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The Liquid Crystalline Behaviour of Certain Analogous Biphenyl and 2- and 4- Phenylpyridine Systems

being a thesis submitted to The
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of Philosophy

by

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1977

PREFACE

I wish to thank the Council for National Academic Awards for their sponsorship for three years, whilst undertaking the degree of Doctor of Philosophy.

I would like to extend my sincere gratitude to both Dr R.C. Wilson, and especially Dr D.J. Byron for their supervision, guidance and friendship throughout my stay at Trent Polytechnic, Nottingham.

I also wish to thank Dr G.W. Gray at Hull University for his kind permission to use their differential thermal analysis facilities during the course of this work.

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NOMENCLATURE

Throughout the Thesis, the following nomenclature will be used:

C-N : transition from crystal to nematic mesophase.
C-S : transition from crystal to smectic mesophase.
C-I : transition from crystal to isotropic liquid.
S-N : transition from smectic mesophase to nematic mesophase.
S-S : transition from smectic mesophase to smectic mesophase.
N-I : transition from nematic mesophase to isotropic liquid.
S-I : transition from smectic mesophase to isotropic liquid.

1. History

The observation of Reinitzer[1] in 1888 when he heated a sample of cholesteryl acetate marked the discovery of liquid crystals, although myelin structures, which were described by Virchow[2], were known in 1854. Reinitzer's work was confirmed by Lehmann[3], an excellent experimentalist, whose high-spirited publications soon excited interest in this new field. After this initial work, a wide range of mesomorphic compounds was prepared, notably by Vorländer[4] and Lehmann[3] and by Gatterman who was the first person to synthesise a nematogen.

The Swarm Theory of the nature of liquid crystals proposed by Bose[5] (1909) found approval and acceptance by many authors and his theory was developed into a mathematical form by Ornstein and his collaborators[6-8]. An alternative theoretical approach to the nature of liquid crystals was developed by Zocher[9], Oseen[10] and Frank[11] and is known as the Continuum Theory of Liquid Crystals. This theory is mainly concerned with nematogens but it has been extended to include smectic mesophases.

In 1922 came the great work of Friedel[12], in which he proposed a clarified systematisation of and nomenclature for liquid crystals which has since been widely adopted. The only controversial feature was Friedel's unwillingness to recognise polymorphism which we now know to exist in smectogens.

A large group of compounds exhibiting mesomorphic behaviour but which differ from liquid crystals, was recognised by Timmermanns[13] in 1935. This class of compounds was called Plastic or Cubic Crystals. Further discussion of this type of liquid crystal is inappropriate here.

Since the early 1960s, with the recognition of the important applications of liquid crystals in the electronic industry, interest in liquid crystals has escalated. Many more applications of liquid crystals have been found, e.g. in chromatography, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, etc. By the mid-1970s research in liquid crystals had progressed to a stage when its achievements had resulted in the term 'liquid crystals' being a household phrase.

2. General Comments on Liquid Crystals

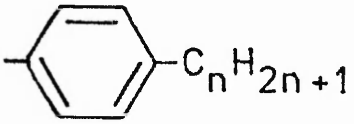
Crystalline solids are formed by crystal lattices that are comprised of regular arrangements of ions or molecules, the patterns of which extend and repeat in three dimensions, so constituting the ordered crystal lattice. The crystal solid possesses both three-dimensional long range positional order and orientational order. It is a well ordered system, and on heating to the isotropic liquid, both the positional and orientational order are lost, although small, isolated, transient cybotactic groups containing some order will still exist. Thus on heating, the system is transformed from a well ordered array of ions or molecules to the predominant disorder of the isotropic liquid. This destruction of long range order on melting occurs at a precise temperature, namely the melting point. However, this one step process is not universal, for the transformation from order to disorder can occur in well defined steps as the temperature is raised. These intermediate phases or mesophases will have properties which are intermediate between those of the ordered crystal lattice and those of the disordered isotropic liquid, i.e. they will have fluid characteristics coupled with a considerable degree of organisation of the ions or molecules. Compounds which possess this middle phase or mesophase are called Mesogens, which are of two types; amphiphilic and non-amphiphilic.

Amphiphilic Compounds

The molecules of amphiphilic compounds have two distinctly different regions, based on solubility behaviour. One of these regions is termed lipophilic, i.e. dissolving in hydrocarbons, but not in water, and the other region is termed hydrophilic, dissolving in water and not in hydrocarbons. Thus because of the dual nature of the molecules, amphiphiles are miscible with both water and organic solvents. Examples of

hydrophilic groups are: $CH_3(CH_2)n \cdot CO_2^{\ominus}Na^{\oplus}$, $SO_3^{\ominus}K^{\oplus}$.
Examples of lipophilic groups are:

$-OC_nH_{2n+1}$,



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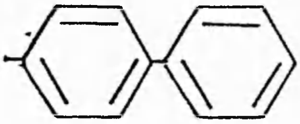


n is usually 2-20.

Typical amphiphiles are the alkali metals salts of aliphatic carboxylic acids, and sulphonic acids, alkyl ammonium sulphates, phospholipids, etc.

The order in the amphiphilic mesophases is based, not on structural arrangements of the individual molecules, as in the case of non-amphiphilic mesophases, but on the arrangement of multimolecular units, called 'aggregates' or 'micelles'. The shapes of these micelles are determined by inter-molecular forces operating both within and at the surface of the micelles. If the micelles are in sufficiently close proximity and thermal motion is not too strong, these inter-micellar forces cause the micelles to adopt a thermodynamically stable arrangement, showing a minimum potential energy. This constitutes the mesophase, of which M_1, G and M_2 are anisotropic optically birefringent mesophases and S_{1c}, V_1, V_2 and S_{2c} are cubic optically isotropic mesophases[14].

Non-Amphiphilic Compounds

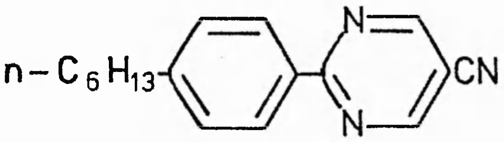
These consist of molecules which do not have a dual nature and have no marked affinity for water. These essentially lipophilic compounds may however contain one or more moderately polar groups, e.g.

$$-\underset{\displaystyle \overset{\|}{O}}{C}-O- \ , \ -OR \ , \ -CN \ , \ -NO_2$$

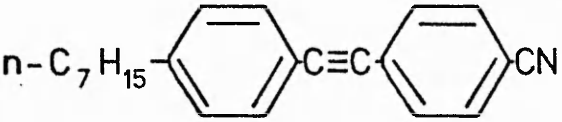
etc., and can be described as being typically covalent organic compounds, which dissolve more readily in organic solvents than in water. Some typical examples of non-amphiphilic mesogens are given overleaf (p. 6).

The terms 'thermotropic' and 'lyotropic' have also been used to distinguish liquid crystals. Those formed by heating are termed thermotropic and the liquid crystals formed by the addition of a solvent are termed lyotropic. Unfortunately, many amphiphilic compounds are lyotropic and the terms are used synomymously, and the same is true of thermotropic and non-amphiphilic compounds. However, there are many examples of this misuse of this nomenclature.

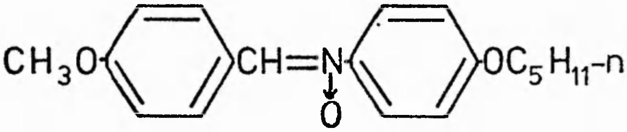
Aerosol OT, a typical amphiphile exists as a liquid crystal at room temperature, i.e. with no solvent present, and anhydrous amphiphiles such as phospholipids, form liquid crystals when heated. Also the types of mesophases formed by an amphiphilic-solvent system are themselves sensitive to temperature, i.e. the so-called lyotropic mesophases are 'temperature



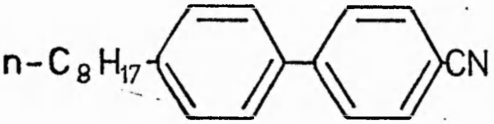
$$\mathrm{C} \xrightleftharpoons{86^\circ} \mathrm{S_A} \xrightleftharpoons{101{\cdot}5^\circ} \mathrm{N} \xrightleftharpoons{103^\circ} \mathrm{I}$$



$$\mathrm{C} \xrightleftharpoons{59^\circ} \mathrm{N} \xrightleftharpoons{67{\cdot}5^\circ} \mathrm{I}$$



$$\mathrm{C} \xrightleftharpoons{112^\circ} \mathrm{N} \xrightleftharpoons{120^\circ} \mathrm{I}$$



$$\mathrm{C} \xrightleftharpoons{21^\circ} \mathrm{S_A} \xrightleftharpoons{32{\cdot}5^\circ} \mathrm{N} \xrightleftharpoons{40^\circ} \mathrm{I}$$

dependent'. The picture becomes even more confused when it is remembered that the so called thermotropic mesophases of non-amphiphilic mesogens may take up a small amount of organic solvent and still retain their liquid crystal properties.

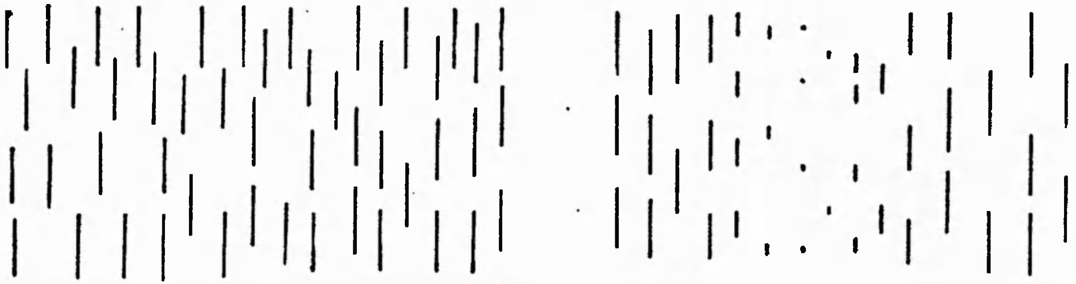
It seems sensible therefore to classify the mesogens in terms of whether they are amphiphiles or non-amphiphiles and not in terms reflecting their formation. Thus the amphiphile Aerosol OT gives amphiphilic phases, irrespective of their mode of formation. Similarly, mesophases formed by non-amphiphiles are non-amphiphilic irrespective of their mode of formation.

The mesophases of the non-amphiphilic compounds can be classified into two distinct types which have been designated by Friedel[12] as 'smectic' and 'nematic'. The smectic term was coined by Friedel from the Greek σμεγμα, meaning grease (soap-like), or slime. In the smectic mesophase, there is a statistically parallel arrangement of the molecules in layers and the centres of gravity of these molecules are mobile in two directions; rotation is permitted about one axis. The layers are free to slide over one another and only in the more highly organised smectic phases, e.g. S_B and S_E (structured layers), do head-to-tail correlations occur over a few molecular lengths. It can be conceived that polymorphism, i.e. differing types of mesophases, can occur in smectogens due to the mobility of the layers which can give rise to different molecular arrangements. This and the differing orientation of the molecules within the layers can account for most of the observed types of smectic polymorphs[15, 16].

The nematic term was coined by Friedel[12] from the Greek νημα, meaning thread. In the nematic structures the only restriction on the arrangement of the molecules is that the molecules preserve a statistically parallel (i.e. nearly parallel) orientation of the long, molecular axes with the centres of gravity of the molecules mobile in three directions and rotation also permitted about one axis. The direction of this axial arrangement (the director) changes continuously throughout the bulk of the melt in accordance with the marked increase in fluidity of the nematic phase, relative to the smectic mesophase.

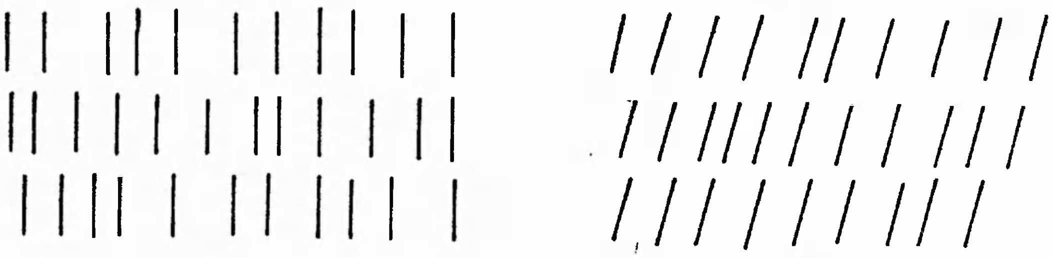
A third phase, the cholesteric mesophase, so called because it is shown mainly by cholesteryl derivatives, has a structure which is similar to the nematic mesophase but which is modified by the presence of a chiral centre. In the cholesteric mesophase the molecules pack parallel to each other within one plane but the planes lie at a well defined angle to one another along the normal to these planes. The effect is to cause a helical twist axis at right angles to the long axes of the chiral molecules. Even though structurally the cholesteric phase is regarded as similar to nematic mesophase, optically it is very much different to both the smectic and nematic phases, exhibiting some unique optical characteristics (see later).

The structures of all three phases, the smectic, nematic and cholesteric mesophases are represented diagrammatically in Figure 1.



NEMATIC

CHOLESTERIC



SMECTIC

TILTED SMECTIC

Figure 1 - Structures of Mesomorphic Phases

Molecular Parameters for the Mesogens

Even a quick inspection of the structure of the non-amphiphilic mesogens on page 6 can show one common geometrical feature of the mesogens; all the compounds are elongated, descriptively termed rodlike or preferably lathlike. Bernal and Crowfoot[17] carried out X-ray studies on the solid states of a limited number of mesogens and concluded that in the crystal state two structures are possible, namely:

i) A layer crystal lattice in which the molecules lie with their long axes parallel and their ends in a line forming a three dimensionally organised arrangement of molecular strata, in which the long axes may be tilted or orthogonal to the planes;

ii) A crystal lattice in which the molecules are not arranged in layers but are aligned parallel to each other, in a head-to-tail manner, with the ends of any one molecule arranged approximately half way along the lengths of the adjacent molecules. No molecular strata exists.

Thus liquid crystal formation can be looked upon as the stepwise thermal degradation of the intermolecular forces in either a layered or non-layered crystal lattice which destroys the well ordered arrangement of the molecules in that crystal lattice, to give a two-dimensional smectic mesophase or a one-dimensional nematic/cholesteric mesophase. The sequence shown in Figure 2 exemplifies the above statement. The smectic mesophase may be formed from the layer crystal lattice because of the mobility of the layers (T). Further breakdown of the intermolecular forces may result in the formation of the isotropic liquid (T_3), or an intermediate nematic mesophase (T_1) formed by a simple translation of the molecules in the direction of their long axes. The nematic phase will then pass to the isotropic liquid on further heating (T_2). The layer lattice can of course change directly to the nematic phase (T_4) without the formation of a smectic phase. However, the non-layer crystal lattice can only give a nematic phase and, on further heating, the isotropic liquid. The possible sequences of phase transition are therefore:

$C \longrightarrow N \longrightarrow I$, $C \longrightarrow S \longrightarrow I$, $C \longrightarrow S \longrightarrow N \longrightarrow I$.

The stepwise degradation in the order of a system from the three-dimensional crystal lattice to the zero order of the isotropic liquid is exemplified by the sequence below:

$C \longrightarrow S_B \longrightarrow S_A \longrightarrow N \longrightarrow I$.

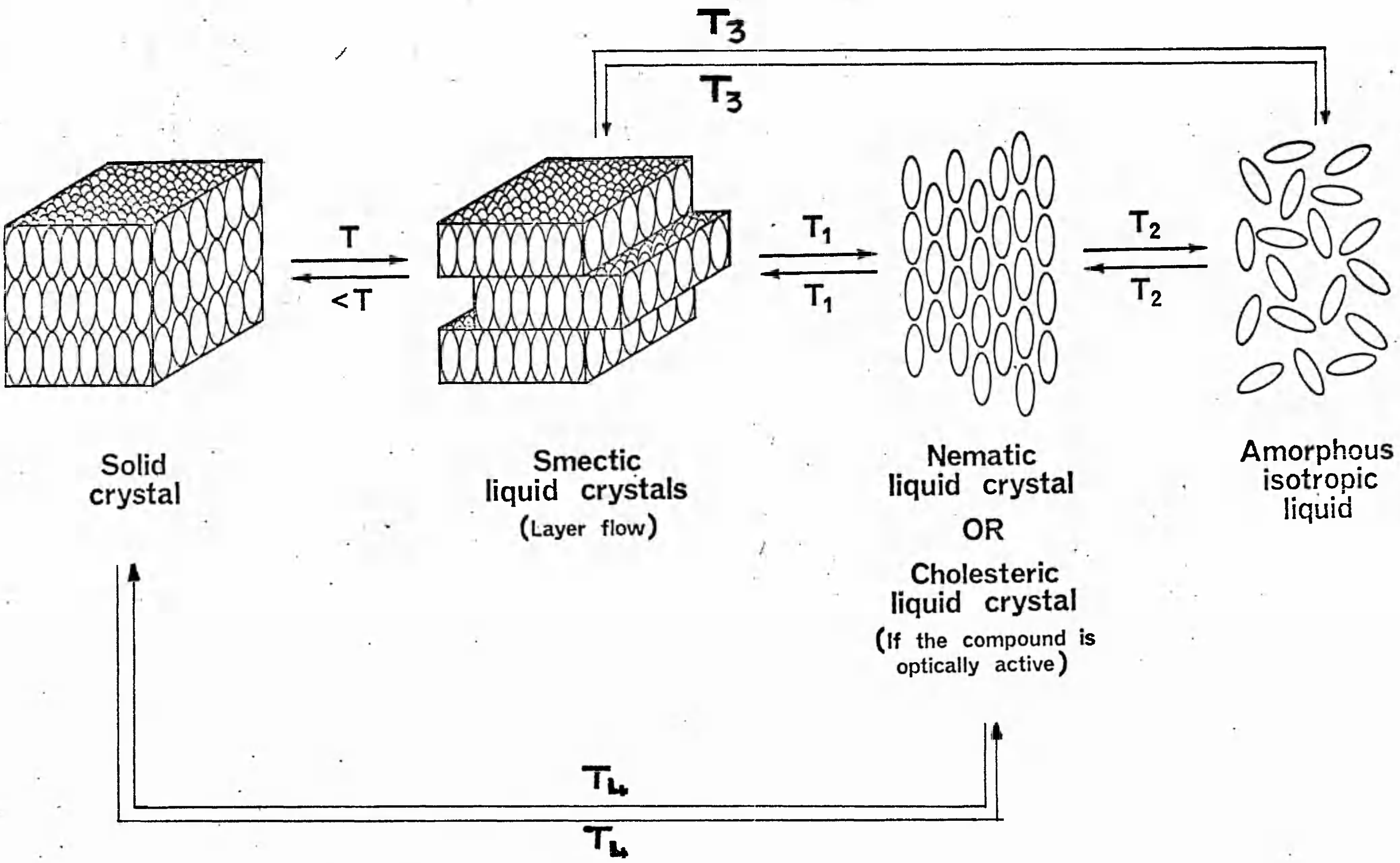


Figure 2 - Mesomorphic Pathways

The smectic mesophases, S_B and S_A, involve a layered structure giving rise to a two-dimensional ordered system. However, in the case of the S_B mesophase, the molecules within the layers are more highly organised (they are hexagonally packed) and so are more highly ordered than are the molecules in the S_A mesophase. In the nematic mesophase, no strata are found and this approximates to a one-dimensional fluid.

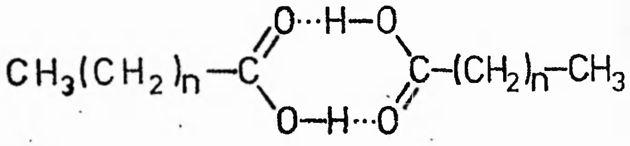
Probably the most important feature of the mesogens is the anisotropic nature of the intermolecular forces. These forces could arise from several interactions; e.g. dipole-dipole, dipole-induced dipole and induced dipole-induced dipole interactions, and the anisotropy of these forces would arise between molecules having an anisotropy of their polarizabilities or of their dipolarities. An anisotropic intermolecular force results in the magnitude of such a force varying from one plane in the crystal lattice to another. Thus in the case of the formation of the smectic phase, the lateral intermolecular forces are stronger than the terminal forces and, on heating, the weaker terminal forces will breakdown first, allowing the layers to slide over one another. Without this anisotropy of the intermolecular forces, all the forces within the molecule will breakdown simultaneously at a definite temperature and the crystal lattice will change directly to the isotropic liquid, without the formation of a mesophase. Thus, anisotropy of molecular geometry is fundamental for the formation of non-amphiphilic mesophases because this gives rise to an anisotropy of the intermolecular forces. As the lathlike molecules tend to be more globular in shape, so the anisotropy of polarizability and dipolarity will approximate to zero and the intermolecular forces will be equal in all directions. Such a case is found in plastic crystals, where the molecules are globular in shape. In plastic crystals the molecules possess long range positional order but are oriented with respect to neighbouring molecules in a completely disordered manner, i.e. the spherical molecules occupy points in a crystal lattice but are capable of free rotation. The resulting plastic crystal lattice is less rigid than that of a liquid crystal and on further heating the positional order is lost and the isotropic liquid is formed. There are thus two limiting shapes for molecules, namely:

i) the anisotropic, lathlike shape of the molecules of the non-amphiphilic liquid crystals.

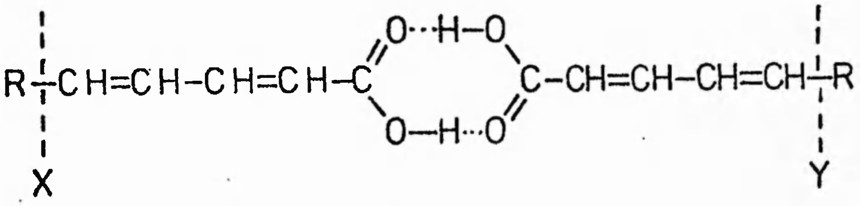
ii) the globular shape of the molecules for the plastic crystals (whose shape anisotropy tends to zero).

Most organic molecules possess a molecular geometry which lies in a region intermediate between these two extremes, i.e. the molecular shape is neither globular nor particularly elongated. As a consequence, an 'ordinary' melting point (C-I) is observed, because the thermal energy input can cause adverse rotational and translational motions within a particular system and the anisotropic intermolecular forces may be inadequate to cope with such motions, resulting in the total breakdown of the lattice and the formation of the isotropic liquid.

If elongation is taken to the extreme, as in the case of the long chain n-alkanes, the flexible chain can coil and bend making packing difficult and no liquid crystals are formed by these hydrocarbons. This illustrates the third criterion for the formation of a mesogen; rigidity. If the flexible n-alkyl chain of the carboxylic acid (I) in Figure 3 is strengthened by the introduction of a pair of double bonds, as in the 2,4-dienoic acid (II), the sp^2 hybridised bonds restrict the rotation and bending, and hence the rigid core part of the molecule (from X to Y) is quite extensive. These unsaturated acids are mesogens, e.g. II, R = ethyl.



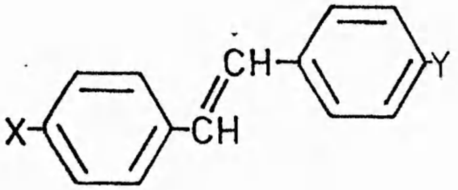
(I)



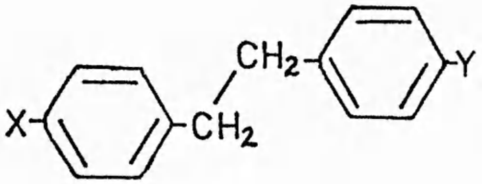
(II)

Figure 3 - Rigidity and Flexibility of Alkyl Chains

Rigidity and anisotropy of polarizability normally accompany each other. Consider the structures (III) and (IV). In the trans-Stilbenes(III) the structure is more rigid because the π-bond of the group linking the rings restricts rotation. However, with the 1,2-diphenylethanes (IV), the zig-zag elongated conformation can be destroyed by rotation about the central bond of the groups linking the rings. Furthermore, the conjugation of the planar aromatic rings can be transmitted through the -CH=CH- linking group but not through the $-CH_2-CH_2-$ linking group. This not only increases rigidity but also enhances the anisotropy of polarizability in the trans-Stilberes (III). Consequently, the tendency of Stilberes to form mesogens is greater than that of the 1,2,-diphenylethanes.



(III)



(IV)

To summarise, three criteria must be fulfilled for a compound to be a potential mesogen, namely:

i) Anisotropy of the intermolecular forces;

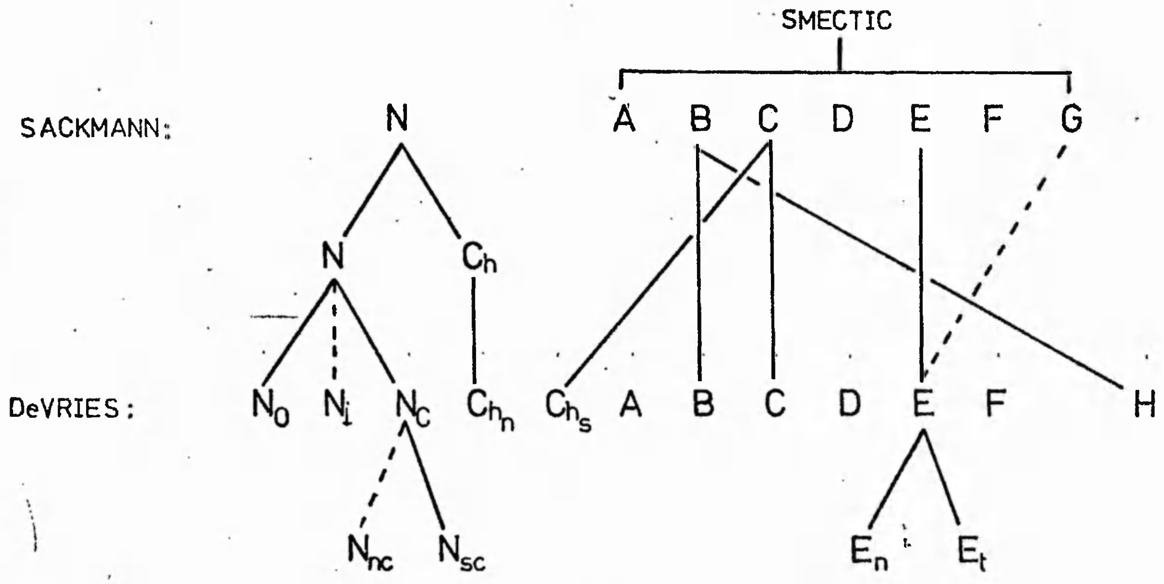
ii) Elongated shape of the molecule;

iii) Rigidity.

3. Classification and Properties of Non-Amphiphilic Liquid Crystals

a) Classification:

There are two prime modes of classification of non-amphiphilic liquid crystals; one by Sackmann and Demus[15] and the other by DeVries[16]. A summary of the two classifications is shown in Figure 4.



N = NEMATIC

N_o = ORDINARY NEMATIC

N_i = INTERMEDIATE NEMATIC

N_c = CYBOTACTIC NEMATIC

E_n = NORMAL SMECTIC E

E = TILTED SMECTIC E

N_{nc} = NORMAL CYBOTACTIC NEMATIC

N_{sc} = SKEWED CYBOTACTIC NEMATIC

C_h = CHOLESTERIC

Ch_n = NEMATIC CHOLESTERIC

Ch_s = SMECTIC CHOLESTERIC

Figure 4 - Classification of Liquid Crystals

The classification of Sackmann and Demus is based on the Rule of Selective Miscibility which states "all liquid crystalline modifications which exhibit an uninterrupted series of mixed crystals in binary systems without contradiction, can be marked with the same symbol". That is, if two liquid crystals are miscible in all proportions, then they belong to the same type. In Figure 5 an idealised phase diagram has been constructed to illustrate this point.

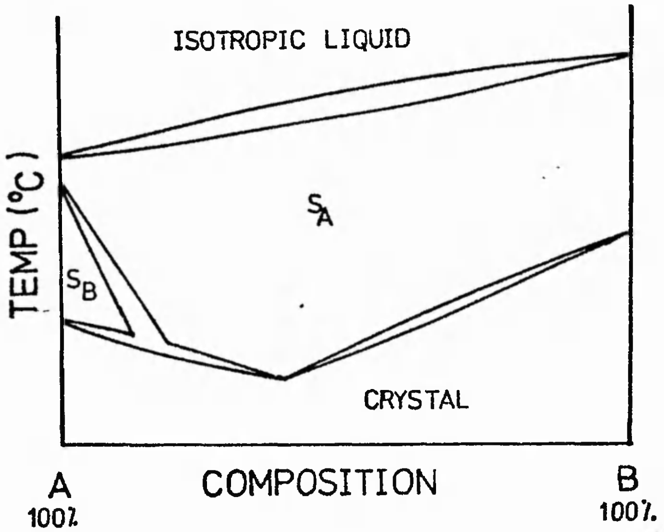


Figure 5 - Ideal Phase Diagram for Two Smectogens A and B Having a S_A Phase

Usually one of the compounds involved is the standard (A). A series of binary mixtures of known composition for each of the components A and B is made up and the transition temperatures are determined by microscopy. From the plot of temperature versus composition it is apparent that there is a continuous region of miscibility across the composition range for smectic A (S_A), whereas the composition line for smectic B (S_B) falls away sharply, as the concentration of component B in the binary mixture is increased. Thus the component B shows the following sequence of phase transitions:

$$C \rightleftharpoons S_A \rightleftharpoons I.$$

By the use of phase-composition diagrams it is usually possible to confirm the types of mesophase present in a polymorphic smectogen.

DeVries based his classification of polymorphic liquid crystals on structural evidence, and not on optical evidence, using X-ray diffraction techniques. By examining the X-ray diffraction patterns he concluded that polymorphism can also be extended to nematic mesophases. DeVries argued that in the normal nematic (N_O), the molecules are free to move, with respect to their neighbours in the direction of their long axis, whilst in the so-called cybotactic nematics, the molecules are regularly arranged in groups (cybotactic groups), and within these groups the molecules are no longer free to move in the direction of their long axis. However, in some recent papers by Sackmann and Demus[15], de Gennes[18] and Steger et al[19], the cybotactic groups are regarded as pretransitional phenomena.

The classification of Sackmann and Demus has been modified (Figure 6) to include some more recently recognised mesophases.

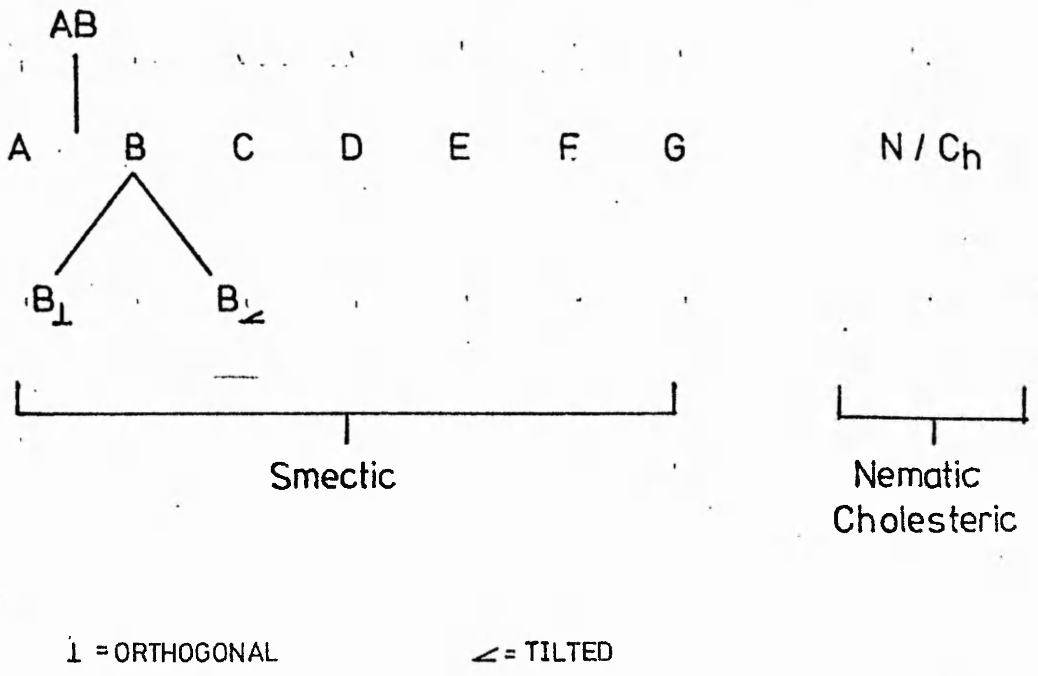


Figure 6 - Classification of Liquid Crystals by the Rule of Selective Miscibility

b) Structure of the Smectic Mesophase:

The smectic mesophase exists because, at a precise temperature, the weaker terminal cohesive forces within the layered crystal lattice breakdown and the layers then have the ability to slide over one another. Different smectic modifications (polymorphism) exist primarily because of the extent of molecular orientation and the degree of order within and between the layers. The classifications of Sackmann and DeVries has led to the identification of eight smectic modifications, denoted S_A to S_H, of which some are identical (Figure 4). Three of the smectic modifications, the S_A, S_B and S_E phases have their long molecular axis orthogonal to the layers. The most common of all the smectic phases is the smectic A phase (S_A), in which both the position and the orientation of the molecules within the layers are disordered. The extent of disorder manifests itself in liquid-like properties and only localised density variations in the layers gives the smectic A phase some crystal-like properties. The smectic B phase also has a layer arrangement, but in contrast to the smectic A phase, the long molecular axis are ordered within the layers, i.e. the S_B phase has structured layers. X-ray work[20] has shown that a hexagonal close packed arrangement exists within the layers. Neither smectic A or B phases are ferroelectric.

A very similar modification is the smectic E phase in which the rotational freedom about the long axis of the molecules is restricted, so producing the chevron arrangement (Figure 7) of the molecules within the layers. This causes a slight distortion in the average hexagonal symmetry, compared with the smectic B phase. In the S_E phase the three dimensional ordering of the molecules gives rise to orthorhombic symmetry.

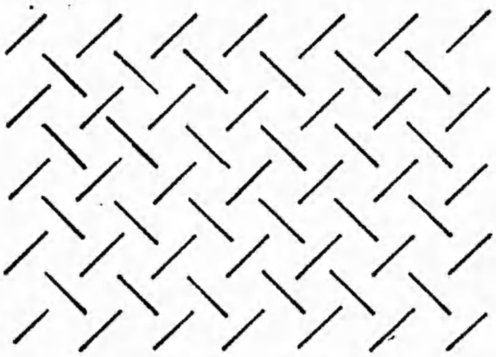


Figure 7 - Chevron Arrangement in Smectic E, Looking Down the Molecular Axis

The tilted version of the smectic modifications have the molecules inclined with respect to the layers. These types of phases have caused the most confusion concerning their identification. No ambiguity exists, however, for the smectic C phase which can be regarded as a tilted version of the smectic A phase. The behaviour and nature of the tilt in the smectic C phase is still not fully understood.

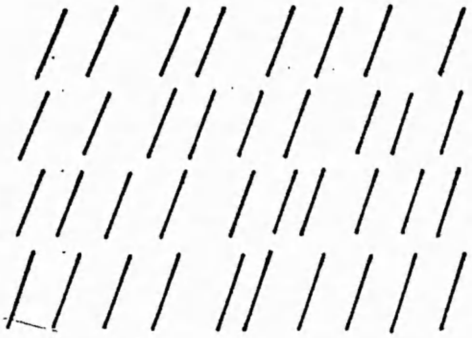


Figure 8 - Structure of Smectic C Phase

A tilted version of the smectic B phase, $S_{B\angle}$ is known (Figure 9) although slight variation in the X-ray diffraction pattern of some $S_{B\angle}$ phases has led DeVries to classify some of them as S_H. There has been much discussion about the relationship between $S_{B\angle}$, $S_{E\angle}$ (tilted smectic E), S_G and S_H phases and it now seems probable that the S_H, S_G and $S_{E\angle}$ phases are identical (designated S_G), and that they differ from the smectic $B\angle$ phase. This difference is very similar to that in which the orthogonal S_B and S_E phases differ from each other. The restriction of the rotational motions of the molecules manifests itself in the ordered chevron arrangement found in the S_G phase.

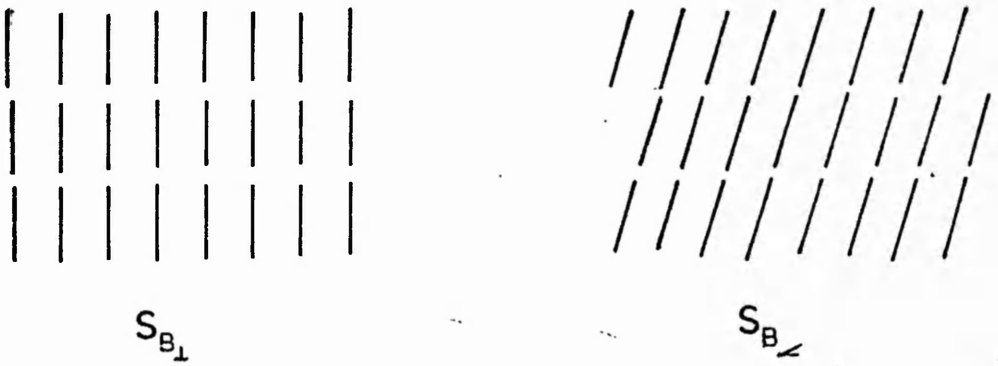


Figure 9 - Structures of Smectic $B_\perp$ and Smectic $B_\angle$ Phases

Very little is known of S_D and S_F phases since very few mesogens exhibit this type of smectic modification. In one particular case[21] the S_D phase is optically extinct between two birefringent mesophases (Figure 10).

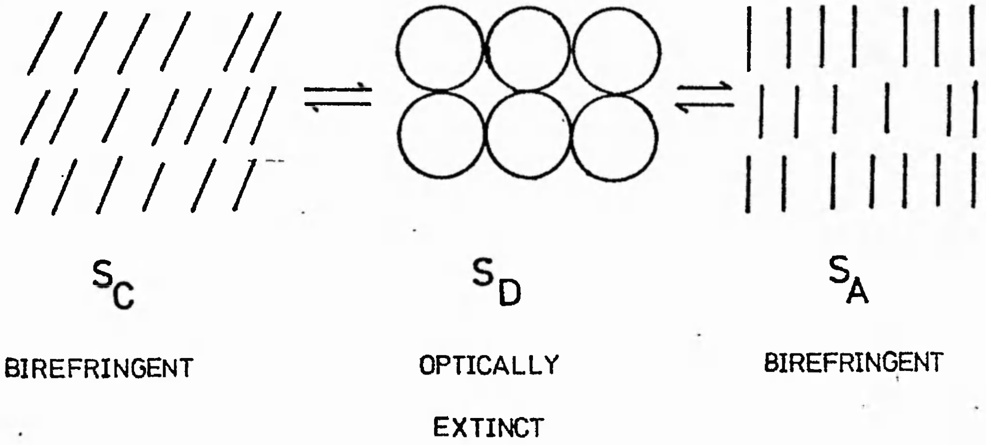


Figure 10 - The Optically Extinct S_D Phase Between Two Birefringent Smectic Phases

Instead of a single process in which the molecules in the layers become orthogonal to the layer plane ($S_C \longrightarrow S_A$), there exists an intermediate mesophase, smectic D, in which the molecules are packed together as micelles. This process is also encountered with lyotropic liquid crystals, where the cubic (rotational) mesophases, V_1 and V_2, which are optically isotropic, lie between the anisotropic optically birefringent mesophases M_1, G and M_2.

The smectic F phase has unstructured layers and is closely related to S_C. The diameter of the sharp inner ring in the X-ray diffraction pattern decreases in the order $S_F \longrightarrow S_C \longrightarrow S_A$, indicating an increase in layer thickness, presumably due to the decrease in tilt angle.

An interesting new development is the idea of an $I \rightleftharpoons S_{AB}$ transition, suggested by Coates and Gray[22], to overcome the need to envisage the transition $S_B \rightleftharpoons I$ observed by Billard et al[23] in which the system would have suddenly changed from the complete disorder of the isotropic liquid, to one involving structured layers (S_B), without the formation of a smectic phase with an unstructured layer (e.g. S_A). The S_{AB} (or $S_B \rightleftharpoons I$) transition has certain characteristics which are similar to both $S_A \rightleftharpoons I$ and $S_B \rightleftharpoons I$ transitions.

Both chiral smectic F and chiral smectic C[24] phases have been prepared in which the tilt direction rotates progressively through the bulk of the phase in a helix manner (the angle of tilt remaining constant). Coates and Gray[24] from miscibility studies also suggest that chiral $S_{B\angle}$ phase is also capable of existence.

The various smectic modifications adopt a variety of optical textures. These have been fully investigated and discussed by a number of authors, and various features are recognised as being characteristic of a particular smectic modification. A detailed discussion of all the optical textures is beyond the scope of this introduction, but the articles by Coates and Gray[21], Sackmann and Demus[15], Brown[25,26] and Saupe[14] give excellent accounts and photographs of all the textures found in the polymorphism of smectogens.

The most common type of smectic mesophase, the smectic A phase, which when cooled directly from the isotropic liquid, manifests elongated sharp-pointed particles known as bâtonnets. In thick samples, these bâtonnets coalesce to give the focal-conic texture in which the characteristic feature is the elliptical disclination lines at the liquid crystal-glass interface. To each elliptical disclination line belongs a second line that follows the branch of a hyperbola, and for the ellipse and hyperbola to be related as a focal-conics, the locus of the vertices of the cone of resolution whose bases are the ellipse, must be the hyperbola which passes through the focus of the ellipse and whose plane is at right angles to the plane of the ellipse. Such an arrangement will meet the requirement that the system possesses a minimum potential energy and the simplest case for the focal-conic arrangement is where the ellipse is a circle, and the hyperbola a straight line passing through the centre of the circle (Figure 11).

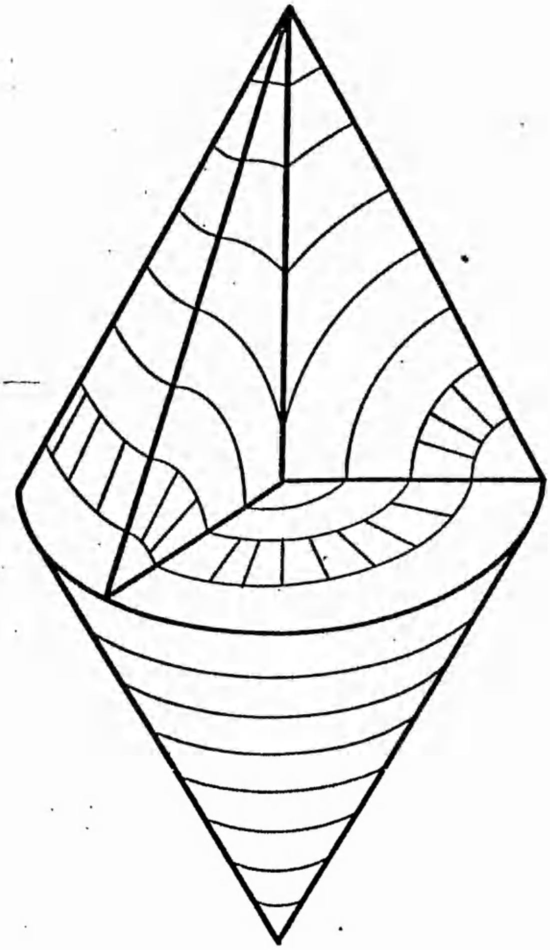


Figure 11 - Focal Conic Domain

In thinner layers, volume restrictions prevent the growth of the focal-conics in the bulk of the mesophase and the fan-shaped focal-conic texture is formed. A coverslip displacement often changes this fan texture suddenly to a pseudo-isotropic texture in which the molecular layers are parallel to the plane of the film.

The homogeneous texture is due to strong molecular ordering in the mesophase and the birefringent areas correspond exactly to the crystalline areas from which it was derived. If there is no attachment between the molecules of the mesogen and the glass supporting surface, then the homeotropic texture is observed. A special case of the homeotropic texture are the Grandjean Terraces (Figure 12) in which the stratification is denoted by a sharp step or edge, whose perimeter is made up of a narrow chain of focal-conic groups. This is the only place where the homeotropic nature of the Grandjean Terraces (Stepped Drops) is incomplete.

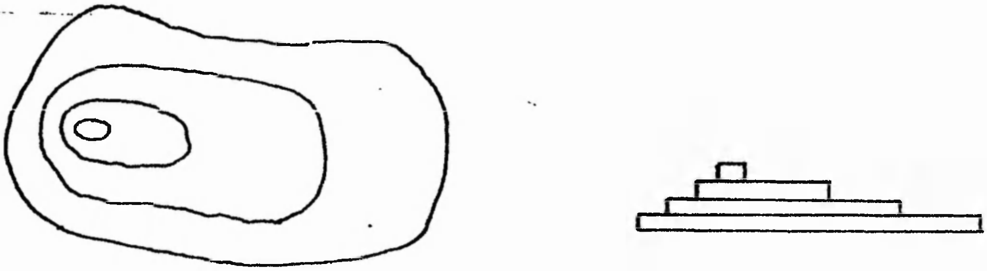


Figure 12- Grandjean Terraces

c) Structure of the Nematic Mesophase:

The only structural restriction to complete disorder in the nematic mesophase is that the long axes of the molecules maintain a parallel, or nearly parallel arrangement. The centres of gravity of the molecules are mobile in three directions and rotation about one axis is permitted. Thus in nematic liquid crystals, there is long-range orientational order but no long-range correlation of the molecular centres.

A fundamental difference between the smectic and nematic mesophases occurs when a thin sample of a nematogen is mounted between a slide and a cover slip and observed using a microscope while the sample is allowed to cool slowly from the isotropic liquid. Whilst the smectic A mesophase appears as bâtonnets, the nematic mesophase separates as tiny, spherical drops which coalesce to give one of the many nematic textures.

The threaded texture is the most common texture of the nematic liquid crystal; a texture from which the mesophase has derived its name. These threads appear to be partly or wholly anchored to the supporting surface, and have varying shapes and lengths. This type of surface adhesion is typical of nematic liquid crystals. However, the essentially parallel molecular arrangement at the glass supporting surfaces, becomes highly distorted (especially in thick samples) in a complex manner in the bulk of the mesophase. The threads are lines of discontinuity in the anisotropic medium about which the medium is structurally built.

If the glass surfaces are rubbed in one direction prior to the preparation of the mesophase, the prepared surface will align the molecules parallel to the supporting surface, giving a strong birefringent melt. This is known as the homogeneous texture, and has an obvious anology with the homogeneous texture of the smectic mesophase. There are, however, two fundamental differences. Microscopic examination of the nematic texture would reveal that the melt is not static, but continuously in motion (Brownian motion) with the molecules suddenly changing their orientation as they pass from one area to another. A cover slip displacement on the smectic homogeneous texture would destroy the parallel alignment of the molecules, resulting in the formation of the focal-conic texture. The nematic homogeneous texture is not destroyed by such a displacement.

In thinner films, the schlieren texture is observed, with point-like singularities. These singularities are vertical threads and may be characterised by the number of dark brushes that appear when observed between crossed polarisers. Points with two or four brushes are commonly found (cf smectic schlieren texture).

The fourth texture is the pseudoisotropic texture, where the optical axis is oriented perpendicular with respect to the planes of the slide and coverslip.

d) Structure of the Cholesteric Mesophase:

As the name indicates, cholesteric liquid crystals were first observed with cholesteryl derivatives, e.g. cholesteryl benzoate, acetate, propionate, etc. Non-sterodial molecules can also show cholesteric properties if the molecule has a chiral centre. In fact, the cholesteric liquid crystal has been shown by Robinson[27] to be a special kind of nematic liquid crystal.

The structure of the cholesteric mesophase is very similar to that of the nematic, i.e. long-range orientational order, but no long-range translational order, with unidirectional alignment of the molecules within a given layer. However, in the cholesteric mesophase the individual layers are stacked so that the direction of the long axes of molecules in one layer is displaced slightly from the direction of the long axes in the adjacent layer, tracing a helix, the optical axis of which is perpendicular to the layers. A schematic representation of the cholesteric mesophase is shown in Figure 13.

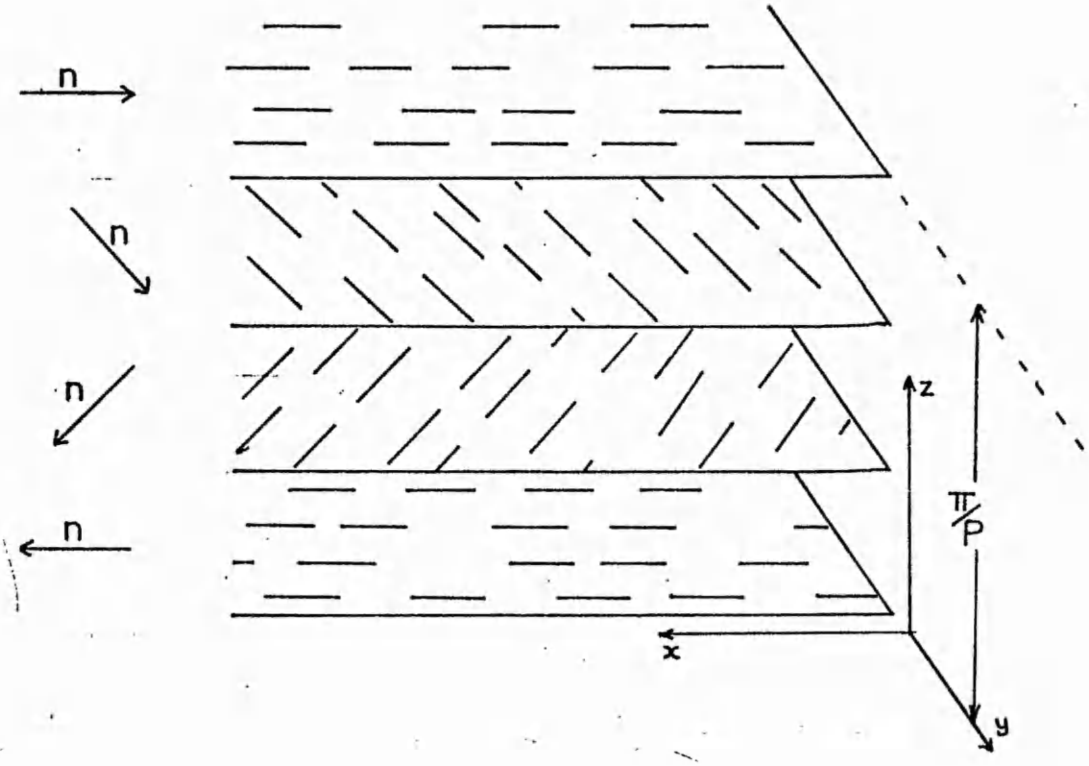


Figure 13 - The Structure of the Cholesteric Mesophase.

Clearly, in reality the nematic liquid crystal is merely a cholesteric phase with a zero value of P, the pitch. The pitch and the reflection colours, which are a notable feature of the cholesteric liquid crystal, are strongly temperature dependent (thin, homogeneous, aligned layers of cholesteric liquid crystals are good temperature sensors, changing colour at precise temperature values). Usually, the pitch decreases as the temperature increases and the reflection band shifts to shorter wavelengths (the blue end of the electromagnetic spectrum). However, some cases are known where the converse is true. Cholesteric liquid crystals also show very strong optical rotatory power, which can be as large as

50 complete rotations per millimetre, and they can be either dextro- or leavo-rotatory.

When a cholesteric mesophase is formed, the usual texture adopted is the focal-conic one, provided that there is no cover slip displacement. The focal-conic groups are small and confused, although a large number of cholesteric mesophases do contain well defined focal-conic areas. This confused state is, in fact, a 'homoeotropic' condition formed by the rapid coalescing of a large number of small, indistinguishable particles and whose molecular arrangement is not known. Like the smectic mesophase, bâtonnets are observed when the isotropic liquid is cooled to form the focal-conic texture. The texture is optically negative and uniaxial, unlike the smectic and nematic mesophases which have the property of positive uniaxial or biaxial crystals.

A cover slip displacement transforms the focal-conic texture to the planar texture, where the twist axis is perpendicular to the plane of the film, and alignment discontinuities in the mesophase result in a crack-like pattern in the texture. The planar texture can also show reflection colours. If the supporting surfaces have been prepared for parallel alignment, a feature known as Grandjean steps or threads is observed, where the threads follow lines of equal thickness and are connected with a discontinous change in pitch.

The structures, textures and optical properties of the smectic, nematic and cholesteric mesophases are summarised in Table 1 which is based on that presented by Brown[28] (see p. 36).

4. The Effect of Molecular Geometry on the Properties of Non-Amphiphilic Liquid Crystals

a) General Considerations:

With very few exceptions, meaningful correlations of the melting points of a series of similar compounds with their chemical composition do not exist. The main reason for this is that the melting point of a solid is a one-step process in which the three-dimensional geometrical arrangement of the molecules suddenly collapses to give a disordered isotropic liquid. This process will involve a great deal of energy in order to break down the intermolecular cohesive forces between the ends, sides and planes of the molecules in the crystal lattice. The process does not occur in a predictable manner, especially if the polarizability and/or the permanent dipole of the compound are high. Crystal packing plays an important role in the one-step melting-point

Table 1 - Polymesomorphism of Non-Amphiphilic Liquid Crystals

Class	Optical Properties	Textures	Structures	Examples
Nematic	Uniaxially positive	Schlieren; threaded; marbled; pseudo-isotropic; homogeneous	Parallelism of long molecular axes	p-Azoxyanisole; p-methoxybenzylidene-p-n-butylaniline
Cholesteric	Uniaxially negative; or isotropic, optically active	Focal conic with Grandjean steps; homogeneous; isotropic	Nematic packing in planes; superimposed twist in direction perpendicular to the long axes of the molecules	Cholesteryl nonanoate
Smectic A	Uniaxially positive	Focal conic (fan-shaped or polygon); stepped drops; homogeneous; pseudoisotropic	Layer structure; molecular axes orthogonal to the layers; random arrangement within the layers	Diethylazoxybenzoate
Smectic B	Uniaxially or biaxially positive	Mosaic; stepped drops; pseudoisotropic; homogeneous; schlieren	Layer structure; molecular axes orthogonal or tilted to the layers; hexagonal arrangement within the layers	Ethyl ethoxybenzylideneaminocinnamate; terephathal-bis-butylaniline
Smectic C	Biaxially positive	Broken focal conic; schlieren; homogeneous	Layer structure; molecular axes tilted to the layers; random arrangement within the layers	Dodecyloxyazooxybenzene
Smectic D	Isotropic	Isotropic; mosaic	Cubic structure	$4'$-Octadecyloxy-$3'$-nitro-diphenyl-4-carboxylic acid

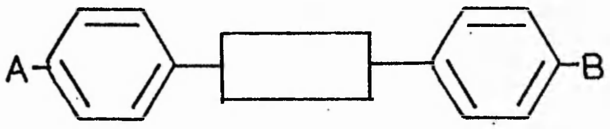
Table 1 continued

Class	Optical Properties	Textures	Structures	Examples
Smectic E	Uniaxially positive	Mosaic; pseudoisotropic	Layer structure; molecular axes orthogonal to the layers; ordered arrangement within the layers	Di-n-propylterphenyldicarboxylate
Smectic F	Uniaxially positive	Schlieren; broken focal conic with concentric axes	Layer structure	2(4-n-pentylphenyl)-4-(4-n-pentyloxyphenyl)-pyrimidine
Smectic G	Uniaxially positive	Mosaic	Layer structure with ordered arrangement within the layers	2-(4-n-pentylphenyl)-5-(4-n-pentyloxyphenyl)-pyrimidine

process and predictions of the effect of molecular geometry on the properties of the liquid crystal are difficult.

Nevertheless, some rationalisation is possible. At the outset, it should be emphasised that there is no correlation between the C-S or C-N transition temperature of liquid crystals and chemical composition. Such transitions involve a great deal of energy in which most of the transitional process from order to disorder is overcome and total disorder being prevented by local intermolecular cohesive forces. However, the transitions N-I, S-N, S-S and S-I are relatively low in their energy demands and molecular geometrical considerations can influence the magnitude of these transitions.

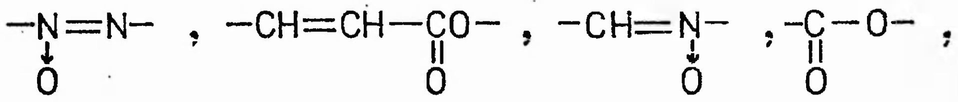
The majority of the non-amphiphilic liquid crystals are aromatic, since aromatic rings are polarizable, planar and rigid, and if suitable substituents are correctly positioned on the aromatic ring, rigid lath-like molecules can be built up. Many of these compounds have the common feature represented by the structure (V). Here, the two p-phenylene rings are joined together by a bridging central group with substituents (which can be hydrogen) in the positions marked A and B.



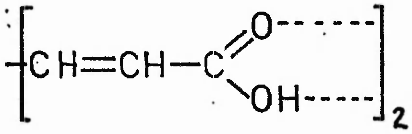
(V)

The effect of different terminal substituents, A and B, will be dealt with later. Examples of the central linking group are as follows:

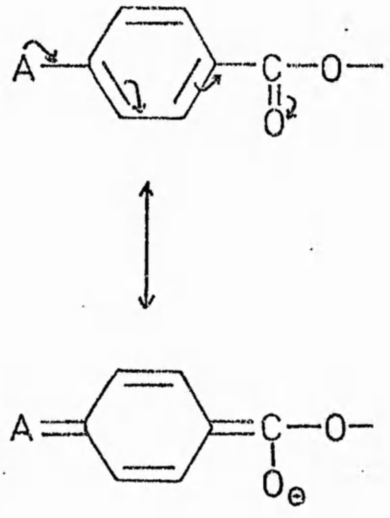
$$-CH{=}CH- \quad ,-(CH{=}CH)_2- \quad ,-C{\equiv}C- \quad ,-N{=}N- \quad ,$$



$$-\underset{\substack{\downarrow\\ O}}{N}{=}N- \quad , -CH{=}CH-\underset{\substack{\|\\ O}}{C}O- \quad , -CH{=}\underset{\substack{\downarrow\\ O}}{N}- \quad ; -\underset{\substack{\|\\ O}}{C}-O- \quad ;$$

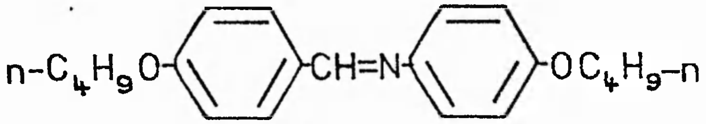


The majority of these groups involve at least one multiple bond or a ring system formed as a result of hydrogen bonding. However, in groups such as -COO or -OCO- in which the double bond is not involved in bridging the two p-disubstituted benzene rings, contributions from resonance structures such as (VI), enhance the molecular rigidity[29]. The linking groups $-OCH_2\,CH_2O$ and $-CH_2CH_2-$ cannot contribute much to the molecular rigidity and consequently are not so frequently encountered as other linking groups.

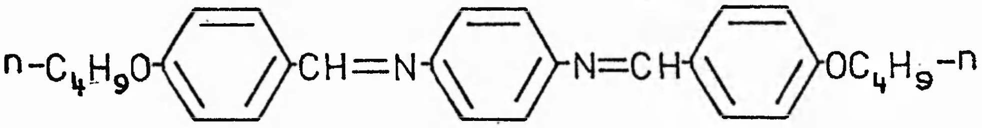


(VI)

If the conjugation of the central linking group is extended, e.g. -CH=CH-COO- or -CH=N-N=CH-, then the lath-like character of the molecules will be increased, giving rise to a greatly enhanced mesomorphic thermal stability, i.e. a higher mesophase-isotropic liquid transition temperature. This transition temperature can also be increased by including a third p-disubstituted benzene ring, especially if the rings are linked by a doubly bonded group. An example of such an increase in mesophase-isotropic liquid transition temperature can be seen by comparison of the structures (VII) and (VIII). The compound (VII) is monotropic (meta-stable mesophase, observed only on cooling the isotropic liquid) and has a N-I transition temperature of 121°C, whilst the N-I transition temperature of compound (VIII) is 297.5°C.

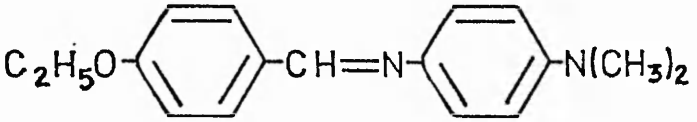


(VII)



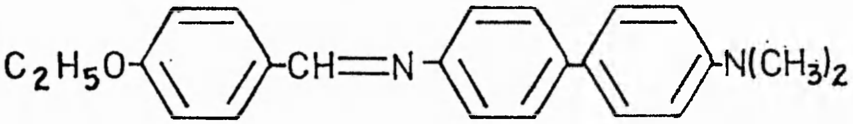
(VIII)

The inclusion of the 4,4 -disubstituted biphenyl function is an excellent way to promote mesophase thermal stability because the system is rigid and if nearly planar, will allow conjugation within the molecule. An example of this particular enhancement of mesophase thermal stability is illustrated by the comparison of the structures (IX) and (X).



C—I ,140°; [I—N , 102°]

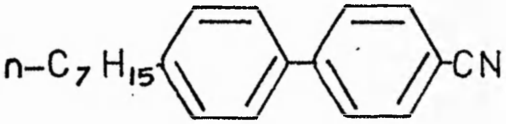
(IX)



C—N , 208° ; N—I , 274°

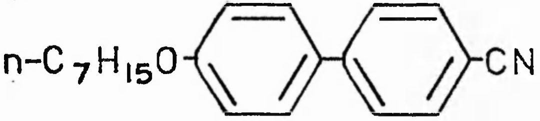
(X)

The biphenyl ring has such strong mesophase-promoting tendencies, that the simple 4,4'-disubstituted biphenyls (i.e. with no central linking group present) can be mesogens. Excellent examples of this are the 4'-n-alkyl (XI) and 4'-n-alkoxy-4-cyano-biphenyls (XII) prepared by Gray[30] and his co-workers.



N-I, 42°

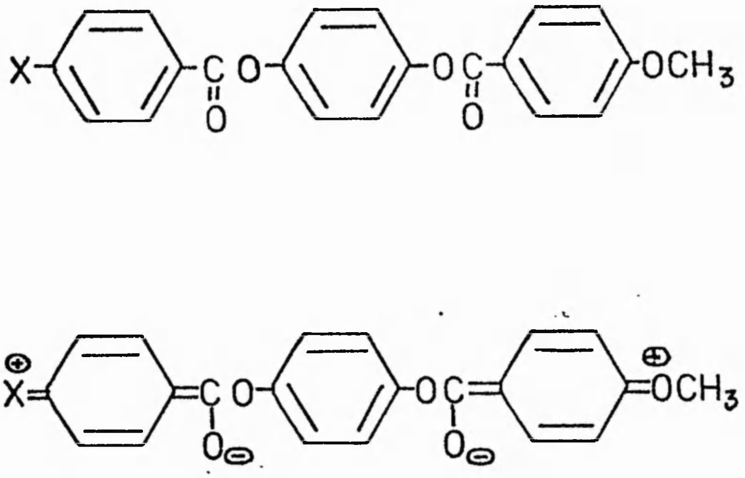
(XI)



N-I, 75°

(XII)

Dewar and Goldberg[31] have drawn attention to the important role of the p-disubstituted benzene ring in the formation of mesogens. These authors observed that the mesophase-promoting characteristics of such a system are not only inherent in its shape and rigidity, but because its electronic effect also permits conjugative interactions to operate between the p-substituents as indicated by the following example (XIII):



(XIII)

The exact role of the lateral and terminal substituents and of the central linking group in mesogens is reviewed in the following three sections.

b) <u>The Role of the Terminal Substituent in Mesogens</u>

This can conveniently be divided into two sections:

i) Examination of a homologous series of mesogenic compounds, in which the terminal substituent $Me(CH_2)_n$- or $Me(CH_2)_nO$- is progressively lengthened by successive methylene groups.

ii) The influence of small, compact groups, e.g. CN, NO_2, halogen, etc., on the properties of mesogens.

i) Homologous Series of Mesogenic Compounds

Some seventy homologous series or parts of homologous series of mesogens have been examined[32]. When the liquid crystal transition temperature, e.g. N-I, S-I, S-N, S-Ch, Ch-I and some S-S transitions temperatures, for a homologous series are plotted against the number of carbon atoms in the n-alkyl or n-alkoxy chain, smooth curves may be drawn through the points representing like or related transitions. A typical example of this type of plot is found in Figure 14.

The N-I temperatures alternate typically to give two smooth curves, the upper one for the even carbon atoms and the lower one for the odd carbon atoms in the n-alkoxy chain. If the n-alkyl chain is directly attached to the ring, the reverse situation would arise, since the oxygen of the n-alkoxy chain is equivalent to a methylene unit. The odd-even relationship becomes less marked as the series is ascended and in some cases, the two curves will actually merge. The behaviour pattern for the two curves of a homologous series falls into two main

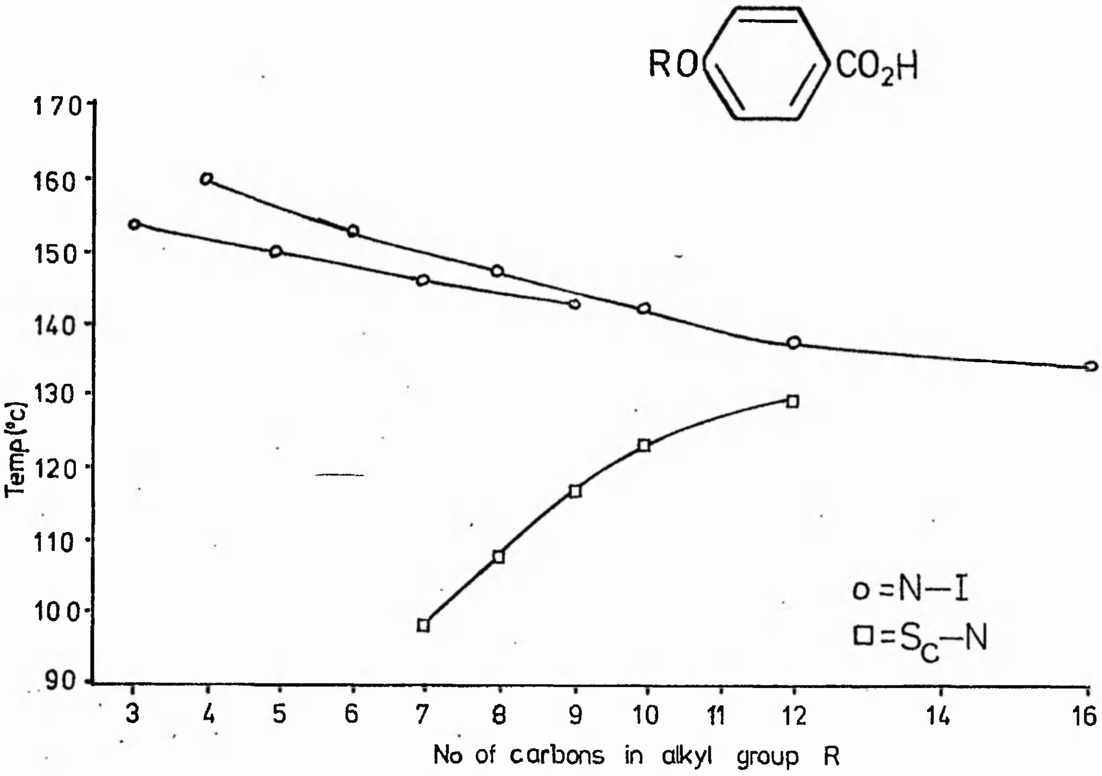


Figure 14 - Transition Temperature -v- Chain Length Plot for 4 -n-alkoxybenzoic acids

groups. The first group is where the curves behave similarly; they both either rise or fall initially and then level out, whilst in the second group, the upper curve may fall and then level out, while the lower curve rises only slightly or stays almost level as the series is ascended. The Figures 14, 15 and 16 give examples of these types.

The odd-even effect in aromatic alkyl ethers is believed to be due to the increased polarizability of the molecule in the direction of the long molecular axis as the length of the n-alkyl chain changes successively from an odd to even value. Assuming a zig-zag

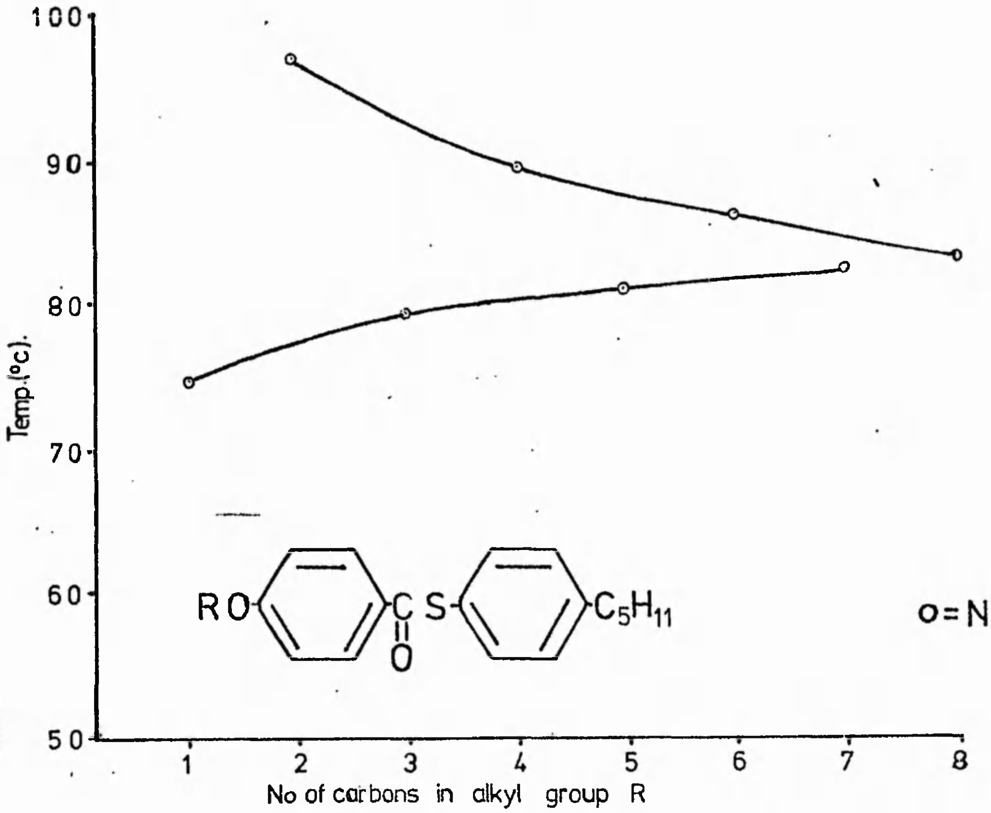


Figure 15 - Transition Temperature -v- Chain Length Plot for 4-pentylphenyl 4′-alkoxypenylbenzthiolates

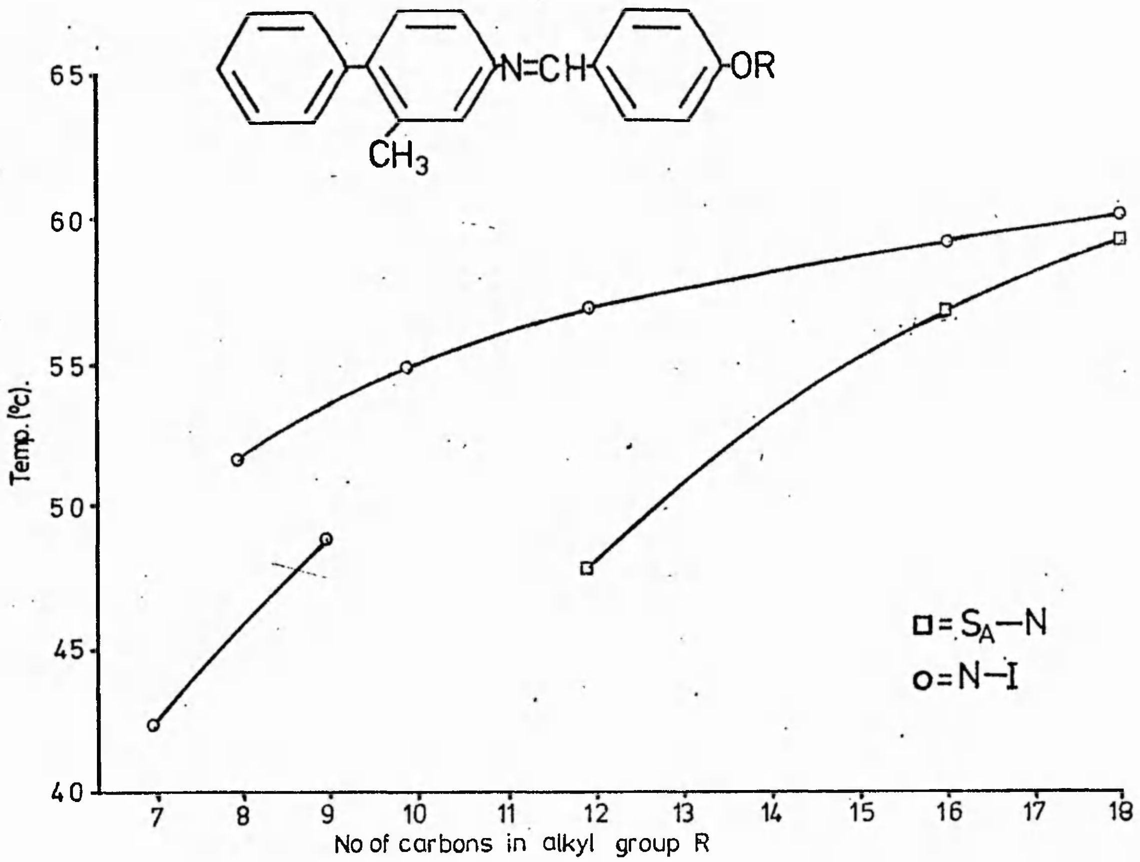


Figure 16 - Transition Temperature -v- Chain Length Plot for 4-(4′-n-alkoxybenzylideneamino)-2-methylbiphenyls

conformation on passing from an odd to an even carbon atom, the new carbon-carbon bond axis will lie closer to the direction of the major molecular axis than it does on passing from an even to an odd carbon atom. In fact, there is almost no increase in polarizability for the latter situation. Thus the anisotropy of molecular polarizability is greater for compounds with an even number of carbon atoms in the n-alkoxy chain. However, as the n-alkyl chain becomes longer, so the chain will flex and bend and come into line with the long molecular axis, and the contribution of each of the additional carbon-carbon bonds to the overall polarizability of the molecule will be about the same, and the alternation effect will be diminished as the series is ascended.

Exceptions to the generally observed trends of the N-I transition temperatures with increasing length of the n-alkyl chain are known, e.g. the 2-(p-n-alkoxybenzylideneamino) fluorenones (Figure 17).

For this series, initially both odd and even N-I transition temperature curves fall to a shallow minimum and then rise slightly before falling again as the length of the n-alkyl

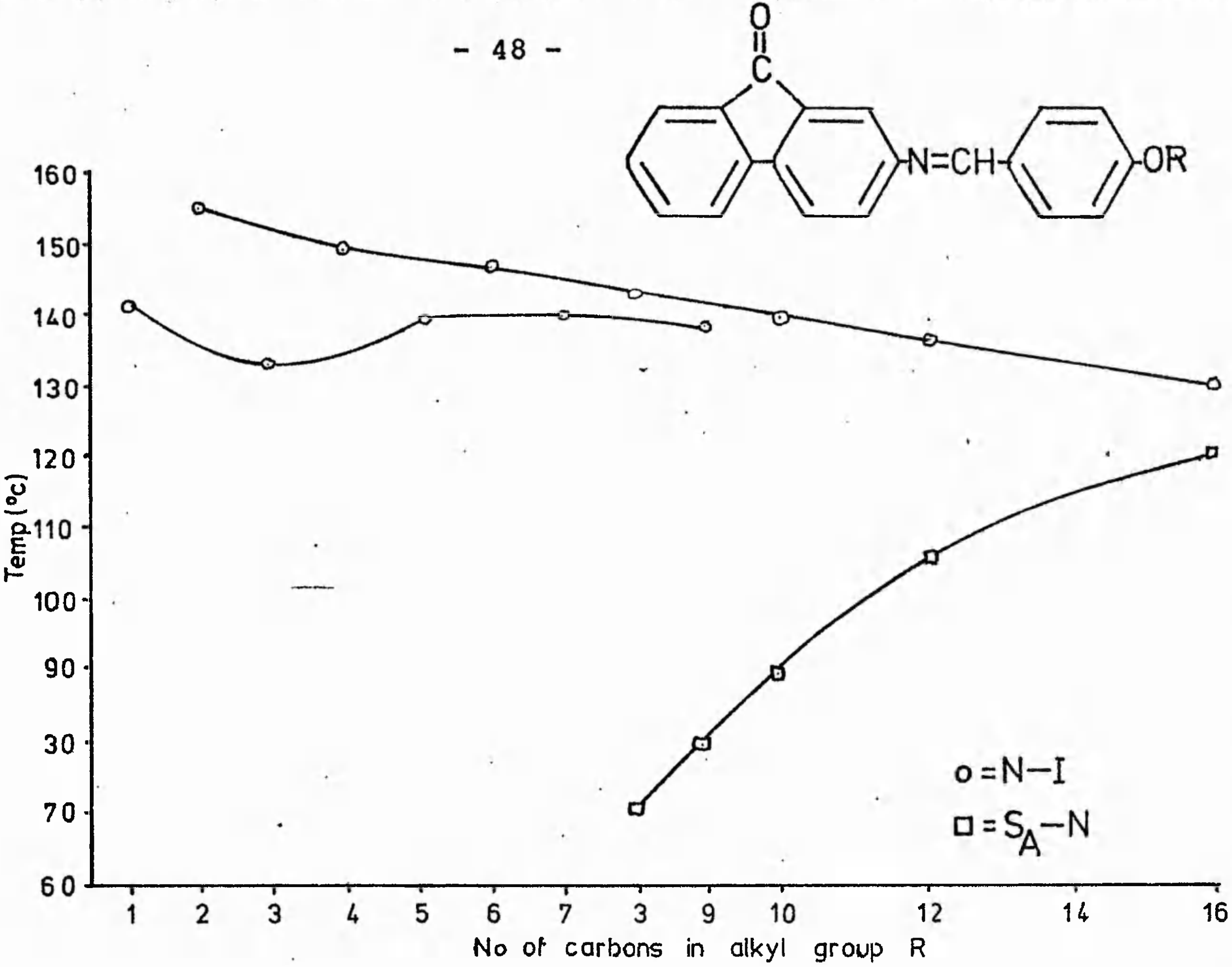


Figure 17 - A Plot of Transition Temperature -v- Chain Length for 2-(4′-n-alkoxybenzylideneamino) fluorenones

chain increases. Although alteration still occurs, the curves are more complex than those usually observed.

The trends found for Ch-I transition temperature curves are very similar to those for N-I transitions. Deviations from strict curve relationships are more frequent in cholesteric liquid crystals, probably due to purification difficulties and the fact that when the cholesteric phase first appears from the isotropic liquid on cooling it is almost optically extinct in transmitted light, and can be easily missed.

In homologous series of purely smectogenic compounds, the odd-even effect is still observed for the S-I transitions, although the trends are slightly different. Three patterns are observed, namely:

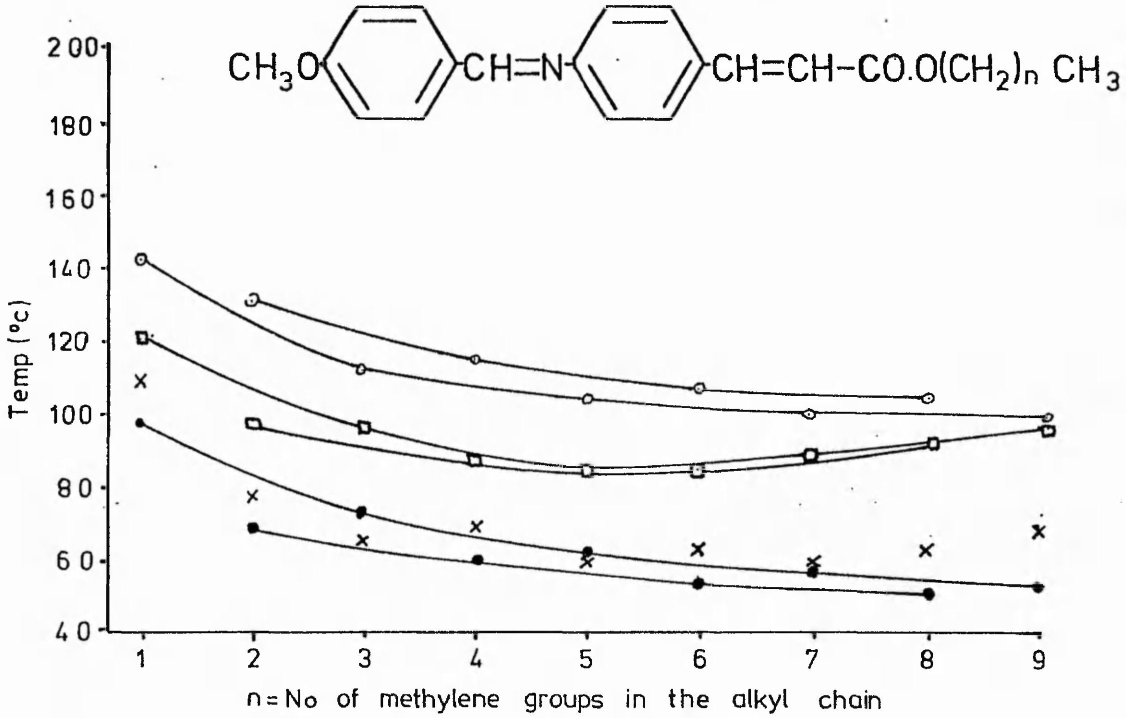
i) both curves rise or fall progressively over the whole range;

ii) both curves rise to an early maximum and then fall;

iii) one curve rises to an early maximum and then falls, while the other falls continuously throughout the homologous series.

For the vast majority of homologous series the odd-even alternation with increasing alkyl chain length is not observed for the S-N transitions and this was thought to be a general occurrence. The points normally lie on one curve which initially rises steeply with increasing n-alkyl chain length and then levels off to become coincident with the falling N-I transition temperature curve. A typical plot is that observed for the 4′-n-alkoxybenzoic acids (Figure 14).

However, more recent studies[14, 33, 34] have shown that the odd-even alternation may occur for S-N transitions. A typical series showing this effect is the n-alkyl 4-(p-methoxybenzylidene-amino) cinnamates transition temperature curves which are depicted in Figure 18.



○ = N—I ; □ = S_A—N ; ● = S_B—S_A ; × = C—N, S_A, or S_B

Figure 18 - A Plot of Transition Temperature -v- Chain Length for n-alkyl 4-(p-methoxybenzylideneamino) cinnamates

For the S_A-N and N-I transition temperatures, the even curve lies above the odd curve, but the alternation of the S_B-S_A transition temperatures is such that the odd curve is uppermost. Thus enhancement of the anisotropy of molecular polarizability stabilises the S_A and N phases, but appears to destabilise the S_B and S_E phases. The reason for this is probably that the S_B and S_E phases are the more highly ordered phases and so lateral cohesive forces are more important in determining the sense of the alternation, i.e. S_B and S_E phases are stabilised more by enhancement of the polarizability across the molecular axis.

Work on the w-phenylalkyl esters has shown that the deviation from a strict lath-like shape only slightly diminishes the S_A thermal stabilities, whereas for the highly ordered S_B and S_E phases, such deviation enhances their thermal stabilities.

ii) Small Compact Groups

Although much work has been carried out in an attempt to recognise a relative 'group efficiency order' for substituents in promoting thermally stable mesophases, only a general trend is apparent. This is due to the complex contribution that the substituent makes to the molecular properties of the mesogen. For example, a terminal substituent may have either attractive or repulsive interactions with the substituent in an adjacent molecule, and lateral interactions with other portions of adjacent molecules are possible. Terminal substituents can also influence the polarizability of the aromatic ring to which they are attached. It must be stressed that the so called group efficiency order is only a general trend and cannot be rigorously applied. There are several examples of small individual terminal group efficiency orders[31, 35, 36, 37] but an average efficiency order often quoted for nematic and cholesteric mesogens is[48]:

$$Ph > NH.CO.CH_3 > CN > OCH_3 > NO_2 > Cl$$

$$> Br > N(CH_3)_2 > CH_3 > F > H$$

Thus, when H in a terminal position is replaced by any of the above substituents, the nematic thermal stability (i.e. the N-I transition temperature) is increased, and the effect is greatest for groups which are compact, polar and polarizable.

The effect of terminal substituents on smectic thermal stability is less clear, mainly due to the fact that very few systems have been studied and considerable variations occur in systems that have been examined. The following two group efficiency orders for smectogens are quoted by Gray[48].

(i) $NH.CO.CH_3 > Ph > Br > Cl > F > N(CH_3)_2 > CH_3 > H > NO_2 > OCH_3 > CN$.

(ii) $Ph > N(CH_3)_2 > CH_3 > OCH_3 > H$.

With the exception of the highly polarizable Ph and NH.CO.Me substituents, the smectic group efficiency order is totally different to the nematic/cholesteric order. The -CN and $-NO_2$ groups are low in the smectic order because these groups have strong dipoles which lie along the molecular axis, and such dipoles give rise to repulsive forces between molecules which lie parallel to one another. However, it is puzzling that the chloro- and bromo-substituents also have a similar, but small dipole but these two substituents lie fairly high up in the smectic order. Clearly the dipole moment is not the only feature that must be considered. The OMe group has a dipole moment which operates across the long molecular axis and hence the OMe group would be expected to enhance smectic thermal stability. However, the OMe group lies low in the smectic order, probably because of rotation about the ring -O bond which aligns the net dipole nearer to the long molecular axis than would initially be envisaged.

c) The Role of the Lateral Substituent in Mesogens

This is best considered under the following three headings:

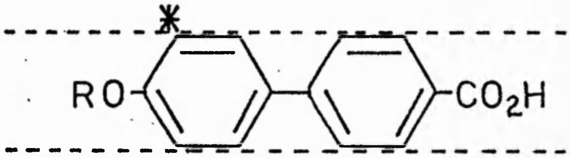
i) Molecular Broadening.

ii) Steric Effects.

iii) Branching of the Terminal Alkyl Chain.

i) Molecular Broadening

The most studied system in relation to molecular broadening is 4'-n-alkoxybiphenyl-4-carboxylic acid (XIV).



(XIV)

The breadth of the molecule can be considered as the smallest cylinder through which the molecule will pass, assuming that the flexible alkyl chain does not interfere. Thus if the breadth is small, the molecules can pack closer together and so enhance the thermal stability of the mesophase.

Any substituent at the $3'$-position (*) will broaden the molecule and so lower the liquid crystal thermal stability.

Opposing this effect is the increase in the molecular polarizability (or dipolarity) that occurs by the substitution of a ring -H by a ring -X. This will increase the lateral intermolecular attractions and so enhance liquid crystal thermal stability.

For the compound (XIV), the introduction of a substituent at the $3'$- position reduces the thermal stability of the nematic mesophase. However, this is not the case for the thermal stability of the smectic mesophase. There is no simple relationship between size and smectic thermal stability because dipole moments do contribute to the layered smectic order, and thus may counteract the destabilising effect of molecular broadening.

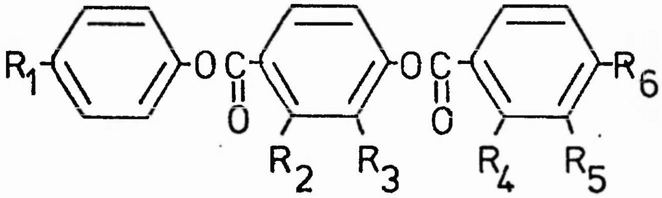
However, in general the effect of the lateral substituent on the mesogen is that:

i) the lateral substituent will decrease N-I transition temperatures, the larger the substituent, the greater the decrease in N-I transition temperature.

ii) The lateral substituent will decrease S-N or S-I transition temperatures more if the molecule is large, but the dependence on molecular size is sometimes counteracted by the substituent's dipole.

There are exceptions to these generalisations usually because the full breadth extension of the substituent is reduced by molecular geometry considerations or other 'side effects', e.g. hydrogen bonding, which can increase the thermal stability of a mesophase.

Di-substitution has an additive effect as demonstrated by VanMeter and Klanderman[78], who prepared a large number of liquid crystalline substituted phenyl 4-benzoyloxy-benzoates (XV). Included in their work were mono- and di-chlorinated compounds. These illustrated the decrease in mesophase thermal stability that occurs due to lateral substitution and also the additive effect of two such substituents. Some of their results are listed in Table 2.



(XV)

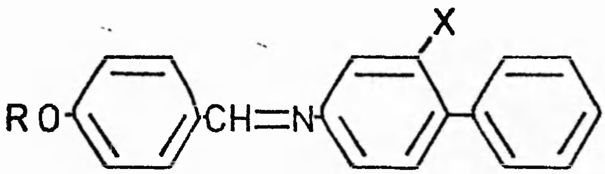
Table 2 - Transition Temperatures for the Esters (XV)

R_1	R_2	R_3	R_4	R_5	R_6	N-I (°)
n-C_5H_{11}	H	H	H	H	n-$C_5H_{11}O$	198.5
n-C_5H_{11}	H	Cl	H	H	n-$C_5H_{11}O$	151
n-C_5H_{11}	H	H	H	Cl	n-$C_5H_{11}O$	168
n-C_5H_{11}	H	Cl	H	Cl	n-$C_5H_{11}O$	123
n-C_5H_{11}	H	H	H	H	Cl	212
n-C_5H_{11}	Cl	H	H	H	Cl	150
n-C_5H_{11}	H	Cl	H	H	Cl	155
n-C_5H_{11}	H	H	Cl	H	Cl	153.5
n-C_5H_{11}	H	H	H	Cl	Cl	149.5
n-C_5H_{11}	H	Cl	Cl	H	Cl	89
n-C_5H_{11}	H	Cl	H	Cl	Cl	[93]

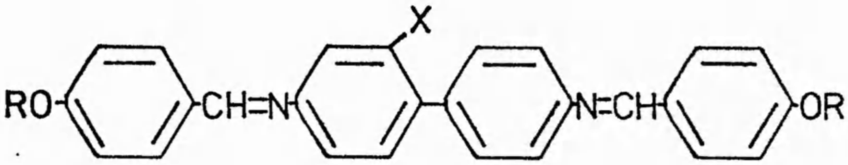
[ ] indicates a monotropic transition

ii) Steric Effects

Even though lateral substitution can broaden the molecule, it can also impose a steric effect on the system by causing a twist about one of the bonds, so that parts of the molecule are rotated out of the plane of the remainder of the molecule. The influence of steric effects on mesophase thermal stability is well illustrated by the Schiff's bases[38, 39] (XVI) and (XVII).



(XVI)



(XVII)

X = F, Cl, Br, I, CH_3 and NO_2

The following discussion typifies the results obtained. In 4′-n-octyloxybiphenyl-4-carboxylic acid, the introduction of a fluoro-substituent into the non-sterically affecting 3 -position decreases the smectic and nematic thermal stabilities by 0.5 and 0.9° respectively, whereas in (XVII) the sterically affecting 2-fluoro-substituent reduces the smectic thermal stability by 58.5° and the nematic thermal stability by 29.4°. The marked decrease in the nematic thermal stability was illustrated by a plot of the N-I transition temperatures for the various 2-substituents against an axis related to the broadening effect of the 2-substituent in (XVI) and (XVII). The plot was a straight line the gradient of which was much greater than that obtained for a range of similarly substituted mesogens in which no steric effects operated. Clearly, an additional factor, the influence of the steric effect, which increases in proportion to the size of the substituent, causes the nematic thermal stability to decrease at a faster rate than expected from a consideration of molecular broadening alone. The steric effect causes the rings to rotate about the 1,1′-bond so that the aromatic nucleii of the biphenyl entity are no longer coplanar (as they are in the solid state of biphenyl itself) and this not only increases intermolecular separation but also the thickness of the molecules in the region of the biphenyl rings, leading to a decrease in the anisotropy of molecular polarizability. Similar results were obtained for the smectic mesophase, but with the added complication that the interference from dipole moment forces impose variable effects on the S-N or S-I transitions. The destabilising steric effect can be of value if it decreases the thermal stability of the crystal-mesophase transition more than the mesophase-isotropic liquid transition.

iii) Branching of Terminal Alkyl Chains

Branching of the alkyl chain will lower the thermal stabilities of both nematic and smectic A phases. The effect is more pronounced when branching occurs at the 1-position (e.g. with a 1-methyl group), of whether the alkyl group is attached to the ring via an oxygen atom, e.g. in esters[40] or ethers[41], or attached directly[42]. The lowering of thermal stability becomes smaller as the methyl group progresses along the chain and the relative effects on the thermal stabilities of the smectic and nematic mesophases depend on the environment of the alkyl group.

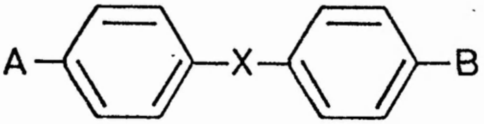
d) The Role of the Central Linking Group in Mesogens

The central linking group governs the mesophase thermal stability rather than the type of mesophase exhibited.

The N-I transition temperatures are enhanced if the central linking group can permit conjugation to occur between the rings. This increases the anisotropy of molecular polarizability, provided the molecule adopts a lath-like configuration. Thus central groups like -CH=N- and -CH=CH-, are rigid and can interact with the π-electrons of the ring. Saturated groups like $-CH_2-CH_2-$ are too flexible and contain no π-electrons for such an interaction with the ring.

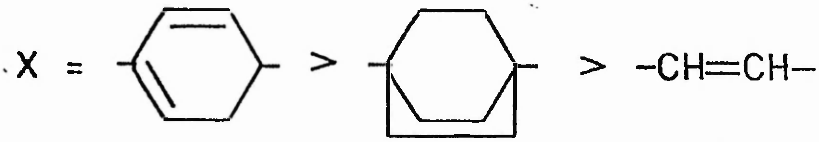
The applications of liquid crystals in the electronics industry depend upon the use of stable, low melting nematogens and cholesterogens, which given enantiotropic mesophases over a range that includes room temperature. An ideal range would be that the mesogen should melt no higher than $-10^{o}C$ and its mesophase should persist until at least $+60^{o}C$. This formidable requirement has not yet been met by a single compound, but eutectic mixtures of low melting mesogens have been prepared, e.g. the mixture E8 (marketed by B.D.H. Chemicals Ltd) has the transition temperatures C-N, approximately $-12^{o}C$; N-I, $70.5^{o}C$.

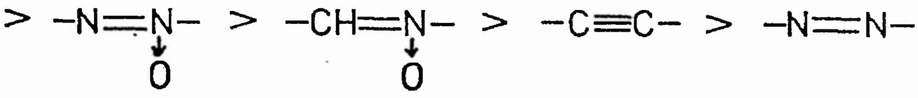
Many low temperature mesogens have a simple molecular structure of the type shown in (XVIII) where A and B are terminal groups and X is a central linking group.



(XVIII)

Gray[43] has produced a 'central linking group efficiency order' based on the structure (XVIII). The order is:





$$> -\underset{\substack{\downarrow \\ O}}{N}{=}N- \;>\; -CH{=}\underset{\substack{\downarrow \\ O}}{N}- \;>\; -C{\equiv}C- \;>\; -N{=}N-$$

> -CO.O- > NONE (i.e. BIPHENYLS).

Thus p-terphenyl derivatives have a high mesomorphic thermal stability, the corresponding biphenyl derivatives have a much lower mesomorphic thermal stability and the other linking groups lie midway between these two extremes.

Just as important as the N-I temperatures are the C-N temperatures of the mesogens, for which a meaningful correlation between melting point and structure does not exist. However, apart from the first three groups in the efficiency order, low melting mesogens can be found with any of the other central groups. In usage of liquid crystals in the electronics industry, the dielectric anisotropy[44-46, 68] of the liquid crystal is a very important property (Figure 19) since the sign and magnitude of $\Delta\epsilon$ governs the use to which the liquid crystal can be put.

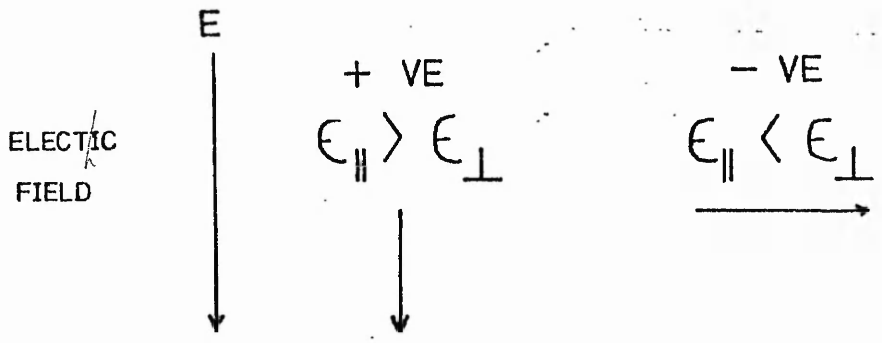


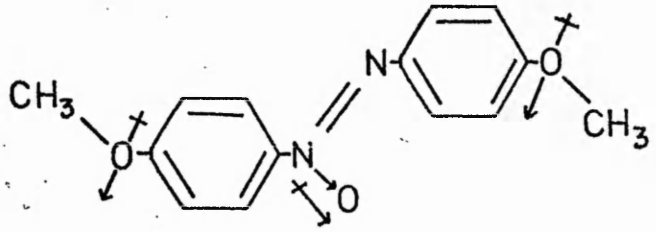
Figure .19 - Dielectric Anisotropy

When the dielectric anisotropy is positive, the director is oriented parallel to the electric field and this can be achieved with A=alkoxy, B=alkyl and X= -CH=N- in structure (XVIII). When the dielectric anisotropy is negative the director is aligned at right angles to the electric field, groups with a strong dipole is needed, e.g. A or B = -C≡N. Sometimes the mesogen may be required to have a dielectric anisotropy which changes sign at higher frequencies. Then there is a tendency to use n-butyl, n-pentyl, n-hexyl, n-heptyl or n-octyl as one of the terminal groups, A or B in structure (XVIII).

e) Features of Molecular Geometry Which Favour Smectic or Nematic/Cholesteric Phase Formation

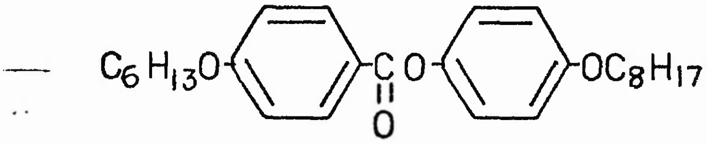
One of the basic problems in liquid crystal chemistry is one that might be termed liquid crystal engineering, i.e. problems relating to the synthesis of liquid crystals that possess precise smectogenic or nematogenic (or cholesterogenic) properties. This problem can be achieved with some degree of certainty, but there are several pitfalls that must be avoided.

The first to be overcome is that concerning the nature of the crystal lattice. Smectic properties can only be exhibited by a mesogen, if the molecules pack in a layered crystal lattice. Without X-ray diffraction data, this inherent property must be assumed. In addition, the intermolecular forces within the crystal lattice must not be too strong, otherwise the melting point of the compound will be high and the thermal motions within the melt may be so great that the cohesive forces are inadequate to maintain the proper alignment of the molecules. A delicate balance exists between the lateral and terminal cohesive forces within a molecule, which not only dictates the potential of a particular system to form liquid crystal phases, but also their type and stability. This balance of the cohesive forces is difficult to predict since their nature, direction and strength can only be judged by qualitative assessment. A good example of this is p-azoxyanisole (XIX) where the $-OCH_3$ groups each have



(XIX)

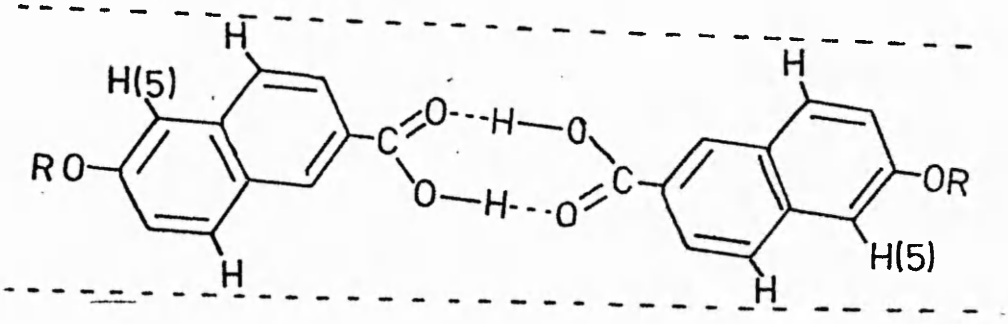
a strong dipole which is directed across the molecular axis. Hence, lateral molecular attractions should be enhanced, so giving a smectogen. However, p-azoxyanisole shows only nematic properties. The reason for this is uncertain, but it may be due to rotation about the ring -O bond resulting in a different orientation than that indicated in (XIX). In addition, the $-OCH_3$ group may interact, by conjugation, with the ring to which it is attached so affecting the dipole. The environment of a particular substituent may vary from one mesogen to another and this can affect the smectic or nematic/cholesteric tendencies of that substituent. The compound (XX) has two long n-alkoxy chains and these substituents in terminal positions are normally smectogenic in nature. However, the



(XX)

compound only shows nematic properties, probably due to conjugation between the carbonyl group of the ester and the ring.

When other considerations have been evaluated, a simple visual error can lead to incorrect predictions about the mesomorphic behaviour of a compound. A compound that looks linear when its structure is written down on paper may, in fact, not be so because some aspect of the molecular geometry has been overlooked. For example, consider the compound (XXI) the 6-n-alkoxy-2-napthoic acid. If drawn incorrectly, the dimer appears linear and hence lateral substitution at the 5-positions might be expected to reduce the smectic and nematic thermal stabilities because of the increase in breadth of the molecule. However, when



(XXI)

written out correctly, paying proper regard to bond angles and lengths as above, a 'gap' exists between the 5-positions and the dotted lines, which indicates the molecular breadth. This 'gap' can accommodate substituents of considerable size without broadening the molecule and thus the increase in molecular polarizability and dipolarity due to the introduction of the substituent at the 5-position will enhance the smectic and nematic thermal stabilities.

This last discussion emphasises how difficult it is to predict the type of liquid crystal which may predominate in a particular system. Nevertheless, the following list, taken from Dr Gray's book[48], indicates that it is possible to predict with some degree of certainty the type(s) of mesophase that a particular mesogen may exhibit.

i) Salts of carboxylic acids and amines are predominantly smectogenic compounds.

ii) Terminal ring-COOR, ring-CH=CHCOOR, ring-$CONH_2$ and ring-OCF_3 groups strongly favour smectic mesophase formation.

iii) Increasing the length of a terminal situated n-alkyl or n-alkxoy chain favours smectic mesophase formation.

iv) Ring-X terminal substituents increase N-I transition temperatures.

v) Ring-X terminal substituents such as -Ph, $-NHCOCH_3$ and $-OCOCH_3$ favour smectic more than nematic mesophase formation.

vi) Ring-X terminal substituents such as -CN, $-NO_2$ and $-OCH_3$ strongly enhance nematic thermal stability and often diminish smectic thermal stability.

vii) Lateral substituents which broaden a molecule markedly reduce the tendency of a compound to form liquid crystals. The thermal stability of a smectic liquid crystal is reduced to a greater extent than that of the nematic liquid crystal if the substituent is either are weakly dipolar, e.g. $-CH_3$, or large and only moderately dipolar, e.g. Br, I.

viii) Lateral substituents which do not broaden the molecule enhance liquid crystal thermal stability; the smectic phase is particularly enhanced if the substituent is dipolar.

ix) Steric effects within a molecule markedly reduce the potential of a compound to form a liquid crystal; smectic thermal stabilities are affected more than nematic thermal stabilities.

5. Aims of this Work

The aims of this present work were the synthesis and evaluation of homologous series of potential mesogenic compounds. The work entailed:

1. the synthesis and comparison of the mesomorphic behaviour of the homologous series of 4-biphenylyl $4''$-n-alkoxybenzoates with the isomeric homologous series of the $4''$-n-alkoxyphenyl biphenyl-4-carboxylates.
2. the synthesis and evaluation of the mesomorphic behaviour of introducing a nitrogen atom into the $4'$- and $2'$- positions of the homologous series of 4-($4'$- and $2'$- pyridyl) phenyl $4''$-n-alkoxybenzoates.
3. the synthesis and evaluation of introducing an N-oxide function into the N-oxides of the homologous series of the 4-($4'$-pyridyl) phenyl $4''$-n-alkoxybenzoates and 4-($4'$-n-alkoxyphenyl) pyridines in relation to their mesomorphic behaviour

and subsequently, the comparison of these two N-oxide homologous series with their analogous cyano compounds.

The relatively low N-I transition temperatures observed for the homologous series of the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates influenced the interest in sterically hindered biphenylyl esters. Subsequently, the homologous series of the 2′-fluoro- and chloro-4-biphenylyl 4″-n-alkoxybenzoates were synthesised, and comparison of their mesomorphic behaviour with that observed for the biphenylyl and 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates was made.

DISCUSSION

Contents

4. The Mesomorphic Transition Temperatures of the Homologous Series of the N-oxides of 4-(4$'$-Pyridyl) phenyl 4$''$-n-Alkoxybenzoates and their Comparison with the Mesomorphic Transition Temperatures of the Homologous Series of the 4-(4$'$-Pyridyl) phenyl 4$''$-n-Alkoxybenzoates.

5. The Mesomorphic Transition Temperatures of the Homologous Series of the N-oxides of the 4(4$'$-n-Alkoxyphenyl) pyridines.

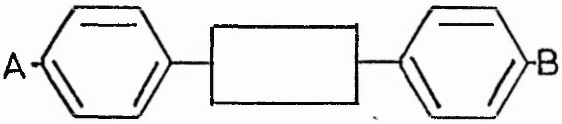
6. Summary.

The key to the graphs of transition temperature against the number of carbon atoms in the n-alkyl chain R are as follows:

○	C-S_A, C-N
△	N-I, S_A-I
▲	S_A-N
●	C-I

1. A Comparison of the Mesomorphic Transition Temperatures of the Homologous Series of the 4-Biphenylyl 4″-n-Alkoxybenzoates and the 4″-n-Alkoxyphenyl Biphenyl-4-carboxylates.

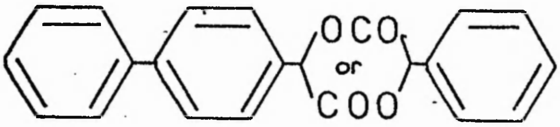
A large number of compounds that form liquid crystals fall into a general structural category indicated by (XXII), where the rectangle represents the central linking group.



(XXII)

The central linking group should ideally extend the rigidity and linearity of the p-disubstituted benzene rings. This may be done by, for example, the incorporation of a multiple bond or rigid hydrogen bonded function in the central group. The extension of the aromatic conjugation by the interaction of the π-cloud of a multiple bond in the central link with the π-electrons of the aromatic rings, generally enhances the mesophase thermal stability of the particular compound. When the central group is an ester linkage, the multiple bond ($\rangle C=O$) lies across the molecular axis, resulting in flexibility. Even though the linearity of the molecule is preserved by the stereochemistry of the ester unit, the flexible linkage results in a less thermally stable mesophase which may be monotropic. The inclusion of a p-disubstituted benzene ring into the A or B positions increases the mesophase thermal stability, since the aromatic nucleus is polarisable, planar and rigid.

The introduction of an ester linking group and a terminal p-disubstituted benzene ring in the structure (XXII) should give rise to a mesogen (XXIII) with enantiotropic mesophases that have relatively low thermal stability, since the monotropic tendencies of the ester linking function are offset by the mesophase-promoting character of the p-disubstituted benzene ring.

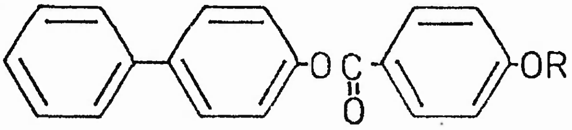


(XXIII)

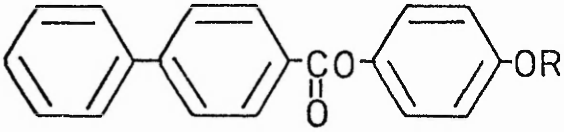
The examination of a homologous series by introducing n-alkyl or n-alkoxy groups at position B enables the mesomorphic properties of the particular type of system to be studied fully. Polymorphism may also occur as the homologous series is extended, and comparison of a number of such homologous series may give information, for example, on the effect of molecular geometry on the properties and thermal stabilities of polymorphic smectic mesophases. The actual homologue for which smectic properties are first observed in a series is of little significance. The main reason for this is that the smectic mesophase may be monotropic and its detection depends upon how far below its melting point the compound can be cooled before crystallisation occurs. The onset of the smectic mesophase is therefore influenced by both the melting point and the supercooling tendencies of the compound. These two factors are related to the crystal structure of the compound, and even within a homologous series, the crystal lattice type may vary irregularly as the series is ascended.

Unusual effects may also be observed as the homologous series is ascended. A good example of this is the series of 2-(4′-n-alkoxybenzylideneamino) fluorenones[43] (Figure 17, p. 48). After exhaustive purifications, the usual alternation between odd and even carbon members of the n-alkoxy series still occurred, but both N-I transition temperature curves fall initially to a shallow minimum and then rise slightly before falling again. This kind of pattern is not common and is difficult to evaluate.

The isomeric series of esters (XXIV) and (XXV) formed the basis of this present work.



(XXIV)



(XXV)

The plot of liquid crystal transition temperatures against the number of carbon atoms in the n-alkyl chain for the 4″-n-alkoxyphenyl biphenyl-4-carboxylates is given in Figure 20.

The N-I transition temperatures alternate in typical fashion with the points fitting two falling curves, the upper curve for the members with an even number of carbon atoms and the lower curve for the members with an odd number of carbon atoms in the n-alkoxy chain.

All the 4″-n-alkoxyphenyl biphenyl-4-carboxylates are enantiotropic except for the methoxy and hexadecyloxy compounds, and as with many homologous series, there is no correlation between the C-N transition temperature (melting point) and the number of carbon atoms in the n-alkyl chain R. All the 4″-n-alkoxyphenyl biphenyl-4-carboxylates are nematogens and no smectic properties were observed, even though most of the esters were cooled to about 96-102° (approximately 20-30° below the C-N transition temperature) before crystallisation occurred.

The plot of the liquid crystal transition temperatures against the number of carbon atoms in the n-alkyl chain for the 4-biphenylyl 4″-n-alkoxybenzoates is given in

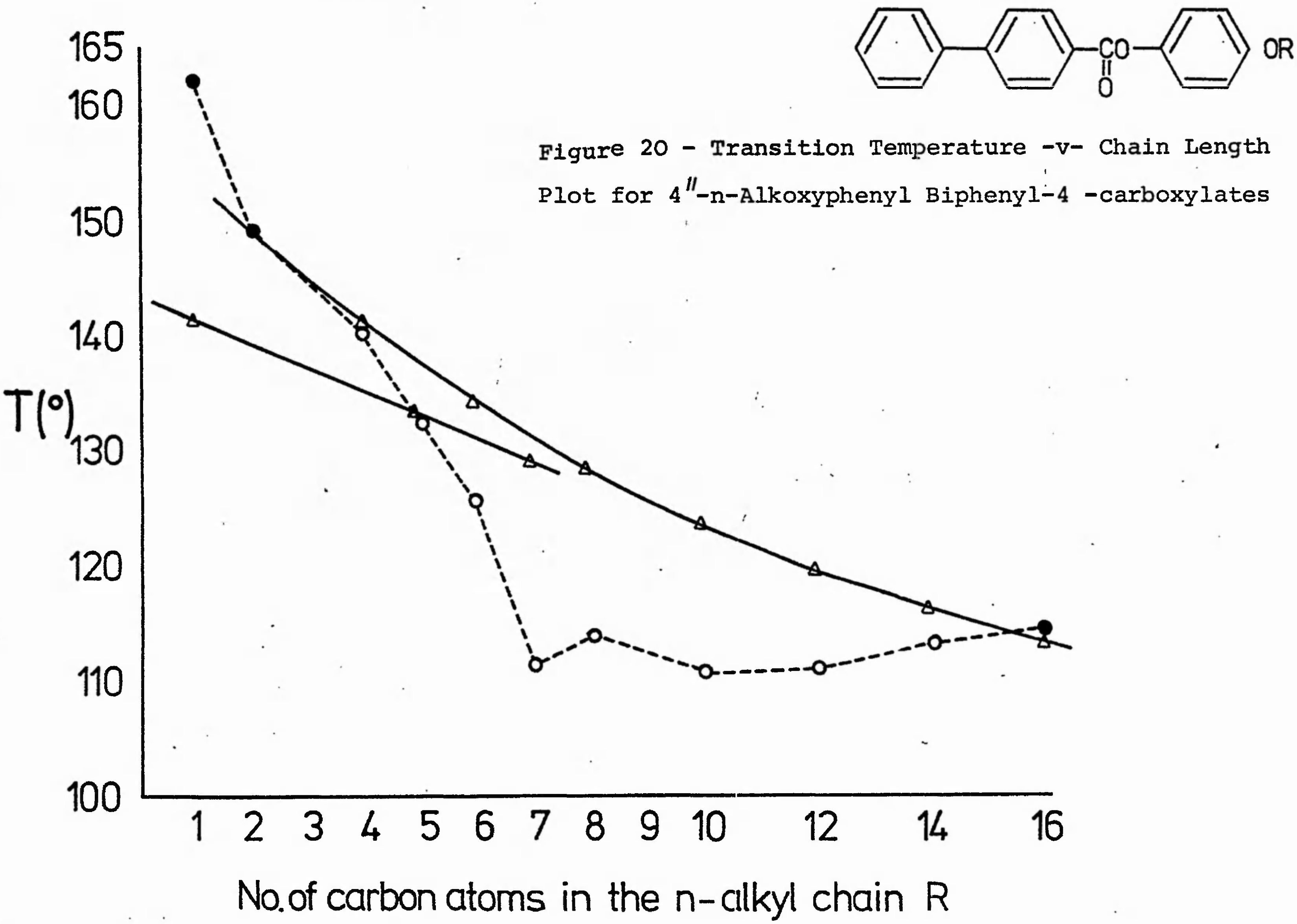


Figure 20 - Transition Temperature -v- Chain Length Plot for 4″-n-Alkoxyphenyl Biphenyl-4 -carboxylates

Figure 21. As with the $4''$-n-alkoxyphenyl biphenyl-4-carboxylates, the N-I transition temperatures alternate on two smoothly falling curves, the upper curve for the members with an even number of carbon atoms and the lower one for members with an odd number of carbon atoms in the n-alkyl chain, R.

In contrast to the previous isomeric esters, smectic mesophases are shown by the n-octyloxy-, -decyloxy-, -dodecyloxy- and -tetradecyloxy- compounds. The S-N transition temperatures do not alternate, but lie on a single smooth curve which initially rises steeply and then levels out, suggesting that if an extended series had been studied, the rising S-N curve would soon merge with the falling N-I curve to give a single S-I curve. The smectic mesophases of the n-octyloxy-, -decyloxy-, -dodecyloxy- and -tetradecyloxy- compounds were shown to be smectic A phases by miscibility studies on mixtures with a compound with a smectic mesophase known to be smectic A [4-(4$'$-pyridyl) phenyl 4$''$-n-tetradecyloxy-benzoate].

There was no correlation between the C-N or C-S transition temperatures (melting points) and the number of carbon atoms in the n-alkyl chain R. The methoxy-, ethyloxy-, n-butyloxy- and -pentyloxy- compounds were all monotropic and the n-octyloxy- and -decyloxy- compounds exhibited monotropic smectic mesophases.

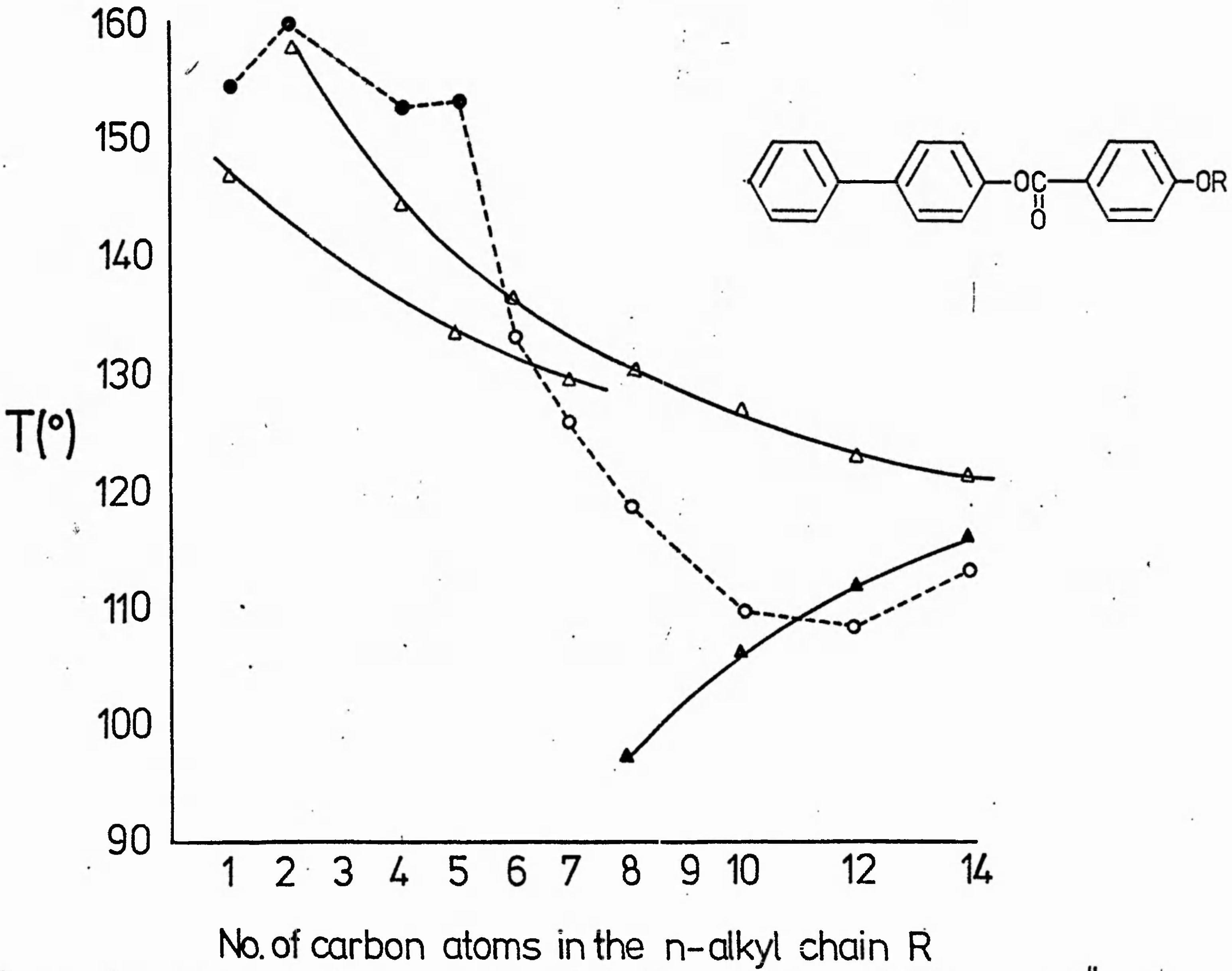


Figure 21 - Transition Temperature -v- Chain Length Plot for 4-Biphenylyl 4″-n-Alkoxybenzoates

For simplicity, the 4-biphenylyl 4″-n-alkoxybenzoates will be designated the 'benzoate esters' and similarly, the 4″-n-alkoxyphenyl biphenyl-4′-carboxylates, the 'biphenyl carboxylate esters'.

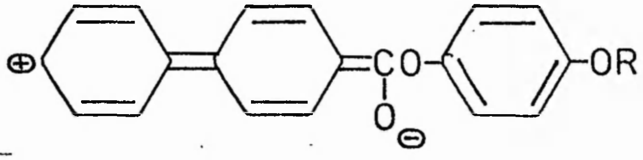
Although the thermal stabilities of the two series are roughly the same, the nematic thermal stabilities of the benzoate esters (Table 3) are in each case higher throughout the homologous series than their counterparts in the biphenyl carboxylate esters. Initially, the difference is quite appreciable but it decreases rapidly as the length of the n-alkyl chain R is increased, until at the n-decyloxy homologue, the difference in the nematic thermal stability begins an increasing trend.

Table 3 - The Difference (ΔT) in the N-I Transition Temperatures of Corresponding 4-Biphenylyl 4″-n-Alkoxybenzoates and 4″-n-Alkoxyphenyl Biphenyl-4-carboxylates

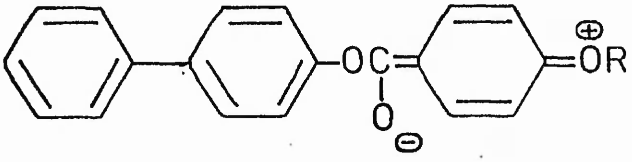
n-R	ΔT Nematic	n-R	ΔT Nematic
CH_3	8°	C_7H_{15}	0.5°
C_2H_5	7.5	C_8H_{17}	2.0
C_4H_9	2.5	$C_{10}H_{21}$	3.5
C_5H_{11}	0.5	$C_{12}H_{25}$	4.0
C_6H_{13}	2.5	$C_{14}H_{29}$	4.5

There seems no obvious reason for these differences in nematic thermal stability. Second order effects on the lateral and terminal cohesive forces as the n-alkyl chain length is increased are probably responsible. These will differ in the two isomeric series of esters. A possible reason for the initial large difference between the benzoate esters and the biphenyl carboxylate esters may be that the n-alkoxy chain can participate in mutual conjugation with the ester carbonyl group in the benzoate esters but not in the biphenyl carboxylate esters, so increasing the polarizability of the former series. This will be discussed shortly. However, it would have been expected that this effect would remain constant throughout the series.

The most striking difference between the two homologous series is the appearance of the smectic mesophase for the benzoate esters, although the only difference in molecular geometry between the two isomeric series is the relative position of the carbonyl moiety of the ester linking function with respect to the n-alkoxy chain. In both cases the π-electrons of the carbonyl group of the central ester linking function can overlap with the π-electrons of the aromatic rings. In the case of the biphenyl carboxylate esters, the conjugation between the carbonyl moiety and the aromatic π-cloud can be transmitted along the biphenyl section of the compound (XXVI), whilst in the case of the benzoate esters, the conjugation involves the ether oxygen of the n-alkoxy chain (XXVII).



(XXVI)

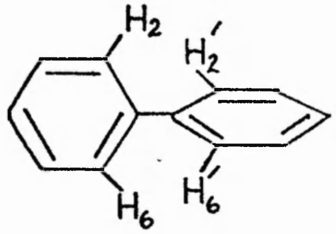


(XXVII)

Such conjugation will increase the dipole vector, since the vector quantity is made up of two components, one of which is the separation of the two charges. The conjugation present in the two esters aids this separation of charges and so enhances the dipole moment of the molecule.

Let us now consider the two esters in turn. For the 4-biphenylyl 4''-n-alkoxybenzoates, maximum overlap of the p-orbitals, and subsequent mutual conjugation between the side chain alkoxy group and the carbonyl oxygen through the aromatic ring, will take place if all these parts of the molecules are coplanar. Thus any factor which opposes coplanarity will reduce the overlap of the p-orbitals and in turn the degree of conjugation. Neubert[47] suggested that in 4,4'-disubstituted phenyl benzoates there is a twist which "principally involves the phenol moiety carbon-oxygen bond, the carbonyl group being in-plane and overlapping with the aromatic π-electrons. This allows a measure of stabilisation including not only the carbonyl group but also the unshared pair overlap between the ether link and the aromatic ring". Thus in disubstituted phenyl benzoates, the geometry of the ester linking function is correct for maximum overlap, making the conjugation between the carbonyl entity and the aromatic ring carrying the n-alkoxy chain very strong.

If we consider the π-overlap of the lone pair of electrons of the oxygen atom of the ester linking function and the π-electrons of the biphenyl rings, we must conclude that this conjugation will not be very significant, partly because the electron donating oxygen atom is in close proximity to a very powerful -M group, the carbonyl group, but principally because of the twist about the $1,1'$-bond of the biphenyl moiety of the ester. In the solid state, biphenyl is coplanar (because of crystal packing requirements) but in solution (or the liquid state), the interplanar angle is about 45^{o} due to the repulsion of the two hydrogen atoms H_2 and H_2' and H_6 and H_6' (XXVIII).



(XXVIII)

The liquid crystalline state is, thermodynamically, very much more like the liquid (or solution) than the solid. Hence such a twist about the 1,1'-bond of the biphenyl moiety of the ester can be envisaged for the mesophases of the esters. The extent to which this twist can affect the electronic transmission from one ring to another has been demonstrated by Berliner and Blommers[52] and by Byron, Gray and Wilson[51]. The work of Byron et. al., involved the comparison of the ionisation constants for 3' and 4'-substituted biphenyl-4-carboxylic acids with the corresponding 3- and 4-substituted benzoic acids. A linear relationship was obtained between a plot of pka values against the Hammett σ-values. The gradient of this plot gave the reaction constant (p-value), which represents the susceptibility of the reaction series to ring substitution and is independent of the nature of the substituent. Byron, Gray and Wilson[51] obtained two p-values, one for the 3'-substituents, the other for the 4'-substituents. For the 4'-substituted biphenyl-4-carboxylic acids, the p-value obtained was +0.45 and that for the 3'-substituted biphenyl-4- carboxylic acids was +0.30. Thus relative to the analogous benzoic acids, a 45% transmission of the electronic effects occurs for a 4'-substituent and a 30% transmission for a 3'-substituent i.e. only about one-third of the electronic effect is transmitted from one ring to the other due to the twist about the 1,1'-bond of biphenyl. These results indicate that in the 4-biphenylyl 4''-n-alkoxybenzoates, the conjugation between the oxygen moiety of the ester linking function across the biphenyl ring system will be seriously curtailed. This will severely limit the separation component of the dipole vector acting along the molecular axis between the oxygen and the biphenyl ring system.

Nevertheless, the 4-biphenylyl 4''-n-alkoxybenzoates can be envisaged as having two separate and distinct regions (Figure 22).

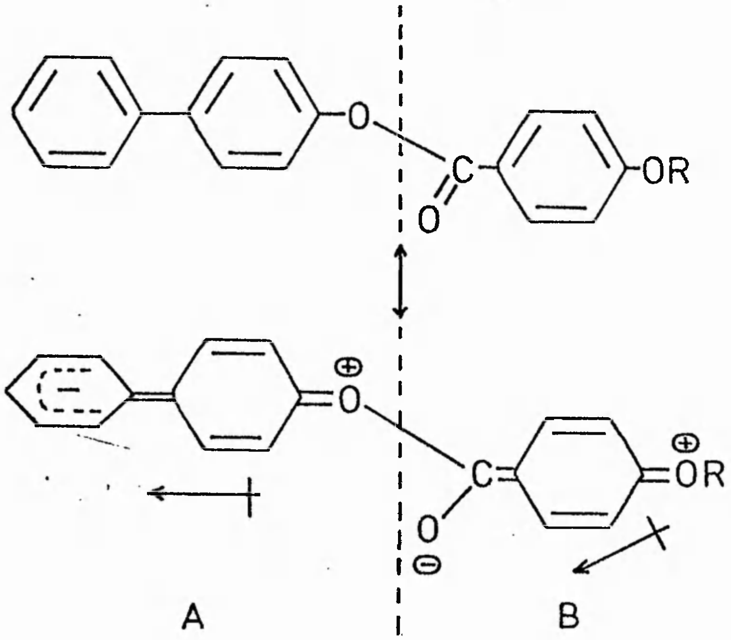


Figure 22 - The Two Distinct Regions of the 4-Biphenylyl 4''-n-Alkoxybenzoate Molecule

In A, the biphenyl region, there is a relatively small dipole which lies along the major molecular axis. Such a dipole will increase the ratio of terminal to lateral cohesive forces and this, along with the packing constraints caused by the twisting about the $1,1'$-bond of the biphenyl ring system, will decrease the potential of the system to form smectic mesophases.

In B, the phenyl region, the strong dipole acting at an angle to the major molecular axis (which increases the lateral intermolecular cohesive forces), and the increase in the packing efficiency as the n-alkyl chain R is lengthened, will increase the potential of the system to form smectic mesophases, which appear at the n-octyloxy compound.

Like the 4-biphenylyl $4''$-n-alkoxybenzoates the molecules of the $4''$-n-alkoxyphenyl biphenyl-4-carboxylates can be divided into two distinct parts, namely; the biphenyl (A) and phenyl (B) regions of the molecule (Figure 23).

In the biphenyl region (A) of the molecule, the carbonyl part of the ester linking function can overlap its π-electrons with the π-cloud of the biphenyl system. However, as with the benzoate esters, extended conjugation does not occur because of the twist about the $1,1'$-bond of the biphenyl system. Hence the separation component of the dipole vector is limited, essentially, to the first

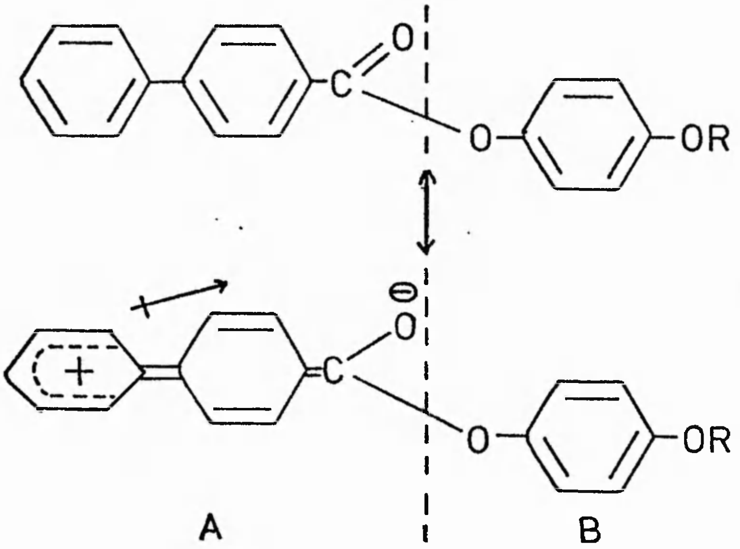


Figure 23 - The Two Distinct Regions of the 4''-n-Alkoxyphenyl Biphenyl-4-carboxylate Molecule

aromatic ring of the biphenyl system. Thus the magnitude of the dipole will be small although its direction will be at an angle to the major molecular axis, (slightly enhancing the tendency of the molecule to form smectic mesophases).

In contrast to the benzoate esters, mutual conjugation of the alkoxy group and the carbonyl group of the ester linking function is not possible in the biphenyl carboxylate series. Since this was responsible for a dipole that made an appreciable contribution to the lateral cohesive forces in the former series, it is not surprising that the carboxylate esters do not show smectic mesophases.

Thus comparison of the two isomeric homologous series of 4-biphenylyl 4''-n-alkoxybenzoates and 4''-n-alkoxyphenyl biphenyl-4-carboxylates, shows that the mode of attachment of the ester linking function has little effect on the nematic thermal stability, but that smectic mesophases are shown only in the series in which the lateral cohesive forces are affected by the dipole resulting from the mutual conjugation of the n-alkoxy group and the carbonyl group of the ester linking function. It should be stressed that in the biphenyl carboxylate ester series (that did not show smectic properties), supercooling of the nematic melt was possible to a temperature (96-102°) well below that at which the smectic mesophases appear in the benzoate ester series, i.e. the non-appearance of smectic mesophases in this series was not merely a function of melting point or the supercooling properties of the melt.

After the synthesis and investigation of the 4-biphenylyl 4″-n-alkoxybenzoates and 4″-n-alkoxyphenyl biphenyl-4-carboxylates had been completed, a short paper by Sadashiva and Subba Rao[53] was published. This described the synthesis and certain of the liquid crystalline properties of members of the homologous series of 4-biphenylyl 4″-alkoxybenzoates (the methoxy- to n-octyloxy-, and the n-decyloxy- and n-dodecyloxy- compounds were investigated). The results of Sadashiva and Subba Rao and those obtained in the present work for these esters appear in Table 4.

Sadashiva and Subba Rao commented that "the plot of the transition temperatures versus the number of the carbon atoms in the alkyl chain......shows the usual odd-even effect". However, the alternation in the N-I transitions is displayed unusually in their paper as a 'zig-zag' graph,

Table 4 - Transition Temperatures for the 4-Biphenylyl 4''-n-Alkoxybenzoates

n-R	Transition Temperature									
	The Present Work					Sadashiva & Subba Rao				
	C-I	C-S$_A$	C-N	S$_A$-N	N-I	C-I	C-S$_A$	C-N	S$_A$-N	N-I
CH_3	155°				[147°]	157-157.5°				[145°]
C_2H_5	160				[157]	161-162				[157.5]
C_3H_7						146-147				[136]
C_4H_9	153				[143]	158-159				[142.5]
C_5H_{11}	153.5				[133.5]	144-145				[113.5]
C_6H_{13}			133°		136.5			132.5°		135.5
C_7H_{15}			126		129.5			128		130
C_8H_{17}			119	[97.5]	130.5			120		131
$C_{10}H_{21}$			110	[106.5]	127			111	[106]	126.5
$C_{12}H_{25}$		108.5°		112	123		110.2°		113.2	124.5
$C_{14}H_{29}$		113-114		116.5	121.5					

[ ] indicates a monotropic transition

joining the points for successive esters rather than in the customary manner, showing two smoothly falling curves which tend towards coincidence as the length of the n-alkyl chain R is increased (Figure 24). When the reported N-I transition temperatures are plotted in this latter manner, it is immediately apparent that their point for the n-pentyloxy- compound lies approximately 20° below its expected position on the lower curve, and that the gradient of this curve is much less than that for the upper curve, so that the two curves rapidly converge as the length of

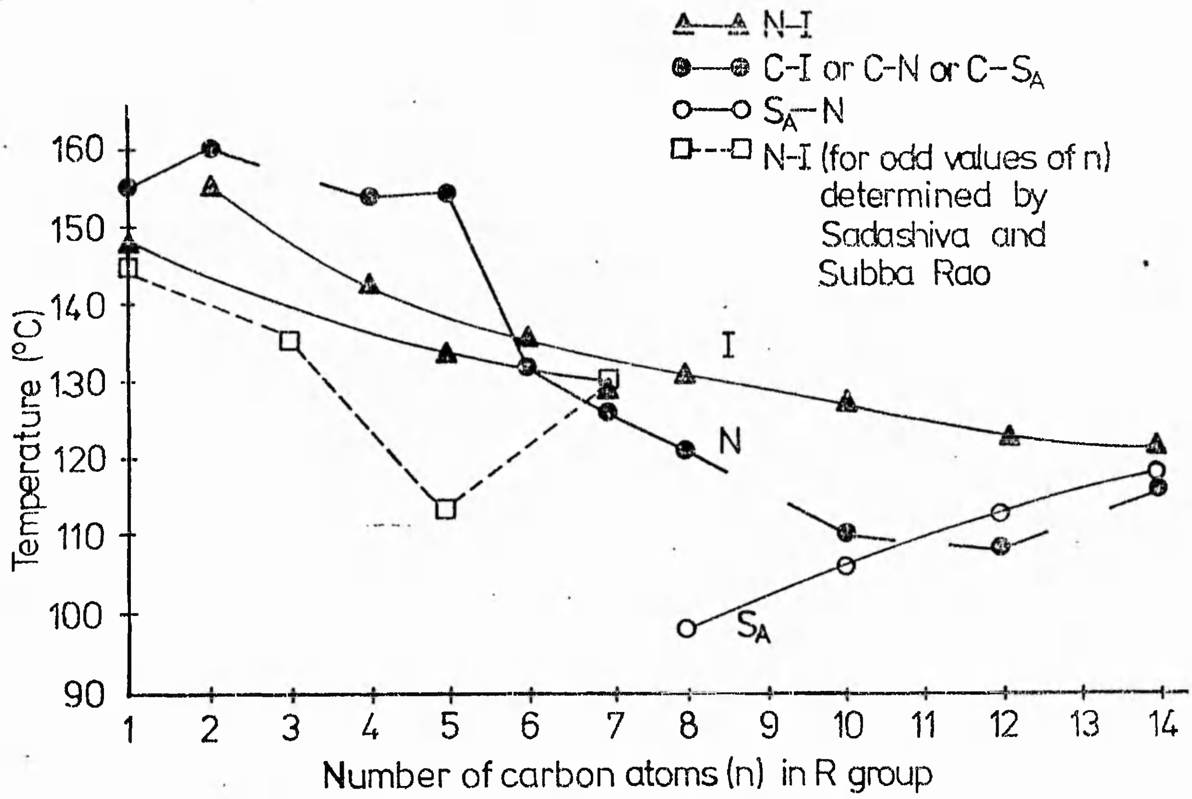


FIGURE 1. Plot of transition temperatures against alkyl chain length (n) for 4-biphenylyl 4''-n-alkoxybenzoates (I)

the 4-biphenylyl 4''-n-alkoxybenzoates (I)

Sadashiva and Subba Rao did not report the monotropic S-N transition at 97.5° noted for the n-octoxy- compound in the present work, nor did they identify the type (smectic A) of the smectic mesophase shown by this series of compounds.

For the esters with an even number of carbon atoms in the n-alkoxy chain, the N-I transition temperatures obtained by Sadashiva and Subba Rao and those obtained in the present work are in reasonable agreement. However for the esters with an odd number of carbon atoms in the n-alkoxy chain, the N-I transition temperature curve of Sadashiva and Subba Rao has a much shallower gradient than that obtained in the present work. Clearly, Sadashiva and Subba Rao's sample of the n-pentyloxy- compound was impure and it is possible that other members of their 'odd' series may also have been slightly contaminated. Although the n-propyloxy- compound was not prepared in the present work, it is estimated that the value reported by Sadashiva and Subba Rao is at least 2° low.

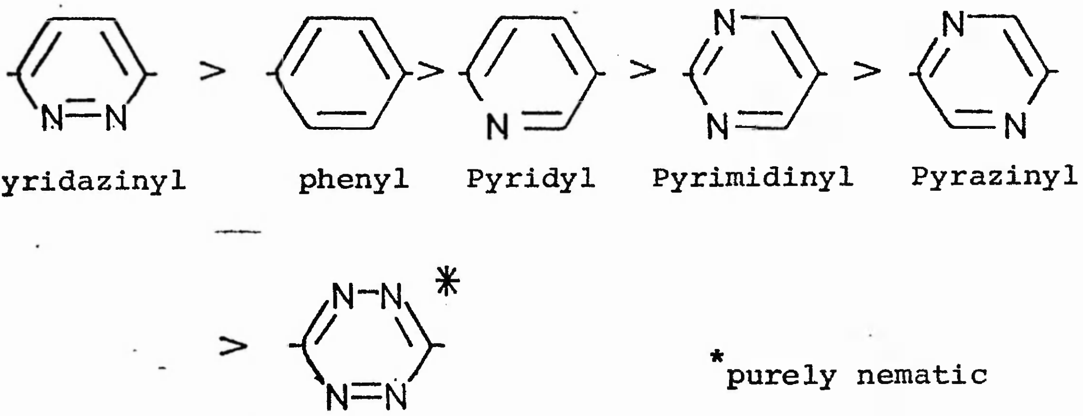
2. A Comparison of the Mesomorphic Transition Temperatures of the Homologous Series of the 4-Biphenylyl 4''-n-Alkoxybenzoates and their 4-(4'-Pyridyl) phenyl and 4-(2'-Pyridyl) phenyl Analogues.

Mesogens containing Heterocyclic Rings.

Relatively very few mesogens containing heterocyclic rings have been synthesed. A recent review by Gray[43] on the systematic work conducted on heterocyclic mesogens emphasised this point. However, three efficiency orders were given by Gray[43]. The first two orders, based on the work of Schubert et al[57, 58] on compounds related to the heterocyclic analogues of substituted terphenyl compounds, show the effect of a heterocyclic central ring system on the smectic behaviour of these compounds. The third efficiency order, based on the work of Nash and Gray[59], obtained from compounds of the type (XXIX) gives an order of influence on the thermal stability of the nematic phase.

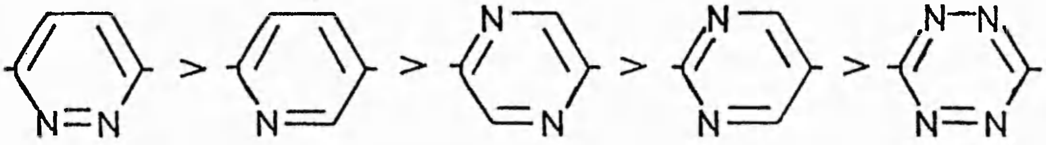
In general, the heterocyclic analogue will give less stable liquid crystals, and in some cases the introduction of a heterocyclic group will inhibit the formation of a

Smectic:

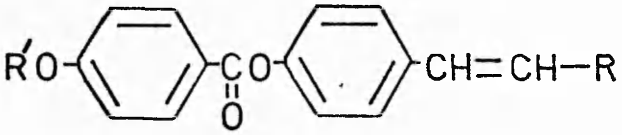


*purely nematic

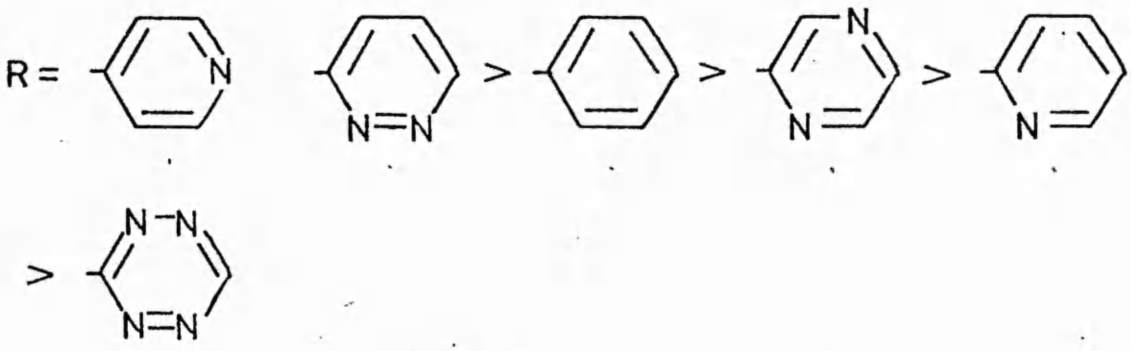
Nematic:



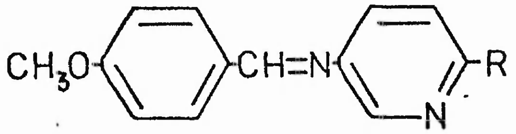
The position of the phenyl group in the nematic order cannot be decided.



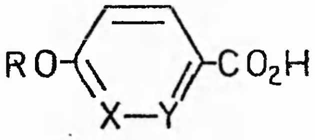
(XXIX)



mesomorphic phase, although the benzene analogue is liquid crystalline. The heterocyclic anils (XXX) and the substituted pyridine carboxylic acids (XXXI) are two good examples of this, although many more are cited in Gray's review[43].



(XXX)



X = N or CH.
Y = CH or N.

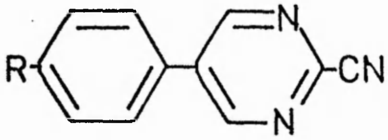
(XXXI)

In the heterocyclic acids prepared by Champa[60], there are some compounds with very low N-I transition temperatures, e.g. R = n-C_3H_7; N-I, 9.3°; R = n-C_4H_9 (the pyridyl analogue of MBBA); N-I, 6.4°, although most of the mesogens gave monotropic mesophases (R = n-C_8H_{17} was enantiotropic). When the methoxy terminal group was replaced by an ethoxy group and R = n-C_4H_9 (the pyridyl analogue of EBBA), two smectic mesophases were observed, even though EBBA itself is a nematogen. This illustrates the marked tendency to form a smectic mesophase that occurs when a pyridine nitrogen atom is introduced in a lateral (as opposed to a terminal) position.

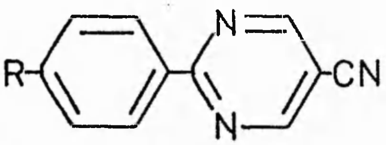
In the case of the substituted pyridine carboxylic acids prepared by Paviluchenko et al[61], the position of the nitrogen (X or Y) in the pyridyl ring determines whether or not the compound exhibits mesomorphic behaviour. In the 4-n-heptyloxypyridine carboxylic acid ($R = n\text{-}C_7H_{15}$, $X = N$, $Y = CH$), the acid gave a enantiotropic nematic phase (N-I, 89.5°) but when X = CH and Y = N, no mesomorphic behaviour was observed for the carboxylic acid. This is probably due to intra-molecular hydrogen bonding between the nitrogen and the carboxylic acid group, which interferes with dimer formation. All the substituted pyridine carboxylic acids prepared by Paviluchenko et al[61] had lower N-I transition temperatures than their benzene analogues[62], and the smectic C phase exhibited by the 4-n-alkoxybenzoic acids (for the n-heptyloxy and subsequent homologues) was not observed in the pyridyl compounds.

Both these examples show the importance of the environment in which the pyridine ring is placed. In the case of EBBA, the replacement of a benzenoid ring by a pyridyl ring causes purely smectic behaviour to be observed, whilst the substituted pyridine carboxylic acids show only nematic properties.

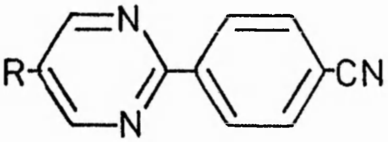
Recent interest in the field effect displays based on the twisted nematic effect has led to a growing demand for liquid crystals with a positive dielectric anisotropy. Classic examples are the n-alkyl- and n-alkoxy-cyanobiphenyls of Gray[63, 64]. However, alkylcyano- and alkoxycyano-phenylpyrimidines[65] (XXXII) to(XXXV)also have a high positive dielectric anisotropy and in the case of the compounds (XXXIII) and (XXXIV), exhibit relatively low enantiotropic nematic mesophases.



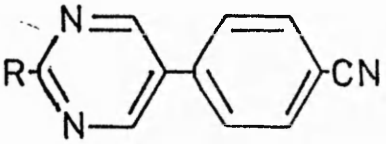
(XXXII)



(XXXIII)



(XXXIV)

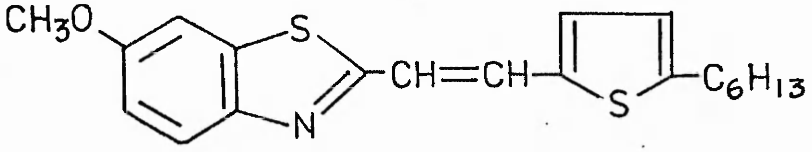


(XXXV)

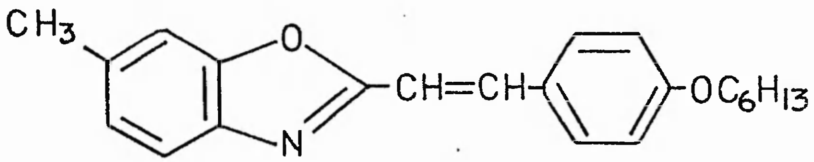
(XXXIII); R = n-C_7H_{15}; C-N, 44.5-45°; N-I, 51°

A recent patent taken out by F. Hoffmann-La Roche[65] concerns many eutectic mixtures involving the alkylcyanophenylpyrimidines (XXXIII) and (XXXIV), several of which also involve the use of 4-cyano-4'-n-heptyl-biphenyl.

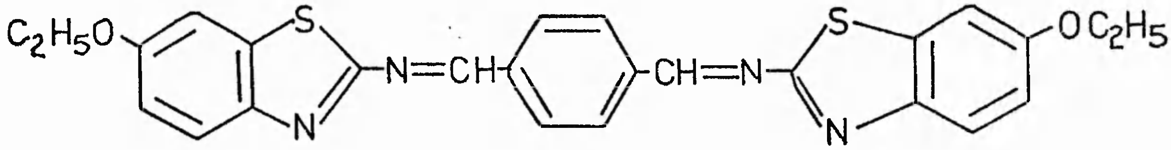
A few other heterocyclic compounds have been found to show mesomorphic behaviour e.g. disubstituted benzazoles (see overleaf) but further synthetic work is needed before a comparison of the effect of molecular geometry on the mesomorphic properties of these compounds can be made.



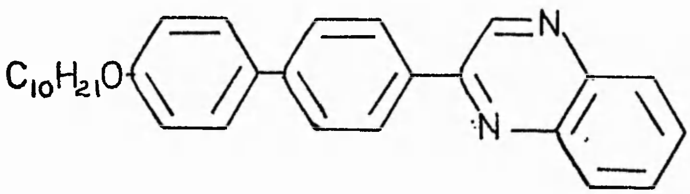
C-N, 74.6°; N-I, [43.2] [61]



C-N, 91.5°; N-I, 122.9° [61]



See Gray[43]



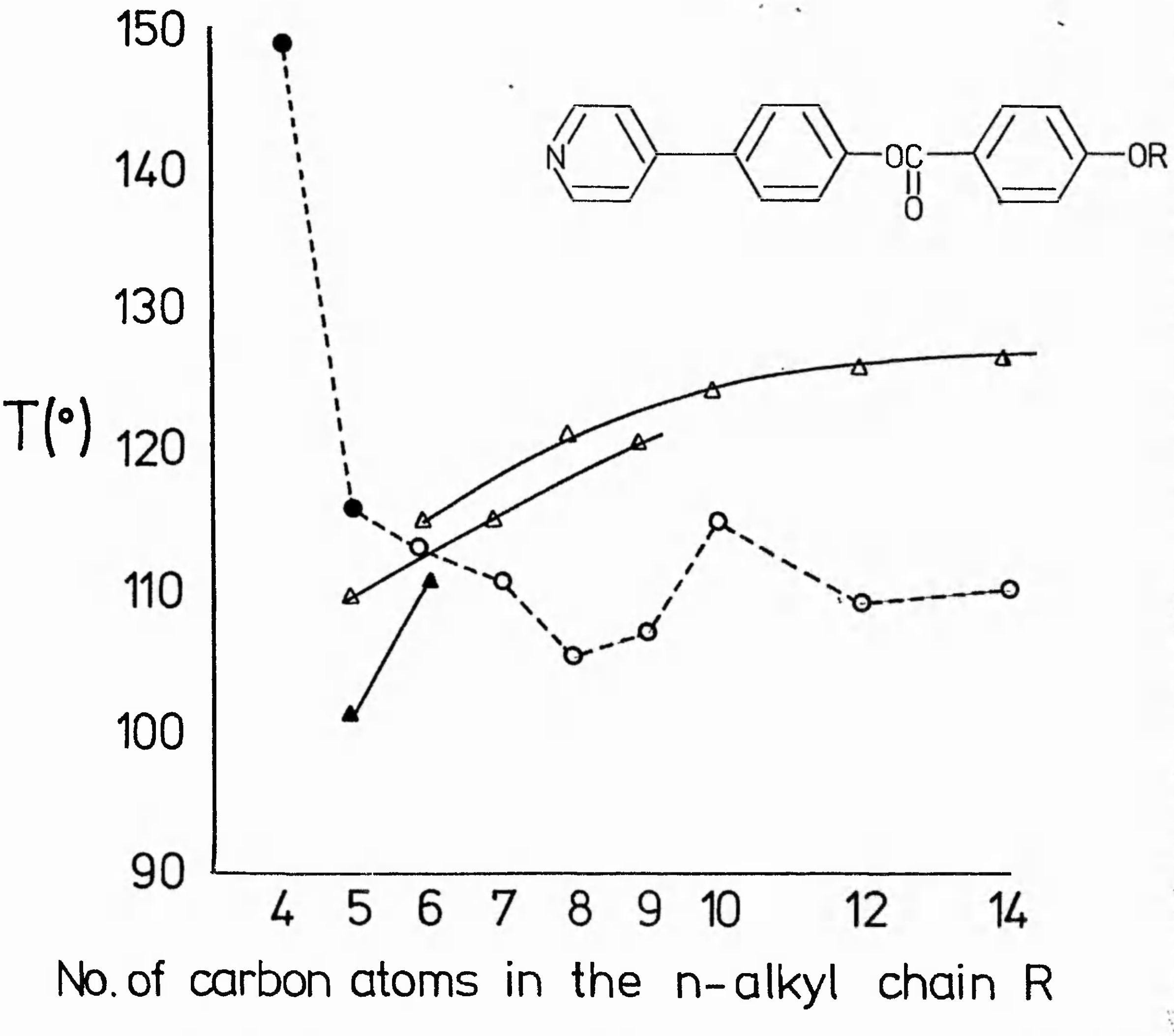
See Gray[43]

In the present work, in an attempt to evaluate the effect of a pyridine nitrogen atom in a 'terminal' as opposed to a 'lateral' position, the mesomorphic thermal stabilities of the 2'- and 4'-pyridylphenyl analogues of 4-biphenylyl 4''-n-alkoxybenzoates have been compared. As there was only a relatively small difference in the mesomorphic thermal stabilities of the isomeric homologous series of 4-biphenylyl 4''-n-alkoxybenzoates and 4''-n-alkoxyphenyl biphenyl-4-carboxylates, there seemed little to be gained from the synthesis and study of the pyridyl phenyl analogues of both of these series of esters.

Principally because the 4-biphenylyl 4''-n-alkoxybenzoates showed both smectic and nematic properties, it was decided to prepare and study their pyridylphenyl analogues, namely the 4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates and the 4-(2'-pyridyl) phenyl 4''-n-alkoxybenzoates. An additional reason for this choice was that the synthetic work involved appeared to be reasonably straightforward. Routes to the 4-(4'-pyridyl)- and 4-(2'-pyridyl) phenols were known and the compounds were readily purified, whereas the synthesis and purification of the corresponding pyridylbenzoic acids (required for the preparation of the pyridylphenyl analogues of the 4''-n-alkoxyphenyl biphenyl-4-carboxylates) seemed to present certain problems. For example, it was found that 4-phenylpyridine resisted Friedel-Crafts acylation in the phenyl ring, and the introduction of the carboxyl group to give 4-(4'-pyridyl) benzoic acid via the diazonium salt involved several steps and resulted in a poor yield. As the acid was zwitterionic, its purification was also more difficult than that of the corresponding phenol.

The Mesophase Transition Temperature of the Homologous Series of the 4-(4′-Pyridyl) phenyl 4″-n-Alkoxybenzoates: The plot of the transition temperatures of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates against the number of carbon atoms in the n-alkyl chain R is given in Figure 25.

Figure 25 - Transition Temperature -v- Chain Length Plot for: 4(4′-Pyridyl) phenyl 4″-n-Alkoxybenzoates



The n-heptyloxy-, -octyloxy-, -nonyloxy-, -decyloxy-, -dodecyloxy and -tetradecyloxy- homologues of this series gave enantiotropic smectic mesophases. For these homologues, no nematic properties were observed. The mesomorphic transition temperature(s) for the n-butyloxy compound was not obtained by optical microscopy, but a small peak was detected on the differential thermal analysis thermogram at 112° during the cooling cycle, prior to crystallisation of the sample. The enthalpy of the transition corresponding to this peak was not determined due to its close proximity to the very large solidification peak. Because of the mesomorphic behaviour of the other homologues of this series, this peak must correspond with the monotropic N-I transition for the n-butyloxy compound. The n-pentyloxy compound gave both monotropic nematic and smectic mesophases, whilst the n-hexyloxy compound exhibited a monotropic smectic phase and an enantiotropic nematic phases.

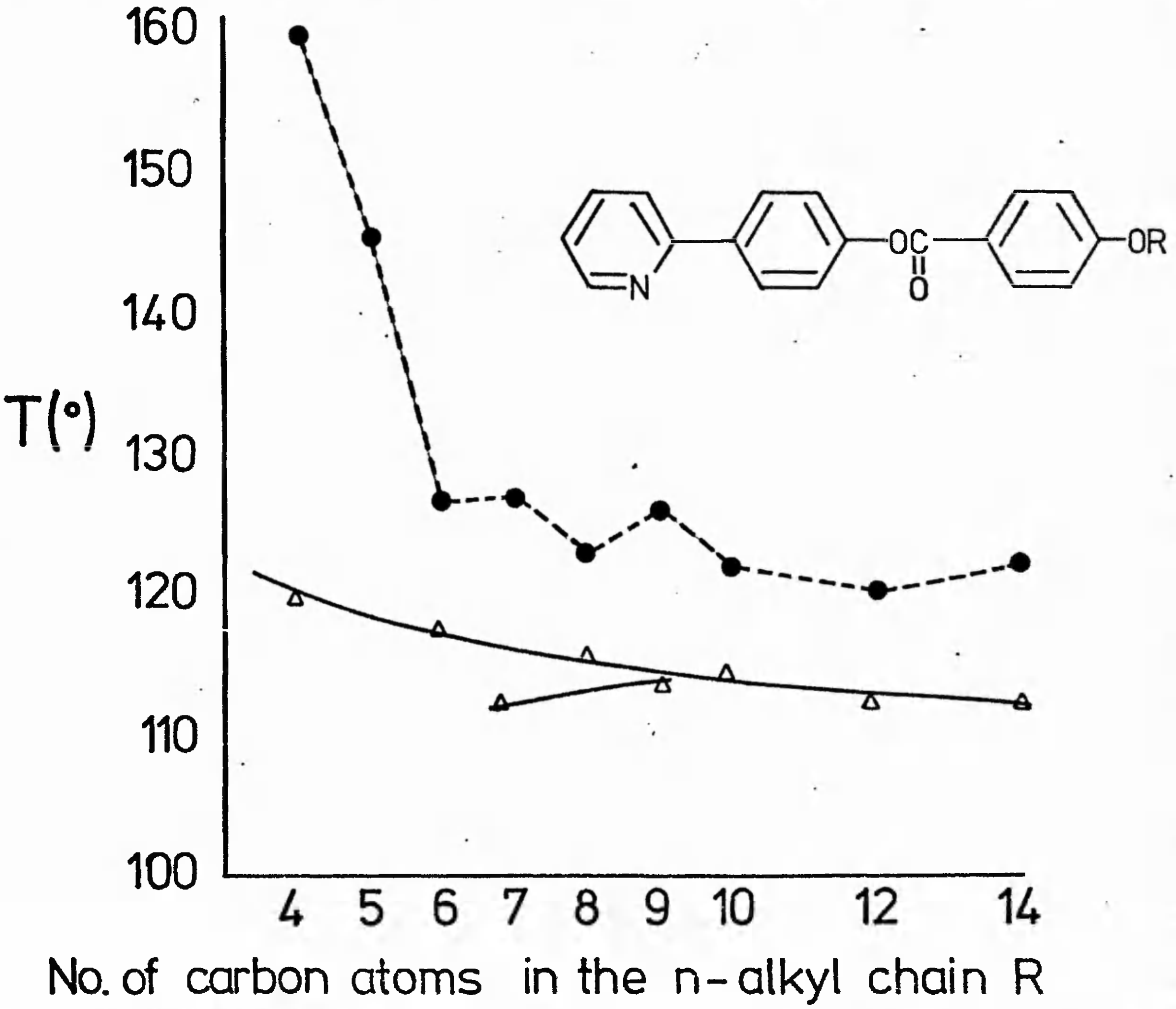
The focal conic fan texture observed by microscopic examination of the birefringent melt, indicated that the smectic mesophase present in these esters was smectic A (S_A). This observation was confirmed by the complete miscibility of this phase over the entire composition range with the known smectic A phase of 4″-n-heptyloxyphenyl 4′-cyanobiphenyl-4-carboxylate (p.268).

The plot of the N-I and S-I transition temperatures shows a typical odd-even alternation with the points fitting two ascending curves, the upper curve for the members with an even number of carbon atoms and the lower curve for the members with an odd number of carbon atoms in the n-alkoxy chain. The rising N-I transition line is characteristic of series in which the N-I transition temperatures are relatively low.

The Mesophase Transition Temperatures of the Homologous Series of the 4-(2′-Pyridyl) phenyl 4″-n-Alkoxybenzoates:

The plot of the transition temperatures of the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates against the number of carbon atoms in the n-alkyl chain R is shown in Figure 26.

Figure 26 - Transition Temperature -v- Chain Length Plot for 4-(2′-Pyridyl) phenyl 4″-n-Alkoxybenzoates

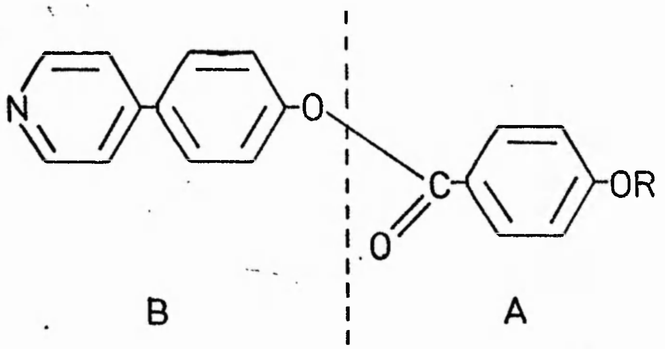


All the homologues in this series gave monotropic nematic mesophases. A possible reason for this is that the geometry of and the dipolar forces within the molecule have a much more pronounced effect on the crystal-mesophase transition than they do on the N-I transition, resulting in the crystal-mesophase transition temperatures reaching higher values than they do for the 4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates, and for the latter part of the analogous biphenyl esters, the 4-biphenylyl 4''-n-alkoxybenzoates. Also the fall in nematic thermal stability as the homologous series is ascended is quite gradual, especially for the initial members of the series. Usually a rapid decrease is observed due to the decreasing terminal attractions as the length of the n-alkoxy chain increases.

The N-I transition temperature for the n-pentyloxy compound was not obtained by optical microscopy because the sample crystallised before any such transition was observed. However, the N-I transition was detected at 108° as a small peak on the differential thermal analysis thermogram during the cooling cycle, but the close proximity of this peak to the large crystallisation peak prevented the measurement of the enthalpy of the N-I transition.

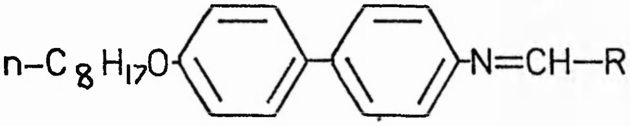
As the homologous series is ascended, the N-I transition temperatures lie on two curves that oppose each other, one a falling upper curve for the members with an even number of carbon atoms and the other an ascending lower curve for the members with an odd number of carbon atoms in the n-alkoxy chain. No smectic properties were observed for the series, even though the later members of this series, i.e. the n-nonyloxy-, -decyloxy-, -dodecyloxy-, and -tetradecyloxy- homologues were supercooled to about 85°.

Comparison of the Mesomorphic Properties of the 4-(4′-Pyridyl) phenyl 4″-n-Alkoxybenzoates and the 4-Biphenylyl 4″-n-Alkoxybenzoates:

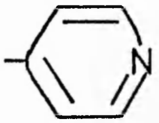


The dipole acting across the long axis in the phenyl region (A) of the molecule will, as in the case of the 4-biphenylyl 4″-n-alkoxybenzoates support the tendency of the molecules to exhibit smectic mesophases. The strong dipole produced by the conjugation between the carbonyl moiety of the central ester linking function and the oxygen atom of the n-alkoxy group, will promote smectic behaviour in the compounds, since the dipole is acting at an angle to the long molecular axis, so increasing the lateral cohesive forces acting between the molecules.

The only structural difference between these two series of compounds is the introduction of the terminal nitrogen in the pyridylphenyl region (B) of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates. The lone pair of electrons on the terminal nitrogen atom could be considered as being equivalent to a 4-substituent in the biphenyl series of esters, in that it can enhance molecular axial polarizability. Clearly, the lone pair of electrons is not exactly equivalent to a 4-substituent and this was demonstrated by Nash & Gray[59] who showed that various 4-substituents in (XXXVI) have a greater effect on the mesophase thermal stability than does the lone pair of electrons on the nitrogen atom of a pyridyl ring.

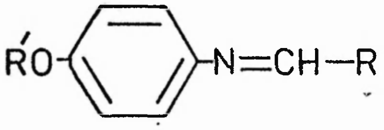


(XXXVI)

R = various substituents, e.g.  .

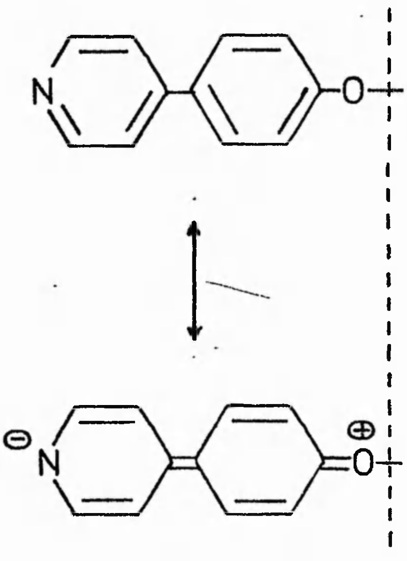
This is expected because the change from a benzene to a pyridine ring causes no significant change in molecular size. This is an important fact to be taken account of when the lateral effect of a pyridyl nitrogen atom is being considered. Nevertheless, the lone pair of electrons of the nitrogen atom will play some part in increasing the molecular polarizability of the molecule, so giving a corresponding increase in the mesophase thermal stability.

The projecting lone pair of electrons of the terminal pyridyl nitrogen atom will cause large repulsive interactions between two 4-pyridyl molecules placed end to end, so reducing the terminal cohesions. The extent of this repulsion was demonstrated by Nash and Gray[59]. In the heterocyclic compound (XXXVII), where R = phenyl and 2- , 3- and 4-pyridyl rings and $R' = n\text{-}C_8H_{17}O$, the compound had pronounced nematic and smectic tendencies. However, when the $n\text{-}C_8H_{17}O\text{-}$ group of the compound was replaced by the R-CH=N- group (R = phenyl and 2- , 3- and 4-pyridyl rings), the mesomorphic character of the dianils was greatly dimished. Neither the di-4-pyridyl nor the di-2-pyridyl compounds were mesogenic, presumably because of the very large repulsions that operate when two pyridyl rings are placed end to end. Thus replacement of a benzene ring by a 4-pyridyl ring causes a reduction in the nematic thermal stability due to repulsive forces, caused by the lone pair of electrons of the terminally positioned nitrogen atom.

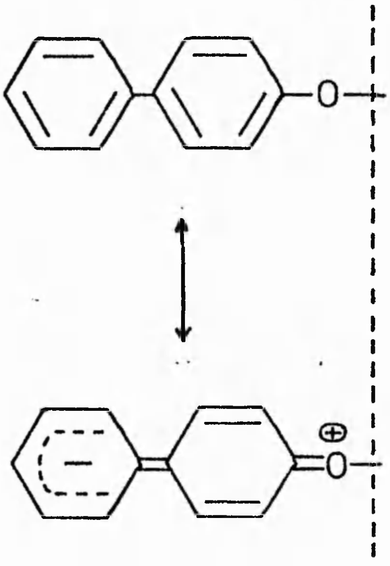


(XXXVII)

The nitrogen atom has a greater electronegativity than the carbon atom (C, 2.5; N, 3.0), and this will enhance the conjugation in the pyridylphenyl region (B) of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates. The contribution of the canonical structures (XXXVIII) and (XXXIX) to the resonance hybrid of this part of the esters will be greater for the pyridylphenyl than for the biphenyl esters, since the negative charge will be more readily accepted by the electronegative nitrogen atom than by the carbon atoms in the terminal ring.



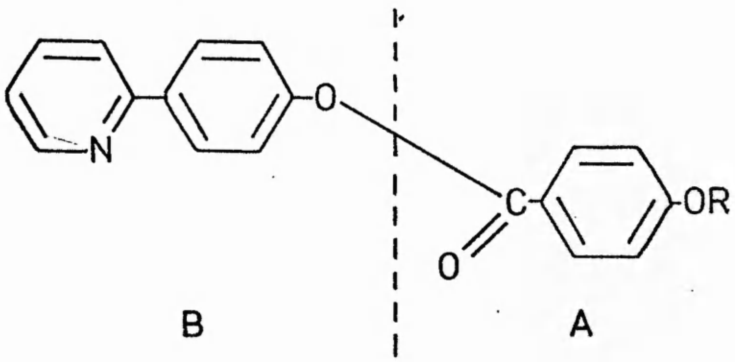
(XXXVIII)



(XXXIX)

Such an effect will increase the overall molecular polarizability of the molecule, but will be dependent on the extent of twisting about the central linkage between the two rings. However, conjugation between the two rings stabilises the molecule and hence because this conjugation is more likely in the pyridylphenyl esters than in the biphenyl esters, the interplanar angle is likely to be less in the former than in the latter esters. It is also probable that packing in smectic mesophases will be more efficient if the interplanar angle is small. Thus the change from a benzene ring to a 4-pyridyl ring alters the intermolecular cohesive forces such that both the tendency for smectic mesophase formation and also the mesomorphic thermal stability are increased.

Comparison of the Mesomorphic Properties of the 4-(2'-Pyridyl) phenyl 4''-n-Alkoxybenzoates and the 4-Biphenylyl 4''-n-Alkoxybenzoates:

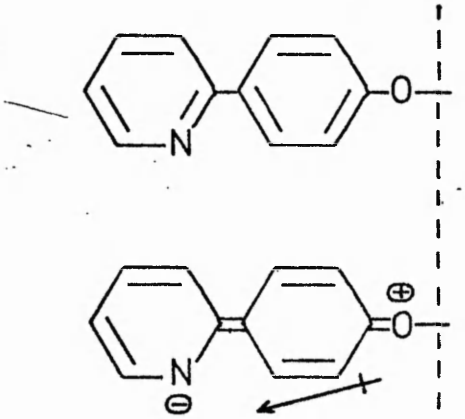


As with the biphenyl esters and the 4′-pyridyl esters, the dipole acting across the long axes of the molecule in the phenyl region A of the 2′-pyridyl esters will support the overall lateral cohesive forces between the molecules and will encourage the formation of and increase the thermal stability of the smectic mesophase. The introduction of the 2′-pyridyl ring in place of the benzene ring gives rise to effects due principally to

i) the greater electronegativity of nitrogen relative to carbon, and

ii) the 'size' of the lone pair of electrons of the laterally positioned nitrogen atom.

As was discussed for the 4′-pyridyl esters, the greater electronegativity of the nitrogen atom should enhance the molecular polarizability of the molecule, giving rise to a dipole which now acts across the molecular axes (XXXX).



(XXXX)

However, the 2′-pyridyl esters do not show smectic properties and hence it seems likely that this conjugation is very largely prevented by the 'size' effect of the lone pair of electrons of the nitrogen atom of the 2′-pyridyl ring, forcing this ring out of plane of the adjacent benzene ring. Lack of planarity of the rings will also cause inefficient packing in the smectic mesophases.

The effect of introducing the 4′-pyridyl ring in place of a benzene ring enhanced the smectic thermal stability of the 4′-pyridyl esters. The nematic properties were restricted to the first two homologues (the pentyloxy and hexyloxy compounds). In the 2′-pyridyl esters, the lone pair of electrons of the nitrogen atoms are laterally disposed. There is no significant increase in molecular breadth when a benzene ring is replaced by a 2′-pyridyl ring (i.e. comparison of biphenyl with 2-phenylpyridine). However, lone pair-lone pair repulsions and lone pair-bond pair repulsions are far greater than bond pair-bond pair repulsions (see footnote), and hence the average

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Footnote: The extent of lone pair-bond pair repulsions is illustrated by the fact that the tetrahedral angle observed in CH_4 (109° 28′) is reduced by the presence of the lone pair of electrons in ammonia to 107° 18′. Similarly, the H-O-H bond angle in water is only 104° 30′ as a result of lone pair-lone pair repulsions.

interplanar angle in 2-phenylpyridine is likely to be much greater than in biphenyl. Thus the conjugation (XXXX) between the ester oxygen atom and the 2′-pyridyl nitrogen atom in the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates is likely to be insignificant. Repulsions between the nitrogen lone pair at the 2′-position and the hydrogen atom at the 2-position in the adjacent benzene ring will give rise to more appeciable twisting about the 1,1′-bond in the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates than in the absence of this effect in the corresponding 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates.

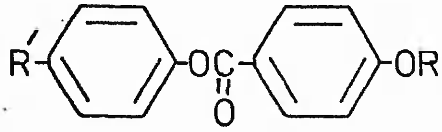
When two laterally positioned nitrogen atoms are in close proximity, the relatively large lone pair-lone pair repulsions between the lone pair of electrons on the nitrogen atoms will reduce the overall lateral cohesive forces operating between the sides of the molecules. This will reduce the ratio of the lateral to terminal cohesive forces and should curtail the smectic behaviour of the 2′-pyridyl esters.

Hence, the dual effect of the lone pair of electrons on the laterally disposed nitrogen atom upon the smectic behaviour of the 2′-pyridyl esters, in reducing both the lateral cohesive forces and the packing efficiency of the molecules in the mesophases, are probably the reasons for the absence of smectic mesophases and the generally lower mesomorphic thermal stability of the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates in comparison with the isomeric

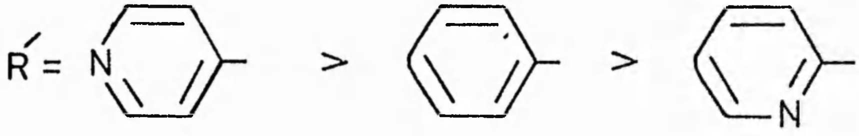
4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates.

It is significant that the general shape of the plot of the N-I transition temperatures against the number of carbon atoms in the n-alkoxy chain is very similar to that obtained for certain 2- and 2′-substituted 4-p-n-alkoxybenzylideneaminobiphenyls[38] (i.e. where the substituent is in a sterically affecting position).

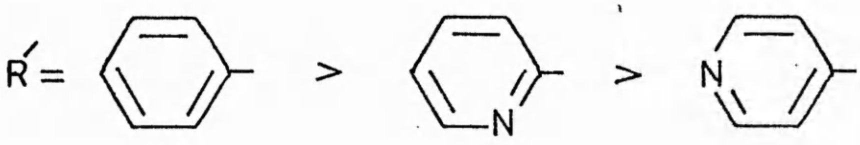
This work on the mesomorphic behaviour of the 4-biphenylyl, 4-(4′-pyridyl) phenyl and 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates gives rise to the following orders of the effect of substituents on smectic and nematic thermal stability.



Smectic Efficiency Order



Nematic Efficiency Order



The phenyl and 2′- and 4′-pyridyl substituents have markedly different effects on the smectic and on the nematic thermal stability. These efficiency orders differ from those quoted by Gray[43], based on the results of structural changes made in a somewhat different environment.

3. The Mesophase Transition Temperatures of the Homologous Series of the 2′-Fluoro- and 2′-Chloro-4-biphenylyl 4″-n-Alkoxybenzoates

This section is sub-divided into three parts:

a) The mesomorphic transition temperatures of the homologous series of 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates;

b) The mesomorphic transition temperatures of the homologous series of 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates; and

c) A comparison of the mesomorphic transition temperatures of the homologous series of:

   i) the 4-biphenylyl 4″-n- alkoxybenzoates;

   ii) the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates;

   iii) the 2′- fluoro-4-biphenylyl 4″-n-alkoxybenzoates; and

iv) the 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates.

It was considered worthwhile to synthesis certain substituted 4-biphenylyl 4″-n-alkoxybenzoates carrying a substituent in a sterically affecting position because the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates showed nematic properties and were relatively low melting. The 2′-fluoro- and -chloro- substituted esters were prepared and their mesophase transition temperatures were measured. The 2′-position as opposed to the 2-position of the biphenyl ring system was chosen as the position of the substituent to avoid any complications due to electronic interactions of the halogeno-substituents, with the carbonyl group of the ester linking function.

a) <u>The Mesomorphic Transition Temperatures of the Homologous Series of 2′-Fluoro-4-biphenylyl 4″-n-Alkoxybenzoates</u>

The plot of the liquid crystal transition temperatures of the 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates against the number of carbon atoms in the n-alkyl chain R, is given in Figure 27.

The n-butyloxy-, -pentyloxy- and -heptyloxy homologues exhibit monotropic nematic mesophases, whilst the n-octyloxy-, -nonyloxy- and -decyloxy- compounds give enantiotropic nematic mesophases. The n-tetradecyloxy- compound also gives a monotropic

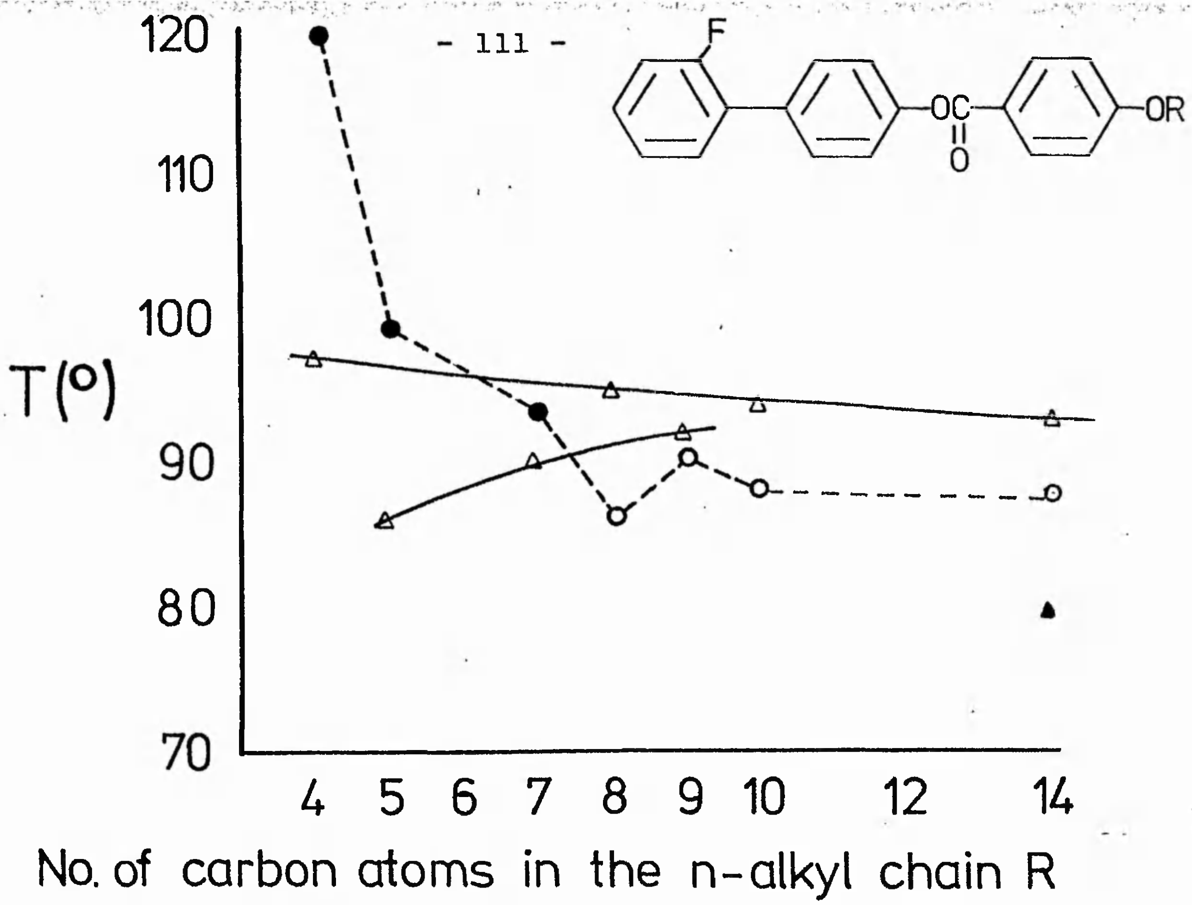


Figure 27 - Transition Temperature -v- Chain Length Plot for 2'-Fluoro-4-biphenylyl 4''-n-Alkoxybenzoates

smectic mesophase which, as a thin sample viewed under the microscope, appears largely homeotropic but with some areas with focal conic and fan texture visible. By observation of the textures under a microscope, the smectic phases were assigned as smectic A.

The general trend of the transition temperatures for this homologous series is very similar to that observed for the 4-(2'-pyridyl) phenyl 4''-n-alkoxybenzoates and for certain 2- and 2'-substituted 4-p-n-alkoxybenzylideneaminobiphenyls[38] in that the N-I transition temperatures show an odd-even alternation with the points fitting two curves, the upper descending curve for the members with an even number of carbons and a lower ascending curve for the members with an odd number of carbon atoms in the n-alkyl chain.

The fluorine atom in the 2$'$-position causes, by its steric effect, an increase in the average interplanar angle due to rotation about the 1,1$'$-bond of the biphenyl system. This, plus the slight increase in molecular breadth caused by the introduction of the small fluoro-substituent into the 2$'$-position, will result in the weakening of the lateral cohesive forces. Gray[32] has suggested an explanation for N-I transition temperature plots which rise with increasing n-alkoxy chain length. It is suggested that if a situation is reached (as in certain sterically affected 2- and 2$'$-substituted 4-p-n-alkoxybenzylidene-aminobiphenyls[38] and the 2$'$-fluoro-4-biphenylyl 4$''$-n-alkoxybenzoates of the present work), where the lateral attractions between molecules are very weak relative to the intermolecular terminal attractions, then the tendency of the terminal attractions to become equivalent to the interactions between hydrocarbon chains may determine the nematic thermal stability. Initially, the relatively strong terminal cohesive forces are insufficient to maintain order in the nematic melt because the lateral cohesive forces are too weak to support the parallel alignment of the molecules. As each successive methylene group is added, the lateral cohesive forces increase so that the parallel alignment becomes possible, and the N-I transition temperature will increase with increasing n-alkyl chain length. Terminal attractive forces then become weaker as the series is ascended, resulting in a gradual reduction in the rate of increase in the N-I transition temperature and a levelling off of the N-I transition line.

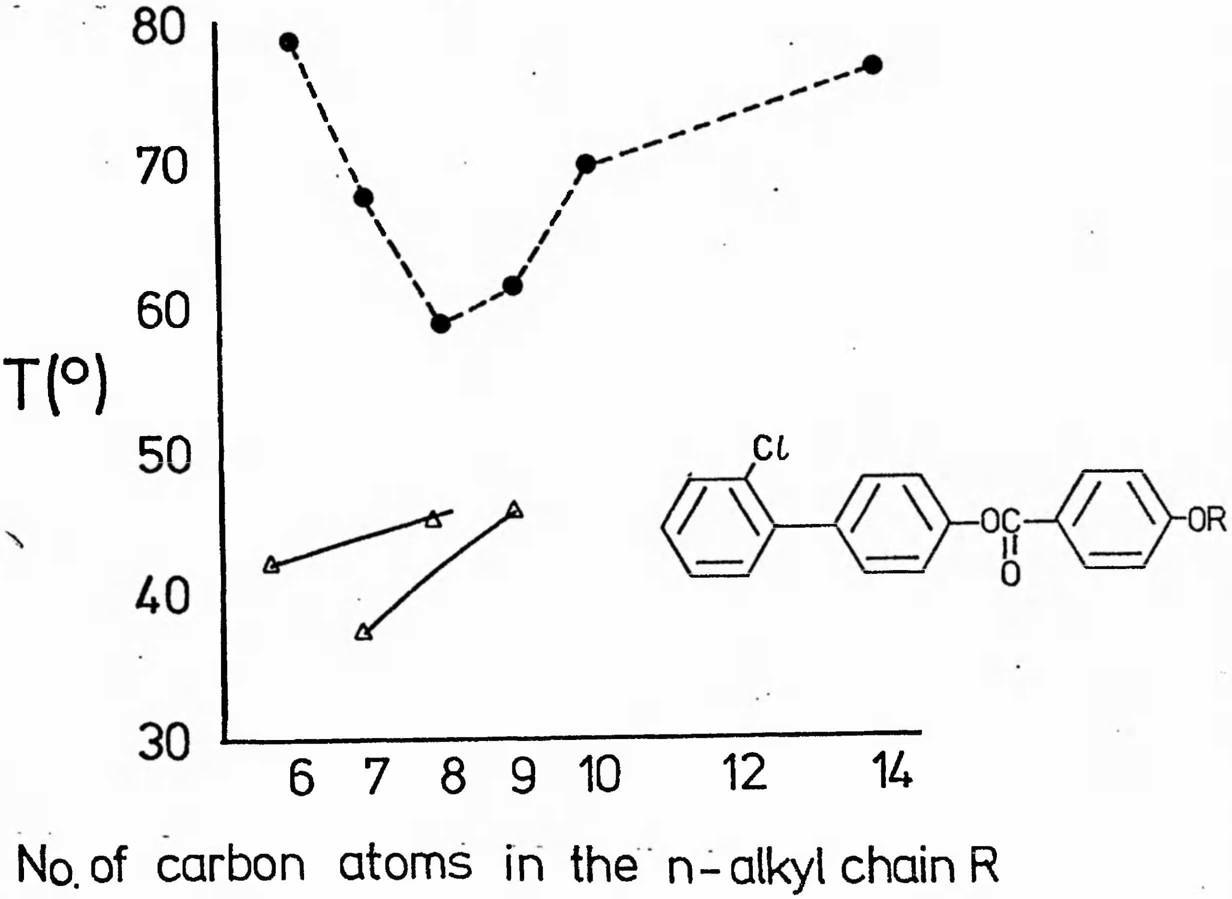
When a series of compounds has smectic character, the position where smectic properties appear depends on the extent of dipole-dipole and induced dipole interactions as well as on dispersion forces, and all three interactions will decrease rapidly with increasing separation of the long molecular axes of adjacent molecules. The 2′-fluoro-substituent is not particularly large and the lateral cohesive forces in the 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates cannot be irreparably affected by the increase in breadth and thickness due to rotation about the 1,1′-bond, since the n-tetradecyloxy-compound exhibits a monotropic smectic A phase. Thus the lateral cohesive forces due to the dipole moment resulting from the conjugation between the carbonyl moiety of the central linking function and the ether oxygen atom are supplemented by the increasing influence of the addition of the methylene units to the n-alkyl chain. When the n-tetradecyloxy-compound is reached, the lateral attractions have increased sufficiently for the molecule to overcome the effects resulting from the introduction of the

2'-fluoro substituent.

b) The Mesomorphic Transition Temperatures of the Homologous Series of 2'-Chloro-4-biphenylyl 4''-n-Alkoxybenzoates

A plot of the liquid crystal transition temperatures of the 2'-chloro-4-biphenylyl 4''-n-alkoxybenzoates against the number of carbon atoms in the n-alkyl chain, R, is presented in Figure 28.

Figure 28 - Transition Temperature -v- Chain Length Plot for 2'-Chloro-4-biphenyly 4''-n-Alkoxybenzoates.



The N-I transitions observed for the n-hexyloxy to the -nonyloxy homologues were all monotropic. No mesophase transition could be detected for the n-decyloxy- and -tetradecyloxy- compounds (these melts could only be supercooled to about 60° prior to crystallisation of the sample). The N-I transition temperatues alternate in a typical fashion with the points now fitting two ascending curves, the upper curve for the members with an even number of carbon atoms and the lower curve for the members with an odd number of carbon atoms in the n-alkoxy chain. In this homologous series, both the N-I transition temperature curves rise as the n-alkoxy chain is lengthened. This is in accord with the expected very low lateral cohesive forces for these esters, caused by the thickening of the molecule resulting from the increase in the interplanar angle due to rotation about the 1,1′-bond of the biphenyl system and by the increase in molecular breadth caused by the introduction of the chloro-substituent in the 2′-position. These very weak lateral cohesive forces in relation to the terminal attractions, will dominate the trend of the N-I transition temperatures as described for the 2′-fluoro-substituted esters.

c) A Comparison of the Mesomorphic Transition Temperatures of the Homologous Series of:

i) the 4-biphenylyl 4″-n-alkoxybenzoates ① ;

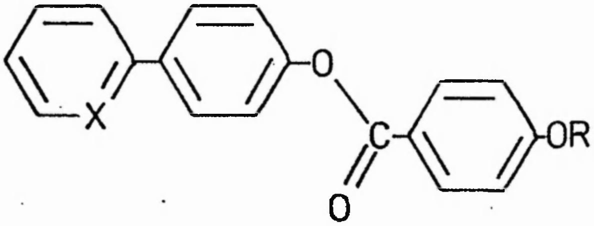
ii) the 4-(2$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates ②;

iii) the 2$'$-fluoro-4-biphenylyl 4$''$-n-alkoxybenzoates ③; and

iv) the 2$'$-chloro-4-biphenylyl 4$''$-n-alkoxybenzoates ④.

The number in the circle given after the name of each of the esters refers to the graph in Figure 29, which enables a comparison to be made of the N-I transition temperatures of the four series of esters.

The figure shows that as X in the four homologous series of 4$''$-n-alkoxybenzoate esters (XXXXI) increases in size (from C-H, to N, to C-F, to C-Cl), the gradients of the N-I transition lines gradually decrease. This tendency is most pronounced for the lines for members with an odd number of carbon atoms.



(XXXXI)

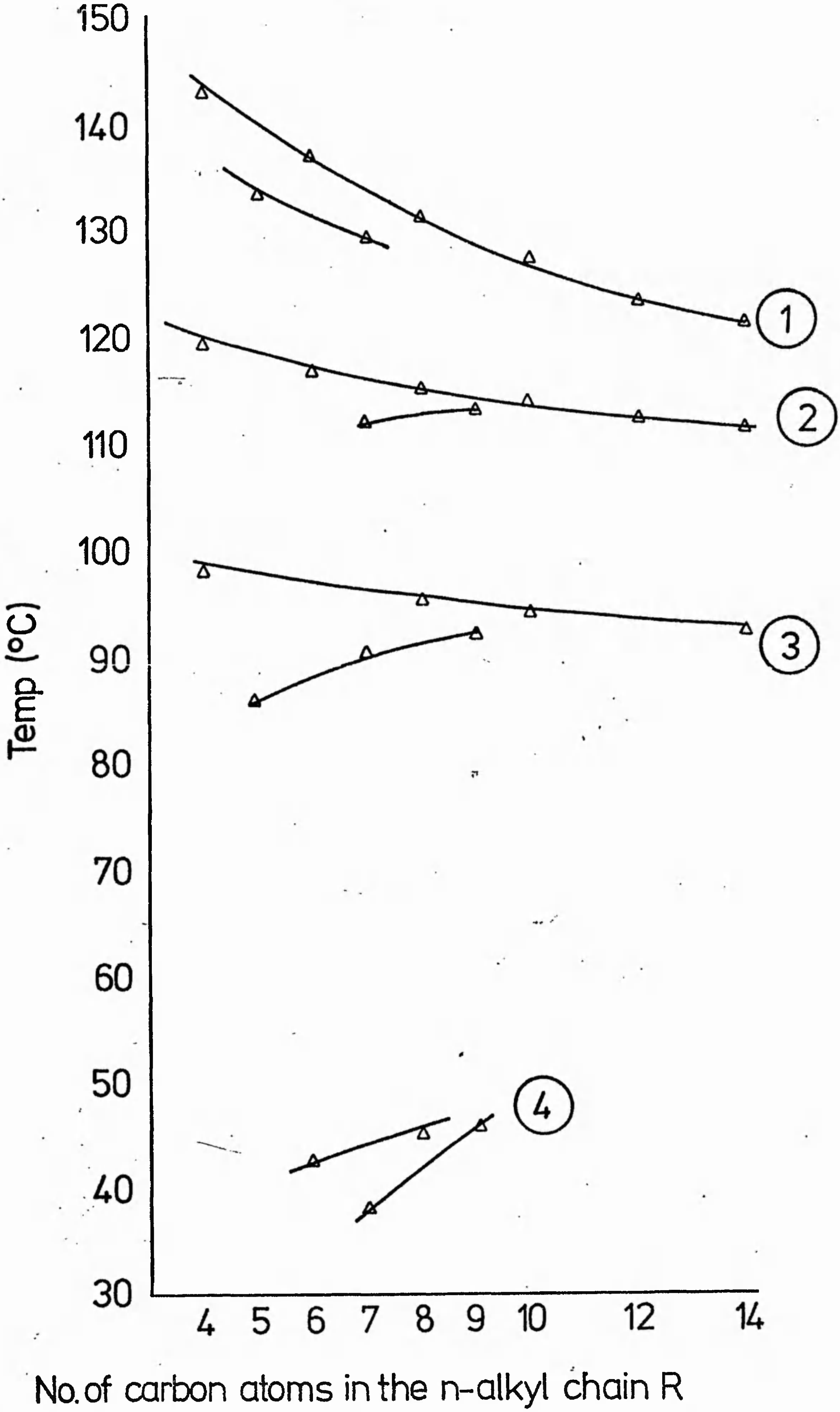


Figure 29 - Comparison of the Mesomorphic Transition Temperatures of the Homologous Series of Certain 4''-n-Alkoxybenzoate Esters

When X = N, the 'odd' curve is almost horizontal whereas for X = C-F, the corresponding curve now rises to meet the falling 'even' curve. When the chloro-substituted esters are reached (X = C-Cl), the 'odd' and 'even' curves both rise. These trends probably reflect the increasing effect of molecular broadening on the lateral cohesive forces as a result of the increasing size of the group X. This may result in the decreasing lateral cohesive forces dominating the N-I transition temperatures.

The numercial differences between the N-I transition temperatures of various members of the 4-biphenylyl, the 4-(2′-pyridyl) phenyl, the 2′-fluoro-4-biphenylyl, and the 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates are given in Table 5.

Table 5 - Differences in the N-I Transition Temperature of Various Homologues of the 4″-n-Alkoxybenzoate Esters

	n-Hexyloxy Homologue		n-Octyloxy Homologue	
4-Biphenylyl (1)	129.5	17.5	130.5	15.5
4-(2′-Pyridyl) phenyl (2)	112	39.5	115	35.5
2′-Fluoro-4-biphenylyl (3)	90	91.5	95	85.5
2′-Chloro-4-biphenylyl (4)	38		45	

Thus to summarise for the four homologous series of 4″-n-alkoxybenzoate esters of the type (XXXXI) studied in this work, the efficiency of the group X in promoting nematic thermal stability is:

X = C-H > N > C-F >> C-Cl

As only two of the series studied showed smectic properties, the smectic order (X = C-H > C-F) is not particularly meaningful.

To conclude this section, it is of interest to note that the N-oxide of 4-(2′-pyridyl) phenyl 4″-n-hexyloxybenzoate was prepared during this work but it did not show mesomorphic properties. The melting point of this compound is 163°. The N→O group is of roughly the same size as the C-F group, but the former group has a very considerable dipole moment (4.52D). Thus the effect on the lateral cohesive forces due to the steric effect of the N-oxide group resulting in twisting about the pyridyl-phenyl bond, and so broadening and thickening the molecule to roughly the same extent as in the 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates, would be expected to be more than compensated by the large dipole moment resulting from the introduction of the N-oxide function. However, presumably this dipole moment is sufficiently large to increase the cohesive forces in the crystal to an extent such that the crystal collapses directly to the isotropic liquid. As the melt of this compound did not supercool more than a few degrees, it was not thought worthwhile to attempt to interpolate to a mesophase transition temperature by measurements on a binary mixture with a mesogen. The synthesis of the N-oxides of other members of the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates was not attempted.

4. The Mesomorphic Transition Temperatures of the N-oxides of the Homologous Series of 4-(4′-Pyridyl) phenyl 4″-n-Alkoxybenzoates and a Comparison with the Mesomorphic Transition Temperatures of the Homologous Series of 4-(4′-Pyridyl) phenyl 4″-n-Alkoxybenzoates

The N-oxides of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates were difficult to purify and were adversely affected by exposure to strong sunlight, their colour changing from white to pale yellow. During slow heating to determine their transition temperatures, appreciable decomposition of the N-oxide occurred. To minimise this decomposition, the N-I (and S-I) transition temperatures therefore had to be determined by insertion of the sample into the heating block only a few degrees below the actual transition temperature. Even then the transitions were not precisely reversible and a repeat determination on a given sample gave a slightly lower value as a result of the progressively increasing decomposition. For this reason, the N-I (and S-I) transition temperatures must be regarded as approximate. Some of the N-oxides exhibited two smectic mesophases. Only the most thermally stable smectic mesophase was identified (as smectic A, by observation of the characteristic focal conic and fan textures by viewing a thin sample under the microscope). Because of the problems associated with the thermal decomposition of the N-oxides, studies of the miscibility of the smectic mesophases with compounds having smectic mesophases of known type were not undertaken.

The N-oxides of the n-hexyloxy- and the -hetyloxy-compounds gave both smectic and nematic mesophases, with the smectic mesophase of the N-oxides of the n-hexyloxy-compound being monotropic. The N-oxides of the n-octyloxy-, -nonyloxy-, -dodecyloxy- and -tetradecyloxy- compounds were all smectogens, and they each exhibited two smectic mesophases. The most thermally stable smectic phase was identified as smectic A.

The plot of the liquid crystal transition temperatures of the N-oxides of 4-(4$^{\prime}$-pyridyl) phenyl 4$^{\prime\prime}$-n-alkoxy-benzoates against the number of carbon atoms in the n-alkoxy chain is shown in Figure 30.

The N-I or S-I transition temperatures show a typical odd-even alternation (except for the N-oxide of the n-pentyloxy- compound which was probably slightly impure), with the points fitting two rising and converging curves as the n-alkyl chain length increases; the upper curve for the members with an even number of carbon atoms and the lower curve for the members with an odd number of carbon atoms in the n-alkyl chain R. The S-N transition temperature curve for the N-oxides of the n-hexyloxy- and n-heptyloxy- compounds rises steeply, suggesting a very strong tendency to form smectic mesophases for this series. This is reflected by the very high S-I transition

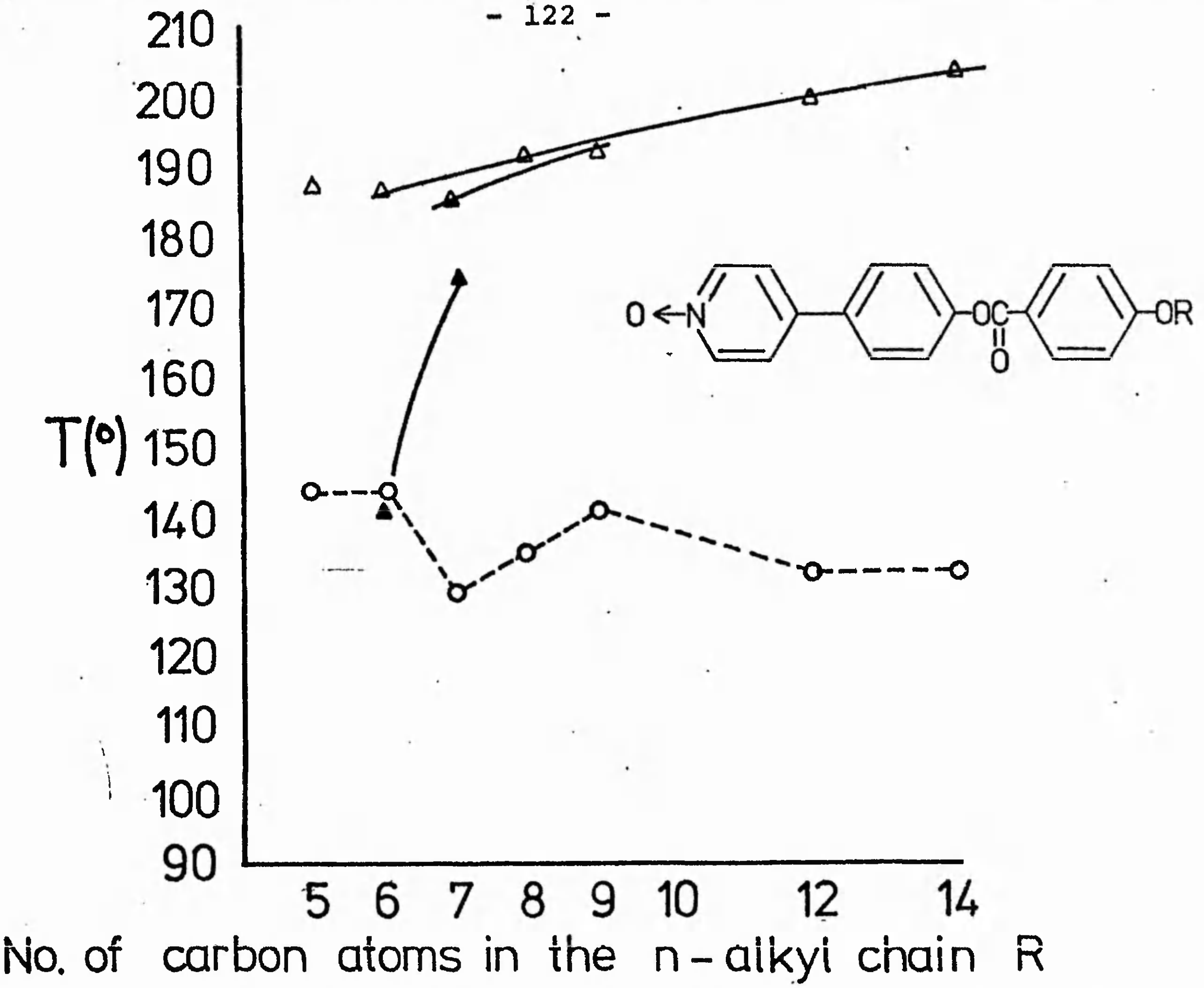
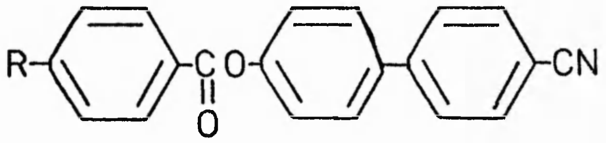


Figure 30 - Transition Temperature -v- Chain Length Plot for the N-oxides of 4-(4$'$-Pyridyl) phenyl 4$''$-n-Alkoxybenzoates.

temperatures of the N-oxides.

A surprising feature of this homologous series is the absence of a nematic mesophase for compounds higher in the series than the n-pentyloxy homologue. The N-oxide function of 4-phenylpyridine-N-oxide is responsible for the dipole moment of 4.52D for this compound. The dipole acts in the direction of the long molecular axis. This should vastly increase the overall molecular polarizability of the molecule, and so enhance both smectic and nematic thermal stabilities. However, such dipoles may give rise to repulsions between the molecules which lie parallel to one another in the layer planes of a smectic liquid crystal. The 4-cyano-4$'$-biphenylyl 4$''$-alkoxybenzoates[72] (XXXXII) provide a good example. The transition temperatures for the hexyloxy and octyloxy compounds of this series are quoted together with the related transition temperatures ( ) obtained in the present work for the corresponding 4-biphenyl 4″-n-alkoxybenzoates.



(XXXXII)

R	C-N, S_B	S_B-S_A	S_A-N	N-I
n-$C_6H_{13}O$	103°(133°)			246°(136.5°)
n-$C_8H_{17}O$	97.3 (119)	138.3°	198.7°(97.5°)	235.3(130.5)

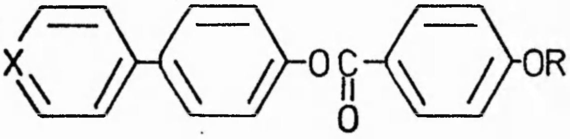
4-Cyanobiphenyl has a dipole moment of 4.33D due to the cyano-substituent. Thus the dipole moments of the cyano and N-oxide group are very similar. Initially, only nematic properties are shown in the series of 4-cyano-4′-biphenylyl 4″-alkoxybenzoate (XXXXII) and hence the terminal cohesive forces must be dominant, with the high dipole moment of the cyano-group playing a significant role. However, as the series is ascended, the gradually increasing lateral cohesive forces become sufficiently strong for smectic properties to appear, although the nematic mesophase still persists at a very high temperature. Both the smectic and the nematic thermal stabilities are high throughout the series due to the presence of highly polar terminal cyano group. The N-oxide function is also highly polar but the N-oxides of 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates show different mesomorphic behaviour to the 4-cyano-4′-biphenylyl 4″-n-alkoxybenzoates.

Smectic properties are dominant in the N-oxide series. The nematic properties initially shown, are soon replaced by smectic behaviour and overall the thermal stability of the N-oxide ,although high, is less than for the 4-cyano-4′-biphenylyl 4″-n-alkoxybenzoates.

The general shape of the plot of transition temperatures against n-alkyl chain length for the N-oxides of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates is very similar to that obtained for the parent esters, the 4-(4′pyridyl) phenyl 4″-n-alkoxybenzoates themselves. For the latter series it was suggested earlier that repulsive interactions between the lone pairs of electrons on the terminal nitrogen atoms of adjacent molecules caused a lowering of the terminal cohesive forces, resulting in a gradually increasing S-I transition temperature as the length of the n-alkyl chain increased. Possibly similar repulsive interactions between dipolar N-oxide functions of adjacent molecules are responsible for the general slope of the plot for the N-oxides. The expected analogy between the N-oxide function and the cyano group does not seem to exist.

To summarise, for the three homologous series of 4'-n-alkoxybenzoate esters of the type (XXXXIII) studied in this work, the efficiency of the group X in promoting smectic thermal stability is:

$X = N \longrightarrow O \gg N > C\text{-}H$



(XXXXIII)

5. The Mesomorphic Transition Temperatures of the N-oxides of the Homologous Series of 4-(4'-n-Alkoxyphenyl) pyridines

The majority of non-amphiphilic liquid crystalline compounds have the general structure (XXII) where the rectangle represents a linking group that extends the rigidity and linearity of the molecule. The linking group influences liquid crystal thermal stability quite markedly. There are many examples of low melting mesogens with unsaturated groups linking the p-disubstituted benzene rings, e.g. the Schiff's base linkage and azo- and azoxy- linkages. These have various disadvantages for use in display devices, e.g. problems of colour and of chemical, electrochemical, or photochemical instability.

Gray and his co-workers showed that the disadvantages could be overcome by removal of the central linking group, provided that the 'end' groups were appropriately chosen. Thus, the 4-n-alkoxy- and 4-n-alkyl-4′-cyano-biphenyls are low melting nematogens, and various mixtures containing these cyanobiphenyls have very low C-N transition temperatures, a long range of temperature during which the mixture is nematic, and a high positive dielectric anisotropy (essentially for use in display cells based on the twisted nematic effect).

Comparison of the mesophase transition temperatures of 4-cyano-4′-biphenylyl 4″-n-hexyloxy and -octyloxy-benzoates with those of the corresponding 4′-n-alkoxy-4-cyanobiphenyls in Table 6 shows that the removal of the Ph.COO— group substantially lowers the smectic and nematic thermal stabilities.

The crystal-mesophase transition temperatures are also lowered, giving low melting enantiotropic mesophases for the 4′-n-alkoxy-4-cyano-biphenyls.

Extending this argument to the N-oxides of 4-(4′-n-alkoxy-phenyl) pyridines in comparison with the N-oxides of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates, it seemed a reasonable expectation that the N-oxides of the 4-(4′-n-alkoxyphenyl) pyridines might be low melting enantiotropic mesogens, since the N-oxide terminal group has a dipole moment roughly equal to that of the 4-cyano-substituent

Table 6 - Comparison of the Mesomorphic Behaviour of the 4-cyano-4′-biphenyl 4″-n-hexyloxy- and -octyloxybenzoates (A) with those of the Corresponding 4′-n-alkoxy-4-cyanobiphenyls (B).

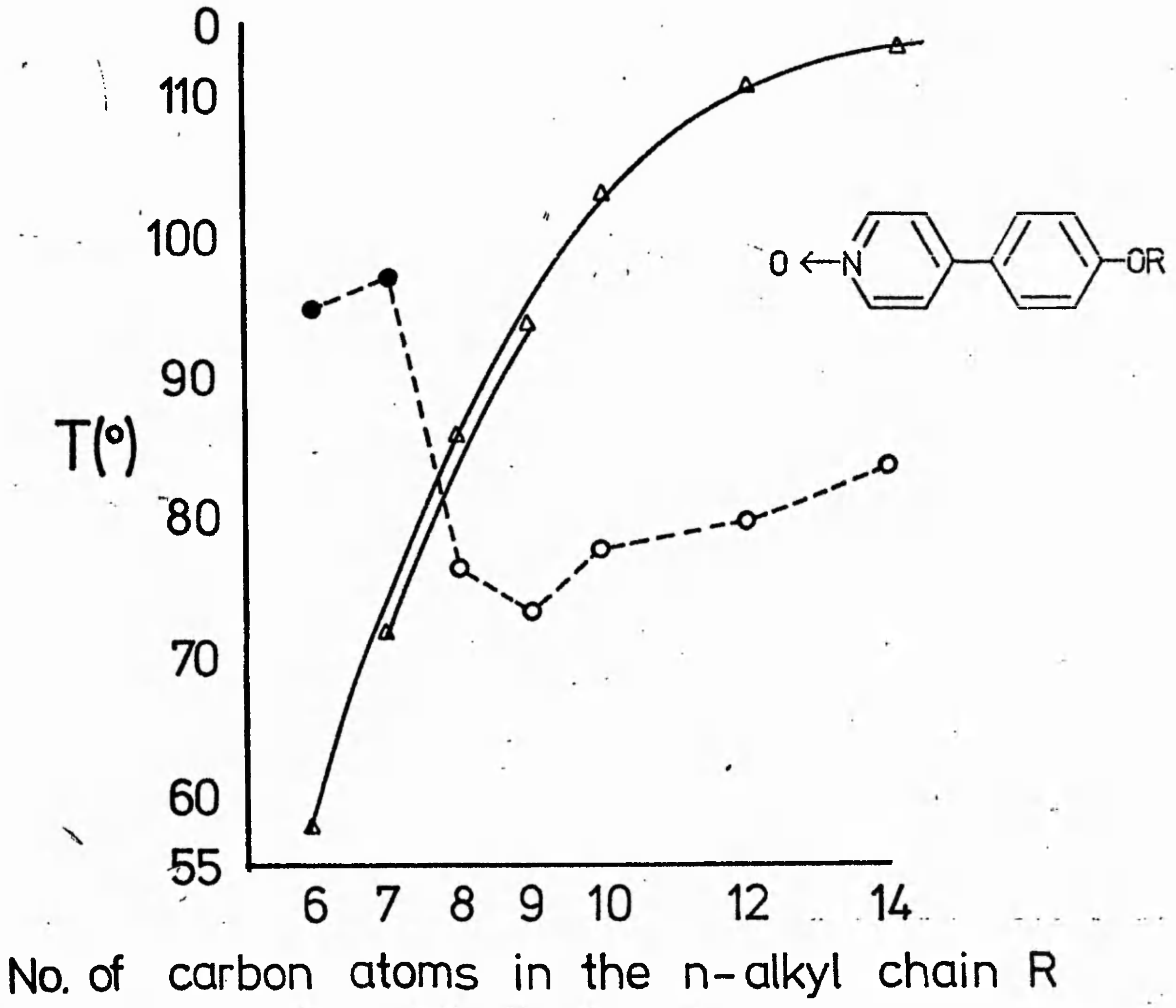
		C-N,S_B	S_B-S_A	S_A-N	N-I
A	$n\text{-}C_6H_{13}O$	103°			246°
	$n\text{-}C_8H_{17}O$	97.3	138.3°	198.7°	235.3
B	$n\text{-}C_6H_{13}O$	58			76.5
	$n\text{-}C_8H_{17}O$	54.5		67	80

of the 4′-n-alkoxy-4-cyanobiphenyls. Although, in contrast to expectations from a consideration of the mesomorphic behaviour of the 4-cyano-4′-biphenylyl 4″-n-alkoxybenzoates, the N-oxides of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates were essentially smectogenic, it was still thought worthwhile to investigate the N-oxides of the 4-(4′-alkoxyphenyl) pyridines.

All the N-oxides of the 4-(4′-n-alkoxyphenyl) pyridines studied showed smectic behaviour, the smectic mesophases of the n-hexyloxy and n-heptyloxy homologues being monotropic. The smectic mesophases were identified as smectic A by observation of the formation of the focal conic and fan textures when an appropriately mounted sample was cooled slowly from the isotropic liquid.

The plot of liquid crystal transition temperatures of the N-oxides of 4-(4′-n-alkoxyphenyl) pyridine against the number of carbon atoms in the n-alkyl chain, R, is shown in Figure 31.

Figure 31 - Transition Temperature -v- Chain Length Plot for the N-oxides of 4-(4′-n-Alkoxyphenyl) pyridine



The S-I transition temperatures alternate typically with the points fitting two steeply rising and converging curves, the upper curve for the members with an even number of carbon atoms and the lower curve for the members with an odd number of carbon atoms in the n-alkoxy chain. The steep rise may be due to the fact that for the early members of the series, the weaker lateral cohesive forces probably govern the S-I transition temperatures. These attractions will increase as the homologous series is ascended and the smectic mesophases will increase in thermal stability. Meanwhile, the terminal attractions will grow weaker, and the probability of interpenetration of the smectic strata increases. For the higher homologues, therefore, the terminal cohesive forces will probably govern the smectic transition temperatures and the S-I transition temperature line will level off (and eventually fall as the homologous series is ascended).

Thus just as the comparison of the N-oxides of 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates with the nematogenic 4-cyano-4$'$-biphenylyl 4$''$-n-alkoxybenzoates showed that the former compounds were smectogenic, the same conclusion emerges when the N-oxides of the 4-(4$'$-alkoxyphenyl) pyridines are compared with the 4-n-alkoxy-4$'$-cyanobiphenyls.

The N-oxides of the 4-(4$'$-n-alkoxyphenyl) pyridines were slightly sensitive to light, turning yellow on prolonged exposure, but did not decompose on heating (in contrast to the N-oxides of the 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates.

6. Summary

The mesomorphic behaviour of the following eight homologous series of compounds has been studied:

i) the 4-biphenylyl 4″-n-alkoxybenzoates;
ii) the 4″-n-alkoxyphenyl biphenyl-4-carboxylates;
iii) the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates;
iv) the 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates;
v) the 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates;
vi) the 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates;
vii) the N-oxides of the 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates; and
viii) the N-oxides of the 4-(4′-n-alkoxyphenyl) pyridines.

The 4″-n-alkoxyphenyl biphenyl-4-carboxylates, and the 4-(2′-pyridyl) phenyl and 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates were purely nematogenic whereas the 4-biphenylyl, 4-(4′-pyridyl) phenyl and 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates exhibited both smectic (smectic A) and nematic mesophases. The N-oxides of 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates were also of this latter type and certain members of this homologous series gave two smectic mesophases, of which the higher (more thermally stable) mesophase was identified as smectic A. The homologous series of the N-oxides of 4-(4′-n-alkoxyphenyl) pyridines were purely smectogenic, the smectic type being assigned as smectic A. Suggestions have been offered to explain the mesomorphic thermal stabilities of the various homologous series and the shapes of the plots of mesophase transition temperatures against the number of carbon atoms in the n-alkoxy chain. Some group efficiency orders, i.e. the effect of substituents on the stabilities of smectic and nematic mesophases have been stated.

With the exception of the N-oxides, the esters and n-alkoxyethers prepared in this work were stable both to heat and prolonged exposure to light. The N-oxides of 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates were sensitive both to light (changing colour from white to pale yellow) and heat (decomposition produced slightly irreversible mesophase transition temperatures). The N-oxides of the 4-(4$'$-n-alkoxyphenyl) pyridines were thermally stable, but on prolonged exposure to light, the colour of the compounds changed from white to pale yellow.

The types of smectic mesophases were assigned by optical microscopy and by miscibility studies with compounds of known smectic type, and certain of the homologous series were studied by differential thermal analysis.

SPECTROSCOPIC DATA & DIFFERENTIAL THERMAL ANALYSIS RESULTS

Contents

d) 2'-Chloro-4-biphenylyl 4''-n-alkoxybenzoates.

e) 4-(4'-Pyridyl) phenyl 4''-n-alkoxybenzoates.

f) 4-(2'-Pyridyl) phenyl 4''-n-alkoxybenzoates.

g) 4-(4'-n-Alkoxyphenyl) pyridines.

4. Mass Spectroscopic Data

a) Comparison of the spectra of 1,4-di-n-tetradecyloxyphenyl diether, the 4''-n-tetradecyloxyphenyl biphenyl-4 - carboxylate and the above ester contaminated with the 1,4-di-n-tetra decyloxyphenyl diether.

b) N-oxide of 4-(4'-pyridyl) phenyl 4''-n-hexyloxybenzoate.

c) N-oxide of 4-(4'-pyridyl) phenyl 4''-n-tetradecyloxybenzoate.

d) N-oxide of 4-(4'-n-tetradecyloxyphenyl) pyridine and of 4-(4'-n-octyloxyphenyl) pyridine.

e) 4-Biphenylyl 4''-n-pentyloxybenzoate.

1. Transition Temperatures by Optical Microscopy and Differential Thermal Analysis

Three methods were used for the detection and identification of mesophases, namely:

i) the melting point capillary technique;

ii) by optical microscopy;

iii) using differential thermal analysis.

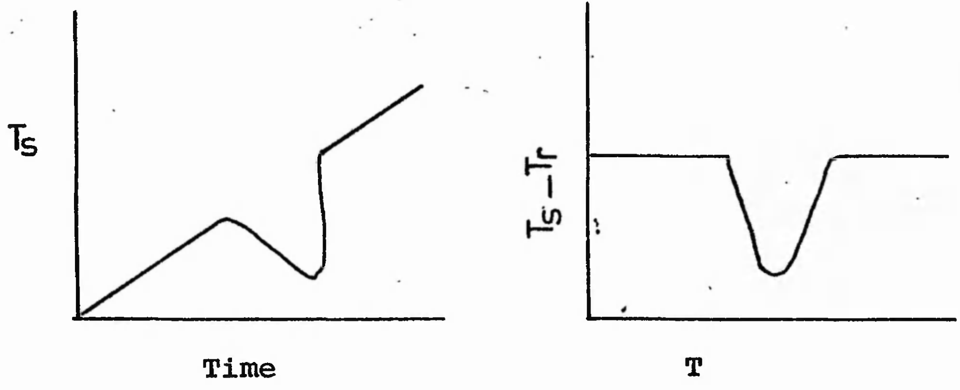
The melting point capillary technique is simple, but useful. It makes use of the rheotropic properties of the mesophases. The solid and the isotropic liquid are distinguished from the smectic mesophase which is opaque and viscous and adheres in droplets to the capillary walls, and from the nematic mesophase which is opaque but mobile and runs freely to the bottom of the capillary tube. The cholesteric mesophase is also opaque and mobile but at some time during the melting process may give rise to irridescent colours.

The melting point capillary technique enables the temperatures at which the various changes occur to be obtained approximately. It has obvious limitations, e.g. monotropic mesophases present certain problems and the polymorphism of smectic mesophases cannot, in general, be detected.

The enthalpies for the transitions between mesophase and mesophase or between mesophase and the isotropic liquid are generally small but they can be readily determined by differential thermal analysis (DTA) or differential scanning calorimetry (DSC).

Differential thermal analysis (DTA) is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material is recorded as a function of the sample, or the inert material, or the furnace temperature as the sample is heated or cooled at a uniform rate. Endothermic enthalpy changes cause corresponding temperature alterations at phase changes, e.g. from crystal to mesophase, mesophase to mesophase or mesophase to isotropic liquid. The temperature changes occurring during these phase transitions are detected by a differential method, such as that illustrated in Figure 32 . If the sample and reference temperatures are T_s and T_r, respectively, then the difference in temperature, $T_s - T_r$ is the function recorded.

Figure 32 - Comparison between Thermal Analysis and DTA



Thermal analysis

DTA

Several different theoretical interpretations of the DTA curves have been suggested. It is inappropriate to discuss these here, but excellent accounts are given by Speil et al[89], Kerr and Kulp[90], Gray[93], Lukaszewski[94] and Pacor[95].

The simplest expression relating the area under a differential curve peak to the various parameters of the sample and the apparatus is given by:

$$\frac{m(\Delta H)}{gk} = \int_{t_1}^{t_2} \Delta T \, dt.........(1)$$

where, m = mass of sample

H = heat of transition

g = geometrical shape constant for the apparatus

k = thermal conductivity of the sample

T = differential temperature

t_1, t_2 = integration limits of the differential curve

The equation (1) is only an approximate relationship, for it neglects differential terms, temperature gradients in the sample, etc. A fuller expression is beyond the scope of this discussion.

In differential thermal analysis, since it is a dynamic temperature technique, the resulting DTA curve (Figure 33) will be dependent on a large number of factors.

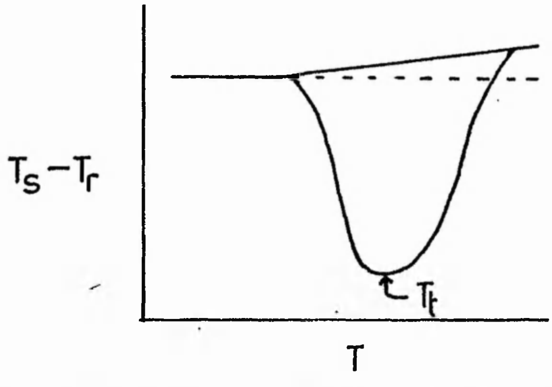


Figure 33 - Generalised D.T.A. Curve

T_t is the Temperature of the Transition.

The key operational parameters are listed in Table 7 & a summary of the operational parameters is given in Table 8. Thus if a large sample size is chosen, a low heating rate is required, which in turn decreases the ΔT sensitivity and peak resolution. A small sample size permits higher heating rates and better peak resolution.

Table 7 - Key Operational Parameters

Sample Size:	
Large	Useful for detecting low-level transitions. Curve peaks are broad giving low resolution and temperature accuracy. Requires slow heating rate.
Small	Good resolution of peaks. Peaks are sharp, permitting fast heating rates.
Heating Rates:	
Fast	Increases sensitivity but decreases resolution and temperature accuracy.
Atmosphere:	Can react with sample. Dynamic preferred over static because it is easier to maintain and reproduce.

Table 8 - Summary of Operational Parameters

Parameter	Maximum Resolution	Maximum Sensitivity
Sample size	Small	Large
Heating rate	Slow	Fast
Sample holder	Block	Isolated container
Volume of sample	Large	Small
Atmosphere	High	Low

In differential thermal analysis, both the enthalpy of transition (area under the curve) and the temperature at which the transition occurs (apex of peak) are given on one thermogram (a heating and a cooling cycle are needed). Thus the choice of parameters is usually a compromise between good resolution and good sensitivity, i.e. small sample size (good resolution) and a fast heating rate (good sensitivity). A typical thermogram is given in Figure 34.

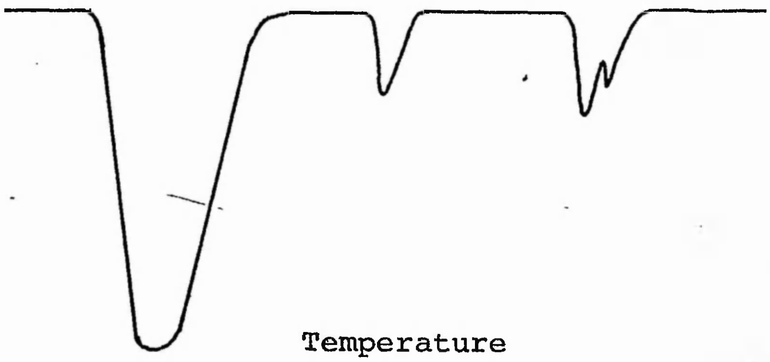


Figure 34 - Representation of a Typical Thermogram

With temperature measurements, no calibration is needed, provided that the thermocouple junction is at 0°. However, for the determination of heat of transitions, the instrument must be calibrated, using the expression:

$$H\bar{m} = kA......(2)$$

where, H = the heat of transition
m = mass of sample
k = calibration coefficient
A = area under the curve.

The calibration coefficient k is determined using a compound with a known transition enthalpy. This compound must conform to certain criteria, e.g. inert, chemically stable, of low vapour pressure, etc. A selection of compounds used as standards in DTA work is presented in Table 9.

The most widely used standard, especially in organic chemistry, is indium wire. The enthalpy of fusion of indium is of the same order of magnitude as the enthalpy of liquid crystal transitions, and the melting point of indium is also conveniently low. Also in wire form, indium is easy to handle and keep pure (the wire is soft and has a low surface area).

Table 9 - Standards Used for DTA and DSC Calibration

Temp. (°)	Standard	ΔHf cal/g	ΔHt cal/g
48.2	Benzophenone	23.5	
69.8	Biphenyl	28.7	
99.3	Phenanthrene	25.0	
125	Ammonium nitrate		12.6
156.4	Indium	6.79	
177.0	Potassium thiocyanate	25.72	
212	Silver nitrate	17.7	
231.9	Tin	14.4	
306.2	Sodium nitrate	44.2	

Differential thermal analysis is mostly used in work on liquid crystals in order to confirm observations made by optical microscopy of the number of mesophases and the temperature(s) of transition associated with a particular mesogen. Its unique function is that enthalpies of transition of any phase changes present in a mesogen may be measured.

The transition temperatures obtained by DTA are often not very accurate (in the present work the accuracy is estimated at $\pm 2^{o}$) and hence a more accurate method of determination of transition temperatures is usually necessary. It is customary to use a hot stage in conjunction with a polarising microscope. When a liquid crystalline compound is mounted as a thin film between a microscope slide and a cover slip, provided that the long molecular axes are oriented parallel to the glass supporting surfaces, the sample exhibits double refraction and the melt is birefringent. Since the isotropic liquid does not exhibit double refraction, this property makes optical microscopy using a polarising microscope one of the most useful methods for the determination of transition temperatures and for the recognition of the types of mesophases.

By melting a small quantity of sample adjacent to a cover slip on a microscope slide, the thin film is formed between the glass surfaces by capillary action. The melt is then allowed to cool. On heating the sample in the hot stage, enantiotropic mesophases may be observed using a polarising microscope. Transition temperatures are measured with a calibrated thermometer. Monotropic mesophases may be detected and their associated transition temperatures measured by cooling the sample below the temperature at which it originally melted. The smectic, nematic and cholesteric mesophases are recognisable by the characteristic optical textures that they adopt when observed with the polariser and analyser of the polarising microscope set 'crossed'. These optical textures are briefly discussed in the Introduction to this thesis. However, in some instances, especially when very clean glass surfaces are used, the mesogenic molecules will adopt a pseudo-isotropic texture in which their long molecular axes are orientated normal to the glass surfaces. In this case, no birefringence occurs and the phase type is difficult to identify.

Results

The transition temperatures were measured by observation of the samples, mounted between microscope slides and cover slips using a polarising microscope (Vickers Instruments, model no. 10A) fitted with a Reichert Kofler hot stage. Measurements of temperature were taken during both heating and cooling cycles. The values quoted are corrected.

The differential thermal analysis was carried out on a Stanton Redcroft 671 differential thermal analyser coupled to an Oxford 3000 recorder. The transition temperature determinations and calorimetric operations were carried out simultaneously, heating the sample from roughly 40° up to about 20° above the mesophase-isotropic liquid transition temperature at a rate of 10° min.^{-1}. The coolant for the cycle was liquid nitrogen and the rate of cooling was 5° min.^{-1}. A static air atmosphere was used in the furnace. The standard used to calibrate the enthalpy transitions was ultra pure indium wire, the thermogram of which was obtained in the same manner. In all determinations alumina was used as the reference since it undergoes no transitions at or below the highest temperatures obtained in this work. The areas under the peaks were measured by cutting out the peaks and weighing them. The unit used for the enthalpies of transition (ΔH) is k.J.mol^{-1}; all monotropic transitions are indicated by square brackets.

Only the compounds in sections a)-d) were analysed by differential thermal analysis.

a) 4-Biphenyl 4″-n-alkoxybenzoates

Transition Temperatures and D.T.A. Results

n-R	C-I		C-S_A		C-N		S_A-N		N-I	
	(°)	ΔH	(°)	ΔH	(°)	ΔH	(°)	ΔH	(°)	ΔH
CH_3	155	37.4							[147]	1.09
C_2H_5	160	34.0							[157]	0.88
C_4H_9	152-153	44.5							[143]	1.22
C_5H_{11}	153.5	44.5							[133.5]	1.13
C_6H_{13}					133	39.5			136.5	1.55
C_7H_{15}					126	39.9			129.5	1.26
C_8H_{17}					119	37.8	[97.5]		130.5	1.18
$C_{10}H_{21}$					110	53.3	[106.5]	1.30	127	1.85
$C_{12}H_{25}$			108.5	60.5			112	2.14	123	1.68
$C_{14}H_{29}$			113-114	65.1			116.5	2.18	121.5	2.18

b) 4″-n-Alkoxyphenyl biphenyl-4 -carboxyates

Transition Temperatures and D.T.A. Results

n-R	C-I		C-N		N-I	
	(°)	ΔH	(°)	ΔH	(°)	ΔH
CH_3	161.5	35.3			[141]	1.43
C_2H_5	149.5	34.4			149.5	1.05
C_4H_9			140	35.3	141	1.30
C_5H_{11}			132.5	37.0	133	1.22
C_6H_{13}			125.5	35.3	134	1.30
C_7H_{15}			111	35.7	129	1.43
C_8H_{17}			114	37.8	128.5	1.22
$C_{10}H_{21}$			110.5	39.1	123.5	1.26
$C_{12}H_{25}$			111.5	52.1	119	1.81
$C_{14}H_{29}$			114	41.6	116	1.26
$C_{16}H_{33}$			114.5	66.4	[113]	2.02

c) 4-(4'-Pyridyl) phenyl 4''-n- alkoxybenzoates and their N-oxides

i) Alkoxybenzoates

Transition Temperatures and D.T.A. Results

n-R	C-I		C-S_A		C-N		N-S_A		S_A-I		N-I	
	(°)	ΔH	(°)	ΔH	(°)	ΔH	(°)	ΔH	(°)	ΔH	(°)	ΔH
C_4H_9	144	42.4									[112]*	-
C_5H_{11}	116	35.3					[101.5]	1.68			[110]	0.55
C_6H_{13}					113	34.9	[110.5]	1.43			115	0.63
C_7H_{15}			111	28.1					115	3.32		
C_8H_{17}			105.5	35.7					121.5	3.32		
C_9H_{19}			107	28.1					121	3.57		
$C_{10}H_{21}$			115	54.2					124.5	3.57		
$C_{12}H_{25}$			109	53.8					126	4.96		
$C_{14}H_{29}$			110	58.0					126.5	4.41		

*This transition was detected by differential thermal analysis. It was not observed optically because the sample crystallised.

ii) N-oxides

n-R	Transition Temperatures				
	C-N	C-S	$S-S_A$	S_A-N	S_A-I	N-I
C_5H_{11}	144°					187°
C_6H_{13}	144			[141°]		187
C_7H_{15}		129.5°		174.5		185.5
C_8H_{17}		135	[128.5°]		191.5°	
C_9H_{19}		141	181		192	
$C_{12}H_{25}$		132	[97.5]		200	
$C_{14}H_{29}$		132	[104.5]		203.5	

d) 4-(2'-Pyridyl) phenyl 4''-n-alkoxybenzoates

n-R	Transition Temperatures and D.T.A. Results			
	C-I		N-I	
	(°)	ΔH	(°)	ΔH
C_4H_9	159	46.2	[119.5]	1.05
C_5H_{11}	145.5	45.4	[108]*	-
C_6H_{13}	126.5	42.8	[116]	1.09
C_7H_{15}	126.5	57.6	[112]	1.72
C_8H_{17}	122	38.7	[115]	1.22
C_9H_{19}	129	65.1	[113]	1.76
$C_{10}H_{21}$	121	59.6	[114]	1.85
$C_{12}H_{25}$	119.5	61.7	[112.5]	2.56
$C_{14}H_{29}$	121.5	67.6	[111.5]	2.18

*This transition was detected by differential thermal analysis. It was not observed optically because the sample crystallised.

e) 2′-Fluoro-4-biphenylyl 4″-n-alkoxybenzoates

n-R	Transition Temperature			
	C-I	C-N	N-S_A	N-I
C_4H_9	119.5°			[97°]
C_5H_{11}	99			[86]
C_6H_{13}	102			[94]
C_7H_{15}	93.5			[90]
C_8H_{17}		86°		95
C_9H_{19}		90		92
$C_{10}H_{21}$		88		94
$C_{14}H_{29}$		88	[79°]	92.5

f) 2′-Chloro-4-biphenylyl 4″-n-alkoxybenzoates

n-R	Transition Temperature	
	C-I	N-I
C_6H_{13}	77°	[41.5°]
C_7H_{15}	67	[37]
C_8H_{17}	58	[44]
C_9H_{19}	60.5	[46]
$C_{10}H_{21}$	70	
$C_{14}H_{29}$	76.5	

g) 4-(4 -n-Alkoxyphenyl) pyridine-1 oxides

n-R	Transition Temperatures		
	C-I	C-S_A	S_A-I
C_6H_{13}	95.5°		[57.5°]
C_7H_{15}	97.5		[72]
C_8H_{17}		76.5°	85.5
C_9H_{19}		73.5	94.5
$C_{10}H_{21}$		78	102.5
$C_{12}H_{25}$		80	110.5
$C_{14}H_{29}$		84	113

2. Nuclear Magnetic Resonance Spectra

The low resolution n.m.r. spectra that appear in this section, were determined on a JEOL JNM-C-60HL 60MHz instrument (internal standard tetramethylsilane).

The alkyl protons from the n-alkoxy chain of all the compounds prepared in this work give a characteristic pattern, which is a common feature in all the n.m.r. spectra. The $-CH_2$ protons adjacent to the oxygen atom of the n-alkoxy chain are strongly deshielded and appear as a downfield triplet at about 4.0δ. The remaining protons of the n-alkoxy chain appear in the alkyl region of the n.m.r. spectrum as two distinct regions; the lower large broad peak (1.5δ) representing the $-(CH_2)_n$ protons and the smaller broad peak (0.9δ) representing the terminal $-CH_3$ of the n-alkoxy chain. For the methoxy and ethoxy compounds, the n.m.r. spectra are consistent with their structures.

The following is a short discussion on the aromatic region of the spectra of the compounds prepared in this work.

The aromatic region of the n.m.r. spectra of 4$''$-n-alkoxyphenyl biphenyl-4-carboxylates (spectrum 1), and the 2$'$-fluoro-and-chloro-4-biphenyl 4$''$-n-alkoxybenzoates (spectrum 3 and 4 respectively) have two distinct doublets in the aromatic region that can be easily identified. The doublet at 8.2δ is associated with the protons (H_A) flanking the carbonyl moiety of the central linking function of the esters which produces a strong deshielding effect, whilst the doublet at 7.0δ is associated with the protons (H_B) that flank the oxygen atom of the n-alkoxy chain. In this case, the oxygen atom shields such protons from the applied field. The assignment of these two doublets is consistent with n.m.r. data[96]. However, in the case of the 4$''$-n-alkoxyphenyl biphenyl-4-carboxylates (spectrum 1), the coupling constant J will differ for H_A and H_B since these protons are on adjacent aromatic rings (for H_A, J = 9.0 Hz; H_B, J = 6.0 Hz).

The n.m.r. spectrum of 4-biphenylyl 4$''$-n-alkxoybenzoates (spectrum 2) is similar to those previously discussed, in that the protons (H_A) which flank the carbonyl group of the central linking function of these esters are at a chemical shift of about 8.2δ, whilst those (H_B) flanking the oxygen atom of the n-alkoxy chain resonate at 7.0δ. Since the two doublets (marked H_A and H_B) are associated with protons on the same aromatic ring, the coupling constant J for these two doublets will be identical (H_A and H_B, J = 9.0 Hz).

In the n.m.r. spectrum for the 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates (spectrum 5), the protons associated with the carbonyl moiety of the central linking function (H_E) and the oxygen atom of the n-alkoxy chain (H_F) can be identified by comparison with the previous spectra. From n.m.r. data[96], the doublet at 8.5δ is associated with the two protons (H_A) flanking the nitrogen atom, which produces a very powerful deshielding effect. The remaining protons (H_B, H_C and H_D) are associated with the multiplet at 7.5δ.

The n.m.r. spectrum of 4-(2$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates (spectrum 6) is complicated in the aromatic region, and only the doublets associated with the proton (H_A) adjacent to the nitrogen atom and the protons (H_k) flanking the oxygen atom of the n-alkoxy chain can be readily assigned. The individual assignment of the pair of overlapping doublets at 8.0 δ is difficult because of the low resolution of the n.m.r. spectrum. However, from n.m.r. data[96], this pair of overlapping doublets may be associated with the protons H_E and H_G. The remaining protons (H_B, H_C, H_D and H_F) cannot be readily assigned.

In the n.m.r. spectrum for the 4-(4'-n-alkoxyphenyl) pyridines (spectrum 7), the doublet associated with the protons flanking the nitrogen atom (H_A, 8.6 δ) and the oxygen atom of the n-alkoxy chain (H_D, 7.0 δ) are easily recognisable. The low resolution nature of the n.m.r. spectrum once again makes it difficult to assign which of the pair of overlapping doublets at about 7.4 δ belongs to H_C and H_B. However, protons attached to the same aromatic ring have identical coupling constants and provided that the coupling constants J_{AB} and J_{CD} are significantly different, then assignment of these overlapping doublets can be made. The coupling constant J_{AB} is 6.0 Hz and this corresponds to the coupling constant shown by the lower of the two overlapping doublets. This doublet is thus designated H_B. The coupling constant of the remaining doublet (J = 9.0 Hz) corresponds to that found for the doublet marked H_D, and thus is designated H_C.

In the n.m.r. spectrum of the N-oxides of 4-(4'-n-alkoxyphenyl) pyridines (spectrum 8), the introduction of the N-oxide function has a pronounced effect on the position of the doublet associated with the protons flanking this function. The other protons are only slightly affected.

Fundamental to the chemistry of N-oxides is the fact that the dipolar ($\geqslant\overset{\oplus}{N}-O^{\ominus}$) moiety is both an electron donor and acceptor by the mesomeric effect[75]. This "push-pull" effect can be expressed by the canonical forms of the type B and C (in Figure 35) which contribute to the resonance hybrid.

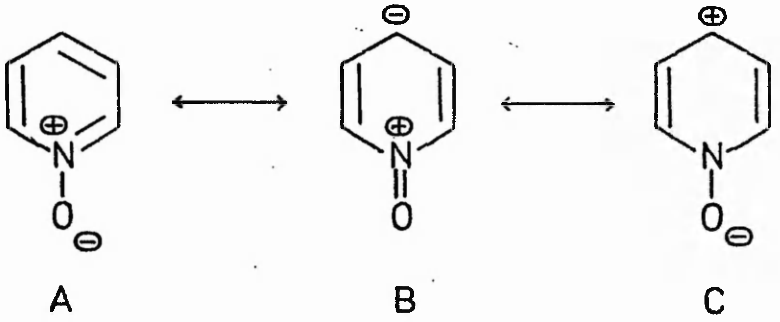


Figure 35 - Three Canonical Structures of Pyridine 1-oxide

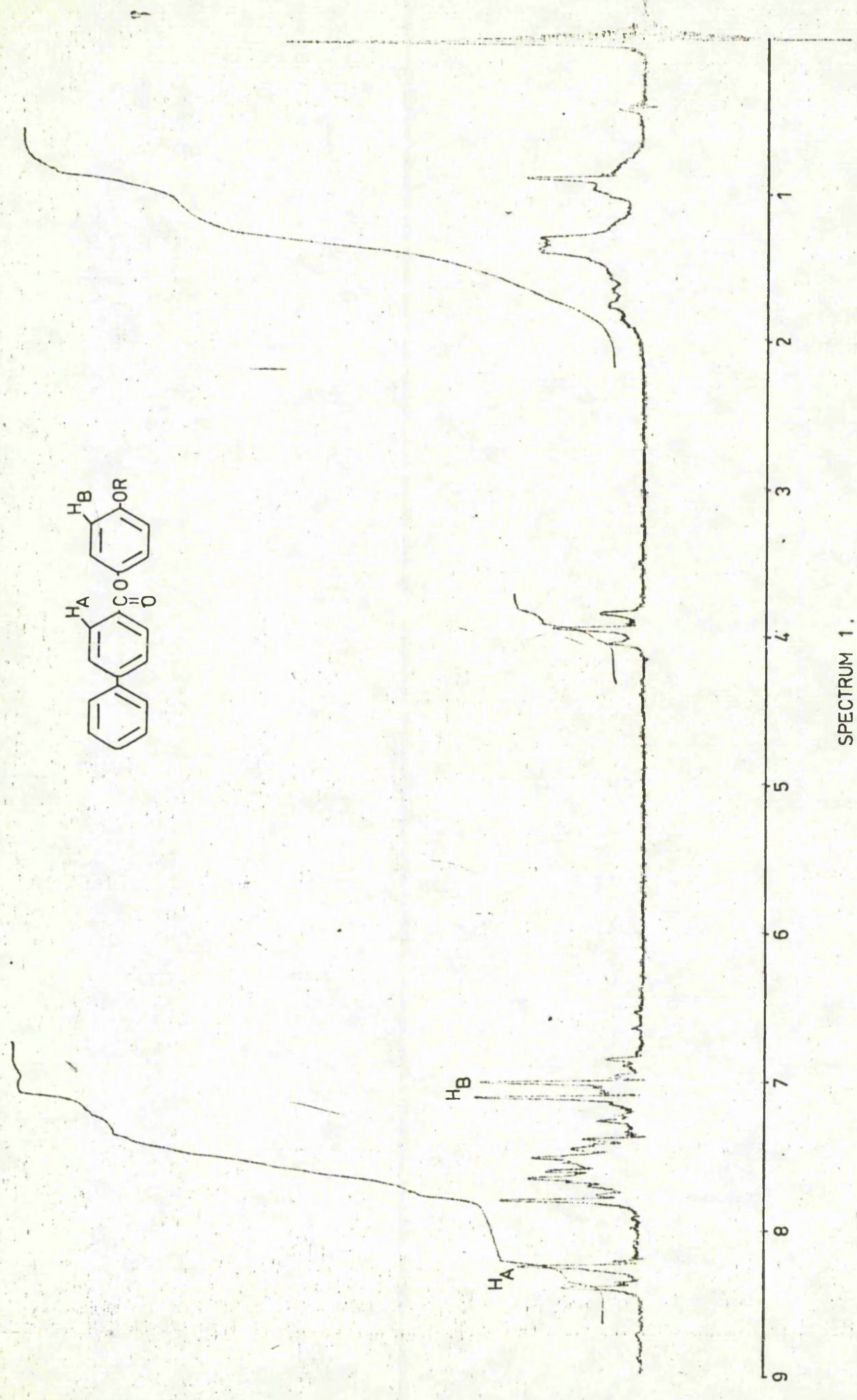
In spectrum 8, the protons which flank the N-oxide function are observed upfield in comparison to the protons flanking the nitrogen atom in 4-(4'-n-alkoxy phenyl) pyridine (spectrum 7). This suggests that back donating by the oxygen atom of the N-oxide function (canonical structure B) has a major influence on the structure of the resonance hybrid. A comparison of the n.m.r. spectra of 4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates and their N-oxides (spectrum 9), also clearly shows this effect, even though the doublet associated with the protons flanking the nitrogen moiety of 4-(4'-pyridyl) phenyl 4$''$-n-alkoxybenzoates is unresolved.

a) 4"-n-Alkoxylphenyl biphenyl-4'-carboxylates

n-CH_3O 3.78 (s, 3H, -OCH_3) ; 7.02 (d, J 6.0 Hz, 2H) ; 7.50 (m, 9H) ; 8.26 (d, J9.0 Hz, 2H)

n-C_2H_5O 1.39 (t,J 6.5 Hz, 3H, -CH_3) ; 4.02 (q, J 6.0 Hz, 2H, -OCH_2) ; 7.02 (d, J 6.0 Hz, 2H) ; 7.48(m,9H) 8.25 (d, J 9.0 Hz, 2H)

n-R	(Br,3H,-CH_3)	(Br,XH)	(t,J6.0Hz,2H,-OCH_2)	(d,J6.0Hz,2H)	(m,9H)	(dJ9.0Hz,2H)
C_4H_9	1.01	1.62 (4)	4.08	7.15	7.61	8.28
C_5H_{11}	0.94	1.55 (6)	4.01	7.12	7.60	8.38
C_6H_{13}	0.95	1.43 (8)	4.03	7.15	7.64	8.35
C_7H_{15}	0.94	1.40 (11)	4.06	7.10	7.73	8.30
C_8H_{17}	0.89	1.32 (13)	3.94	7.02	7.50	8.25
$C_{10}H_{21}$	0.86	1.28 (17)	3.90	6.97	7.47	8.25
$C_{12}H_{25}$	0.90	1.32 (21)	3.95	6.92	7.32	8.14
$C_{14}H_{29}$	0.89	1.32 (26)	4.00	6.86	7.27	8.21
$C_{16}H_{33}$	0.87	1.27 (27)	3.95	7.02	7.53	8.32



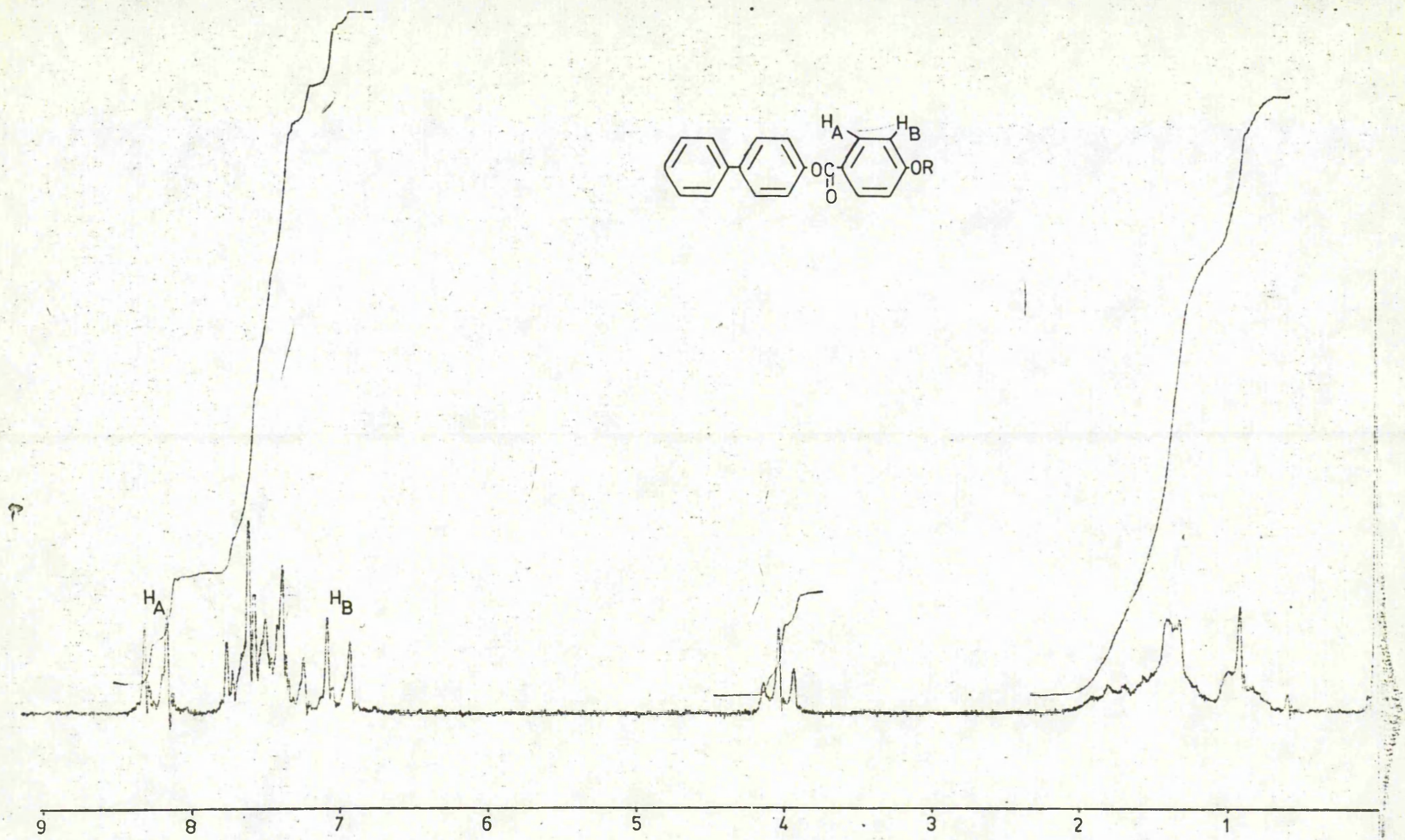
SPECTRUM 1.

b) **4-Biphenylyl 4''-n-alkoxybenzoates**

n-CH_3O 3.88 (s,3H,OCH_3) ; 7.03 (d,J 9.0 Hz, 2H) ; 7.55 (m,9H) ; 8.25 (d,J 4.5 Hz, 2H)

n-C_2H_5O 1.40 (t, J 6.0 Hz, 3H) ; 4.08 (q, J 3.5 Hz, 2H,-OCH_2) ; 6.94 (d, J 4.5 Hz, 2H) ; 7.47 (m, 9H) ; 8.18 (d, J 4.5 Hz, 2H)

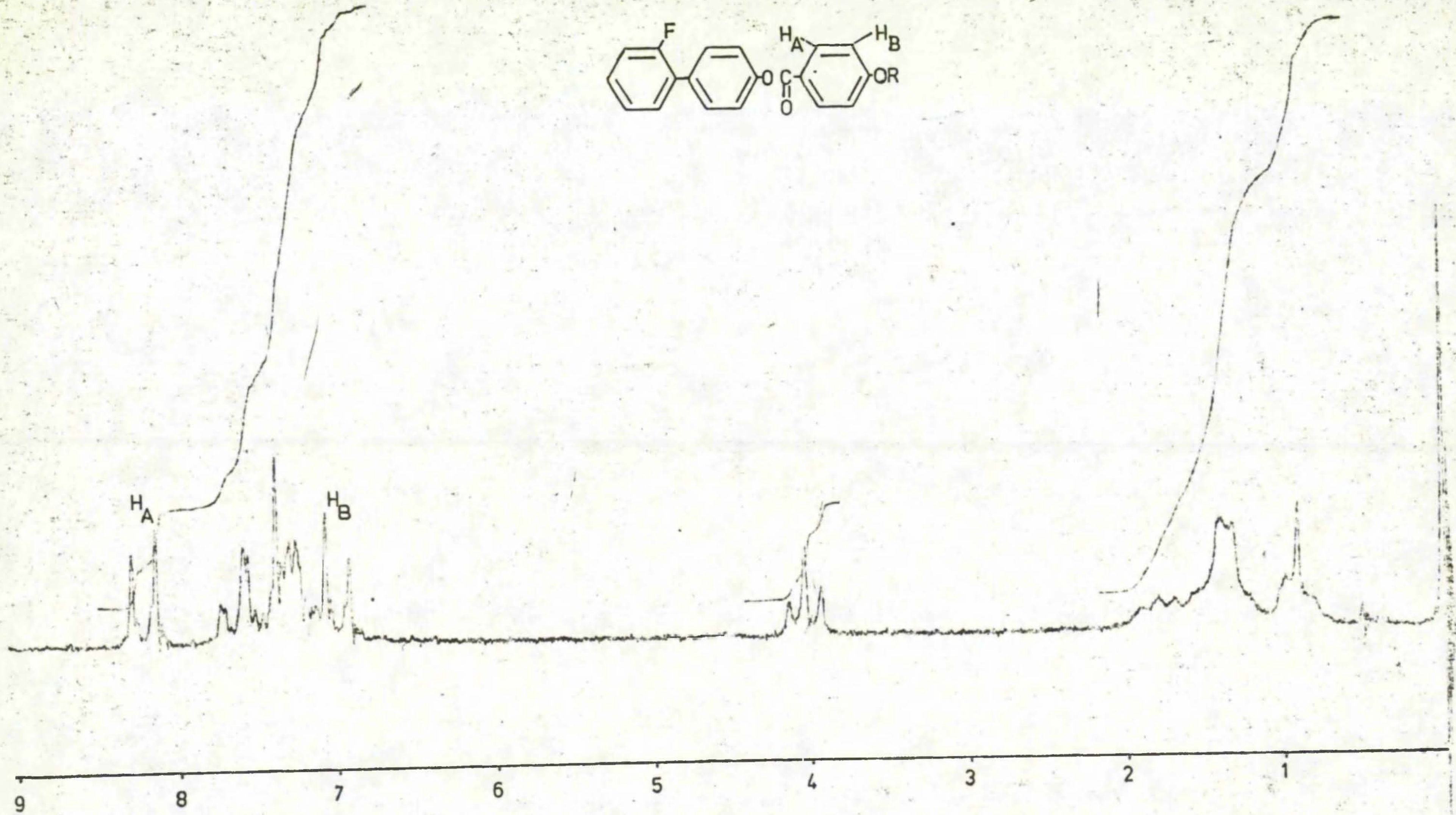
n-R	(Br,3H,-CH_3)	(Br,XH)	(t,J6.OHz,2H,-OCH_2)	(d,J9.OHz,2H)	(m,9H)	(d,J9.OHz,2H)
C_4H_9	1.00	1.65 (4)	4.07	7.04	7.55	8.25
C_5H_{11}	1.00	1.56 (6)	4.09	7.04	7.55	8.30
C_6H_{13}	0.94	1.38 (8)	4.15	7.16	7.65	8.39
C_7H_{15}	0.92	1.36 (11)	4.06	7.04	7.55	8.28
C_8H_{17}	0.92	1.34 (14)	4.03	6.96	7.46	8.18
$C_{10}H_{21}$	0.88	1.30 (17)	4.00	6.94	7.44	8.15
$C_{12}H_{25}$	0.87	1.28 (19)	4.02	6.95	7.45	8.16
$C_{14}H_{29}$	0.85	1.28 (26)	4.02	6.95	7.52	8.18



SPECTRUM 2.

c) $2^{'}$-Fluoro-4-biphenylyl $4^{''}$-n-alkoxybenzoates

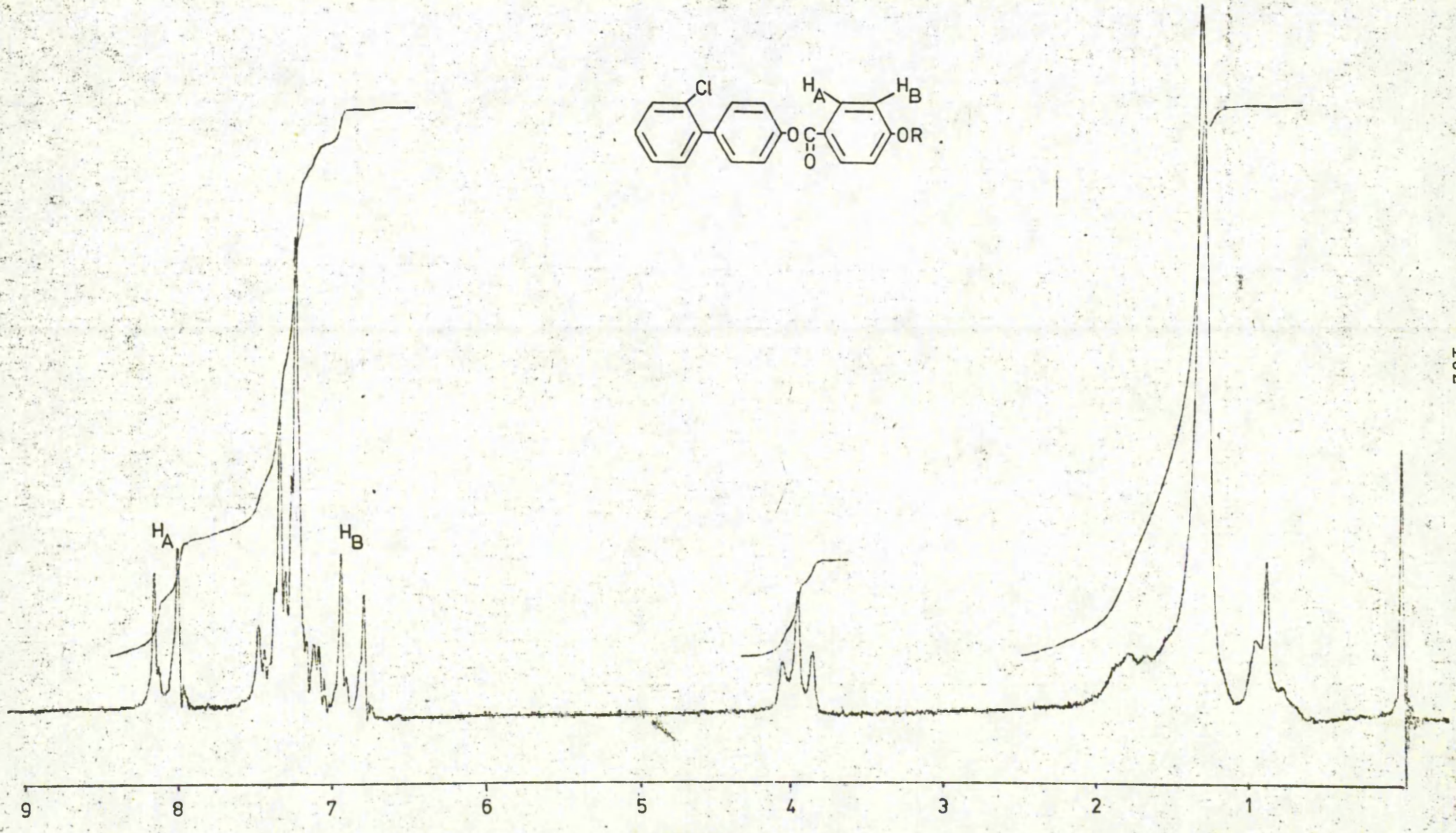
n-R	(Br,3H,-CH_3)	(Br, XH)	(t,J6.0Hz,2H,-OCH_2)	(d,J9.0Hz,2H)	(m,8H)	(d,J9.0Hz,2H)
C_4H_9	0.95	1.56 (4)	4.03	6.95	7.29	8.20
C_5H_{11}	0.92	1.60 (6)	4.00	6.94	7.28	8.18
C_6H_{13}	0.83	1.50 (9)	4.04	6.96	7.25	8.18
C_7H_{15}	0.90	1.55 (11)	4.03	6.97	7.35	8.22
C_8H_{17}	0.87	1.52 (13)	4.03	6.96	7.32	8.21
C_9H_{19}	0.86	1.54 (13)	4.00	6.96	7.32	8.20
$C_{10}H_{21}$	0.90	1.55 (17)	4.02	6.97	7.33	8.20
$C_{14}H_{29}$	0.92	1.57 (26)	4.03	6.97	7.32	8.20



SPECTRUM 3.

d) $2'$-Chloro-4-biphenylyl $4''$-n-alkoxybenzoates

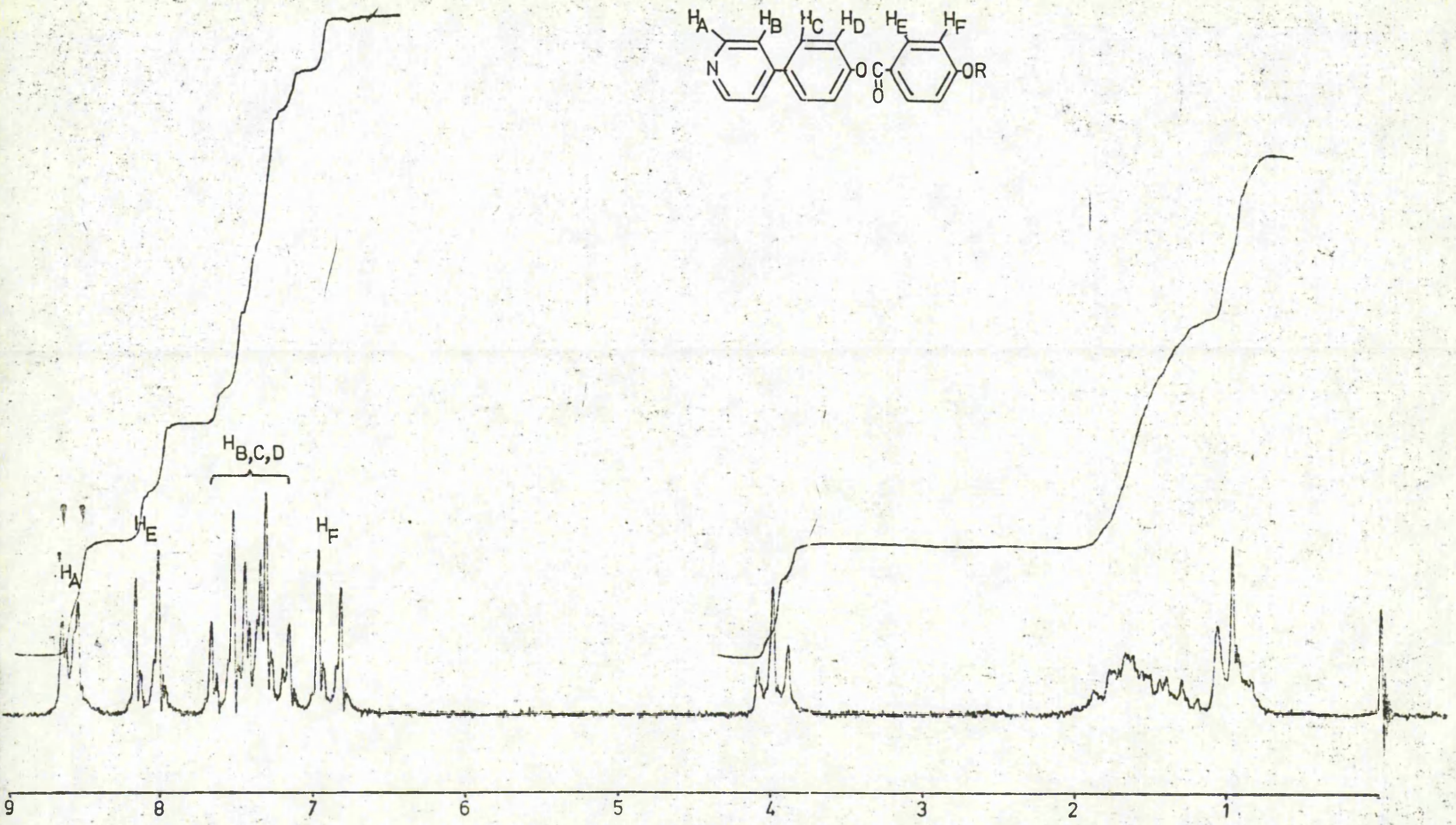
n-R	(Br,3H,-CH_3)	(Br,XH)	(t,J6.OHz,2H,-OCH_2)	(d,J9.OHz,2H)	(m,8H)	(d,J9.OHz,2H)
C_6H_{13}	0.87	1.52 (9)	4.03	7.01	7.39	8.23
C_7H_{15}	0.85	1.53 (12)	4.04	7.00	7.39	8.22
C_8H_{17}	0.82	1.52 (12)	4.02	7.02	7.40	8.22
C_9H_{19}	0.84	1.52 (16)	4.03	7.00	7.40	8.23
$C_{10}H_{21}$	0.80	1.50 (15)	4.08	7.06	7.47	8.32
$C_{14}H_{29}$	0.90	1.48 (26)	4.04	7.01	7.40	8.22



SPECTRUM 4

e) 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates

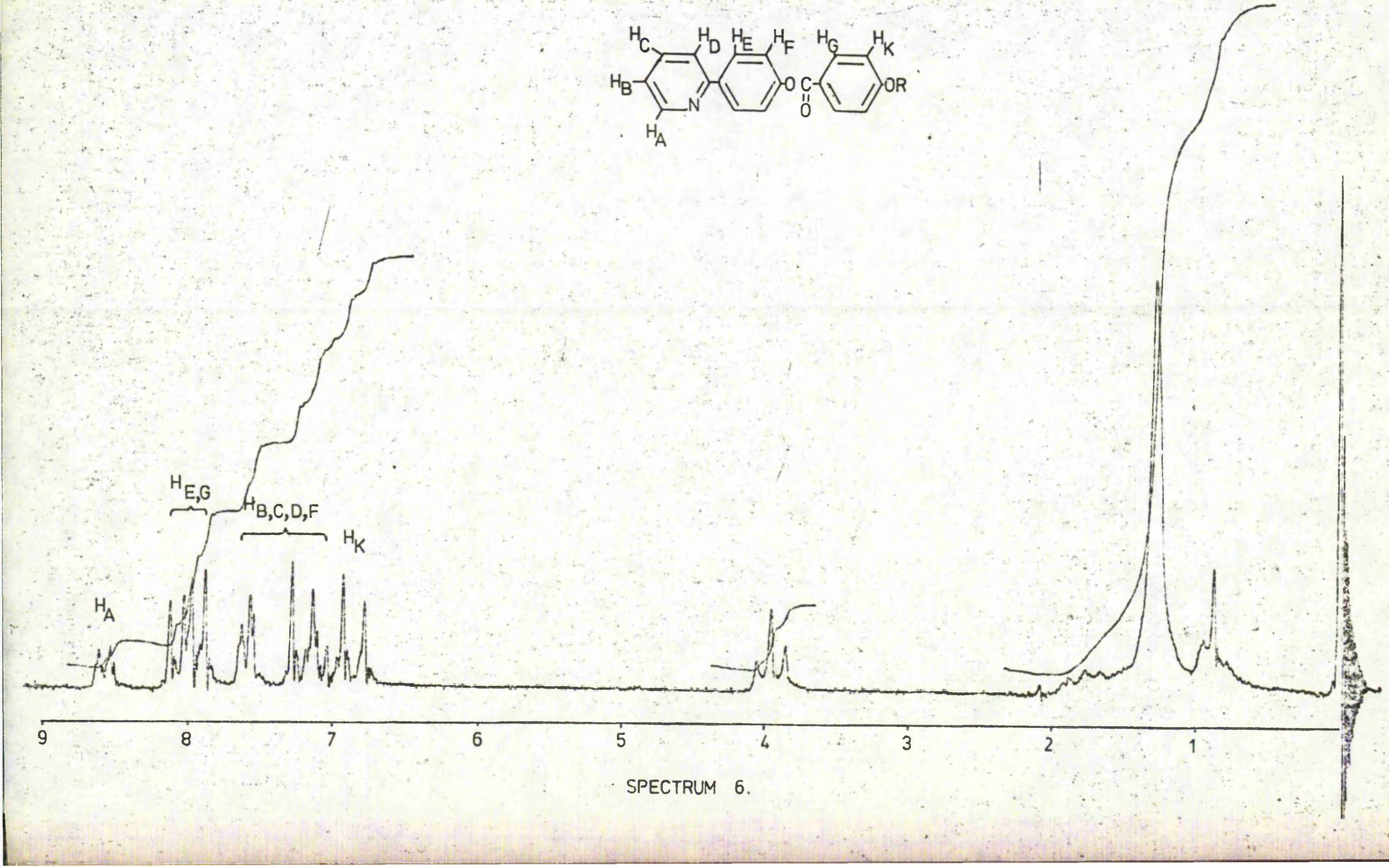
n-R	(Br,3H,-CH_3)	(Br,XH)	(t,J6.OHz,2H,-OCH_2)	(d,J9.OHz,2H)	(m,6H)	(d,J9.OHz,2H)	(d,J6.OHz,2H)
C_4H_9	0.93	1.57 (5)	4.05	7.00	7.55	8.21	8.73
C_5H_{11}	0.94	1.57 (7)	4.06	7.02	7.56	8.24	8.74
C_6H_{13}	0.92	1.54 (9)	4.04	7.01	7.53	8.22	8.72
C_7H_{15}	0.86	1.50 (11)	4.06	7.04	7.56	8.24	8.76
C_8H_{17}	0.88	1.52 (12)	4.01	6.94	7.49	8.13	8.65
C_9H_{19}	0.88	1.56 (15)	4.06	7.04	7.59	8.26	8.75
$C_{10}H_{21}$	0.91	1.53 (16)	4.03	6.98	7.50	8.17	8.68
$C_{12}H_{25}$	0.86	1.53 (21)	4.05	7.02	7.49	8.16	8.68
$C_{14}H_{29}$	0.84	1.52 (25)	4.04	6.99	7.52	8.20	8.70



SPECTRUM 5.

f) 4-(2'-Pyridyl) phenyl 4''-n-alkoxybenzoates

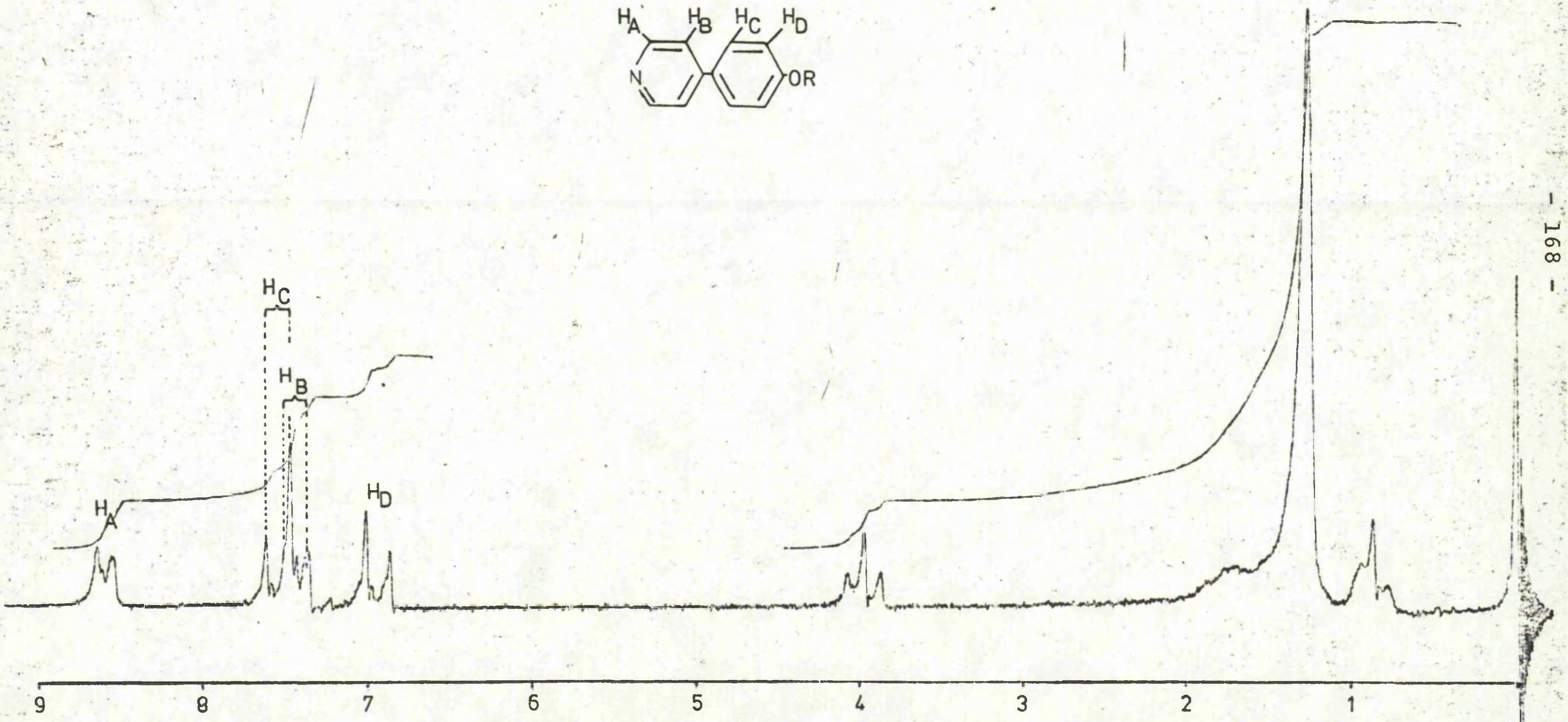
n-R	(Br,3H,-CH$_3$)	(Br,XH)	(t,J6.OHz, 2H,-OCH$_2$)	(d,J9.OHz, 2H)	(d,J9.OHz, 3H)	(d,J5.OHz, 2H)	(d,J9.OHz, 2H)	(d,J9.OHz, 2H)	(d,J5.O Hz,1H)
C_4H_9	0.95	1.56 (4)	4.04	6.92	7.28	7.65	8.02	8.13	8.74
C_5H_{11}	0.87	1.51 (6)	4.00	6.97	7.32	7.72	8.09	8.17	8.72
C_6H_{13}	0.87	1.58 (9)	3.96	6.95	7.34	7.71	8.07	8.19	8.64
C_7H_{15}	0.92	1.52 (11)	4.04	6.97	7.32	7.73	8.09	8.19	8.76
C_8H_{17}	0.88	1.54 (12)	3.98	6.91	7.28	7.68	8.03	8.13	8.70
C_9H_{19}	0.84	1.52 (14)	4.02	6.97	7.32	7.72	8.08	8.18	8.72
$C_{10}H_{21}$	0.87	1.53 (17)	3.98	6.91	7.28	7.68	8.02	8.12	8.68
$C_{12}H_{25}$	0.88	1.54 (20)	4.04	6.98	7.32	7.73	8.09	8.19	8.76
$C_{14}H_{29}$	0.86	1.53 (24)	4.00	6.91	7.27	7.68	8.02	8.12	8.66



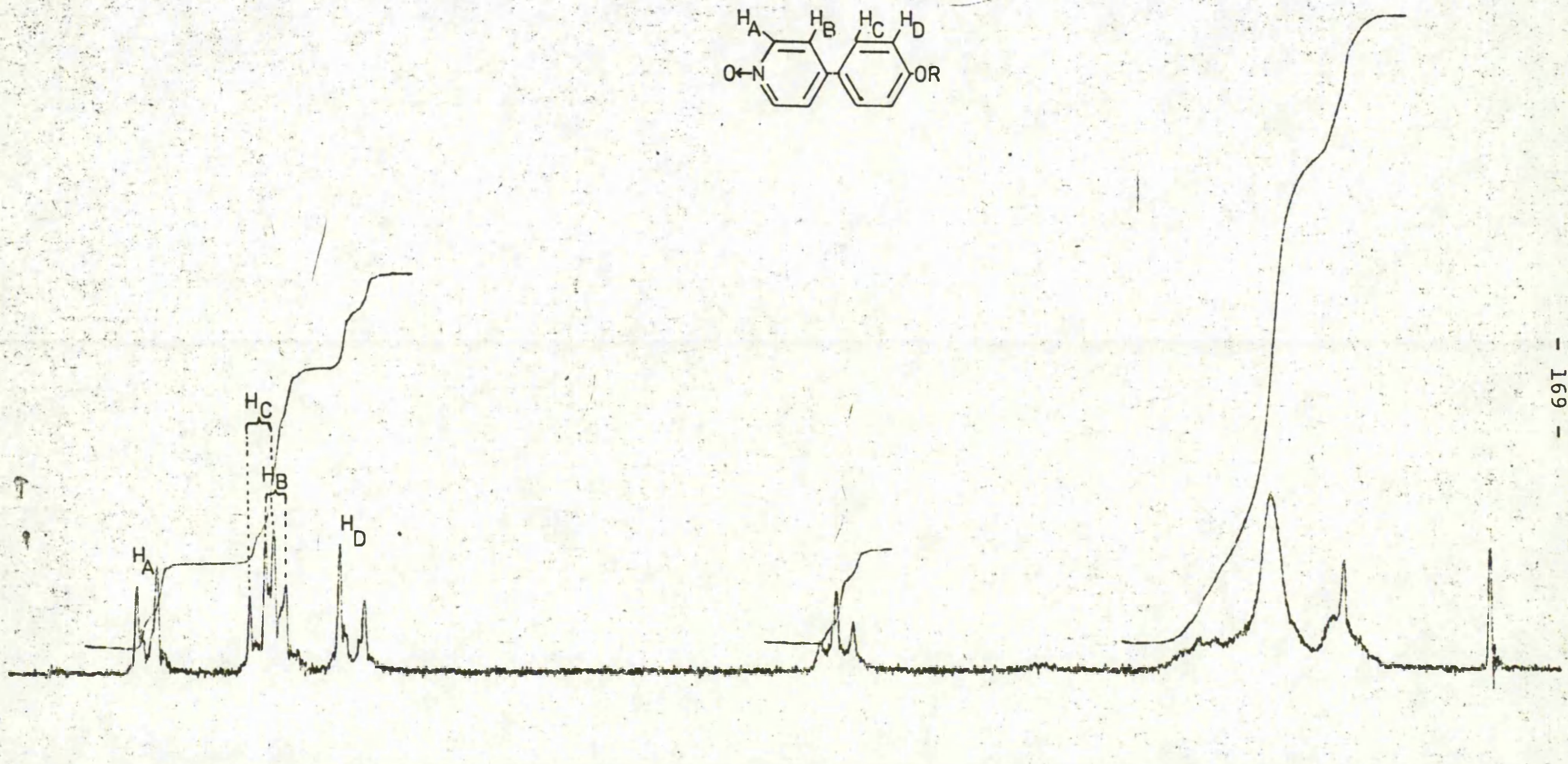
SPECTRUM 6.

g) 4-(4$'$-n-Alkoxyphenyl) pyridines and their N-oxides

n-R	(Br,3H,-CH_3)	(Br, XH)	(t,J6.0Hz, 2H,-OCH_2)	(d,J9.0Hz,2H,D)	(d,J6.0Hz,2H,B)	(d,J9.0Hz,2H,C)	(d,J6.0Hz,2H,A)
C_6H_{13}	0.84	1.49 (8)	3.98	7.00	7.46	7.60	8.62
N-oxide	0.90	1.50 (8)	3.96	6.95	7.50	7.60	8.18
C_7H_{15}	0.85	1.48 (11)	3.98	6.98	7.44	7.58	8.58
N-oxide	0.88	1.52 (10)	4.02	7.01	7.44	7.58	8.18
C_8H_{17}	0.85	1.48 (13)	4.00	7.00	7.46	7.61	8.62
N-oxide	0.88	1.55 (12)	3.98	6.94	7.49	7.58	8.18
C_9H_{19}	0.84	1.54 (16)	4.00	6.98	7.46	7.60	8.65
N-oxide	0.88	1.52 (15)	3.96	6.98	7.48	7.60	8.17
$C_{10}H_{21}$	0.80	1.51 (17)	4.01	7.02	7.48	7.63	8.68
N-oxide	0.84	1.53 (17)	3.96	6.96	7.38	7.46	8.16
$C_{12}H_{25}$	0.84	1.52 (21)	4.00	7.02	7.47	7.62	8.68
N-oxide	0.85	1.53 (21)	4.02	7.02	7.48	7.57	8.24
$C_{14}H_{29}$	0.85	1.52 (27)	4.01	7.01	7.48	7.63	8.67
N-oxide	0.90	1.52 (26)	3.97	7.00	7.50	7.61	8.20



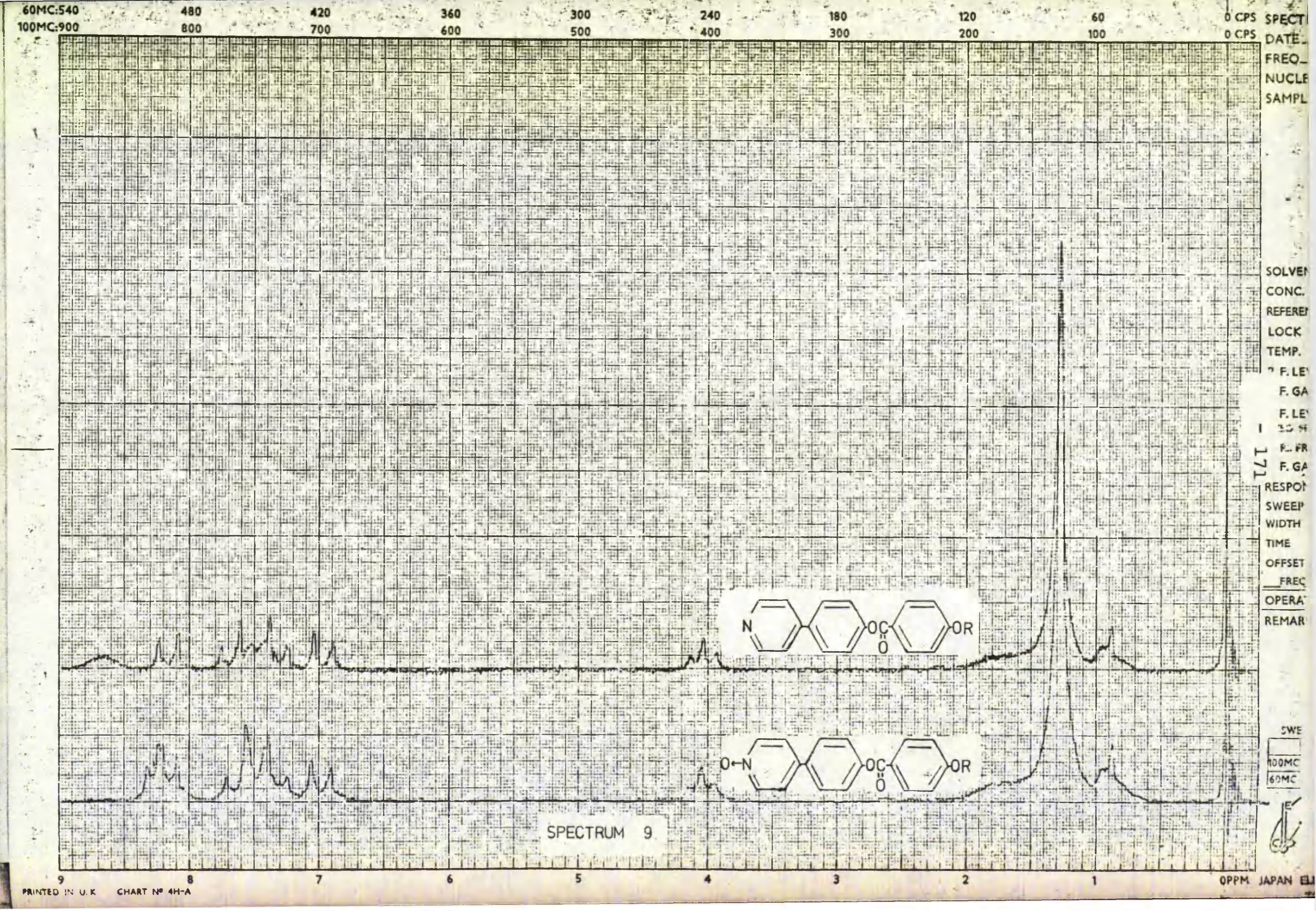
SPECTRUM 7



SPECTRUM 8.

h) N-oxide of 4-($4'$-pyridyl) phenyl $4''$-n-alkoxybenzoates

n-R	(Br,3H,$-CH_3$)	(Br,XH)	(t,J6.OHz,2H,$-OCH_2$)	(d,J9.OHz,2H)	(m,6H)	(d,J9.OHz,2H)	(d,J6.OHz,2H)
C_5H_{11}	0.86	1.49 (6)	4.02	7.01	7.52	8.20	8.33
C_7H_{15}	0.90	1.48 (11)	4.00	7.00	7.51	8.20	8.30
C_9H_{19}	0.88	1.53 (16)	4.00	6.96	7.46	8.18	8.26
$C_{12}H_{25}$	0.84	1.52 (21)	4.01	6.98	7.46	8.16	8.27
$C_{14}H_{29}$	0.85	1.50 (26)	4.04	6.96	7.48	8.17	8.27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800
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SPECTRUM 9

3. Infrared Spectra

The infrared spectra (KBr disc) were determined on a Perkin-Elmer 157G grating spectrophotometer. The wavelengths are in cm^{-1}.

The Infrared Spectra of the Esters

Vibrational mode	(a)	(b)	(c)	(d)	(e)	(f)
C-H str.	2955,2920(m)	2955,2935(m)	2960,2930(m)	2955,2930(m)	2960,2930(m)	2950,2910(m)
CH_2 and CH_3	2845(m)	2860(m)	2860(m)	2875(m)	2855(m)	2855(m)
$\rangle C = O$	1735(s)	1730(s)	1732(s)	1735(s)	1740(s)	1730(s)
Aryl-H	1605(s)	1610(s)	1605(s)	1605(s)	1610(s)	1605(s)
	1580(m)	1580(m)	1580(m)	1580(m)	1580(m)	1580(m)
	1510(s)	1505(s)	1510(m)	1510(m)	1515(m)	1510(m)
	1265(s)	1295(s)	1260(s)	1255(s)	1280(s)	1255(s)
	1215(s)	1245(m)	1210(s)	1200(s)	1218(s)	1205(s)
	1190(s)	1200(s)	1170(s)	1165(s)	1175(s)	1170(s)

a) 4-Biphenylyl 4″-n-alkoxybenzoates

b) 4″-n-Alkoxyphenyl biphenyl-4 -carboxylates

c) 2′-Fluoro-4-biphenylyl 4″-n-alkoxybenzoates

d) 2′-Chloro-4-biphenylyl 4″-n-alkoxybenzoates

e) 4-(4′-Pyridyl) phenyl 4″-n-alkoxybenzoates

f) 4-(2′-Pyridyl) phenyl 4″-n-alkoxybenzoates

The Infrared spectra of 4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates (e) and their N-oxide

Vibrational mode	(e)	N-oxide
C-H str.	2960, 2930 (m)	2950, 2930 (m)
CH_2 and CH_3	2855 (m)	2850 (m)
$\rangle C = O$	1740 (s)	1735 (s)
Ary-H	1610 (s)	1605 (s)
	1580 (m)	1580 (m)
	1515 (m)	1500 (m)
	1280 (s)	1290 (s)
	1218 (s)	1230 (s)
	1175 (s)	1180 (m)

The Infrared spectra of 4-(4'-n-alkoxyphenyl) pyridines (g) and their N-oxides

Vibrational Mode	(g)	N-oxide
C-H str.	2970, 2930 (m)	2960, 2930 (m)
CH_2 and CH_3	2855 (m)	2850 (m)
Aryl-H	1608 (s)	1610 (s)
	1580 (m)	1580 (s)
	1520 (m)	1500 (m)
	1290 (s)	1290 (s)
	1260 (s)	1245 (s)
	1225 (s)	1180 (m)
	1185 (s)	
Aromatic	850 (s)	828 (s)
para-disubstitution	828 (s)	

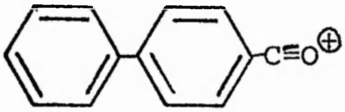
4. Mass Spectroscopic Data

a) Comparison of the mass spectra of:

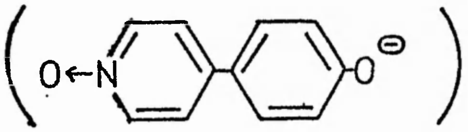
i) 1,4-di-n-tetradecyloxyphenyl diether.

ii) 4-n-tetradecyloxyphenyl biphenyl-4 -carboxylate.

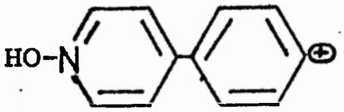
iii) The above ester containated with the diether in i).

(i) m/e	(ii) m/e	(iii) m/e	Assignment
		503	} m$^+$ for (i)
502			
	486	486	m$^+$ for (ii)
475		475	m$^+$ for (i) - $(C_2H_5)^+$
308		308	
	302		
	214		
	181	181	
179			
152	152	152	
136			
	127	127	
110	110	110	
83		83	
69		69	
57	57	57	
55	55	55	
43	43	43	$C_3H_7^{\oplus}$
41	41	41	

b) N-oxide of 4-(4'-pyridyl) phenyl 4''-n-hexyloxybenzoate

m/e	Assignment
391	m$^+$
375	m$^+$ - (O)
360	m$^+$ - (OCH$_3$)
262	
223	
205	m$^+$ - 
191	
186	
171	HO-Pyr.Ph$^\oplus$

c) N-oxide of 4-(4'-pyridyl) phenyl 4''-n-tetradecyloxybenzoate

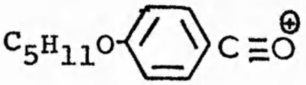
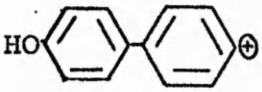
m/e	Assignment
503	m$^+$
487	m$^+$ - (O)
317	$C_{14}H_{29}O.Ph.C\equiv O^{\oplus}$
205	
191	
187	
186	
172	
171	
170	

In both the mass spectra of b) and c), there were many intense peaks below m/e 150, making the spectra very complicated to evaluate below this point.

d) N-oxide of 4-(4'-n-tetradecyloxyphenyl) pyridine (A) and 4-(4'-n-octyloxyphenyl) pyridine (B)

	A			B	
m/e	Abundance	Assignment	m/e	Abundance	Assignment
383	10.6	Molecular ion M^+	299	2.7	Molecular ion M^+
368	12.9		284	1.9	$M^+ - (CH_3)$
367	50.0	$M^+ - (O)$	283	7.7	$M^+ - (O)$
366	7.6		188	2.4	
354	6.0	$M^+ - (CH_2CH_3)$	187	17.1	
340	4.8		172	11.8	
326	4.6		171	100.0	HO.Pyr.Ph$^{\oplus}$
310	3.7		170	3.3	
184	8.2		154	3.1	Pyr.Ph$^{\oplus}$
172	16.8		142	3.6	
171	100.0	HO.Pyr.Ph$^{\oplus}$	133	2.5	
154	3.5	Pyr.Ph$^{\oplus}$	131	3.7	
115	4.1	$HOC_7H_{14}^{\oplus}$	127	3.6	
95	1.8	HOPyr.$^{\oplus}$	115	6.7	$HOC_7H_{14}^{\oplus}$
83	15.1		95	1.9	HO.Pyr$^{\oplus}$
71	7.4	$C_5H_{11}^{\oplus}$	89	3.6	

e) 4-Biphenylyl. 4''-n-pentyloxybenzoate

m/E	Abundance	Assignment
360	19.8	Molecular ion m^+
193	6.1	
192	68.5	
191	100.0	
170	15.2	
169	21.8	
153	1.7	
152	2.0	
141	13.2	
139	4.7	
122	15.1	
121	100.0	
120	9.1	
115	12.6	
93	19.1	
71	2.9	

EXPERIMENTAL

Contents

1. Synthesis of:
   - a) 4-biphenylyl 4″-n-alkoxybenzoates;
   - b) 4″-n-alkoxyphenyl biphenyl-4-carboxylates; and
   - c) 4″-n-heptyloxyphenyl 4′-cyanobiphenyl-4-carboxylate.

2. Synthesis of:
   - a) 2′-fluro-4-biphenylyl 4″-n-alkoxybenzoates; and
   - b) 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates.

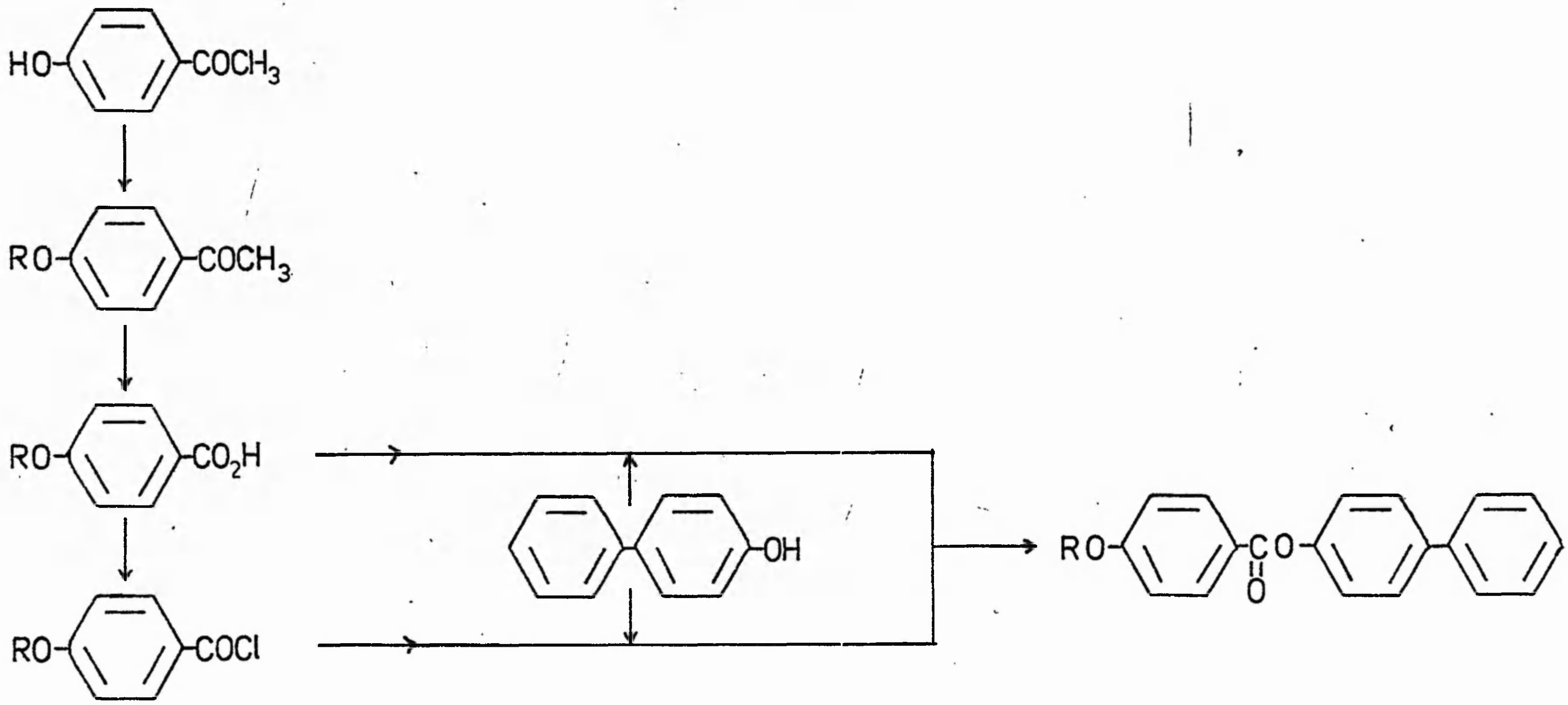
3. Synthesis of:
   - a) 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates;
   - b) 4-(2′-pyridyl)phenyl 4″-n-alkoxybenzoates;
   - c) 4-(4′-n-alkoxyphenyl) pyridines; and
   - d) the corresponding N-oxides of a), b) and c).

4. Miscellaneous:
   - a) Preparation of 4-pyridyl 4′-n-heptyloxybenzoate and 4-pyridyl 4′-n-octyloxybenzoate.
   - b) Classification of the Smectic Mesophases.

All the transition temperatures and melting points recorded in this section are corrected. Unless stated otherwise, thin layer chromatography was carried out on pre-coated alumina plates [Polygramm ALAX N/U.V$_{254}$ (5 x 20 cm^3) from Camlab Cambridge], using chloroform as the solvent. Sometimes pre-coated silica gel plates [Polygramm SIL G/U.V$_{254}$ (5 x 20 cm^3) from Camlab Cambridge] were used with either chloroform, ethyl acetate : benzene (1 : 3) or ethyl acetate : light petroleum (b.p. 60-80 (1 : 1) as the solvent. These exceptions to the alumina/chloroform system will be indicated by S.G/C, S.G/E.A:B or S.G/E.A:P in the text. Both silica gel and alumina t.l.c. plates were developed under ultraviolet light and/or in iodine vapour.

1a) Synthesis of 4-biphenylyl 4″-n-alkoxybenzoates

SCHEME FOR THE 4-BIPHENYLYL 4″-n-ALKOXYBENZOATES



R=n-ALKYL.

4-n-Alkoxyacetophenones

4-Hydroxyacetophenone (13.6g, 0.1 M), anhydrous potassium carbonate (60.0g, 0.4 M) and cyclohexanone (150 cm^3) were placed in a 500 cm^3 flask, fitted with a stirrer and condenser. Whilst stirring, the alkyl bromide (0.16 M) was added and the reaction mixture was then heated under reflux for 4h.

After cooling, the salts were filtered off and washed several times with cyclohexanone. The cyclohexanone was then distilled off, under vacuum, from the combined filtrate and washings. The resulting crude ketones were purified by vacuum distillation, except for the n-heptyloxy, -dodecyloxy and -tetradecyloxy compounds which were purified by recrystallisation from methanol. All the purified ketones gave a single t.l.c. spot (SG/C).

The m.p. and b.p. and percentage yield of each of the 4-n-alkoxyacetophenones prepared in this work are listed in table 10.

Table 10 -Data for the 4-n-alkoxyacetophenones

n-R	m.p. (lit)	b.p. (lit) °/mm	% Yield	Ref
C_2H_5	(39°)	104-105/1.0	88	10
C_4H_9		125-126/0.15 (169-170/13)	96	5
C_5H_{11}		139-141/2.0 (132/0.4)	98	8
C_6H_{13}		147/0.07 (143-145/0.5)	89	8
C_7H_{15}	41° (45)		88	7
C_8H_{17}		163-165/0.5 (161-163/0.4)	79	8
C_9H_{19}		162-164/0.3 (163/0.4)	84	8
$C_{10}H_{21}$	(37°)	192-198/2.5 (194-195/2)	82	7
$C_{12}H_{25}$	48-49°(50)		85	9
*$C_{14}H_{29}$	58-59°		79	

*n-Tetradecyloxyacetophenone (Found: C, 79.2; H, 10.7 $C_{22}H_{36}O_2$ requires C, 79.5: H, 10.9%) was not reported in the literature.

4-n-Alkoxybenzoic Acid

Sodium hydroxide (28.6g) was dissolved in water (135 cm^3). The solution was cooled to below 5° and at or below this temperature, bromine (10.2 cm^3) was added carefully, stirring throughout the addition. The resulting sodium hypobromite solution was kept below 5° until required.

The 4-n-alkoxyacetophenone (0.0434 M) was dissolved in dioxan (102 cm^{3+}) at 35-40°. Keeping the temperature within this range and with continuous stirring, small portions of the sodium hypobromite solution were added dropwise (the reaction was exothermic). When the addition was complete, the solution was stirred at 35-40° for 30 minutes.

The solution was diluted with water (650 cm^3) and 150 cm^3 of the resulting solution was then distilled off. The hot solution was filtered to remove a small quantity of suspended solid and then allowed to cool. Acidification with concentrated hydrochloric acid released the crude acid which was filtered off, washed with water and dried. The crude acid was then purified by recrystallisation from benzene and/or acetone.

The percentage yields and C-I, C-S, C-N, and mesophase transition temperatures of the 4-n-alkoxybenzoic acids prepared by this method are presented in table 11 together with (in parentheses) the corresponding values obtained by Gray[77].

Notes

\+ For the oxidation of n-dodecyloxy- and n-tetradecyloxyacetophenone, the amount of dioxan used was increased to 150 cm^3.

++ Interpolated.

Table 11 - The transition temperatures of 4-n-alkoxybenzoic acids

n-R	Transition Temperature						Yield
	C-I	C-S_A	C-N	S_A-N	S_A-I	N-I	%
C_2H_5	$196^{\circ}(196^{\circ})$						63
C_4H_9			$145^{\circ}(147^{\circ})$			$158^{\circ}(160^{\circ})$	72
C_5H_{11}			124 (124)			150 (151)	73
C_6H_{13}			105 (105)			153 (153)	78
C_7H_{15}		$92^{\circ}(92^{\circ})$		$98^{\circ}(98^{\circ})$		145.5 (146)	75
C_8H_{17}		98.5(101)		109 (108)		147 (147)	85
C_9H_{19}		94 (94)		117 (117)		143 (143)	80
$C_{10}H_{21}$		98 (97)		120 (122)		141 (142)	86
$C_{12}H_{25}$		97 (95)		130 (129)		138 (137)	60
$C_{14}H_{29}$		99			$134^{\circ}(133^{\circ++})$		67

4-biphenylyl 4″-n-alkoxybenzoates

These esters of the 4-n-alkoxybenzoic acids were prepared by the following two methods:

a) Indirectly, via the acid chloride

The preparation of 4-n-biphenylyl 4″-n-octyloxybenzoate exemplifies the method used.

4-n-octyloxybenzoic acid (1.45 g, 1 mol. equiv.) was heated under reflux, with thionyl chloride (10 cm^3) for 2h. The bulk of the thionyl chloride was then distilled off, and the final traces were removed under vacuum.

The acid chloride was added to 4-hydroxybiphenyl (1.0 g, 1 mol. equiv.) in dry pyridine (10 cm^3) and the reaction mixture was heated, under reflux, for 3h.

When cool, the mixture was treated with 5% sulphuric acid (25 cm^3) followed by water (100 cm^3) and the precipitated crude ester was filtered off, washed with water and dried. The ester was dissolved in the minimum amount of chloroform and the unchanged reactants removed by column chromatography on alumina, eluting with chloroform. The column was monitored by t.l.c. and the appropriate fractions were combined before removal of the chloroform. After treatment with decolourising charcoal, the ester was crystallised from acetone and ethanol in turn until the melting point and the mesomorphic transition temperatures were constant.

The percentage yields and the C-I, C-S, C-N and mesophase transition temperatures of the esters prepared by this method are listed in table 12. Elemental analyses are given in table 13.

b) By direct interaction of 4-hydroxybiphenyl with the appropriate 4-n-alkoxybenzoic acid in the presence of boric acid and sulphuric acid[78].

The 4-n-alkoxybenzoic acid (0.005 mol.), 4-hydroxyphenyl (0.0075 mol.), boric acid (0.03 g) and concentrated sulphuric acid (3 drops) were dissolved in redistilled toluene (50 cm^3), which had been dried over sodium, and heated under reflux in a Dean and Stark apparatus for 24h.

After cooling, the toluene was removed under vacuum, and the resulting residue was dissolved in the minimum amount of chloroform. A small quantity of an insoluble impurity was filtered off and the ester freed from unchanged starting materials by column chromatography on silica gel (200 g), eluting with chloroform.

Subsequent work-up and purification were as described in method a).

The percentage yield and C-I, C-S, C-N and mesophase transition temperatures of the esters prepared by this method are listed in table 12. The elemental analyses are given in table 13.

Table 12 -Data for 4-biphenylyl $4''$-n-alkoxybenzoates

n-R	Transition Temperatures (°) C-I	 C-S_A	 C-N	 S_A-N	 N-I	% Yield Method a)	 Method b)
CH_3	155°				[147]		80
C_2H_5	160				[157]		77
C_4H_9	152-153				[143]	70	
C_5H_{11}	153.5				[133.5]	47	
C_6H_{13}			133°		136.5	58	
C_7H_{15}			126		129.5	48	
C_8H_{17}			119	[97.5]	130.5		75
$C_{10}H_{21}$			110	[106.5]	127		72
$C_{12}H_{25}$		108.5°		112	123	63	
$C_{14}H_{29}$		113-114		116.5	121.5	45	

[ ] indicates a monotropic transition

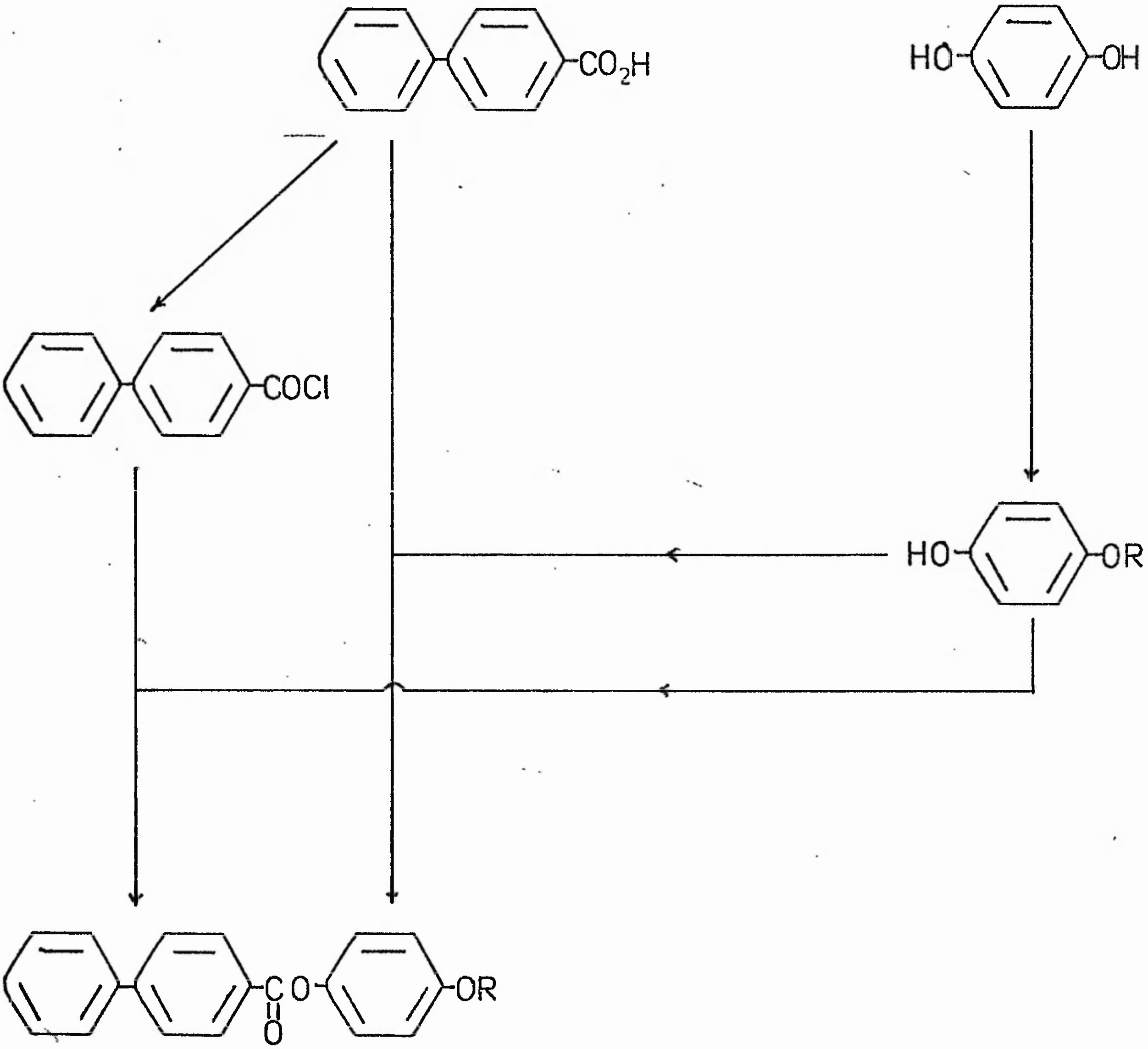
Table 13 -Elemental analyses for the 4-biphenylyl $4''$-n-alkoxybenzoates

n-R	Found %C	Found %H	Molecular Formula	Calculated %C	Calculated %H
CH_3	79.0	5.4	$C_{20}H_{16}O_3$	79.0	5.3
C_2H_5	79.3	5.9	$C_{21}H_{18}O_3$	79.2	5.7
C_4H_9	79.4	6.3	$C_{23}H_{22}O_3$	79.8	6.4
C_5H_{11}	80.2	6.6	$C_{24}H_{24}O_3$	80.0	6.8
C_6H_{13}	80.1	7.0	$C_{25}H_{26}O_3$	80.2	7.0
C_7H_{15}	80.2	7.1	$C_{26}H_{28}O_3$	80.4	7.2
C_8H_{17}	80.7	7.3	$C_{27}H_{30}O_3$	80.6	7.5
$C_{10}H_{21}$	80.7	7.7	$C_{29}H_{34}O_3$	80.9	7.9
$C_{12}H_{25}$	81.2	8.3	$C_{31}H_{38}O_3$	81.2	8.3
	Found			Requires	
$C_{14}H_{29}$	81.5	8.5	$C_{33}H_{42}O_3$	81.5	8.6

Infrared, n.m.r. and mass spectroscopic data and differential thermal analysis results for these esters can be found in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results" (p.132).

1b) Synthesis of 4″-n-Alkoxyphenyl biphenyl-4-carboxylates

SCHEME FOR THE 4″-n-ALKOXYPHENYL BIPHENYL-4-CARBOXYLATES



R=n-ALKYL.

The 4-n-alkoxyphenols were prepared by the alkylation of quinol. A substantial amount of diether contaminates the crude monoether by this method.

The initial work-up procedure (monitored by t.l.c.) seemed to have satisfactorily removed the diether. However, the 4″-n-tetradecyloxy- and -dodecyloxylphenyl biphenyl-4-carboxylates prepared from the appropriate 4-n- alkoxyphenols, despite rigorous purification attempts, had persistently low N-I transition temperatures. Examination of the n-tetradecyloxy ester and the corresponding mono- and diethers by mass spectrometry (p.178) indicated that the ester was impure and that the impurity was the diether.

Re-investigation of the 4-n-alkoxyphenols by t.l.c. showed that in low concentration the contaminating diether was insensitive both to ultraviolet light and to iodine vapour but could readily be detected using Millon's reagent (see note 3). The modified purification procedure for the 4-n-alkoxyphenols could thus be monitored successfully.

4-n-alkoxyphenols

Quinol (20.0 g), methylated spirit (30 cm^3) and the appropriate alkyl bromide (0.18 M) were heated gently under reflux. A solution of potassium hydroxide (10.7 g) in water (30 cm^3) was then added during 1h. After the addition, the solution was heated under reflux for a further 3h (see note 1).

After cooling, the reaction mixture was subjected to t.l.c. The t.l.c. investigation showed that the reaction mixture consisted of some unchanged quinol together with a small quantity of diether and the required monoether. The ethers were separated from the bulk of the unchanged quinol by ether extraction as follows. The reaction mixture was diluted to 150 cm^3 with water and then extracted with ether (300 cm^3) in three portions (see note 2). The ether extracts were combined and treated with 10% aqueous potassium hydroxide (100 cm^3 x 4). The residual aqueous solution was shaken once more with ether (100 cm^3) and all the ether extracts were combined (extract I). The aqueous phase was chilled in ice-water, acidified with concentrated hydrochloric acid and finally extracted with ether (150 cm^3 x 4). The ether extracts were combined (extract II).

Thin layer chromatography indicated that extract I contained mainly the monoether and a small amount of diether of quinol and that extract II contained principally quinol and the remainder of the monoether. The ether extracts were combined and dried ($MgSO_4$). The ether was then removed and the residue extracted several times with light petroleum (b.p. 60-80°). Most of the light petroleum was distilled off, and the remaining solution set aside.

The solid that crystallised out was shown by t.l.c. to be the required monoether but contaminated with some diether. Final purification was achieved by column chromatography on alumina, eluting with chloroform. The fractions collected were monitored by t.l.c. The presence of the diether in the early fractions was established by the development of the plates with Millon's reagent (see note 3). The fractions containing the monoether were combined, the chloroform was removed and the pure 4-n-alkoxyphenol was obtained by recrystallisation to constant m.p. from light petroleum (b.p. 60-80).

The yields (see note 4) and m.p's of the 4-n-alkoxyphenols prepared by this method are listed in table 14.

A literature search revealed no reference to the 4-n-decyloxy-, -dodecyloxy-, -tetradecyloxy-, -hexadecyloxy- and 4-cyclohexyloxy-phenols. The elemental analyses for these compounds are given in table 15.

Table 14 - Data for the 4-n-alkoxyphenols

n-R	Yield (g)	m.p. (lit*)
C_2H_5	4.8	66° (65-66)
C_4H_9	6.7	64-65 (64-65)
C_5H_{11}	5.9	48-49 (49-50)
C_6H_{13}	8.0	47 (48)
C_7H_{15}	7.8	60-61 (60)
C_8H_{17}	7.20, 15.65$^+$	61 (60-61)
$C_{10}H_{21}$	6.2	71.5
$C_{12}H_{25}$	6.15	79-80
$C_{14}H_{29}$	6.10	84-85
$C_{16}H_{33}$	2.1	88-89
Cyclo-C_6H_{13}	3.25^{++}	b.p. 154-156/1.0mm

* Literature values are those reported by Klarmann, Gatyas and Shternov [79].

\+ Preparation scaled up, using 40.0g quinol.

++ Preparation scaled down, using 8.5g quinol.

The di-n-octyloxy-, -dodecyloxy- and -tetra decyloxy-ethers of quinol were isolated during the work-up of the appropriate monoethers. Their m.p's and elemental analyses appear in table 16.

Table 15 - Elemental analyses for 4-n-alkoxyphenols

n-R	Found % C	Found % H	Molecular Formula	Requires % C	Requires % H
$C_{10}H_{21}$	77.2	10.7	$C_{16}H_{26}O_2$	76.8	10.4
$C_{12}H_{25}$	77.9	10.7	$C_{18}H_{30}O_2$	77.7	10.8
$C_{14}H_{29}$	78.3	11.3	$C_{20}H_{34}O_2$	78.4	11.1
$C_{16}H_{33}$	78.9	11.5	$C_{22}H_{38}O_2$	79.1	11.4
Cyclo-C_6H_{13}	75.1	8.0	$C_{12}H_{16}O_2$	75.0	8.3

Table 16 - Data for di-n-alkoxyethers of quinol

n-R	Elemental Analyses					m.p.
	Found		Molecular Formula	Requires		
	% C	% H		% C	% H	
C_8H_{17}	79.4	11.6	$C_{22}H_{38}O_2$	79.0	11.4	56.5-57.5°
$C_{12}H_{25}$	81.0	12.4	$C_{30}H_{54}O_2$	80.7	12.1	74-75
$C_{14}H_{29}$	81.5	12.1	$C_{34}H_{62}O_2$	81.3	12.3	80.5-81.5

General Comment

In retrospect, the method could be simplified by omitting the ether extraction. After dilution of the reaction mixture with water the ethers of quinol would be separated from the bulk of the unchanged quinol by extraction with warm light petroleum (b.p. 60-80°), and the resulting mixture could then be separated into its components as described above by column chromatography.

Notes

1. It was necessary for the solution to be stirred when the n-dodecyl-, n-tetradecyl- and n-hexadecyl-bromides were used.

2. Sometimes the diether would precipitate out at this point. If so, it was filtered off.

3. The plates were sprayed with Millon's reagent and then heated in an oven at 105° for 5 minutes. The diether, if present, appeared as a yellow spot. It was necessary to use Millon's reagent because the diether in low

concentration was insensitive both to ultraviolet light and iodine vapour.

Millon's reagent

Mercury ($3\ cm^3$) was added cautiously to fuming nitric acid ($27\ cm^3$). When the mercury had dissolved, the solution was diluted with an equal volume of water.

4. About 25% of the sample was lost during column chromatography.

4″-n-alkoxyphenyl biphenyl-4-carboxylates

These esters were prepared and purified by the methods described earlier (see page 188). The percentage yields and the C-I, C-N, and mesophase transition temperatures of the esters so obtained are listed in table 17.

Table 17. Data for 4″-n-alkoxyphenyl biphenyl-4-carboxylates

n-R	Transition Temperatures (°)			% Yield	
	C-I	C-N	N-I	Method a)	Method b)
CH_3	161.5°		[141°]		78
C_2H_5	149.5		149.5		74
C_4H_9		140°	141	60	
C_5H_{11}		132.5	133	48	
C_6H_{13}		125.5	134	55	
C_7H_{15}		111	129	62, 56	
C_8H_{17}		114	128.5		75
$C_{10}H_{21}$		110.5	123.5		78
$C_{12}H_{25}$		111.5	119	59	72
$C_{14}H_{29}$		114	116	51, 64	82
$C_{16}H_{33}$		114.5	[113]	48	

[ ] indicates monotropic transition

The 4″-n-cyclohexyloxyphenyl biphenyl-4-carboxylate was not liquid crystalline and had m.p. 136.5-137°.

No reference to the 4″-n-alkoxyphenyl biphenyl-4-carboxylates could be found in the literature and elemental analyses for those prepared in this work are listed in table 18.

Infrared, n.m.r and mass spectroscopic data and differential thermal analysis results for these esters can be found in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results" (p.132).

Table 28- Elemental analyses for 4″-n-alkoxyphenyl biphenyl-4′-carboxylates

n-R	Found % C	Found % H	Molecular Formula	Requires % C	Requires % H
CH_3	79.3	5.5	$C_{20}H_{16}O_3$	79.0	5.3
C_2H_5	78.9	5.5	$C_{21}H_{18}O_3$	79.2	5.7
C_4H_9	79.7	6.6	$C_{23}H_{22}O_3$	79.8	6.4
C_5H_{11}	80.3	7.0	$C_{24}H_{24}O_3$	80.0	6.8
C_6H_{13}	79.9	7.1	$C_{25}H_{26}O_3$	80.2	7.0
C_7H_{15}	80.3	7.5	$C_{26}H_{28}O_3$	80.4	7.2
C_8H_{17}	80.5	7.4	$C_{27}H_{30}O_3$	80.6	7.5
$C_{10}H_{21}$	81.1	7.9	$C_{29}H_{34}O_3$	80.9	7.9
$C_{12}H_{25}$	81.5	8.1	$C_{31}H_{38}O_3$	81.2	8.3
$C_{14}H_{29}$	81.7	8.8	$C_{33}H_{42}O_3$	81.5	8.6
$C_{16}H_{33}$	82.1	9.2	$C_{35}H_{50}O_3$	81.7	9.0
cyclohexyl	82.9	6.6	$C_{25}H_{24}O_3$	83.3	6.7

1c) Synthesis of 4″-n-heptyloxyphenyl 4′-cyanobiphenyl -4-carboxylate

The synthetic methods used in the preparation of 4″-n-heptyloxyphenyl 4′-cyanobiphenyl-4-carboxylate were those used by Coates and Gray[80].

Preparation of 4-acetyl-4′-bromobiphenyl

Anhydrous aluminium chloride (14g, 0.1M) and 4-bromobiphenyl (18.6g, 0.08M) were dissolved in dry nitrobenzene (85 cm^3) and to the stirred solution, acetyl chloride (8.3g, 0.1M) was added, keeping the temperature below 20°C. The dark solution was then stirred at room temperature for 6 h. The reaction mixture was poured onto a mixture of ice (100g), water (25 cm^3) and concentrated hydrochloric acid (50 cm^3) in order to break down the complex. The nitrobenzene layer was separated, washed with water and dried ($CaCl_2$). The calcium chloride was filtered off and the nitrobenzene removed from the filtrate by vacuum distillation. After treatment with decolourising charcoal, the ketone was recrystallised from ethanol, affording 4-acetyl-4′-bromobiphenyl as a white crystalline solid, 17.2g (78%), m.p. 129.5-130°. Byron, Gray and Wilson[51] report a m.p. of 129.5-130° for 4-acetyl-4′-bromobiphenyl.

4-Acetyl-4′-cyanobiphenyl

4-Acetyl-4′-bromobiphenyl (13.0g) was stirred and heated under reflux, for 8h with cuprous cyanide (6.5g) and N,N-dimethylformamide (25 cm^3). After cooling, the mixture was poured into a warm solution of iron (III) chloride (19g), concentrated hydrochloric acid and water (30 cm^3) and stirred for 30 min. After cooling the mixture was shaken with chloroform (4 x 100 cm^3) and then dried ($MgSO_4$). The magnesium sulphate was filtered off and the chloroform and N,N-dimethyl formamide were removed from the filtrate by distillation, under reduced pressure.

The crude product was purified by column chromatography on alumina, eluting with chloroform. Recrystallisation from ethanol gave 4-acetyl-4'-cyanobiphenyl as a white crystalline solid, 6.1g (62%), m.p. 117-118°. Coates and Gray[80] report a m.p. of 118° for this compound.

4'-cyanobiphenyl-4-carboxylic acid

This was prepared by the hypochlorite oxidation[81] of 4-acetyl-4'-cyanobiphenyl.

To a solution of sodium hydroxide (9.2g) in water (20 cm^3), ice was added to make the final volume about 80 cm^3. At 0°, chlorine gas was bubbled into the solution until it was neutral to litmus. Then, a solution of sodium hydroxide (1.7 g) in water (5 cm^3) was added and the hypochlorite solution was warmed to 55° when 4-acetyl-4'-cyanobiphenyl (4.55g) was added. The temperature was raised to 65° and maintained at this temperature for 90 min. The excess of hypochlorite was removed by the addition of sodium metabisulphite (2.5g) in water (10 cm^3), and the solution was carefully acidified (to avoid excess frothing) with 4-M aqueous hydrochloric acid. The precipitated acid was filtered off, washed with water and dried. Recrystallisation from glacial acetic acid gave the 4$'$-cyanobiphenyl-4-carboxylic acid as a very pale brown solid, 3.1g (68%). The mesomorphic acid had the following transition temperatures: C-N, 258-259°; N-I 311°. Coates and Gray[80] report C-N, 263°; N-I, 315°.

<u>4$''$-n-heptyloxyphenyl 4$'$-cyanobiphenyl-4-carboxylate</u>

4$'$-Cyanobiphenyl-4-carboxylic acid (1.12g, 1 mol. equiv.) was heated, under reflux, with thionyl chloride (10 cm^3) for 3h. The bulk of the thionyl chloride was then distilled off and the final traces were removed under vacuum.

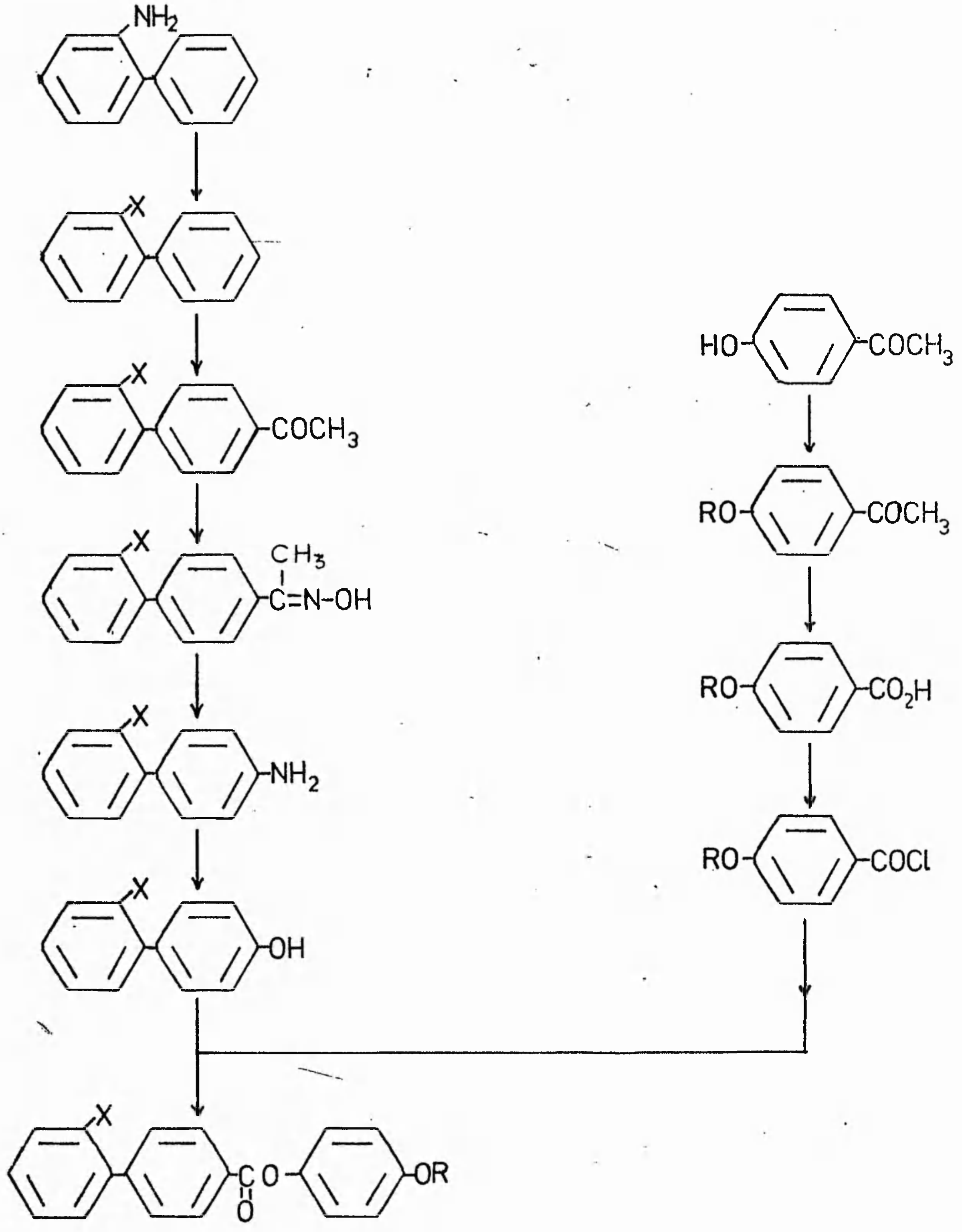
The acid chloride was heated, under reflux, with 4-n-heptyloxyphenol (1.04g, 1 mol. equiv.) in dry pyridine (10 cm^3) for 3h. After cooling, the mixture was treated with 5% aqueous sulphuric acid (25 cm^3) and water (100 cm^3) and the precipitated ester was filtered off and washed with water. The crude ester was dissolved in chloroform and the solution was washed several times with saturated aqueous sodium carbonate and finally with water. The chloroform was then removed and the ester was treated with decolourising charcoal, and then recrystallised from ethanol until the mesophase transition temperatures were constant. The esterification gave a yield of 52% of 4$''$-n-heptyloxyphenyl 4$'$-cyanobiphenyl-4-carboxylate, C-S_A, 121.5°; S_B-S_A, [110.6°] ; S_A-N, 151.2°; N-I, 240.7°. (Found: C, 78.8; H, 6.7; N, 3.2. $C_{27}H_{27}NO_3$ calculated for C, 78.5; H, 6,5; N, 3.4%).

The mesophase transition temperatures of the 4″-n-heptyloxyphenyl 4′-cyanobiphenyl-4-carboxylate reported by Coates and Gray[80] were as follows: C-S_A, 121.5°; S_A-N, [108.5] ; N-I, 241°. Correspondence with these authors established that these transition temperatures had been incorrectly abstracted from the original laboratory notes, and that the actual values recorded for their sample of the n-heptyloxy ester were: C-S_A, 121.5°; S_B-S_A, [108.5] ; S_A-N, 153.1°; N-I, 241°.

Dr Gray then kindly measured the transition temperatures of the author's sample of the n-heptyloxy ester using his laboratory's Mettler hot stage. The transition temperatures for the two samples are in excellent agreement.

2a) Synthesis of 2'-fluoro-4-biphenylyl 4"-n-alkoxybenzoates

SCHEME FOR THE 2′-HALOGENO-4-BIPHENYLYL 4″-n-ALKOXYBENZOATES



R= n-ALKYL.

X= Cl, Fl.

The methods used for the preparation of 2-fluorobiphenyl, 4-acetyl-2'-fluorobiphenyl and its oxime, and 4-amino-2'-fluorobiphenyl were as reported by Byron, Gray and Wilson[51].

2-fluorobiphenyl

2-Aminobiphenyl (31.3g, 0.19M) was dissolved in a mixture of concentrated hydrochloric acid (75 cm^3) and water (75 cm^3) by heating. The well stirred solution was cooled rapidly to 0°, and the resulting fine suspension of the amine hydrochloride was diazotised by the dropwise addition of a solution of sodium nitrite (13.5 g, 0.195M) in water (30 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards.

To the solution of the diazonium salt, sodium borofluoride (33,5g, 0.3M) in water (55 cm^3) was added, with stirring, during 30 min. Thirty minutes after the addition was completed, the yellow precipitate of biphenyl-2-diazonium borofluoride was filtered off, washed in turn with saturated aqueous sodium borofluoride, ethanol, and ether, and then dried in a desiccator under vacuum overnight. A second batch of the diazonium borofluoride was prepared on the same scale and the two products were combined. The overall yield was 92g (93%).

The diazonium borofluoride was decomposed, initially by gentle heating, when a controlled exothermic reaction occurred, and finally by heating the tarry mass more strongly for several minutes. The 2-fluorobiphenyl was steam distilled from the residue and extracted from the distillate with ether. The ether extract was dried ($MgSO_4$), and the ether removed. Recrystallisation of the residue from methanol gave 2-fluorobiphenyl as a white crystalline solid, 41.5g (66%), m.p. 72-73°. Byron, Gray and Wilson[51] report a m.p. of 72-73° for 2-fluorobiphenyl.

4-acetyl-2′-fluorobiphenyl

Anhydrous aluminium chloride (42.0g, 0.3M) and 2-fluorobiphenyl (41.5g, 0.19M) were dissolved in dry nitrobenzene (250 cm^3). To the well stirred solution, acetyl chloride (25g, 0.3M) was added below 20°, and the dark solution was stirred at room temperature for 24h. The solution was poured onto a mixture of ice (330g), water (75 cm^3) and concentrated hydrochloric acid (150 cm^3), in order to break down the complex. The nitrobenzene layer was separated from the aqeuous layer and dried ($CaCl_2$). The calcium chloride was filtered off and the nitrobenzene removed by distillation, under reduced pressure. The residue was distilled under vacuum and the large fraction b.p. 128-129°/0.15 mm was collected. The crude ketone was obtained as a yellow solid, 41.8g. Several recrystallisations from light petroleum (b.p. 60-80°) gave the 4-acetyl-2′-fluorobiphenyl as a white crystalline solid, 35.8g (70%), m.p. 86-87°. Byron, Gray and Wilson[51] report a m.p. of 85.5-86.5° for this compound.

4-acetyl-2'-fluorobiphenyl oxime

A solution of 4-acetyl-2'-fluorobiphenyl (7.5g, 0.035M) and hydroxylamine hydrochloride (6.75g), in a mixture of ethanol (17 cm^3) and pyridine (50 cm^3) was heated under reflux for 3h. Most of the solvent was then removed under reduced pressure, and the residue was diluted with water (500 cm^3). The precipitated oxime was filtered off, washed with water and dried in a vacuum desiccator. Recrystallisation from ethanol gave the oxime of 4-acetyl-2'-fluorobiphenyl as a white solid, 7.45g (93%), m.p. 147-148°. Bryon, Gray and Wilson[51] report a m.p. of 147-148° for this compound.

The above preparation was carried out several times and the yields varied from 92 to 96%.

4-amino-2'-fluorobiphenyl

4-Acetyl-2'-fluorobiphenyl oxime (29.8g, 0.13M) was suspended in dry benzene (800 cm^3), to which phosphorus pentachloride (40g) was added, and the whole was heated under reflux for 30 min. After cooling, a solution of concentrated hydrochloric acid (80 cm^3) in ethanol (1600 cm^3) was added and the resulting solution was heated, under reflux, for 7h. After cooling, the bulk of the solution was removed, under reduced pressure, and the amine hydrochloride was basified with 4M-aqueous sodium hydroxide. The free base was extracted with ether, the extract was dried ($MgSO_4$) and the ether removed. The residue was distilled, under vacuum (122-124°/0.15mm) to afford 4-amino-2'-fluorobiphenyl as a cream coloured solid, 17.6g (77%), m.p. 50-52°. Byron, Gray and Wilson[51] report a m.p. of 52-54° for this compound.

2′-fluoro-4-hydroxybiphenyl

4-Amino-2′-fluorobiphenyl (16.5g, 0.088M) was dissolved in a boiling solution of 40% aqueous sulphuric acid (150 cm^3) and glacial acetic acid (45 cm^3). The well stirred solution was cooled rapidly to 0°, and the resulting fine suspension was diazotised by the dropwise addition of a solution of sodium nitrite (6.2g, 0.091M) in water (100 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards.

The cold solution of the diazonium salt was added dropwise, slowly initially and then faster, to a boiling solution of 40% aqueous sulphuric acid (200 cm^3). When the addition was complete, the solution was heated under reflux for 30 min., cooled, and then diluted with water (1,500 cm^3). The resulting precipitate was filtered off, washed with water and then digested with M-aqueous sodium hydroxide (1200 cm^3). The insoluble material was filtered off and the cooled filtrate was acidified with 4M-aqueous hydrochloric acid. The free phenol was filtered off, washed with water and dried. The yield was 11.9g (72%).

The 4-hydroxy-2′-fluoro-4-hydroxybiphenyl was sublimed under vacuum (120°/0.2mm) and the resulting yellow solid was recrystallised several times from chloroform to give the 2′-fluoro-4-hydroxybiphenyl as a white crystalline solid, 10.65g (64%), m.p. 135-137°. (Found: C, 76.5; H, 4.8. $C_{12}H_9OF$ C, 76.6;

H, 4.8%). ν max (KBr) 3450 cm^{-1}; broad OH stretching band.

2$'$-fluoro-4-biphenylyl 4$''$-n-alkoxybenzoates

These esters were prepared by heating the acid chloride of the appropriate 4-n-alkoxybenzoic with 2$'$-fluoro-4-hydroxybiphenyl under reflux, in dry pyridine, as described earlier (p.188). After cooling the reaction mixture, the pyridine was removed under reduced pressure, the resulting solid was dissolved in the minimum amount of chloroform and the unchanged reactants were removed by column chromatography on alumina (60 g), eluting with chloroform. The fractions from the column were monitored by t.l.c. and the appropriate fractions containing the ester were combined prior to the removal of the bulk of the chloroform. After treatment with decolourising charcoal the chloroform was removed and the esters were crystallised from acetone and from ethanol in turn, until the m.p. and the mesomorphic transitions were constant.

The yield, m.p., and the mesomorphic transition temperatures of the esters prepared by this method are listed in Table 19 . The elemental analysis appear in Table 20.

Table 19- Data for 2'-fluoro-4-biphenylyl 4''-n-alkoxybenzoates

	Transition Temperatures (°)				%
n-R	C-I	C-N	S_A-N	N-I	Yield
C_4H_9	119.5°			[97°]	58
C_5H_{11}	99			[86]	70
C_6H_{13}	102			[94]	65
C_7H_{15}	93.5			[90]	73
C_8H_{17}		86°		95	56
C_9H_{19}		90		92	64
$C_{10}H_{21}$		88		94	66
$C_{14}H_{29}$		88	[79°]	92.5	52

[ ] indicates a monotropic transition

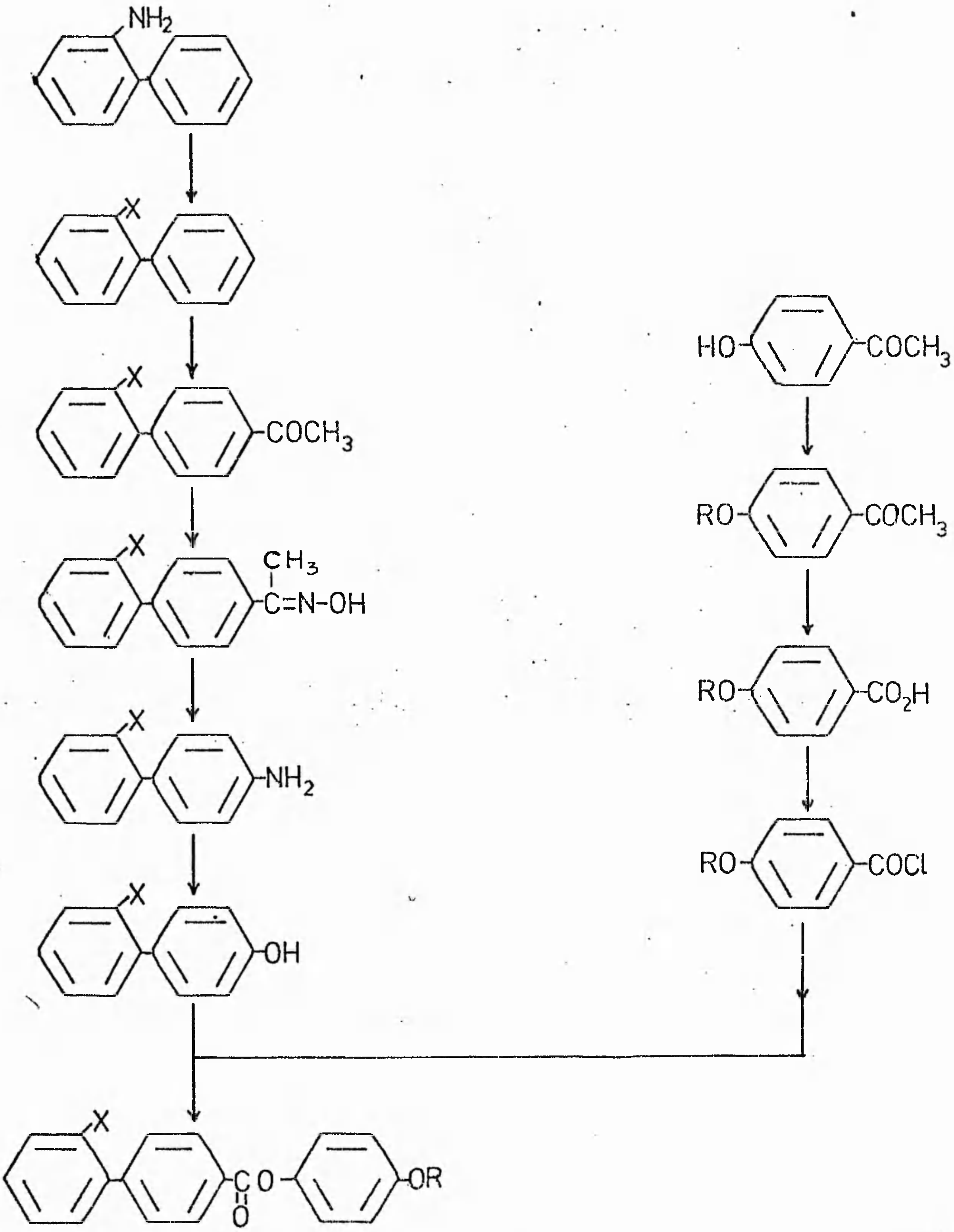
Table 20- Elemental Analysis for 2'-fluoro-4-biphenylyl 4''-n-alkoxybenzoates

	Found		Molecular	Requires	
n-R	%C	%H	Formula	%C	%H
C_4H_9	75.6	5.7	$C_{23}H_{21}FO_3$	75.8	5.8
C_5H_{11}	75.8	6.3	$C_{24}H_{23}FO_3$	76.2	6.1
C_6H_{13}	76.5	6.6	$C_{25}H_{25}FO_3$	76.5	6.4
C_7H_{15}	76.6	6.9	$C_{26}H_{27}FO_3$	76.9	6.7
C_8H_{17}	77.1	7.1	$C_{27}H_{29}FO_3$	77.1	6.9
C_9H_{19}	77.3	7.4	$C_{28}H_{31}FO_3$	77.4	7.1
$C_{10}H_{21}$	77.9	7.5	$C_{29}H_{33}FO_3$	77.7	7.4
$C_{14}H_{29}$	78.6	8.3	$C_{33}H_{41}FO_3$	78.6	8.1

Infrared, and n.m.r. spectroscopic data of these esters can be found in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results".

2b) Synthesis of 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates

SCHEME FOR THE 2′-HALOGENO-4-BIPHENYLYL 4″-n-ALKOXYBENZOATES



R= n-ALKYL.

X= Cl, Fl.

The methods used for the preparation of 2-chlorobiphenyl and 4-acetyl-2′-fluorobiphenyl were those reported by Byron, Gray and Wilson[51].

2-Chlorobiphenyl

2-Aminobiphenyl (42.0 g, 0.22M) was dissolved in concentrated hydrochloric acid (75 cm^3) and water (75 cm^3) by heating. The well stirred solution was cooled rapidly to 0°, and the resulting fine suspension of the amine hydrochloride was diazotised by the dropwise addition of a solution of sodium nitrite (16.5 g, 0.24M) in water (50 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards.

The solution of the diazonium salt was added, slowly and with stirring, to copper (I) chloride (35g) in concentrated hydrochloric acid (130 cm^3). To allow the complex to break down slowly,the reaction mixture was set aside to stand overnight. The 2-chlorobiphenyl was extracted with ether, the extract was dried ($MgSO_4$) and the ether was then removed. The residue was distilled under reduced pressure and the large fraction b.p. 84-86°/0.15 mm was collected. The crude product was recrystallised from aqueous methanol and the 2-chlorobiphenyl was obtained as a white crystalline solid, 34.5 g (73%), m.p. 32-33°. Byron, Gray and Wilson[51] report a m.p. of 32-33° for this compound. The preparation of 2-chlorobiphenyl was repeated on half the above scale. The yield was 15.0 g (64%).

4-acetyl-2′-chlorobiphenyl

Acetylation of 2-chlorobiphenyl was carried out by the Friedel-Crafts method used to prepare 4-acetyl-2′-fluorobiphenyl (p.210). Recrystallisation of the 4-acetyl-2′-chlorobiphenyl from aqueous methanol gave a white solid, 42.0 g (82%), m.p. 53°. Byron, Gray and Wilson[51] report a m.p. of 54-55° for this compound.

4-acetyl-2′-chlorobiphenyl oxime

A solution of 4-acetyl-2′-chlorobiphenyl (26.0 g, 0.11M) and hydroxylamine hydrochloride (21.0 g) in a mixture of ethanol (50 cm^3) and pyridine (155 cm^3) was heated under reflux for 8h. Most of the solvent was removed, under reduced pressure, and the resulting suspension was diluted with water (1600 cm^3). The oxime was extracted with chloroform, the extract was dried ($MgSO_4$) and the chloroform was removed. The crude product was recrystallised from the minimum amount of methanol. The oxime of 4-acetyl-2′-chlorobiphenyl was obtained as a white solid, 15.8 g (57%), m.p. 136-137° (Found: C, 68.4; H, 5.2; N, 5.9. $C_{14}H_{12}NOCl$ requires C, 68.4; H, 4.9; N, 5.7%).

The preparation of the oxime was repeated using 16.0g of 4-acetyl-2′-chlorobiphenyl. The yield was 8.95 g (53%).

4-amino-2′-chlorobiphenyl

4-Acetyl-2′-chlorobiphenyl oxime (22.0 g, 0.09M) was suspended in dry benzene (550 cm^3). Phosphorus pentachloride (27.5g) was then added, and the whole was heated under reflux for 30 min. After cooling, concentrated hydrochloric acid (55 cm^3) in ethanol (1100 cm^3) was added and the resulting solution was heated under reflux for 7h. After cooling, most of the solvent was removed under reduced pressure and the suspension of the amine hydrochloride was made alkaline with 4M-aqueous sodium hydroxide. The free amine was extracted with ether, the extract was dried ($MgSO_4$), and the ether was then removed. The residue was distilled under reduced pressure and the large fraction b.p. 148°/0.1 mm was collected. The 4-amino-2'-chlorobiphenyl was obtained as a pale yellow solid, 14.2 g (55%), m.p. 39-41°. Byron, Gray and Wilson[51] report a m.p. of 42-43° for 4-amino-2'-chlorobiphenyl.

2'-Chloro-4-hydroxybiphenyl

4-Amino-2'-chlorobiphenyl (14.2g, 0.07M) was dissolved in a boiling solution of 40% aqueous sulphuric acid (100 cm^3) and glacial acetic acid (30 cm^3). The well stirred solution was cooled rapidly to 0°, and the resulting fine precipitate was diazotised by the dropwise addition of a solution of sodium nitrite (4.95 g, 0.072M) in water (40 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards.

The cold solution of the diazonium salt was added dropwise, slowly initially and then faster, to a boiling solution of 40% aqueous sulphuric acid (200 cm^3). After the addition, the solution was heated under reflux for 30 min., cooled and then diluted with water (1500 cm^3). The product was extracted with ether, the extract was dried ($MgSO_4$) and the ether was removed. The residue was digested with M-aqueous sodium hydroxide (1000 cm^3). The insoluble material was filtered off and the cooled filtrate was acidified with 4M-aqueous hydrochloric acid. The free phenol was extracted with chloroform, the extract was dried ($MgSO_4$), and the bulk of the chloroform then removed. The crude phenol was chromatographed on a column of silica gel (250g), eluting with chloroform. The fractions from the column were monitored by t.l.c. (S.G./A), and the fractions containing the phenol (Rf about 0.15) were combined and the chloroform was then removed. The yield of the crude yellow phenol was 9.2 g. Recrystallisation from chloroform gave the 2′-chloro-4-hydroxybiphenyl as a white solid, 8.1g (57%), m.p. 91° (Lit[82], 90.5-91°C).

2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates

The preparation and purification of these esters was carried out in an analogous fashion to the 2′-fluoro-4-biphenylyl 4″-n-alkoxybenzoates (p.188). The percentage yield, m.p. and mesomorphic transition temperatures of the 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates are listed in Table 21. The elemental analyses of these esters are presented in Table 22

Table 21 - Data for 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates

n-R	Transition Temp. C-I	 N-I	% Yield
C_6H_{13}	77°	[41.5°]	52
C_7H_{15}	67	[37]	42
C_8H_{17}	58	[44]	47
C_9H_{19}	60.5	[46]	61
$C_{10}H_{21}$	70		60
$C_{14}H_{29}$	76.5		66

[ ] indicates a monotropic transition

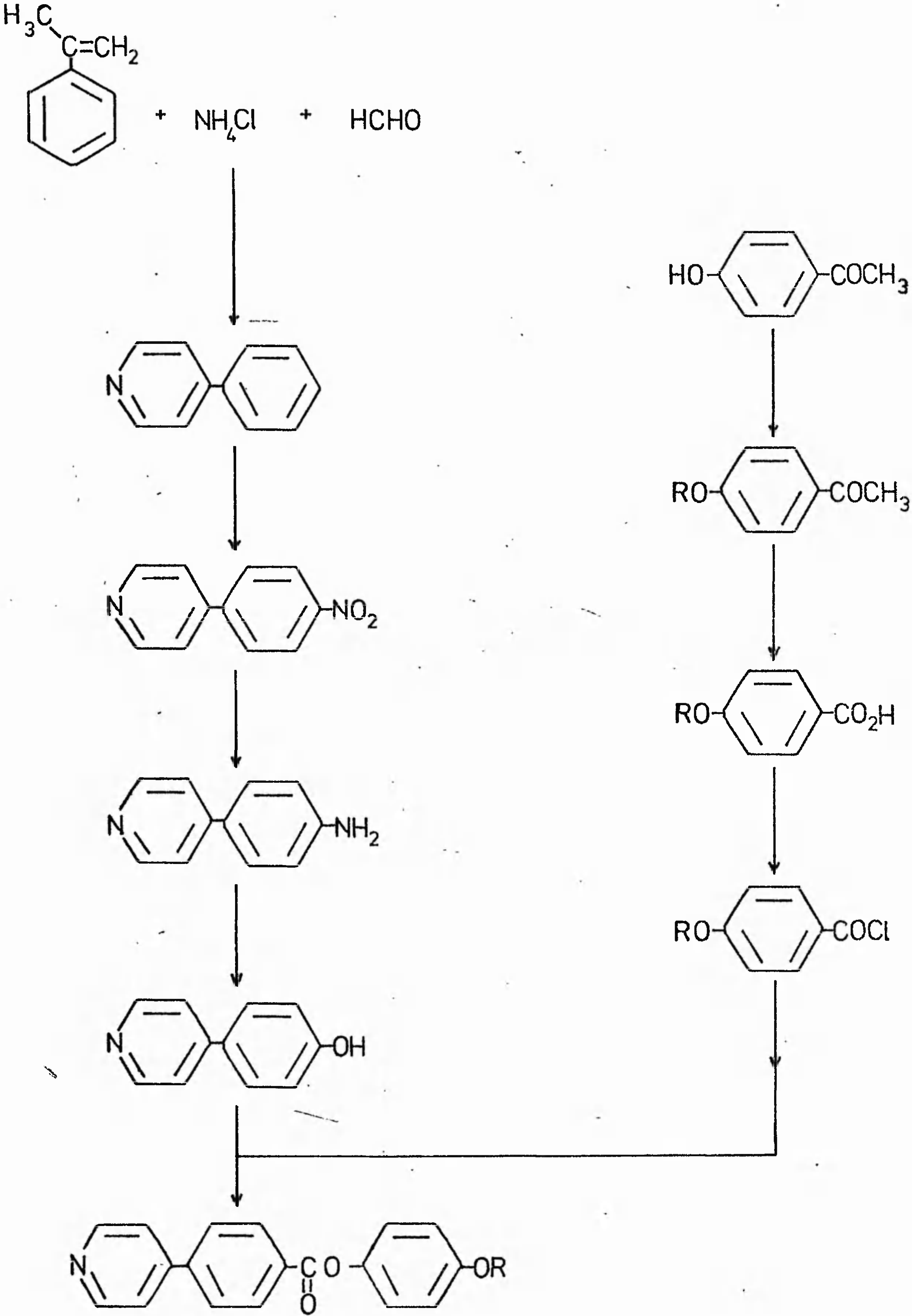
Table 22 - Elemental analyses for 2′-chloro-4-biphenylyl 4″-n-alkoxybenzoates

n-R	Found %C	 %H	 %Cl	Molecular Formula	Requires %C	 %H	 %Cl
C_6H_{13}	73.1	6.2	8.6	$C_{25}H_{25}ClO_3$	73.4	6.1	8.7
C_7H_{15}	74.2	6.6	8.6	$C_{26}H_{27}ClO_3$	73.9	6.4	8.4
C_8H_{17}	74.6	6.9	7.9	$C_{27}H_{29}ClO_3$	74.2	6.6	8.1
C_9H_{19}	74.8	7.1	8.0	$C_{28}H_{31}ClO_3$	74.6	6.9	7.9
$C_{10}H_{21}$	75.0	7.2	-	$C_{29}H_{33}ClO_3$	74.9	7.1	-
$C_{14}H_{29}$	75.9	7.9	-	$C_{33}H_{41}ClO_3$	76.1	7.9	-

Infrared and n.m.r. spectroscopic data for these esters can be found in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results".

3a) Synthesis of 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoates

SCHEME FOR THE 4-(4′-PYRIDYL)PHENYL 4″-n-ALKOXYBENZOATES



R = n-ALKYL.

4-Phenylpyridine

Ammonium chloride (216g) was dissolved in 38% aqueous formaldehyde (670 cm^3) at 65^oC, and whilst stirring and maintaining the temperature in the range 60-65^oC (the reaction is exothermic), α-methylstyrene (236g) was added slowly over a period of 30-40 mins. The reaction mixture was then left stirring for 2h after which time the temperature had dropped to about 35^oC. Methanol (500 cm^3) was then added and the solution was stirred for a further 1h. The solution was then set aside for 2 days.

The methanol was evaporated off, under reduced pressure, until a precipitate was observed. The resulting suspension was hydrolysed by stirring with concentrated hydrochloric acid (600 cm^3) on a water-bath for 4h. When the solution had cooled it was diluted with water (800 cm^3) and made alkaline with concentrated aqeuous ammonia. The crude amine was extracted with toluene (4 x 500 cm^3). The extract was dried ($MgSO_4$) and the toluene removed. The residue was distilled under vacuum to give 4-phenyl-1,2,3,6-tetrahydropyridine as a pale yellow oil (b.p. 94-120^o/0.5 mm). The yields obtained from several preparations varied from 32 to 39%.

The 4-phenyl-1,2,3,6-tetrahydropyridine (105g) was dehydrogenated by heating the amine with sulphur (42.6g) at 145^o for 2h. The temperature was then increased to 175^o and maintained at 170-175^o for 24h. When the mixture had cooled, the solid residue was dissolved in warm benzene (800 cm^3) and the 4-phenylpyridine was extracted with 4M-aqueous hydrochloric acid (5 x 200 cm^3). The aqueous phase was basified with 50% aqueous ammonia and the free amine was extracted with benzene (4 x 250 cm^3). The benzene extract was dried ($MgSO_4$), the benzene removed, and the residue was distilled under vacuum. The large fraction (b.p. 100-104°/1.3 mm) was collected. The crude 4-phenylpyridine was then purified by recrystallisation from light petroleum (b.p. 60-80°). The 4-phenylpyridine was obtained as a white solid, m.p. 74-75°. Schmidle and Mansfield[83] report a m.p. of 74° for this compound. In several preparations, some carried out on double the scale, the yields obtained varied from 14 to 25%.

<u>4-(4′-nitrophenyl) pyridine</u>

4-Phenylpyridine (74.0g) was added to a stirred solution of concentrated sulphuric acid (250 cm^3) in fuming nitric acid (21.0 cm^3) in small aliquots at 20°. After the addition was completed, the reaction mixture was heated at 100° (oil bath) for 45 min. The reaction mixture was cooled and then carefully poured into water (1250 cm^3) and the solution was made alkaline with 50% aqueous ammonia. The mixture of isomeric nitrophenylpyridines was filtered off and washed with water. The 4-(4′-nitrophenyl) pyridine was separated from other isomers (principally the 3′-nitro-isomer) by fractional recrystallisation from 4M-aqueous hydrochloric acid (700 cm^3, then 300 cm^3). The hydrochloride of the 4'-nitro-isomer was the least soluble and was filtered off and basified with 10% aqueous ammonia. After washing with water, the free base was purified by recrystallisation from ethanol. The 4-(4'-nitrophenyl) pyridine was obtained as a pale yellow solid, 31.6g (33%), m.p. 123-124°. Katritzky and Simmons[85] report a m.p. of 124-125° for this compound. The mother liquors from the recrystallisation of the hydrochloride of 4-(4'-nitrophenyl) pyridine were basified, and the resulting solid was twice recrystallised from 5M-aqueous nitric acid. The 4-(3'-nitrophenyl) pyridine was liberated on basification with concentrated aqueous ammonia, and the free base was recrystallised from ethanol. Yellow needles of 4-(3'-nitrophenyl) pyridine, 18.1g (19%), m.p. 109-110° were obtained. Katritzky and Simmons[85] report a m.p. of 109-110°.

The nitration of 4-phenylpyridine was carried out several times using different quantities of 4-phenylpyridine. The yields varied from 27 to 40% (average, 37%).

4-(4'-aminophenyl) pyridine

To a stirred solution of 4-(4'-nitrophenyl) pyridine (22.0g) and hydrazine hydrate (20 cm^3) in ethanol (900 cm^3) at 50°C, small portions of 5% palladium on charcoal (5.2g) were added. The solution was then heated under reflux for 90 min.

The catalyst was then filtered off from the hot reaction mixture and the volume of ethanol in the filtrate was reduced to about 150 cm^3. On cooling, the 4-(4'-aminophenyl) pyridine crystallised out and was filtered off. Recrystallisation from ethanol gave the 4-(4'-aminophenyl) pyridine as a white crystalline solid, 15.8g, (89%), m.p. 234-235°. Forsyth and Pyman[86] report a m.p. of 232-234° for this compound.

In several preparations, yields varied from 83 to 95% (average, 87%).

4-(4'-hydroxyphenyl) pyridine

4-(4'-Aminophenyl) pyridine (23.0g, 0.14M) was dissolved in concentrated hydrochloric acid (65 cm^3) and water (100 cm^3), by heating. The stirred solution was then cooled rapidly to 0°, and the resulting fine suspension of the amine hydrochloride was diazotised by the dropwise addition of sodium nitrite (12.0g, 0.17M) in water (100 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards, when a small quantity of insoluble material was removed by filtration.

The diazonium salt was diluted with water (4,000 cm^3), stirred vigorously, and heated to 60°. This temperature was maintained for 1h., after which it was raised to 75°C for 1h, and finally to 90° for a further 30 min.

After cooling, the solution was made slightly alkaline with 20% aqueous ammonia and the resulting precipitate was filtered off, washed with water and dried.

The crude phenol(13.0g, 0.76M) was dissolved in boiling ethanol (200 cm^3) and the insoluble material was filtered off. The filtrate was added to a solution of picric acid (17.4g, 0.76M) in ethanol (100 cm^3) and on cooling, the picrate was filtered off and washed several times with ether. The phenol was liberated by the addition of the picrate to a warm saturated solution of lithium hydroxide (700 cm^3). After cooling, the precipitated salt was filtered off and dissolved in 2M-aqueous hydrochloric acid. The solution was made slightly alkaline with 20% aqueous ammonia and cooled. The crude 4-(4$'$-hydroxyphenyl) pyridine was filtered off, washed with water and dried. After treatment with decolourising charcoal and several recrystallisations from ethanol the 4-(4$'$-hydroxyphenyl) pyridine was obtained as a white solid, 10.5g (45%), m.p. 254-255^o. Butterworth, Heilbron and Hey[88] report a m.p. of 253-254^o for this compound.

A small portion of the picrate of 4-(4$'$-hydroxyphenyl) pyridine was recrystallised several times from ethanol. It had a m.p. of 260-262^o (Found: C, 50.6; H, 2.9: N, 13.9. $C_{17}H_{12}N_4O_8$ requires C, 51.0; H, 3.0; N, 14.0%).

The preparation of 4-(4′-hydroxyphenyl) pyridine was carried out several times and the yields obtained varied from 43 to 66% (average, 57%).

4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates

These esters were prepared by heating under reflux the acid chloride of the appropriate 4-n-alkoxybenzoic acid and the 4-(4′-hydroxyphenyl) pyridine in dry pyridine. The experimental procedure for the preparation of the 4-n-alkoxybenzoic acids is described on p.185, and the method for the preparation and purification of their 4-(4′-pyridyl) phenyl esters was the same as that used for the 4-biphenylyl 4″-n-alkoxybenzoates (p.188).

Esterification via the direct interaction of the 4-(4′-hydroxyphenyl) pyridine with the appropriate 4-n-alkoxybenzoic acid in the presence of boric acid and sulphuric acid[78] was unsuccessful.

The percentage yield and C-I, C-S, C-N and mesophase transition temperatures of these esters are listed in Table 23. The elemental analyses are given in Table 24.

Table 23- Data for 4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates

	Transition Temperatures						%
n-R	C-I	C-S_A	C-N	S_A-N	S_A-I	N-I	Yield
C_4H_9	148.5°					[112°]*	48
C_5H_{11}	116			[101.5°]		[110]	43
C_6H_{13}			113°	[110.5]		115	62
C_7H_{15}		111°			115°		52
C_8H_{17}		105.5			121.5		66
C_9H_{19}		107			121		74
$C_{10}H_{21}$		115			124.5		75
$C_{12}H_{25}$		109			126		61
$C_{14}H_{29}$		110			126.5		49

[ ] indicates a monotropic transition.

*This transition was detected by differential thermal analysis. It was not observed optically because the sample crystallised.

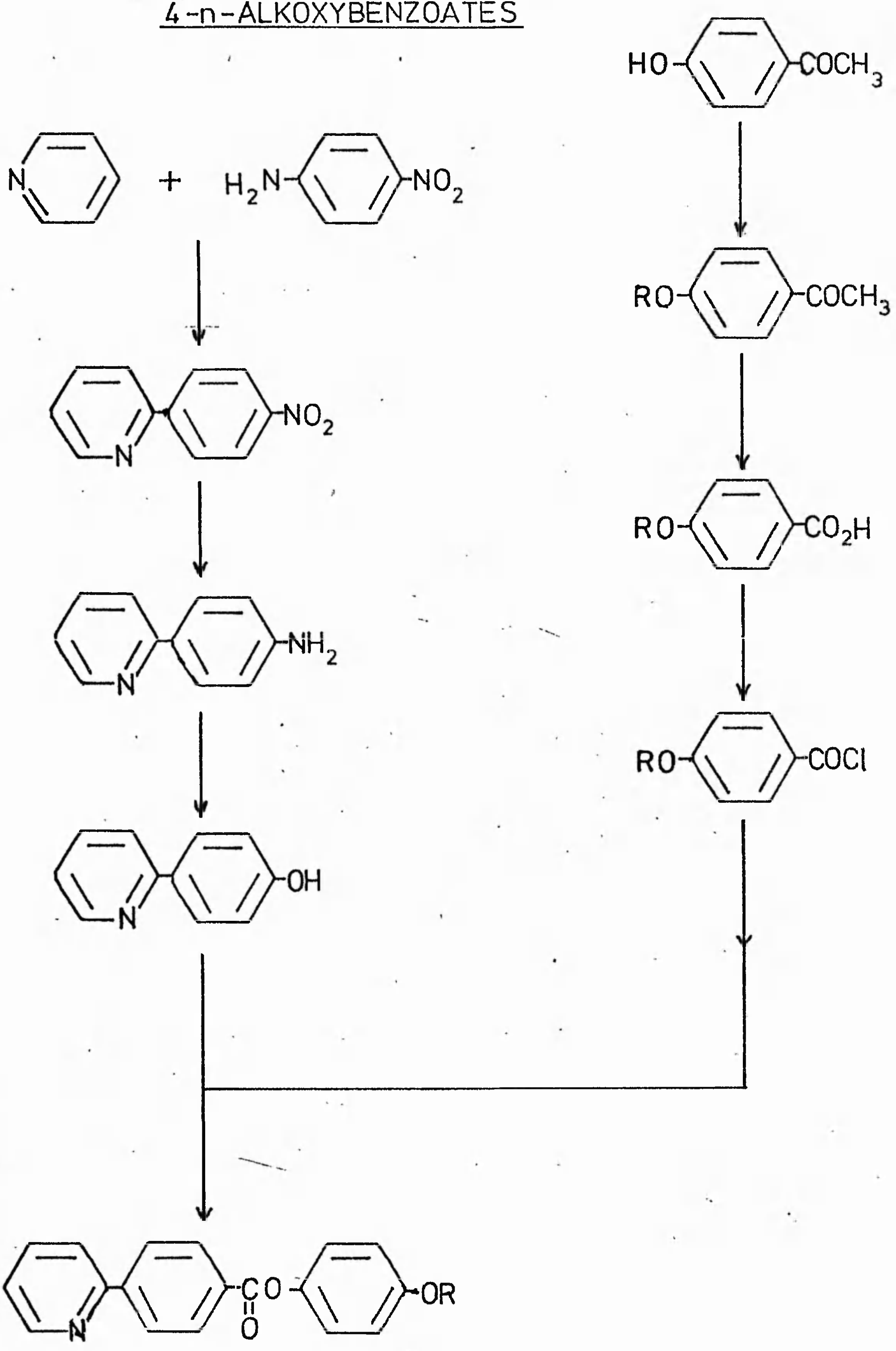
Table 24- Elemental Analyses for 4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates

	Found			Molecular	Requires		
n-R	%C	%H	%N	Formula	%C	%H	%N
C_4H_9	75.9	6.1	3.9	$C_{22}H_{21}NO_3$	76.1	6.1	4.0
C_5H_{11}	76.3	6.5	3.9	$C_{23}H_{23}NO_3$	76.5	6.4	3.9
C_6H_{13}	76.8	6.7	3.6	$C_{24}H_{25}NO_3$	76.8	6.6	3.7
C_7H_{15}	76.9	7.1	3.8	$C_{25}H_{27}NO_3$	77.1	6.9	3.6
C_8H_{17}	77.1	7.4	3.2	$C_{26}H_{29}NO_3$	77.4	7.2	3.5
C_9H_{19}	77.7	7.6	3.4	$C_{27}H_{31}NO_3$	77.7	7.4	3.4
$C_{10}H_{21}$	77.8	7.9	3.0	$C_{28}H_{33}NO_3$	78.0	7.7	3.2
$C_{12}H_{25}$	78.3	8.1	3.0	$C_{30}H_{37}NO_3$	78.4	8.1	3.1
$C_{14}H_{29}$	78.9	8.7	2.9	$C_{32}H_{41}NO_3$	78.9	8.4	2.9

Infrared, n.m.r. and mass spectroscopic data and differential thermal analysis results for these esters can be found in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results".

3b) Synthesis of 4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates

SCHEME FOR THE 4-(2′-PYRIDYL)PHENYL 4″-n-ALKOXYBENZOATES



R=n-ALKYL.

2-(4′-nitrophenyl) pyridine

4-Nitroaniline (140g, 0.99M) was dissolved in concentrated hydrochloric acid (250 cm^3) and water (250 cm^3), by heating. The stirred solution was then cooled rapidly to 0^o, and the resulting fine suspension of the amine hydrochloride was diazotised by the dropwise addition of sodium nitrite (72g, 1.04M) in water (150 cm^3). The temperature was maintained at 0-5^o throughout the addition and for 30 min. afterwards.

The diazonium salt was subjected to a Gomberg reaction by adding it slowly, over a period of 3h, to pyridine (1,000 cm^3), stirred, at 40^o. After the addition, the reaction mixture was heated on a water-bath for 1h. The cooled solution was diluted with water (8,000 cm^3) and the yellow-brown solid was filtered off, washed with water and dried. The crude mixture of 2-, 3-, and 4-(4′-nitrophenyl) pyridines was dissolved in benzene (300 cm^3) and chromatographed on a short column of alumina (100 g), eluting with benzene. This gave a very much cleaner product. All the fractions from the column were combined and the benzene removed, giving the mixture of the isomeric nitrophenyl pyridines as an orange-brown solid, 135.0 g (78%), m.p. 105-115^o.

The above procedure was repeated three more times and the yields obtained were 73, 78 and 74%. The 2-(4′-nitrophenyl) pyridine was separated from the 3- and 4-isomers by column chromatography followed by recrystallisation from 4M-aqueous hydrochloric acid. The column chromatography was carried out on alumina (1800 g; ratio, mixed isomers : alumina of 1 : 18), eluting with benzene. The fractions leaving the column were monitored by t.l.c. and the fractions containing the more rapidly eluted 2-isomer were combined and the benzene was removed. To ensure complete removal of the contaminating 3-isomer, the solid was recrystallised from hot 4M-aqueous hydrochloric acid (100 cm^3) and the precipitated amine hydrochloride was filtered off and basified with 20% aqueous ammonia. The liberated 2-(4′-nitrophenyl) pyridine was filtered off, washed with water and recrystallised several times from methylated spirit. The resulting white crystalline solid, 34.0 g (22%), had a m.p. of 130-131°. Forsyth and Pyman[86] report a m.p. of 130.5-131.5 for 2-(4′-nitrophenyl) pyridine.

The preparation and purification of 2-(4′-nitrophenyl) pyridine as described above was carried out several times during the course of this work. The yields obtained were 22, 20, 19, 17 and 16%.

<u>2-(4′-aminophenyl) pyridine</u>

To a stirred solution of 2-(4′-nitrophenyl) pyridine (22.0g), hydrazine hydrate (20 cm^3) and ethanol (900 cm^3) at 50-55° was added, in small portions, 5% palladium on charcoal (4.0g). When the addition was complete, the mixture was heated, under reflux, for 90 min. The charcoal was filtered off from the hot solution and the ethanol was removed from the filtrate to afford the crude 2-(4′- aminophenyl) pyridine.

Recrystallisation from ether gave 2-(4′-aminophenyl) pyridine as a white solid, 12.5g (67%), m.p. 97°. Forsyth and Pyman[86] report a m.p. of 98°.

This reduction procedure was carried out several times; and the percentage yield varied from 61 to 70%.

2-(4′-hydroxyphenyl) pyridine

2-(4′-Aminophenyl) pyridine (20.0g, 0.12M) was dissolved in a warm solution of concentrated hydrochloric acid (75 cm^3) and water (150 cm^3). The stirred solution was cooled rapidly to 0°, and the resulting fine suspension of the amine hydrochloride was diazotised by the dropwise addition of sodium nitrite (8.5 g, 0.123M) in water (60 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards.

The diazonium salt was diluted with water (4,000 cm^3) and, while stirring vigorously, the temperature of the solution was raised to 70°. This temperature was maintained for 90 min., after which the temperature was increased to 90° for 1h. After cooling, the solution was made slightly alkaline with 20% aqueous ammonia and the dark brown precipitate was filtered off, washed with water and dried.

The crude product was recrystallised from chloroform to give the pure 2-(4′-hydroxyphenyl) pyridine as a pale buff solid, 12.2g (61%), m.p. 161°, Butterworth, Heilbron and Hey[88] report a m.p. of 160° for this compound.

The above preparation was carried out several times. The yields obtained varied from 52 to 62%.

4-(2′-pyridyl) phenyl 4″-n-alkoxybenzoates

These esters were prepared by heating under reflux the acid chloride of the appropriate 4-n-alkoxybenzoic acid and the 2-(4′-hydroxyphenyl) pyridine in dry pyridine. The experimental procedure for the preparation of the 4-n-alkoxybenzoic acids is described on p.185, and the method for the preparation and purification of their 4-(2′-pyridyl) phenyl esters was the same as that used for the 4-biphenylyl 4″-n-alkoxybenzoates (p.188).

Ester formation by the direct interaction of 2-(4′-hydroxyphenyl) pyridine with the appropriate 4-n-alkoxybenzoic acid in the presence of boric acid and sulphuric acid[78] was unsuccessful.

The percentage yields obtained and the C-I and mesophase transition temperatures of these esters are listed in Table 25. The elemental analyses are given in Table 26 .

Table 25 - Data for 4-(2'-pyridyl) phenyl 4''-n-alkoxybenzoates

	Transition Temperatures		%
n-R	C-I	I-N	Yield
C_4H_9	159°	[119.5°]	68
C_5H_{11}	145.5	[108*]	75
C_6H_{13}	126.5	[116]	78
C_7H_{15}	126.5	[112]	73
C_8H_{17}	122	[115]	70
C_9H_{19}	129	[113]	63
$C_{10}H_{21}$	121	[114]	76
$C_{12}H_{25}$	119.5	[112.5]	80
$C_{14}H_{29}$	121.5	[111.5]	51

[ ] indicates a monotropic transition.

*This transition was detected by differential thermal analysis. It was not observed optically because the sample crystallised.

Table 26- Elemental Analyses for 4-(2'-pyridyl) phenyl 4''-n-alkoxybenzoates

	Found			Molecular	Requires			%
n-R	%C	%H	%N	Formula	%C	%H	%N	Yield
C_4H_9	76.4	6.2	4.0	$C_{22}H_{21}NO_3$	76.1	6.1	4.0	58
C_5H_{11}	76.3	6.4	4.1	$C_{23}H_{23}NO_3$	76.5	6.4	3.9	55
C_6H_{13}	77.0	6.8	3.8	$C_{24}H_{25}NO_3$	76.8	6.6	3.7	72
C_7H_{15}	77.1	6.9	3.9	$C_{25}H_{27}NO_3$	77.1	6.9	3.6	60
C_8H_{17}	77.4	7.4	3.7	$C_{26}H_{29}NO_3$	77.4	7.2	3.5	70
C_9H_{19}	77.6	7.2	3.4	$C_{27}H_{31}NO_3$	77.7	7.4	3.4	63
$C_{10}H_{21}$	78.2	7.7	3.2	$C_{28}H_{33}NO_3$	78.0	7.7	3.2	76
$C_{12}H_{25}$	78.5	8.0	3.3	$C_{30}H_{37}NO_3$	78.4	8.1	3.1	46
$C_{14}H_{29}$	79.1	8.5	3.0	$C_{32}H_{41}NO_3$	78.9	8.4	2.9	48

Infrared, n.m.r. and mass spectroscopic data and differential thermal analysis results for these esters can be found in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results".

3c) Synthesis of 4-(4'-n-alkoxyphenyl) pyridines

The 4-(4′-n-alkoxyphenyl) pyridines were difficult to prepare. Four synthetic routes were tried, namely

1. A synthetic method used by Chennat and Eisner[91] for the preparation of the dimethyl esters of 4′-substituted 4-phenylpyridinedicarboxylic acids.

2. A modification of a method used by Schmidle and Mansfield[83] for the preparation of 4-phenylpyridine and related compounds.

3. A method based on the copper (I) catalysed conversion of aryl halides into alkyl aryl ethers by Bacon and Rennison.[92]

4. Direct alkylation of 4-(4′-hydroxyphenyl) pyridine.

Methods 1 and 2 are essentially Hantzsch Pyridine Syntheses in which a β-dicarbonyl compound (2 moles) is condensed with an aldehyde (1 mole) and ammonia (1 mole). In the case of the Chennat and Eisner[91] method, an acetylenic compound, namely methyl propiolate, replaces the β-dicarbonyl compound and aromatic aldehydes were always used. The preparation of 4-n-heptyloxyphenylpyridine by this method was unsuccessful because of:

i) the low yield of the intermediate dimethyl 1,4-dihydro-4-(4′-n-heptyloxy phenyl) pyridine-3,5-dicarboxylate, and

ii) the difficulty of decarboxylating the dicarboxylic acid obtained from this by hydrolysis. Because of the high cost of the starting material, the method was therefore not viable.

The method of Schmidle and Mansfield[83], in which the β-carbonyl compound is replaced by α-methylstyrene and the aldehyde used is formaldehyde, was modified by the use of α-methyl-4-n-heptyloxystyrene in place of α-methylstyrene. The substituted α-methystyrene was prepared by the alkylation of 4-hydroxy-acetophenone and the resulting ether was converted to the tertiary alcohol via a Grignard reaction using iodomethane. The tertiary alcohol was dehydrated by heating with p-toluenesulphonic acid affording the α-methyl-4-n-heptyloxystyrene directly. The low yield of 4-n-heptyloxy phenylpyridine obtained by this method limited its usefulness as a general synthetic route to the 4-(4′-n-alkoxyphenyl) pyridines.

Nucleophilic and reductive substitution are frequent competitive reactions between aryl halides and nucleophiles in the presence of copper and its compounds. For the preparation of alkylaryl ethers Bacon and Rennison[92] used the fact that the substitution reaction becomes predominantly nucleophilic if the catalyst is changed from copper (I) oxide to the copper (I) halides. In the present work an attempt was made to prepare 4-butyloxyphenyl pyridine, using both compounds of 4-(4′-bromo-and-iodophenyl) pyridine. Reductive substitution predominated because in each case the product was 4-phenylpyridine.

The fourth synthetic route attempted was the direct alkylation of 4-(4′-hydroxyphenyl) pyridine, using three slightly different modifications. The first two of these, namely, using a non-polar solvent and using the hydrochloride of 4-(4′-hydroxyphenyl) pyridine in a polar solvent, both left the starting material essentially unchanged. However, by changing the solvent to N,N-dimethylformamide, the 4-(4′-hydroxyphenyl) pyridine was alkylated quite readily with the appropriate alkyl halide in the presence of anhydrous potassium carbonate giving the corresponding 4-(4′-alkoxyphenyl) pyridine. Several of these ethers were prepared in yields varying from 67 to 86%, but none of them exhibited liquid crystal behaviour. All the 4-(4′-alkoxyphenyl) pyridines prepared in this work were new compounds.

1. Chennat and Eisner's Method

4-n-Heptyloxybenzaldehyde

A stirred mixture of 4-hydroxybenzaldehyde (12.2g), anhydrous potassium carbonate (60g), n-heptylbromide (28.6g) and cyclohexanone was heated under reflux for 3h.

After cooling, the potassium carbonate was filtered off and washed with a little cyclohexanone. The cyclohexanone was removed from the combined filtrate and washings and the product was distilled, under vacuum (b.p. 130-132°/ 0.3mm) to afford a very pale green liquid, 19.8g (90%), ν max. 2920, 2850, 1690, 1600, 1580, 1510, and 830cm^{-1}, n.m.r. ($CDCl_3$) δ = 0.95 (br, 3H,-CH_3), 1.62 (br, 11H), 3.96 (t, J6.0Hz 3H,-OCH_2), 6.90 (d, J9.0Hz, 2H), 7.75 (d,J9.0Hz, 2H), 9.75 (S, 1H,-CHO).

Dimethyl 1,4-dihydro-4-(4'-n-heptyloxyphenyl) pyridine-3,5-dicarboxylate

Methyl propiolate (3.1g, 0.037M), n-heptyloxybenzaldehyde (4.05g, 0.018M), ammonium acetate (1.42g, 0.018M) and glacial acetic acid (4cm^3) were warmed together on a water-bath for 15 min. After cooling, the thick oil was diluted with 1:1 ethyl acetate:light petroleum (b.p. 60-80°) and then chromatographed on a column of silica gel (60g), eluting with 1:1 ethyl acetate:light petroleum (b.p. 60-80°). The fractions that came off the column were monitored by t.l.c. (SG/E.A.:P). The fractions that corresponded with the 3 lower spots (Rf value in the range 0.4 to 0.5) were combined and the solvent removed. The residue was dissolved in methanol and treated with charcoal. Recrystallisation from methanol gave an off-white solid, 0.35g, m.p. 132-134° (Found; C, 68.2; H, 7.0; N, 3.4. $C_{22}H_{29}O_5N$

requires C, 68.4; H, 7.3; N, 3.6%).

2. Schmidle and Mansfield's Method

4-n-Heptyloxyacetophenone (41.7g, 89%) was obtained as described previously (p.184), on twice the scale.

α-Methyl-4-n-heptyloxystyrene

All the apparatus, reactants and solvents were thoroughly dried.

To magnesium turnings (4.9g) in ether (20cm^3) was added iodomethane (28.4g) in ether (30cm^3) at such a rate that the ether boiled gently throughout the addition. When the addition was complete, the mixture was heated for approximately 15 min. to dissolve most of the magnesium turnings. After cooling, a solution of 4-n-heptyloxyacetophenone (23.4g) in ether (35 cm^3) was added dropwise to the vigorously stirred etheral solution of the Grignard reagent. When the addition had been completed, the reaction mixture was heated under reflux, on a water-bath for 1h.

After cooling, the reaction mixture was poured carefully onto 10% ammonium chloride (200cm^3) and ice (200g), to break down the complex and the product was extracted with ether (3 x 250 cm^3). The ether extract was then dried (K_2CO_3), the potassium carbonate filtered off and the ether removed.

The residue was heated, under reflux, with p-toluenesulphonic acid (1g) for 1h. After cooling, the reaction mixture was extracted with ether (150 cm^3) and the p-toluene sulphonic acid was removed by shaking the ether extract with 10% sodium hydroxide solution (2 x 50cm^3). The ether extract was then washed with water (2 x 100cm^3) and dried ($MgSO_4$).

The ether was evaporated off and the residue distilled under vacuum b.p. 114-115°/0.35 mm, affording the α-methyl-4-n-heptyloxystyrene as a white crystalline solid, 12.0g (52%), m.p. 37° (Found: C, 82.5; H, 10.4. $C_{16}H_{24}O$ requires C, 82.8; H, 10.3%).

4-(4′-n-heptyloxyphenyl) pyridine

Ammonium chloride (5.57g) was dissolved in a warm, stirred mixture of 38% formaldehyde (20 cm^3), dioxan (15 cm^3) and water (5 cm^3). Whilst the solution was heated under reflux, a solution of α-methyl-4-n-heptyloxy-styrene (12.0g) in dioxan (25 cm^3) was added slowly, with stirring. After the addition had been completed, the reaction mixture was heated, under reflux, for 1h. After cooling, methanol was added to the solution which was then stirred for 1h. The reaction mixture was then set aside, for 24h.

The methanol was removed from the bulk of the solution until a solid separated out, and then the suspension was hydrolysed by heating with concentrated hydrochloric acid (125 cm^3), with stirring, on a water-bath for 4h (frothing occurred). After cooling, the reaction mixture was diluted with water (300 cm^3) and then basified with 50% aqueous ammonia. The resulting tetrahydropyridine was then extracted with chloroform, dried ($MgSO_4$) and the chloroform was removed. The tetrahydropyridine (14.8g) in dry nitrobenzene (45g) was dehydrogenated by stirring for 6h under nitrogen with 5% palladium on charcoal (1g), at a temperature of 135°C. A condenser was fitted to the apparatus to allow the continuous removal of water. After cooling, an excess of dilute hydrochloric acid was added to the reaction mixture, and the insoluble material was filtered off. Non-basic materials were removed from the filtrate by extraction with toluene. The aqueous phase was then basified with 4M-aqueous sodium hydroxide and the liberated amine was extracted with toluene. The extract was dried ($MgSO_4$) and the toluene removed. The residue was dissolved in ether and to this solution was added an excess of an etheral solution of picric acid. The picrate crystallised out and was filtered off, washed with ether, and then added to saturated aqueous lithium hydroxide. The liberated amine was extracted with ether (3 x 100 cm^3). The ether extract was washed with water (2 x 50 cm^3), dried ($MgSO_4$), concentrated to a smaller volume and then subjected to chromatography on a short column of alumina (5g), eluting with ether. All the fractions from the column were combined and the ether removed. After treatment with decolourising charcoal, the resulting 4-(4$'$-n-heptyloxyphenyl) pyridine was recrystallised several times from light petroleum (b.p. 60-80°) and thus obtained as a white solid, 0.32g, m.p. 57° (Found: C, 80.7; H, 8.7; N, 4.9. $C_{18}H_{23}NO$ requires C, 80.3; H, 8.6; N, 5.2%).

3. Bacon and Rennison's Method

4-(4'-Aminophenyl) pyridine was prepared from 4-phenylpyridine via the nitro-compound as described previously (p.226).

4-(4'-Iodophenyl) pyridine

4-(4'-Aminophenyl) pyridine (6g) was diazotised as described earlier (p.228).

To the stirred diazonum salt was added, dropwise, a solution of potassium iodide (6.2g) in water (15 cm^3). When the addition was complete, the solution was stirred for 1h. The solution was then warmed to 60° and this temperature was maintained for 45 min., after which the temperature was raised to 80° for 15 min. The excess of iodine was removed by the addition of sodium bisulphite until the colour changed from deep purple to orange. The mixture was cooled and the solid was filtered off, washed with water and dried. Thin layer chromatography (S.G/E.A:B) established that the crude product was not unchanged 4-(4'-aminophenyl) pyridine nor 4-(4'-hydroxyphenyl) pyridine. Recrystallisation from ethanol and then from n-butanol gave 4-(4 -iodophenyl) pyridine as a pale buff coloured solid, 3.1g (31%), m.p. 212° (Found: C, 46.9; I, 45.2. $C_{11}H_8NI$ requires C, 46.9; I, 45.2%).

The filtrate was worked-up by basification with 20% aqueous ammonia and the resulting precipitate was filtered off and washed with water. Thin layer chromatography (S.G./E.A:B) indicated that the compound was 4-(4'-hydroxyphenyl) pyridine. Recrystallisation from ethanol gave the compound as a very pale yellow solid, 3.8g (63%), m.p. 251-252°. Butterworth, Heilbron and Hey[88] report a m.p. of 253-254° for this compound.

4-(4'-Bromophenyl) pyridine

4-(4'-Aminophenyl) pyridine (4g, 0.024 m) was dissolved in hydrobromic acid (15 cm^3) and water (15 cm^3), by warming. The stirred solution was then cooled rapidly to 0°, and the resulting fine suspension of the amine hydrobromide was diazotised by the dropwise addition of sodium nitrite (1.8g, 0.026M) in water (25 cm^3). The temperature was maintained at 0-5° throughout the addition and for 30 min. afterwards.

The diazonium salt was added dropwise to a stirred solution of copper (I) bromide (4.1g) in hydrobromic acid (10 cm^3) and when the addition was complete, the solution was stirred at room temperature overnight. The solid was filtered off and basified with 10% aqueous ammonia and the liberated amine was filtered off and washed with water. The product was treated with boiling n-butanol and the insoluble material was filtered off. The n-butanol was removed from the filtrate and the residue was dissolved in methylated spirit, treated with decolourising charcoal, and the hot solution set aside. On cooling, 4-(4'-bromophenyl) pyridine crystallised out as a white solid, 3.25g (59%), m.p. 130-131° (Found: C, 56.6, Br, 39.3. $C_{11}H_8NBr$ requires C, 56.4; Br, 34.2%).

4-(4'-n-Butyloxyphenyl) pyridine

All the apparatus, reagents and solvents were thoroughly dried.

Freshly cut sodium (0.69g) was dissolved in warm n-butanol (12 cm^3) under an atmosphere of nitrogen and with stirring. When dissolution was complete, freshly distilled 2,4,6-trimethylpyridine (10 cm^3), copper (I) iodide (0.95g) and the halogenophenylpyridine (bromo-compound, 2.34g; iodo-compound, 2.81g) was added. Finally, more 2,4,6-trimethylpyridine (20 cm^3) was added and the solution was heated under reflux, in an atmosphere of nitrogen, with stirring, for 24h. After cooling, the insoluble material was filtered off and washed with 2,4,6-trimethylpyridine. The filtrate and washings were combined and the 2,4,6-trimethylpyridine removed by vacuum distillation (b.p. 44-46°/1.8 mm).

In both instances, the product was vacuum distilled, the large fraction (b.p. 114-122°/2.0 mm) was collected and then dissolved in light petroleum (b.p. 60-80°) and treated with decolourising charcoal. A white crystalline compound, m.p. 73° was obtained. A mixed melting point with pure 4-phenylpyridine was undepressed, indicating that the product was 4-phenylpyridine.

4. Direct alkylation of 4-(4'-hydroxyphenyl) pyridine

a) Using a non-polar solvent

4-(4'-Hydroxyphenyl)pyridine (1.7g, 0.01M), anhydrous potassium carbonate (6.0g, 0.04M) and cyclohexanone (25 cm^3) were placed in a 100 cm^3 flask fitted with a stirrer and condenser. Whilst stirring, n-heptyl bromide (2.9g, 0.016M) was added and the reaction mixture was heated, under reflux, for 3h.

After cooling, the salts were filtered off and washed several times with cyclohexanone. The cyclohexanone was then distilled off from the combined filtrate and washings. Thin layer chromatography on the resulting residue indicated that it was unchanged 4-(4'-hydroxyphenyl) pyridine [the 4-(4'-n-heptyloxyphenyl) pyridine obtained by Schmidle and Mansfield's method fluoresced in ultraviolet light].

b) From the hydrochloride of 4-(4'-hydroxyphenyl) pyridine

The hydrochloride was prepared by dissolving the 4-(4'-hydroxyphenyl) pyridine (0.5g) in warm, dry tetrahydrofuran (30 cm^3). Keeping the solution cool, hydrogen chloride gas was passed through the solution and the precipitated amine hydrochloride was filtered off and washed with ether.

The amine hydrochloride was added to a stirred solution of n-heptylbromide (0.53g) in dry N,N-dimethylformamide which was then heated, under reflux, for 8h. After cooling, the N,N-dimethylformamide was removed by vacuum distillation leaving behind a yellow-brown solid, which on examination by t.l.c., was found to be the starting material.

c) Using a polar solvent

A stirred reaction mixture containing 4-(4'-hydroxyphenyl) pyridine (2.0g, 0.0118M), n-heptyl bromide (3.1g, 0.0174M), anhydrous potassium carbonate (7.0g, 0.066M) and dry N,N-dimethylformamide (45 cm^3) was heated, under reflux, for 8h.

After cooling, the salts were filtered off and washed several times with dry N,N-dimethylformamide. The N,N-dimethylformamide was distilled off, under vacuum, from the combined filtrate and washings. The desired product was then distilled off, under vacuum. The pale yellow solid, 3.6g (68%) was heated with decolourising charcoal and recrystallised several times from light petroleum (b.p. 60-80°) to give 4-(4'-n-heptyloxyphenyl) pyridine as a white crystalline solid, 2.8g (53%), m.p. 57-58° (Found: C, 80.3; H, 8.6; N, 5.2. $C_{18}H_{23}NO$ requires C, 80.5; H, 8.7; N, 5.1%).

The above procedure typifies that used for the synthesis of several 4-(4'-n-alkoyxphenyl) pyridines. These are listed in Table 27, together with the percentage yields, melting points and elemental analyses.

Table 27- Data for the 4-(4'-n-alkoyxphenyl) pyridines

n-R	Elemental Analysis Found %C	%H	%N	Molecular Formula	Requires %C	%H	%N	% Yield	m.p.
C_6H_{13}	80.1	8.4	5.6	$C_{17}H_{21}NO$	80.0	8.2	5.5	70	62°
C_8H_{17}	80.5	8.7	5.0	$C_{19}H_{25}NO$	80.6	8.8	5.0	86	67
C_9H_{19}	80.5	9.4	4.6	$C_{20}H_{27}NO$	80.8	9.1	4.7	67	65-66
$C_{10}H_{21}$	81.4	9.6	4.3	$C_{21}H_{29}NO$	81.0	9.3	4.5	82	72-73
$C_{12}H_{25}$	81.6	10.0	4.3	$C_{23}H_{33}NO$	81.4	9.7	4.1	78	73-74
$C_{14}H_{29}$	82.0	9.9	4.0	$C_{25}H_{37}NO$	81.7	10.1	3.8	70	75.5-76.5

Infrared and n.m.r. data for these ethers are given in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results".

3d) Synthesis of the N-oxides of:
4-(4'-pyridyl) phenyl 4''-n-alkoxybenzoates;
4-(2'-pyridyl) phenyl 4''-n-alkoxybenzoates; and
4-(4'-n-alkxoyphenyl) pyridines.

The N-oxides were prepared by two methods:

a) Using m-chloroperoxybenzoic acid

b) Using hydrogen peroxide in glacial acetic acid.

It was found that the latter method gave the best results and was easier to carry out.

a) Using m-chloroperoxybenzoic acid

To a cooled, stirred solution of 4-(4'-n-heptyloxyphenyl) pyridine (1.0g) in chloroform (5 cm^3) was added, dropwise, a cold suspension of m-chloroperoxybenzoic acid (0.65g) in chloroform (5 cm^3). After the addition, the yellow solution was stirred at room temperature for 3h. The complex was then broken down by shaking the chloroform solution with 2M-aqueous sodium hydroxide. The chloroform layer was separated from the aqueous layer, dried ($MgSO_4$) and the volume of chloroform in the filtrate reduced to about 10 cm^3.

The N-oxide was chromatographed on a column of alumina (100 g), eluting with chloroform. The fractions leaving the column were monitored by t.l.c. (the N-oxide had an Rf value of approximately 0.10) and the appropriate fractions containing the N-oxide were combined and the chloroform was removed. After treatment with decolourising charcoal, the N-oxide was recrystallised several times from aqueous acetone, then from light petroleum (b.p. 60-80°), and finally from AnalaR light petroleum (b.p. 60-80°).

The N-oxides of 4-(2′-pyridyl) phenyl 4″-n-hexyloxybenzoate and 4-(4′-pyridyl) phenyl 4″-n-heptyloxybenzoate were also prepared by this method. Other N-oxides were prepared by the hydrogen peroxide method.

b) Using hydrogen peroxide

The 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoate or the 4-(4′-n-alkoxyphenyl) pyridine (2.0g) was added to a solution of glacial acetic acid (5 cm^3) in 100 vol. hydrogen peroxide (2 cm^3). The solution was warmed to 80° and this temperature was maintained for 24h. An additional amount of hydrogen peroxide (2 cm^3) was added after 12h. The chilled reaction mixture was then basified with 20% aqueous sodium hydroxide. At this stage, the N-oxide of the 4-(4′-pyridyl) phenyl esters were filtered off, whereas those of the 4-(4′-n-alkoxyphenyl) pyridines were extracted with chloroform. In both cases, the N-oxide was purified by column chromatography on alumina (100 g), eluting with chloroform. The eluate was monitored by t.l.c. and the appropriate fractions were combined before the removal of the solvent. The yields varied from 60 to 84%.

The N-oxides were treated with decolourising charcoal and recrystallised several times from the minimum amount of acetone or aqueous acetone, and finally from AnalaR light petroleum (b.p. $60-80^{o}$). The melting points, C-I, C-S, C-N and mesophase transition temperatures are listed in Table 28.

Table 28- Data for the N-oxides

			Transition Temperature				
n-R	C-I	C-S$_A$	C-N	S-S$_A$	S$_A$-N	S$_A$-I	N-I
N-oxides of 4-(4$'$-n-alkoyxphenyl) pyridine							
C_6H_{13}	95.5^{o}					[57.5^{o}]	
C_7H_{15}	97.5					[72]	
C_8H_{17}		76.5^{o}				85.5	
C_9H_{19}		73.5				94.5	
$C_{10}H_{21}$		78				102.5	
$C_{12}H_{25}$		80				110.5	
$C_{14}H_{29}$		84				113	
N-oxides of 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoate							
		C–S					
C_5H_{11}			144^{o}				187^{o}
C_6H_{13}			144		[141^{o}]		187
C_7H_{15}		129.5^{o}			174.5		185.5
C_8H_{17}		135		[128.5]		191.5	
C_9H_{19}		141		181		192	
$C_{12}H_{25}$		132		[97.5]		200	
$C_{14}H_{29}$		132		[104.5]		203.5	

[ ] indicates a monotropic transition

The N-oxide of 4-(2$'$-pyridyl) phenyl 4$''$-n-hexyloxybenzoate was not liquid crystalline and had a m.p. of 163°.

The elemental analyses are listed in Table 29.

Table 29- Elemental Analysis for the N-oxides

	Found			Molecular	Requires		
n-R	%C	%H	%N	Formula	%C	%H	%N
N-oxides of 4-(4$'$-n-alkoxyphenyl) pyridine							
C_6H_{13}	75.3	7.7	5.0	$C_{17}H_{21}NO_2$	75.3	7.8	5.2
C_7H_{15}	75.5	8.3	5.0	$C_{18}H_{23}NO_2$	75.8	8.1	4.9
C_8H_{17}	76.0	8.2	4.7	$C_{19}H_{25}NO_2$	76.3	8.4	4.7
C_9H_{19}	76.4	8.9	4.4	$C_{20}H_{27}NO_2$	76.7	8.6	4.5
$C_{10}H_{21}$	76.9	9.0	4.2	$C_{21}H_{29}NO_2$	77.1	8.9	4.3
$C_{12}H_{25}$	77.3	9.6	4.1	$C_{23}H_{33}NO_2$	77.7	9.3	3.9
$C_{14}H_{29}$	78.1	9.6	3.8	$C_{25}H_{37}NO_2$	78.3	9.7	3.7
N-oxides of 4-(4$'$-pyridyl) phenyl 4$''$-n-alkoxybenzoate							
C_5H_{11}	73.3	6.1	3.6	$C_{23}H_{23}NO_4$	73.2	6.1	3.7
C_6H_{13}	76.6	6.5	3.5	$C_{24}H_{25}NO_4$	76.8	6.4	3.6
C_7H_{15}	73.9	6.8	3.3	$C_{25}H_{27}NO_4$	74.1	6.7	3.5
C_8H_{17}	74.7	6.7	3.3	$C_{26}H_{29}NO_4$	74.5	6.9	3.3
C_9H_{19}	74.6	7.3	3.1	$C_{27}H_{31}NO_4$	74.8	7.2	3.2
$C_{12}H_{25}$	75.6	7.8	2.8	$C_{30}H_{37}NO_4$	75.8	7.8	2.9
$C_{14}H_{29}$	76.0	8.3	2.8	$C_{32}H_{41}NO_4$	76.3	8.2	2.8
N-oxides of 4-(2$'$-pyridyl) phenyl 4$''$-n-heptyloxybenzoate							
C_6H_{13}	77.0	6.6	3.8	$C_{24}H_{25}NO_4$	76.8	6.4	3.6

Infrared, n.m.r. and mass spectroscopic data for these N-oxides are given in the section entitled "Spectroscopic Data and Differential Thermal Analysis Results".

4. Miscellaneous Experimental Work

4a) Synthesis of 4-pyridyl 4′-n-heptyloxy- and -octyloxy-benzoates

Isonicotinoyl chloride

Isonicotinic acid (10g) was heated under reflux with thionyl chloride (100 cm^3) for 3h. The bulk of the thionyl chloride was removed by distillation, and the final traces removed by warming under reduced pressure. Recrystallisation from a mixture of dry chloroform and light petroleum (b.p. 60-80°) afforded the isonicotinoyl chloride as an off-white solid, 8.65g (75%). The m.p. was not determined.

4-Pyridyl 4$'$-n-heptyloxy- and -octyloxy-benzoates

These esters were prepared by heating under reflux, the isonicotinoyl chloride (1.41g, 0.01M) and the appropriate n-alkoxyphenol (0.01M) [n-heptyloxyphenol, 2.08g; n-octyloxyphenol, 2.22g] in dry pyridine. The experimental procedure for the preparation of the n-alkoxyphenols is described on (p.195), and the method for the preparation and purification of the 4-pyridyl 4$'$-n-alkoxybenzoates was the same as that used for the 4-biphenylyl 4$'$-n-alkoxybenzoates (p.188).

The yields obtained, the melting points and the elemental analyses are presented in Table 30.

Table 30 - Data for 4-pyridyl 4 -n-heptyloxy- and -octyloxy-benzoate

n-R	m.p. (°)	% Yield	Elemental Analysis						
			Found			Molecular Formula	Requires		
			%C	%H	%N		%C	%H	%N
C_7H_{15}	83	40	72.7	7.5	4.3	$C_{19}H_{23}NO_3$	72.8	7.3	4.5
C_8H_{17}	82	52	73.2	7.8	4.2	$C_{20}H_{25}NO_3$	73.4	7.6	4.3

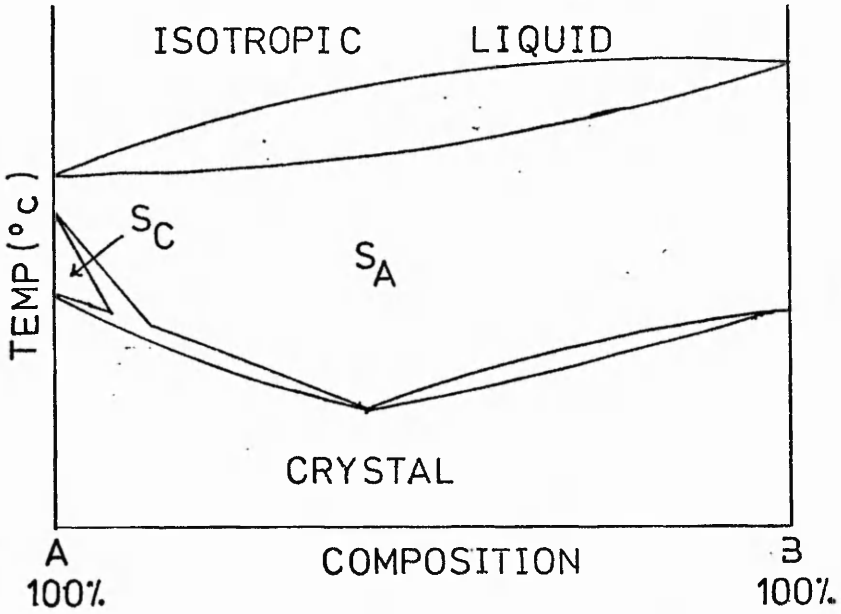
4b) Identification of the Smectic Mesophases Exhibited by the Compounds Prepared in the Present Work

Assignment of the Smectic Mesophases

One of the most difficult problems in the field of liquid crystals is the identification of the various types of smectic mesophases. There are two basic classifications of the polymorphism of non-amphiphilic smectic mesophases: one by DeVries [16], which is based on the structure of the mesophases determined by X-ray diffraction; the other by Sackmann and Demus [15], which uses the 'Rule of Selective Miscibility'. An account of both classifications is given in the introduction to this thesis. That most frequently used is the simpler classification of Sackmann and Demus.

Their rule is based on experimental observations; for example if the smectic mesophase formed by a binary mixture of two smectogenic liquid crystals is continuous, homogenous and miscible across the entire composition range (i.e. from 100% of one component to 100% of the other), then the smectic mesophases of the two compounds are of the same type. If the converse is true, the smectic mesophases of the two compounds are of different types. The phase diagram (Figure 36) shows the type of composition diagram observed for the case where the smectic mesophase of components A and B are the same.

Figure 36 - Ideal Phase Diagram for Two Smectogens A and B Having Identical Smectic Mesophase



Procedure for the Construction of a Composition Diagram

The diagram is constructed by plotting the composition of a binary mixture, in which one of the components has known smectic properties (i.e. a standard), against the mesophase transition temperature of the mixture, over an appropriate composition range which may extend from 100% of one component to 100% of the other.

For a given composition, the correct amount of each of the two components is weighed out onto microscope slides and the components are thoroughly mixed. The mixture is then melted and a cover slip is placed near the melt so that capillary action draws the melt between the cover slip and microscope slide. On examination with the polarising microscope, the mesophase transition temperatures are observed during the heating and cooling cycles of the hot stage, and a plot of these transition temperatures against the binary mixture composition enables the composition-temperature plot to be constructed and hence permits the type of the unknown smectic mesophase to be identified.

Initial observation (using the polarising microscope) of the textures indicated that the smectic mesophases exhibited by the compounds prepared in this work were of the smectic A type. This was confirmed by miscibility studies using 4′-n-heptyloxyphenyl 4′-cyanobiphenyl-4-carboxylate[80] (designated by the symbols CB7) as the S_A standard.

The composition diagrams of CB7 with 4-(4′-pyridyl) phenyl 4″-n- alkoxybenzoates and of 4-(4′-pyridyl) phenyl 4″-n-alkoxybenzoates with 4-biphenylyl 4″-n-alkoxybenzoates illustrates the results obtained.

i) Binary mixture of CB7 and 4-(4′-pyridyl) phenyl 4″-n-tetradecyloxybenzoate

The diagram of composition against temperature was plotted (Figure 37) from the results shown in Table 31 Both components of the phase diagram form a continuous miscible homogeneous region over the whole composition range of the smectic A mesophase of CB7.

The nematic mesophase of CB7 falls away rapidly as its concentration in the binary mixture decreases. The S_B phase of CB7 also falls away so sharply that at the 80:20 composition ratio of CB7:4-(4′pyridyl) phenyl ester, crystallisation occurred before the S_B phase could be

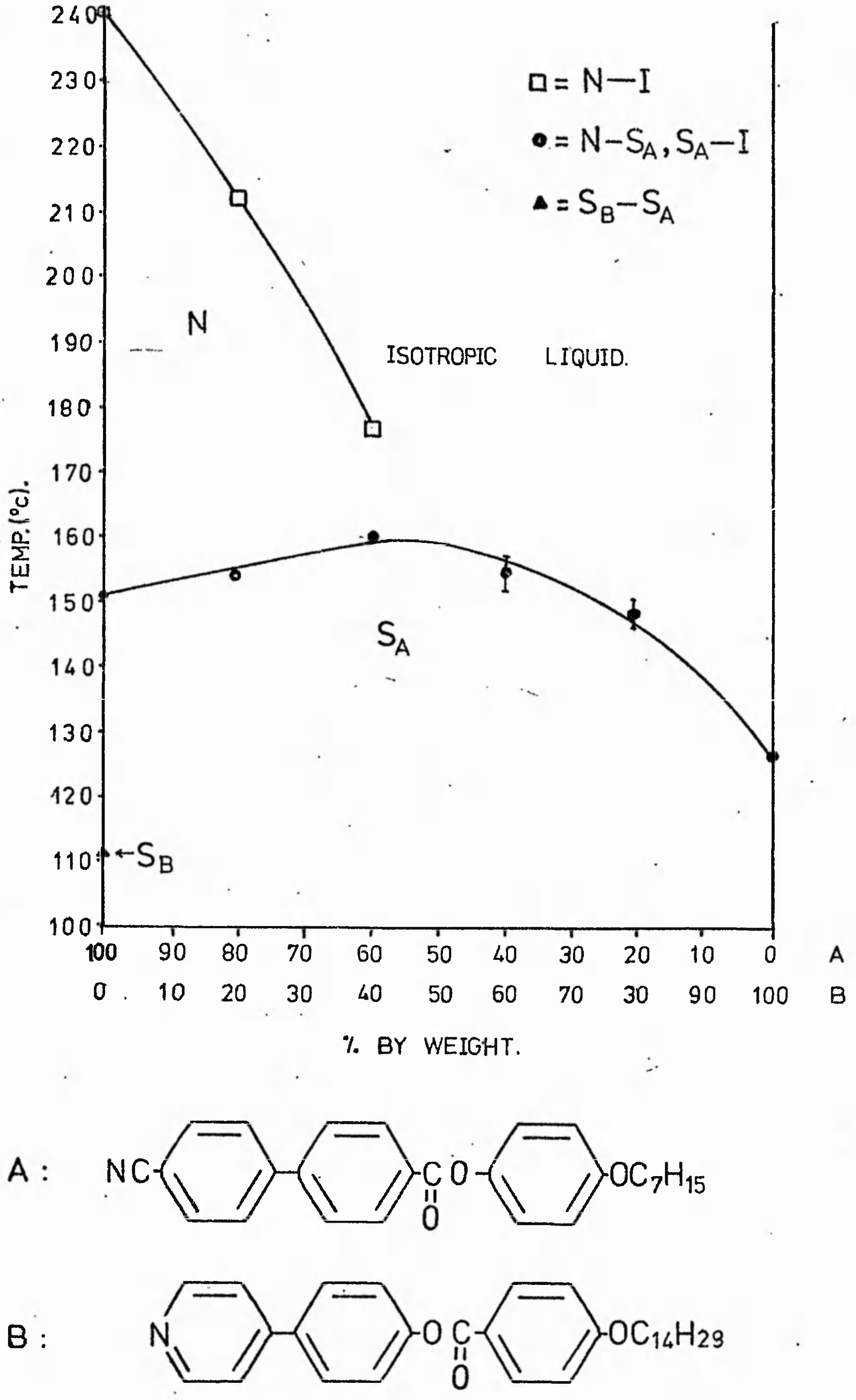


Figure 37 - Compositional Diagram for the Binary Mixture of CB7 and 4(4′-Pyridyl)phenyl 4″-n-Tetradecyloxybenzoate

observed. From these results, it was concluded that the 4-(4′-pyridyl) phenyl ester was a pure smectogen, exhibiting a smectic A mesophase.

Table 31 - Transition temperatures for various compositions of the binary mixture of 4-(4′-pyridyl) phenyl 4″-n-tetradecyloxybenzoate with CB7

CB7:B	Transition Temperature			
% Weight	S_B-S_A	N-I	N-S_A	S_A-I
100 : 0	111°	240°	151°	
80 : 20	*	211°	154.5	
60 : 40		175.5-178	159.5	
40 : 60				152.5-156°
20 : 80				147-150
0 : 100				126.5

B = 4-(4′-pyridyl) phenyl 4″-n-tetradecyloxybenzoate

* crystallised at 91°

ii) Binary mixture of 4-(4′-pyridyl) phenyl 4″-n-tetradecyloxybenzoate and 4-biphenylyl 4″-n-dodecyloxybenzoate

A composition diagram (Figure 38) was constructed from the results shown in Table 32. The biphenyl esters have both smectic and nematic mesophases but (Figure 38) the nematic properties soon give way to a smectic mesophase, which appears as a continuous miscible homogeneous region across the whole composition range. Thus the smectic mesophase of 4-biphenylyl 4″-n-dodecyloxybenzoate is

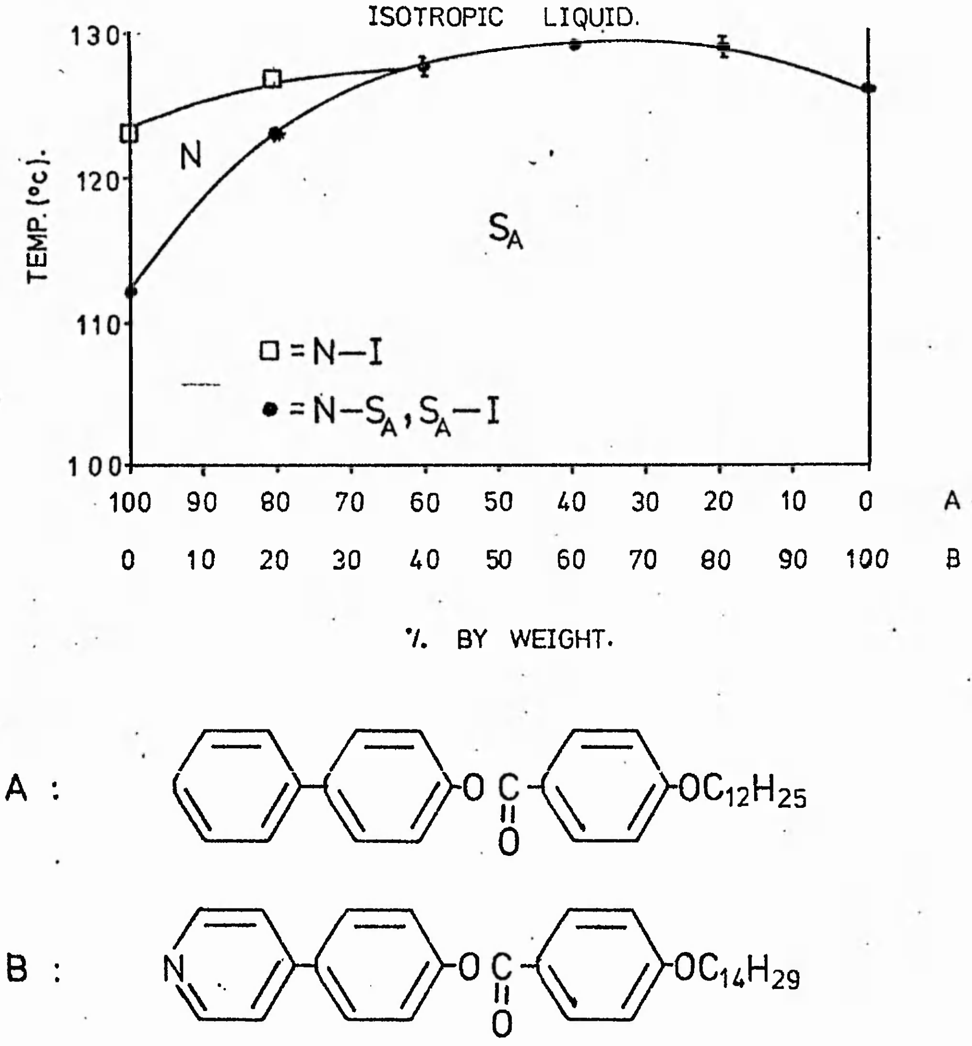


Figure 38 - Compositional Diagram for the Binary Mixture of the 4-(4′-Pyridyl) phenyl 4″-n-Tetradecyloxybenzoate and 4-Biphenylyl 4″-n-Dodecyloxybenzoate

smectic A.

Table 32 – Transition temperatures for various compositions of the binary mixture of 4-(4′ pyridyl) phenyl 4″-n-tetradecyloxybenzoate with 4-biphenylyl 4″-n-dodecyloxybenzoate

A:B % by weight	Transition Temperature $N-S_A$	 S_A-I	 $N-I$
100 : 0	112°		123°
80 : 20	123		126.5-127,5
60 : 40		128-129°	
40 : 60		129	
20 : 80		128.5-129.5	
0 : 100		126.5	

The smectic mesophases of all the smectogenic liquid crystals prepared in this work were of the smectic A type.

The nature of the smectic-smectic mesophase transitions of the N-oxides of the 4-(4′ -pyridyl) phenyl 4″-n-alkoxybenzoates was not investigated. In relation to the completion of the synthetic work, this assignment was of low priority, but will be carried out before publication of data on these compounds.

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The Liquid Crystalline Behaviour of Certain Analogous Biphenyl and 2- and 4-Phenylpyridine Systems

Summary of a thesis submitted to the
Council for National Academic Awards for the degree of
Doctor of Philosophy
by
DAVID LACEY, BSc
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In order to compare the mesomorphic properties of certain biphenyl and 2- and 4-phenylpyridine systems, seven homologous series of esters were studied, namely the:

(i) 4-biphenylyl 4"-n-alkoxybenzoates;
(ii) 4"-n-alkoxyphenyl biphenyl-4-carboxylates;
(iii) 2'-fluoro-4-biphenylyl 4"-n-alkoxybenzoates;
(iv) 2'-chloro-4-biphenylyl 4"-n-alkoxybenzoates;
(v) 4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoates;
(vi) 4-(2'-pyridyl)phenyl 4"-n-alkoxybenzoates;
(vii) N-oxides of 4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoates.

The 4-(4'-n-alkoxyphenyl)pyridines and their N-oxides were also investigated.

The 4-biphenylyl 4"-n-alkoxybenzoates and the 4"-n-alkoxyphenyl biphenyl-4-carboxylates provided the foundation on which subsequent work was based. These isomeric esters have almost the same N-I transition temperatures but only in the former series are smectic properties observed. An explanation for this behaviour is offered.

The effect of replacing -CH= in the 2- and the 4-position of the biphenyl system by a hetero-N atom was studied by measurement of the transition temperatures of the 4-(2'-pyridyl)phenyl and 4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoates. The effect of the terminal N-atom of the 4-pyridylphenyl esters is to enhance the smectic properties, whereas the effect of the lateral N-atom of the 2-pyridylphenyl esters is to lower both the m.p. and the N-I transition temperatures. This latter effect is attributed to broadening of the molecule due to twisting about the inter-ring bond. For this reason the 2'-fluoro- and -chloro-4-biphenylyl 4'-n-alkoxybenzoates were investigated. In both series of halogeno-substituted biphenyl esters twisting about the 1,1'-bond results in substantial lowering of both the m.p. and the N-I transition temperature, although several of the esters exhibited monotropic mesophases.

4'-Alkyl- and 4'-alkoxy-4-cyanobiphenyls are low melting nematogens that are used extensively in electro-optical display devices. In order to compare the effect on mesophase thermal stability of the cyano-group and the heterocyclic N-oxide function, the 4-cyano-4'-biphenylyl 4"-n-alkoxybenzoates and the N-oxides of the 4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoates were studied. The latter series is essentially smectogenic but problems arose in the measurement of their mesophase transition temperatures because of the inherent thermal and photo sensitivity of these compounds. The N-oxides of the 4-(4'-n-alkoxyphenyl)pyridines were also investigated as a type of heterocyclic 'analogue' of the 4-alkoxy-4'-cyanobiphenyls. The compounds were not as low melting (73.5-97.5°) as was hoped and showed smectic properties, some of which were monotropic. These compounds were affected by prolonged exposure to light.

Miscibility studies, optical microscopy and differential thermal analysis were used to investigate the various types of mesophase. Suggestions to explain the trends of the mesomorphic thermal stabilities of the various homologous series are offered, along with some group efficiency orders.