NOTTINGHAM POLYTECHNIC

(in collaboration with MERCK LTD.)

SYNTHESIS AND PROPERTIES OF SOME FLUORINATED BIPHENYL MESOGENS

being a Thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the degree of Doctor of Philosophy

by

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Dedicated to my parents Mr. and Mrs. Sujan Singh **MATHARU** for their endless support and encouragement over the years.

Acknowledgements

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Equipment used during this work

1. All infra-red spectra were recorded with a Perkin-Elmer 157 grating spectrophotometer.
2. All nuclear magnetic resonance spectra were determined using an Hitachi Perkin-Elmer R-24B N.M.R. spectrophotometer.
3. Measurements of transition temperatures and microscopic observations of mesophase textures were made using a Vickers M75 polarising microscope in conjunction with a Mettler FP52 hot-stage, and FP5 control unit.
4. Birefringence, dielectric constants and viscosity measurements were made at Merck Ltd. (formerly BDH Chemicals Ltd.), Poole, using their own equipment.

The following abbreviations are used in the discussion and reaction schemes:

DMSO - Dimethylsulphoxide

DMF - Dimethylformamide

DCM - Dichloromethane

THF - Tetrahydrofuran

TMB - Trimethyl borate

1.6M BuLi - 1.6M n-Butyllithium in hexane

BMS - Borane dimethylsulphide

PCC - Pyridinium chlorochromate

DCC - Dicyclohexylcarbodiimide

TFA - Trifluoroacetic acid

*p*TSA - *para*-Toluenesulphonic acid

INTRODUCTION

1. INTRODUCTION

1.1 HISTORICAL

The liquid crystalline phase is a state of matter that is observed in certain materials intermediate between the crystalline solid and the isotropic liquid.

The credit for the discovery of and early pioneering work on liquid crystals belongs to Reinitzer[1] and Lehmann.[2] In 1888, Reinitzer noted that a pure sample of cholesteryl benzoate melted to give a turbid fluid at 145.5°C which clarified at 178.5°C. On cooling the clear liquid he also observed an unusual colour effect (the iridescent colour phenomena now known to be a characteristic of many cholesteric phases). Other cholesterol derivatives gave rise to similar effects, and Reinitzer informed Lehmann of his observations. Lehmann, who studied the melting behaviour with the aid of polarising microscope, confirmed Reinitzer's findings and introduced the term '*liquid crystal*' to describe Reinitzer's newly discovered phenomenon. Lehmann later showed that many other compounds, e.g. ammonium oleate and *p*-azoxyanisole exhibited the liquid crystal state.

Not surprisingly, other chemists were attracted by the new discovery and many new materials were synthesised within a short span of years. In 1890, Gattermann[3] synthesised derivatives of azoxybenzene which were the first liquid crystalline compounds with a completely known chemical structure. Vorländer[4] investigated a large number of compounds in order to study the relationship between molecular structure and liquid crystallinity. By 1908 about 170 liquid crystalline compounds were available and he was able to conclude that compounds that gave rise to liquid crystals had an enlongated, lath-like molecular structure.

The first classification of liquid crystals on a structural basis was proposed by Friedel[5] in 1922 who classified the 42 liquid crystalline compounds known to him as nematic, smectic and cholesteric. Friedel opposed Lehmann's term 'liquid crystal' because he considered that the intermediate state was neither a true liquid nor a true solid, and he introduced the term mesophase which stresses the intermediate nature of observed liquid crystalline phases without associating them with the crystalline solid or the isotropic liquid. It should be noted that Friedel's studies did not take account of the existence of smectic polymorphism and the first compound showing smectic polymorphism was synthesised by Vorländer.[6]

At the same time, active research was being carried out by theoreticians on the nature of the liquid crystalline state. Two hypotheses were proposed, namely the continuum or distortion hypothesis and the swarm hypothesis.

The continuum hypothesis was initially proposed by Zocher[7] in 1922. His theory was based on the interpretation of the effects of a magnetic field on the nematic structure. Although his work was substantiated by others such as Oseen,[8] the hypothesis had its limitations when attempting to interpret the properties of light extinction and wall effects.

The swarm therory was initially proposed by Bose[9] and rigorously promoted by Ornstein and Kast.[10] At the time, this theory was favoured in preference to the continuum theory. The theory assumes that the molecules in the mesomorphic state are not orientated in the same direction throughout the whole medium but are grouped in aggregates or swarms. The molecules in the swarm lie parallel or approximately so, but in a direction that is random to the direction of orientation of the molecules of other swarms in the medium. A principal attraction of the swarm theory was its ability to explain the turbid appearance of the mesomorphic state as being due to the scattering of light by the swarms.

With the passage of subsequent years, leading to the advent of the Second World War, there was a sharp decline in the extent of research into the liquid crystal field. Even so, some important academic and theoretical developments were made. Maier and Saupe[11] developed a uniform theory of dielectric behaviour. After the war, following initial work by Weygand,[12] Gray[13] and his co-workers concentrated work on relationships between the mesomorphic state and chemical structure. Extensive microscopic and X-ray investigations of liquid crystalline compounds by Sackmann and Demus[14] led to classification of smectic types A, B, C, D, E, F and G. More recently, smectic types H, I, J and K have been characterised.

Following the recognition in the late 1960s, of the important applications of liquid crystals, principally as materials for display devices (L.C.D.s) in the electronics industry, a very rapid upsurge of interest in liquid crystals resulted. This has continued to the present day with an increasing necessity for collaboration between liquid crystal scientists inorder to produce novel liquid crystalline materials to meet newer challenges.

1.2 CLASSIFICATION

Matter may exist in three forms: solid, liquid and gas. Solids may be crystalline or amorphous. In the crystalline solid, the centres of mass of the molecules are fixed and located on a regular three-dimensional lattice. As a consequence, Bragg reflections are intense and correspond to the lattice planes. In general, the crystalline solid retains a high degree of positional and dimensional (orientational) order.

To understand the nature of liquid crystals, it is necessary to recall that at the melting point of a crystal, the solid is converted into an isotropic liquid. The centres of mass of the molecules are no longer fixed resulting in a loss of positional order. However, certain substances which are rigid, elongated and lath-like in shape and are said to be geometrically anisotropic, show different behaviour. On heating these compounds, they may not pass directly to the isotropic liquid nor return directly to the crystalline solid on cooling the isotropic melt but may adopt an intermediate structure which may flow like a liquid, but which still possesses the anisotropic physical properties characteristic of a crystalline solid. This is referred to as the liquid crystalline or mesomorphic state which may be defined as an intermediate state of matter that exists between the crystalline solid and the isotropic liquid. Compounds which exhibit the liquid crystalline state are known as liquid crystalline or mesomorphic compounds.

The melting point and clearing point define the temperature range over which the liquid crystal is stable, and several mesophases with slightly differing molecular arrangements may exist over this range of temperature.

Friedel[5] distinguished three types of mesophase, namely, smectic, nematic, and cholesteric mesophases.

1. Smectic mesophase. The name smectic is derived from the Greek word *smectos* meaning soap-like. In the smectic phase, the molecules are stratified and possess orientational and positional order. The centres of the molecules, on average, are arranged in equidistant planes. The molecules may be aligned either perpendicular to the layers or at an acute angle to the layers. Depending upon the arrangement of the molecules in the layers, the smectic mesophase can exist as several polymorphic modifications. These were not acknowledged by Friedel.
2. Nematic mesophase. The name nematic is derived from the Greek word *nematos* meaning thread-like. The molecules possess long range positional order, i.e. statistically, the molecules tend to align parallel to each other, the direction of alignment being represented by, $\tilde{n}$, the director. In fact, the nematic threads visible when a thin section of a nematic phase is viewed with a polarising microscope, are abrupt discontinuities in the director, i.e. deviations in the direction of alignment of the statistically parallel molecules within the sample.
3. Cholesteric mesophase. The name cholesteric is used because such mesophases were originally restricted in their occurrence only to derivatives of cholesterol. The cholesteric state can be visualised as a layered nematic state on which a natural twist of the director occurs through the layers. The average direction of the molecules in each layer is uni-directionally skewed either clockwise or anti-clockwise to the layer just above or below it thus tracing a natural right- or left-handed helix. The longitudinal distance over which the angle of twist has made one complete 360° revolution is defined as the pitch.

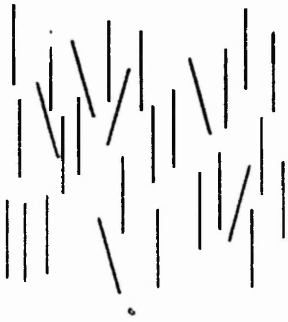
The molecular arrangements in the smectic, nematic and cholesteric mesophase are shown diagrammatically in ***Figure 1.***

Mesogenic compounds can be classified according to their structure as *amphiphilic* or *non-amphiphilic.*

1. Amphiphilic compounds. These are characterised by having in the same molecule two groups which show greatly different solubility properties. These groups are
   i) a hydrophilic portion of the molecule which tends to be water soluble, and
   ii) a lipophilic group which tends to be water insoluble and soluble in hydrocarbons.

   Depending upon the relative contribution of each of the molecular portions, amphiphilic compounds may range from essentially hydrophilic to predominantly lipophilic. Amphiphiles can be either anionic, cationic, or non-ionic.

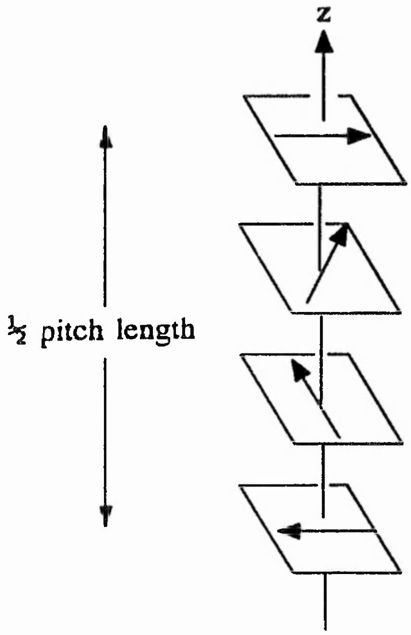
   In solutions of amphiphiles there is a tendency for like groups in the molecules to associate. A common arrangement is to form micelles which may adopt a spherulitic or lamellar-like structure. Micelles are stabilised by a balance between the electrostatic attractions (hydrophilic groups) from resultant charges on ions and dipoles and the weaker dispersive forces associated with movements of electrons. When the micelles are in sufficiently close proximity, the inter-micellar forces cause the micelles to adopt a thermodynamically stable arrangement, i.e. one with minimum potential energy, and this constitutes a mesophase.[15] The present work is not concerned with amphiphilic compounds and therefore the mesophases formed by amphiphilic compounds will not be discussed further.



NEMATIC

SMECTIC

TILTED SMECTIC



The arrow indicates the direction of the molecular long axes (ñ) in each sheet. z is the helical axis and is orthogonal to the plane of each sheet.

HELICAL ARRANGEMENT OF CHOLESTERIC

Figure 1. The molecular arrangements in the nematic, smectic and cholesteric mesophase.

2. Non-amphiphilic compounds. These compounds contain molecules which do not possess regions of differing solubility. Essentially, they are hydrophobic in character containing one or more polar groups, for example, -OR, $-NO_2$, -CN, which tend to dissolve more readily in organic solvents than in water. The nature of non-amphiphilic compounds will be discussed in more detail later.

Liquid crystalline compounds may also be classified according to the manner in which they are formed. Compounds which form mesophases due to the action of heat are termed *thermotropic*, whilst compounds which form mesophases due to the action of solvent are termed *lyotropic*. However, this classification is rather ambiguous since the transition temperatures of thermotropic liquid crystals are markedly affected by the addition of solvents. Similarly lyotropic mesophases are influenced by heat, and compounds giving lyotropic mesophases may also form thermotropic mesophases on heating. Hence, both thermotropic and lyotropic behaviour is characteristic of all mesophases and the use of the terms amphiphilic and non-amphiphilic is regarded as a more fundamental classification.

At this stage, before attempting to discuss the structure of liquid crystals, it is appropriate briefly to comment on plastic crystals. The first plastic crystal was observed by Lehmann when he viewed AgI under a polarising microscope but it was not until 1935 that plastic crystals were classified as such by Timmermanns.[16] Essentially plastic crystals are composed of 'globular' or spherical molecules for which the barriers to rotation are small relative to the lattice energy. As the temperature of such a material is raised, a point is reached at which the molecules become energetic enough to overcome these rotational energy barriers, but not sufficiently energetic to break up the lattice.[17] The result is a phase in which the molecules are translationally well ordered but are rotationally disordered, i.e. a disordered or plastic crystal. Further increase in temperature leads to complete disorder of the lattice giving rise to the isotropic liquid. When viewed through a polarising microscope, the mesophase appears to be optically isotropic and hence microscopic investigation is rather difficult.

1.3 STRUCTURE

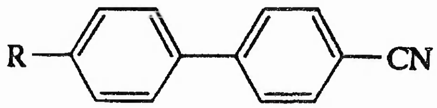
Compounds which form thermotropic liquid crystals may be low molar mass or high molar mass (polymeric). Generally, they are geometrically anisotropic and possess an elongated, rigid, lath-like molecular structure. Such compounds are also defined as *calamitic*. However, during the last fifteen years the possibility that other types of molecular structure may give rise to liquid crystals has been investigated. New liquid crystalline compounds which deviate from the conventional lath-like (calamitic) structure have been discovered.[18] Perhaps the most important of these are the *discotic* compounds.[19] Other types include the following:

1. Polycatenar compounds[20] which are liquid crystalline compounds possessing more than two flexible chains, e.g. bi-forked compounds,[21] phasmidic compounds.[22]

2. Twin mesogens, also called *Siamese twin mesogens*,[23,24] which consist of two mesogenic units which may be linked in various ways. The twins may be considered as precursors of polymer liquid crystals.

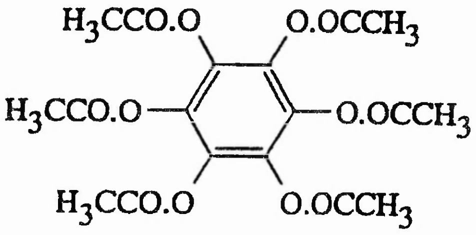
Examples (**1**-**5**) of the above types are shown in ***Figure 2***.

Initial X-ray diffraction studies of the structures of mesosphases formed by lath-like compounds were carried out by Hückel[25] and de Broglie and Friedel.[26] Hückel concluded that the X-ray diffraction patterns of the nematic phase are similar to those of the liquid and de Broglie and Friedel showed that the molecules in the smectic phase lie in equidistant parallel strata. Herrmann[27] obtained information on the angle made by the intersection of the molecular long axes with the smectic layer planes.

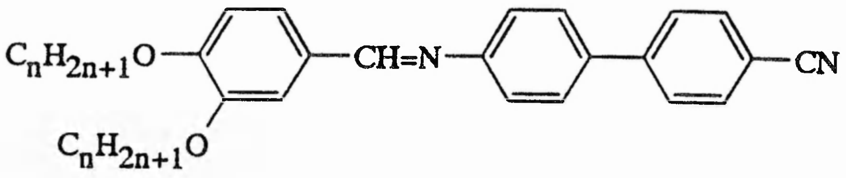


R = C_nH_{2n+1} (K series)
= $C_nH_{2n+1}O$ (M series)

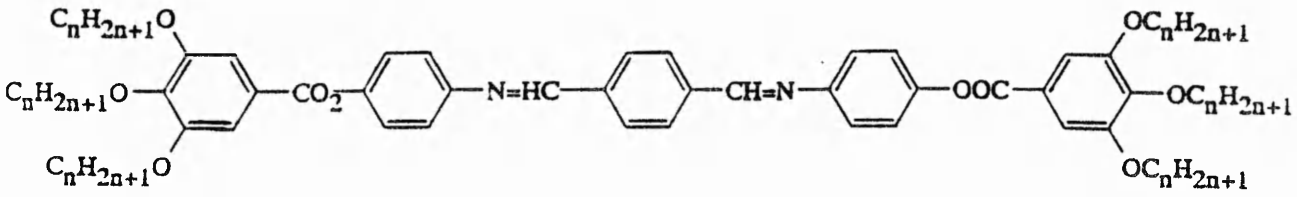
(1) Calamitic



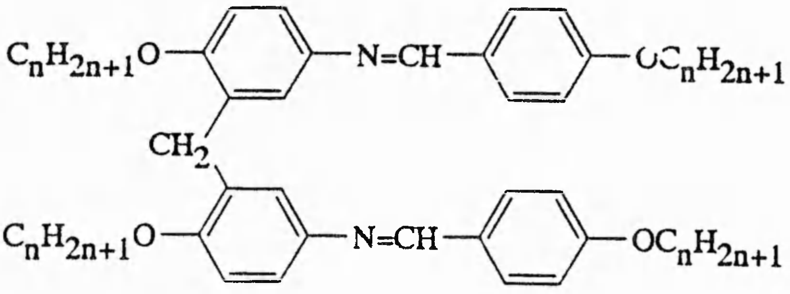
(2) Discotic



(3) Bi-forked



(4) Phasmidic



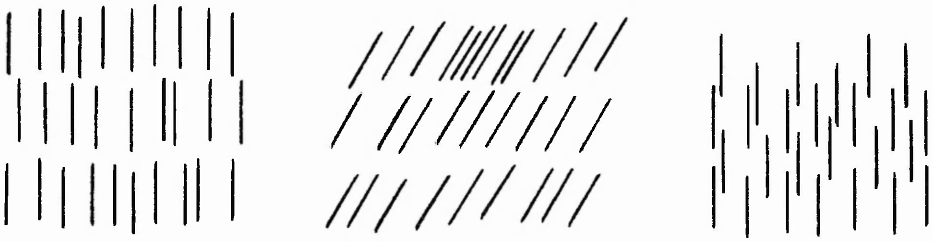
(5) Siamese twins

Figure 2. Examples of liquid crystalline compounds

Later X-ray investigations, especially by Bernal and Crowfoot,[28] who studied the crystalline state of mesogenic compounds, established that in the crystalline state two types of crystal lattice are possible. *Figure 3* exemplifies the two extreme lattice types.

1. A layer 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 layer planes.

2. A non-layer 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 i.e. an imbricated structure in which no molecular strata exist.



a. Orthogonal

b. Tilted

LAYER LATTICES

NON-LAYER LATTICE

Figure 3. Two possible arrangements of the crystal lattice

There are two essential criteria for a liquid crystal to form:

1. The cohesive forces operating between the sides of the elongated molecules must be both anisotropic and of suitable magnitude.

   Anisotropy of molecular geometry gives rise to anisotropy of intermolecular forces, and hence the forces maintaining order in the crystal lattice breakdown in stages on heating. If the cohesive forces are very strong, the melting point may be very high and so prevent the existence of an ordered liquid crystal after melting. However, if the intermolecular forces are weak, the residual cohesions after melting occurs may be too weak to maintain order.

2. The elongated molecules must be rigid.

   In the absence of rigidity, flexing occurs along the length of the molecule and this may prevent liquid crystal formation.

In general, compounds which have a layer crystal lattice possess weak terminal forces between the molecules holding the layers together compared with the lateral attractive forces which act between the sides of the molecules within the layers.

$$\text{CRYSTAL} \xrightarrow{T_1} \text{SMECTIC} \overset{T_2}{\rightleftarrows} \text{NEMATIC} \overset{T_3}{\rightleftarrows} \begin{array}{l}\text{ISOTROPIC}\\ \text{LIQUID}\end{array}$$

Thus, on heating to T_1, the terminal forces weaken so that the layers may become free to rotate and slide over one another giving rise to a *smectic* liquid crystal. On heating to a higher temperature T_2, the lateral intermolecular forces may weaken sufficiently for the molecules to slide out of the layers giving rise to the *nematic* phase. At a higher temperature T_3 , the residual terminal and lateral cohesive forces weaken and the nematic phase converts into the amorphous *isotropic* liquid.

Alternatively, a layer lattice may give the following sequence(s)

crystal $\rightleftharpoons$ smectic $\rightleftharpoons$ isotropic liquid

crystal $\rightleftharpoons$ nematic $\rightleftharpoons$ isotropic liquid

A non-layer lattice normally gives only the nematic phase. However, it has been found[29] that when the molecular structure incorporates a cyano-group, a non-layered crystal lattice, upon heating, may give rise to a smectic phase comprised of interdigitated bilayers, usually with an anti-parallel arrangement of molecules. Schematic representations of possible bilayer arrangements for the alkylcyanobiphenyls (K series) are shown in ***Figure 4***.

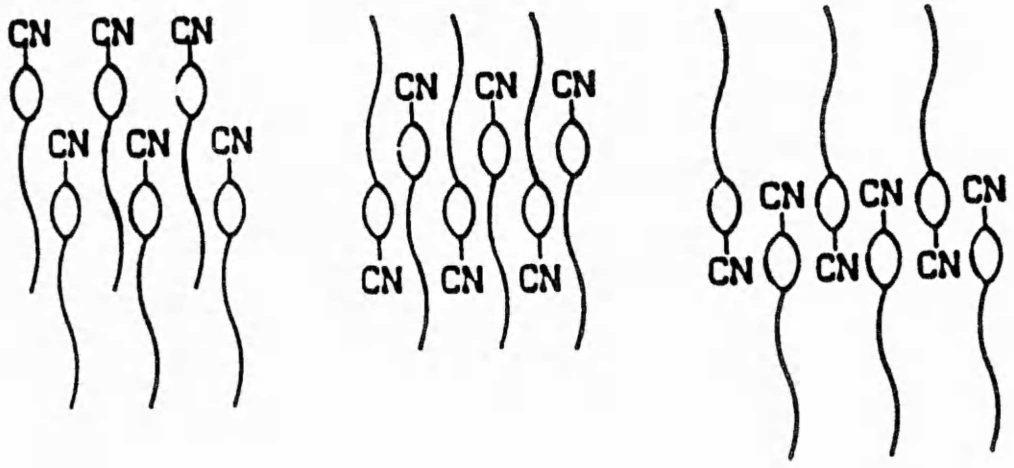


Figure 4. Possible structures for an inter-digitated bilayer for the smectic A phase - the 'tails' represent flexible alkyl chains

1.4 TEXTURES AND POLYMORPHISM OF LIQUID CRYSTALS

Observation of liquid crystals in linearly polarised light utilising a polarising microscope is the simplest and most often used method for their study. The characteristic patterns and features seen when a thin layer of liquid crystal is observed by means of a microscope in polarised light, caused by defects, are known as optical textures. Different textures due to different defects are shown by different liquid crystal phase types. An advantage of examining liquid crystal phases by optical microscopy is that suitable molecular alignments of the specimen may be achieved, e.g. by surface preparation.[30] The most common molecular alignments are the homeotropic and homogeneous (planar) arrangements as shown in ***Figure 5.***

1. Homeotropic alignment. The molecules are arranged with their optic axes parallel to the viewing direction, i.e. for lath-like molecules, orientation is such that their long axes are normal to the supporting surface.

   The homeotropic alignment can be achieved in a variety of ways. The simplest way is to use very clean glass supports, and to heat the material to the isotropic liquid and allow it to run between the coverslip and slide by capillary action. More reliable methods usually involve the use of surfactants. Surfactants commonly used are polar compounds with long alkyl chains. Two alternative types of surfactant may be used:

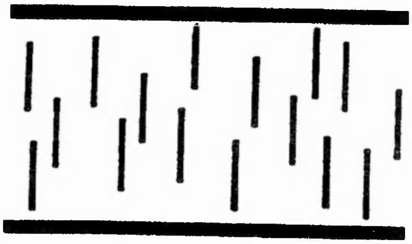
   i) surfactants that bond to the glass surface, e.g. trichlorooctadecylsilane;
   ii) surfactants that do not react with the glass surface, e.g. lecithin.

   The homeotropic alignment finds several uses, e.g. in the identification of mesophases; as a precursor for paramorphotic textures (see later); in the construction of display devices; and for the determination of the optical rotation in chiral liquid crystals.

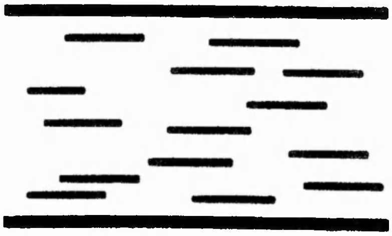
2. Homogeneous or planar alignment. The molecules lie parallel to the glass slide and perpendicular to the viewing direction in the microscope. Thus when a sample is placed between crossed polarisers it will extinguish light when the optic axes of the molecules are parallel to either of the axes of the polarisers.

The homogeneous alignment can be readily obtained by rubbing the glass surface in a uniform direction or by using surfactants and polymer solutions such as nylon 66 in *m*-cresol, polyvinyl alcohol or poly-1,4-butyleneterephthalate.

Homogeneous preparations are useful for the determination of pitch length in chiral smectics, the determination of polarisation direction in ferroelectrics, and for the construction of display devices.



1. Homeotropic



2. Homogeneous

Figure 5. Homeotropic and homogeneous molecular alignments

1.4.1 NEMATIC STATE

Nematic liquid crystals differ structurally from the isotropic liquid only in the parallel orientation of the long axes of their molecules. Nematic mesophases are the least ordered of the various mesophases. Upon cooling the isotropic melt, the nematic phase begins to separate at the clearing point in the form of spherical droplets known as nematic droplets.

The homogeneous texture is commonly recognised as the nematic marbled texture. The texture consists essentially of a large number of nearly homogeneous regions with different orientations of the optical axes. These regions when viewed between crossed polarisers impart a rock-like appearance to the texture. The interference colours within any given area are nearly always constant.

In non-homogeneous orientations (usually thicker layers) the schlieren texture is readily observed. The optical characteristics of this texture are dark brushes which have irregular curved shapes and correspond to extinction positions of the nematic liquid. Such patterns emerge as a direct result of disclinations or singularities, which are regions of discontinuity of order at molecular level. Schlieren brushes emanate from both point singularities and the ends of line singularities and contain either two or four brushes. If the disclination lines lie more or less parallel to the supporting surface they appear as threads, their ends being attached to the glass surfaces.

The homeotropic texture appears optically extinct. It is characterised by displacing the coverslip and observing *flashes* as the originally dark field of view brightens for an instant. Homeotropic textures are observed in very thin films that are influenced by capillary forces.

1.4.2 SMECTIC STATE

Smectic mesosphases may adopt the homeotropic or homogeneous alignment depending upon:

1. The nature of the sample;
2. the way in which the mesophase is formed, e.g. by heating the solid, by cooling the isotropic liquid, or by cooling the nematic phase and;
3. the nature and cleanliness of the supporting surface (as discussed earlier).

Unlike the nematic phase, smectic phases have stratified structures, with the long axes of the lath-like molecules parallel to each other in the layers. The long axes of the molecules may be approximately normal or inclined to the layer planes.

Smectic polymorphism arises as a direct result of variations in the arrangement of molecules within a given layer and on the extent of long range positional order between layers, i.e. layer correlation. Sackmann and Demus[32] originally classified seven smectic polymorphs S_A , S_B , S_C ,...S_G on the basis of miscibility relationships of liquid crystal modifications in binary systems. Their work was supported by optical microscopy and X-ray analyses. Newer smectic polymorphs have been identified namely S_I , S_J , S_K and S_H, plus the chiral analogues of S_C , S_I and more recently S_A.[32] The structures and textures of the various polymorphic modifications will be reviewed later.

When attempting to classify smectic mesophases by thermal optical microscopy, the textures usually observed are paramorphotic, i.e. the textures are usually derived from, and therefore have features of, the preceding phase. Alternatively, if the material is first heated to the isotropic liquid and then cooled into the smectic mesophase, the mesophase that forms first will exhibit its natural texture. Both homeotropic and homogeneous aligned samples may exhibit paramorphotic textures. Usually it is advantageous to observe both alignments together on the same slide when identifying mesophase types.

In order to identify smectic polymorphs it is necessary to know the thermodynamic sequence of occurrence of mesophases. The following sequence lists the mesophases in the order that they occur on heating and cooling.

Isotropic liquid, N, S_A, S_D, S_C, $S_B{}^h$, S_I, $S_B{}^c$, S_F, S_J, S_G, S_E, S_K, S_H

Thermodynamic sequencing for lath-like molecules

In using this sequence for identification purposes it should always be remembered that the sequence takes no account of the occurrence of new phases and that re-entrant phases can confuse the situation.

The homeotropic alignment of molecules within a layered structure gives an optically extinct field of view when observed between crossed polarisers. If the sample is viewed in the absence of a coverslip, a series of steps or terraces are observed (*Figure 6*). This occurs primarily for the S_A phase and is rarely seen for the S_C phase. These were first observed by Grandjean[33] who coined the term *Grandjean* *steps*. The steps are seen as lines where homeotropy is incomplete. They are not of equal height, however, as the height of each step corresponds to a multiple of the layer spacing.

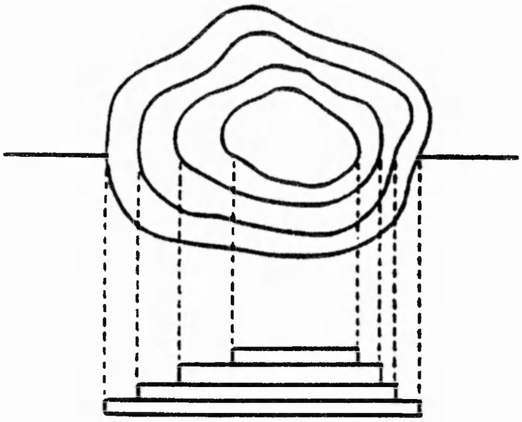


Figure 6. Schematic representation of the arrangement of Grandjean steps

In the homogeneous texture, the field of view appears birefringent when viewed between crossed polarisers. This suggests that the molecules within the layers are no longer perpendicular to the layer planes, or, more likely, that the layers are no longer parallel to the glass surface. The homogeneous texture is complicated by many types of defects which give rise to a variety of optical textures. Recently, Kléman[34] has reviewed the physics of defects. Such a treatment is not appropriate in the present context, although the more common types of defect and the optical texture they produce will now be briefly discussed.

Defects giving rise to focal-conic fan textures consist of two line singularities that have a con-focal arrangement. In essence, the defect consists of a line singularity (hyperbola) running through a closed elliptical disclination (*Figure 7*). The latter forces the layered structure to be curved and is termed a Dupin cyclide.[35]

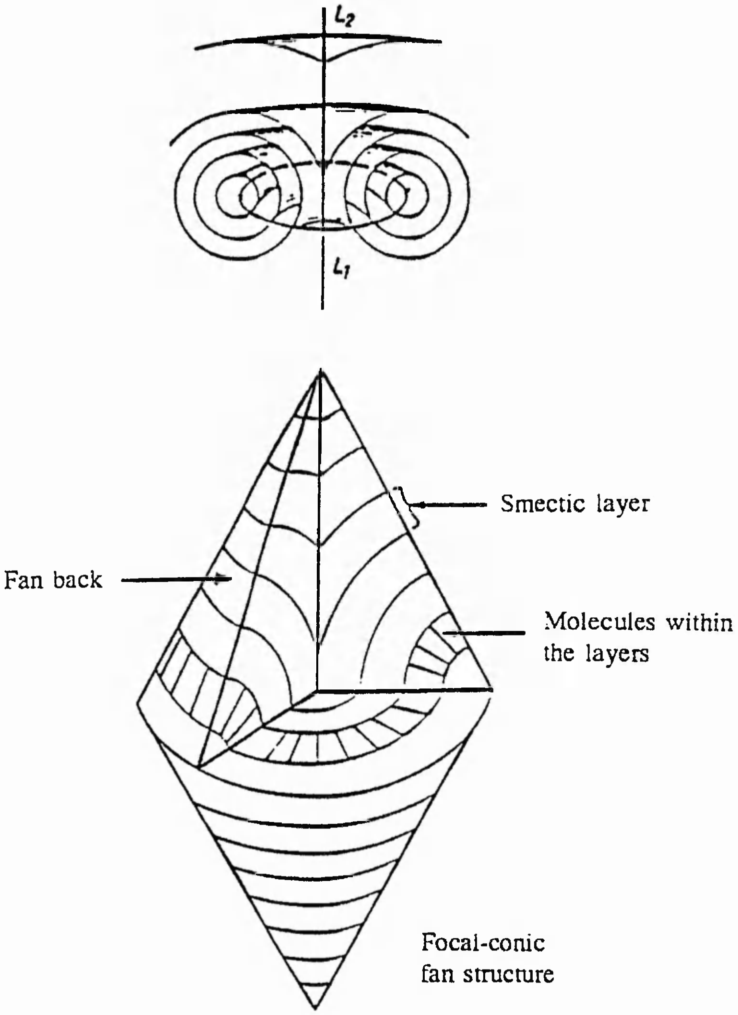


Figure 7. Arrangement of a line singularity (L_1) passing through a closed elliptical singularity (L_2)

When this structure is viewed with an optical microscope between crossed polarisers, the ellipse and hyperbola appear as dark lines or a black cross.

Defects giving rise to platelet or mosaic textures arise from discontinuities in the layer planes as shown in *Figure 8.* Such platelet or mosaic textures consist of highly coloured, optically homogeneous regions (grains) with non-regular boundaries (grain boundaries). When the phase has greater fluidity the grain boundaries become 'softer' and blurred. The smectic B (S_B) phase shows such a characteristic mosaic texture.

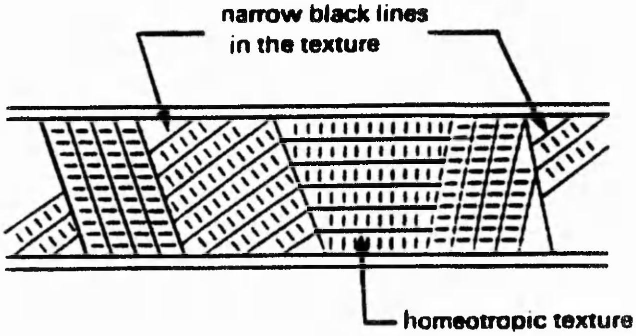


Figure 8. Possible arrangements of the layers for the mosaic texture of the smectic B phase

Smectic A phase (S_A)

Within the layers of the S_A phase, the molecules are aligned parallel to the layer normal and are uncorrelated with respect to the centre of mass position, except over very short distances. The molecules are free to rotate about their long axes and thus the layers are individually fluid. A classical representation of the S_A phase is shown in *Figure 9.*

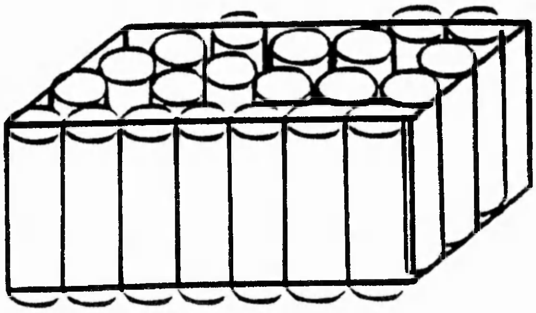

Simple 3-D model

Figure 9. Schematic representation of the smectic A phase

The layer spacing (*d*) in S_A phase is normally close to but somewhat shorter than the molecular length (*l*). However, in compounds containing strongly polar groups, for example, alkyl- or alkoxy-cyanobiphenyls, the lamellar spacing is larger than the calculated molecular length.^{36,37} The ratio lamellar spacing:molecular length is of the order 1.4 : 1 and this has been interpretated in terms of a semi-bilayer or interdigitated arrangement of molecules. This structure is commonly referred to as the S_Ad structure which is shown in ***Figure 10.***

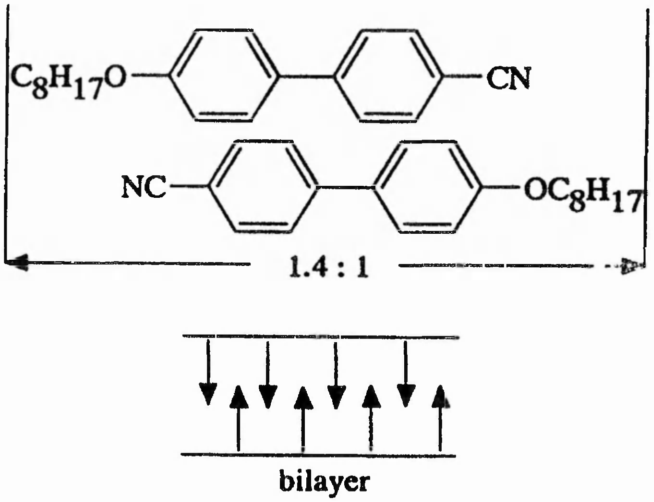


Figure 10. Schematic representation of the S_Ad structure

Smectic B phase (S_B)

The molecules are arranged in layers with the molecular long axes orthogonal to the layer planes. Within a given layer, the molecules are positioned in a hexagonally close-packed array as shown in ***Figure 11.***

Unlike the S_A phase, the hexagonal net restricts free rotation and rotation is only permitted in a co-operative manner^{38} about the molecular long axes. The layers can possess short range order in which case the phase is termed hexatic B (S_B^h).

When there is extensive long range correlation between the layers the phase is then termed crystal B (S_B^c).

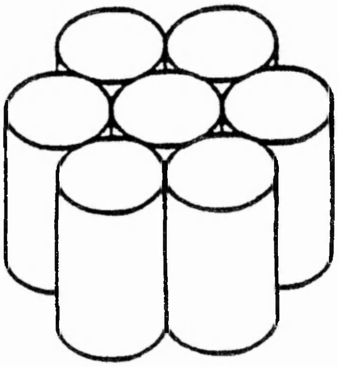


Figure 11. Hexagonal close packed arrangement of the molecules within the smectic B phase

Both types of S_B phase exhibit two natural textures (homeotropic and mosaic textures) and one paramorphotic texture (focal-conic fan texture). In the latter, the backs of the fans appear very smooth and clear compared with the frequently grained appearance of the S_A fans. At the S_A-S_B transition, lines (known as transition bars) across the backs of the fans are usually observed[39] when the phase change is to crystal S_B, whereas these are not normally seen when the phase is hexatic S_B.

Smectic C phase (S_C)

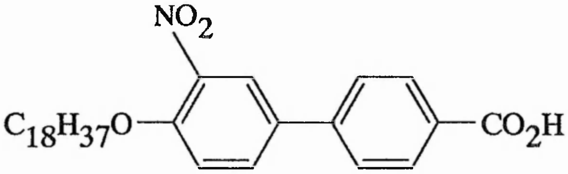
The structure of the S_C phase is similar to that of the S_A phase except that the molecules are tilted with respect to the layer plane.[41] Hence, the layer spacing of the S_C phase is less than that of the corresponding S_A phase.

Natural textures exhibited by the S_C phase are the focal-conic fan texture and the schlieren texture. The latter is characterised by the appearance of point singularities associated with only four brushes. Paramorphotic textures are the broken focal-conic fan texture (derived from S_A focal-conic fans) and the schlieren texture (derived from a homeotropic S_A phase).

Smectic D phase (S_D)

The mesophase classified as S_D possesses a cubic structure and is optically isotropic. Early X-ray studies[40] suggested the possibility of a cubic lattice consisting of spherical micelles. Later work comparing the S_D phase with similar phases found in lyotropic systems indicates that the S_D phase may not be of micellar type but is composed of disc-like aggregates[41,42] of molecules which stack to form short cylinders with pointed ends. These then become arranged in a hexagonal array.

Interestingly, depending upon the cooling rate, the S_A phase may directly convert into the S_D phase or into the metastable S_4 phase which forms on super-cooling. Lydon[43] has proposed a discotic-like structure for the S_4 phase. Compound (6) shows such anomalous behaviour.



(6)

When observed between crossed polarisers, the S_D phase appears as black optically isotropic regions. These areas often have distinctive shapes, e.g. rectangles, squares and rhombs.

Smectic E phase (S_E)

The S_E modification is a layered structure with a degree of order more closely approaching that of a crystalline solid than that shown by S_A, S_B, and S_C modifications.

X-Ray diffraction studies show the molecules to be orthogonal to the layer planes.[44] Doucet et al.[45] showed that the S_E phase is biaxial even though it is not connected with a tilted arrangement of the molecules. The reason for this is that the molecules adopt a chevron or orthorhombic arrangement as shown in ***Figure 12***. Restricted rotation about the molecular axes is possible but only if the molecules oscillate through <180° in a concerted 'flapping' manner.[46]

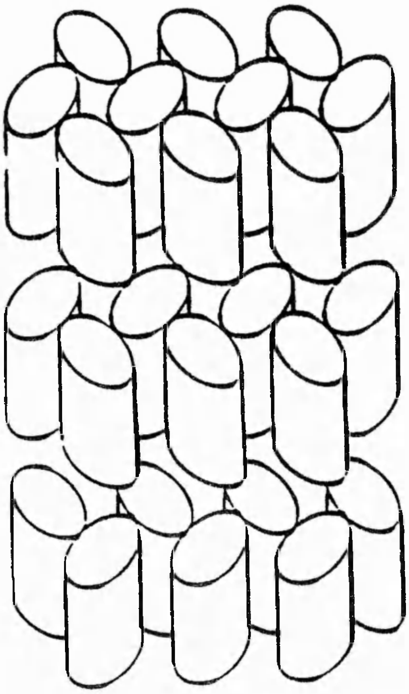


Figure 12. Chevron or herringbone packing arrangement of the molecules in the smectic E phase - ellipses show the molecular cross-sections and indicate co-operative 'flapping' motion required for rotation about the long axes

The natural texture of the S_E phase appears as an undulating mosaic texture. However this is very rarely observed. More commonly observed, are the paramorphotic textures which can be of the following types:

1. Focal-conic fan texture - from S_A or S_B fans and is characterised by concentric permanent arcs running across the backs of fans;
2. Mosaic texture - from the mosaic texture of S_B;
3. Platelet texture - from a homeotropic S_A or S_B texture.

Smectic F phase (S_F)

The S_F phase has a layered structure which closely resembles the S_C phase, i.e. molecules are tilted with respect to the layer planes. However, the phase is positive uniaxial, whilst the S_C phase is positive biaxial.

The molecules within a given layer are arranged into pseudo-hexagonal nets with a tilt angle of approximately 20°.[47] ***Figure 13*** represents a simplified structure of the S_F phase. Between the layers there is poor correlation. However within the layer there is long range bond orientational order but only short range positional order. Between the layers there is very little positional correlation but there is extensive orientational correlation.

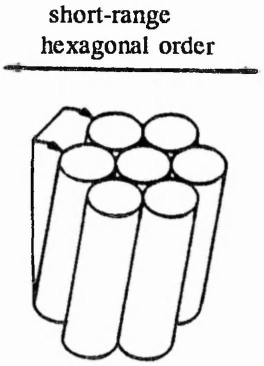
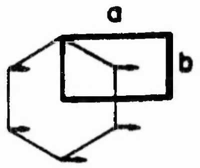


Figure 13. Structure of the smectic F phase

With regard to the tilt direction, in the S_F phase the tilt is towards the side of the pseudo-hexagonal net[48] (***Figure 14***) in contrast with the S_I phase where the tilt direction is towards the apex of the pseudo-hexagonal net.



tilt to side of
hexagonal net (S_F)

Figure 14. Local structure of the smectic F phase - the arrows denote the tilt direction of the molecules

The S_F phase is rarely observed separating directly from the isotropic liquid, but when it does so it can adopt two natural textures, namely, the schlieren-mosaic texture and the cylindrical, spherulitc or fan-type texture.

The S_F phase forms a variety of paramorphotic textures depending upon the preceding mesophase type. When the S_F phase appears on cooling the S_C phase, the schlieren areas are converted into a schlieren-mosaic texture and the S_C focal-conic fan texture changes to S_F fans which have a well-defined broken appearance with black patches. When formed on cooling a homeotropic S_A phase, the S_F phase appears as a true mosaic.

Smectic G phase (S_G)

X-Ray studies[49] showed that the structure of the S_G phase is similar to that of the S_F phase. The molecules are arranged in pseudo-hexagonal nets which are tilted with respect to the layer normal. However, unlike the S_F phase, there is extensive long range layer correlation suggesting a highly ordered structure. This is shown diagrammatically in ***Figure 15.***

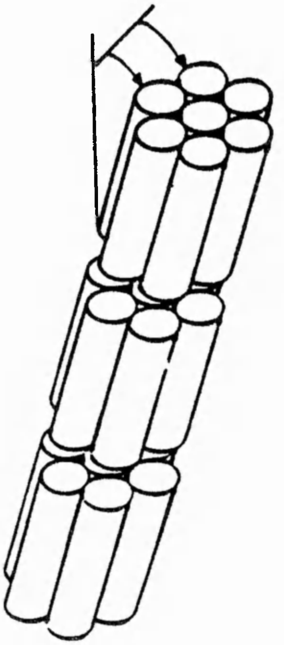


Figure 15. Structure of the smectic G phase

The natural texture of the S_G phase is the mosaic or platelet-type texture but very few materials give an I - S_G transition. Paramorphotic textures tend mainly to be of the focal-conic fan type derived from S_A , S_B , S_C or S_F (from which the S_G fans take on a chequered, patchwork appearance) or the mosaic texture usually derived from homeotropic S_A or S_B.

Smectic H phase (S_H)

The S_H phase has a similar structure to the S_E phase. The molecules are arranged in pseudo-hexagonal nets but are slightly tilted with respect to the layer normal. As with the S_E phase, the loss of rotational freedom[50] forces the molecules in the pseudo-hexagonal nets to adopt a herringbone arrangement. The tilt direction is towards the side of the (pseudo) hexagonal net and the layers are highly correlated as shown in ***Figure 16.*** The S_H phase has monoclinic symmetry.

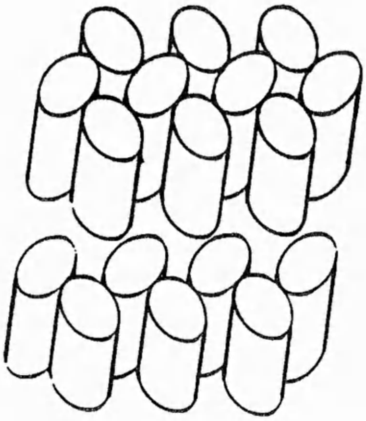


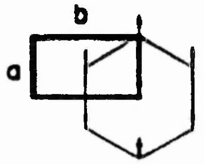
Figure 16. Diagrammatic representation of the layer structure of the smectic H phase

The S_H natural texture has not yet been observed. However, the S_H phase exhibits a variety of paramorphotic textures, principally the focal-conic fan texture and the mosaic texture.

Smectic I phase (S_I)

The S_I phase is similar to the S_F phase. However detailed X-ray diffraction studies by Gane et al.[48] have established that in the S_I phase the molecules within a given pseudo-hexagonal net are tilted towards an apex, i.e. a < b, as shown in ***Figure 17.***

The natural texture of the S_I phase is of a mosaic type, and is very rarely observed. More commonly observed are the paramorphotic focal-conic fan and schlieren textures. It is possible to distinguish between S_I and S_F phases by optical microscopy. In particular the S_I phase gives a schlieren texture that is difficult to bring into optical focus.



tilt to apex of
hexagonal net (S_I)

Figure 17. Local structure of the smectic I phase - the arrows denote the tilt direction of the molecules

Smectic J and Smectic K phases (S_J and S_K)

The structures of the S_J and S_K phases[51] (formerly referred to as S_G' and S_H') are analogous to those of the S_G and S_H phases, respectively, except that the tilt direction of the molecular long axes in the layers of the three-dimensional crystal structures are to the apex rather than the side of the pseudo-hexagonal net. Therefore for S_J $a < b$ and for S_K $a > b$.

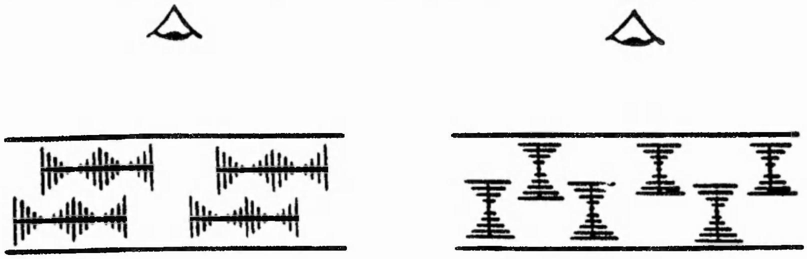
1.4.3 CHOLESTERIC STATE

Friedel[5] suggested that the cholesteric state was a special kind of nematic structure. A nematic phase can be formed either by compounds composed of achiral molecules or of chiral molecules provided that a racemic mixture of left-handed and right-handed species is present. When the sample is optically active, i.e. consists entirely or contains an excess of one enantiomer, the chiral nematic or cholesteric mesophase results.

Comparing the nematic and the cholesteric phase, the following observations are important:

1. Both phases are completely miscible. Addition of a small amount of a chiral component changes a nematic phase into a long pitch cholesteric phase.
2. Racemic mixtures give a nematic phase. At a certain composition, the pitch becomes infinite. At this compensation point, there are no anomalies in any other physical properties that would indicate a phase change difference between a nematic and a cholesteric phase.[52]
3. Both possess similar X-ray patterns showing no long-range correlations.

Due to the helical structure, the cholesteric phase has unique optical properties. The mesophase can exist in three different textures.[53] These differ only in the degree and direction of ordering of the helices relative to the observer. If the helices are at right angles to the optic axes, the focal-conic (or undisturbed) texture forms. This texture is birefringent but optically inactive. If the helices are aligned with their axes approximately parallel to the light path, the Grandjean (planar or disturbed) texture forms. This texture readily forms when the focal-conics are disturbed by mechanical shear. These orientations are shown schematically in *Figure 18.*



FOCAL-CONIC
a.

GRANDJEAN
b.

Figure 18. Orientations of helical (long lines) and molecular axes (short lines) relative to the observer for (a) focal-conic texture and (b) Grandjean texture

A third texture is the ***homeotropic state.*** This texture is transparent, has very slight birefringence, and no optical activity.

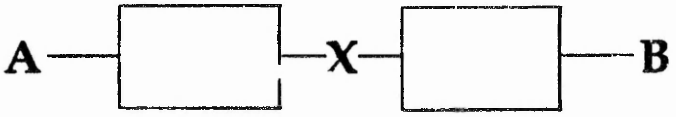
The Blue phases

The blue phases are difficult to detect as they occupy a temperature span of less than 1°C between the cholesteric phase and the isotropic liquid. These new phases are termed BPI, and BPII which have cubic structures, and BPIII the structure of which has not been fully elucidated. The present work is not concerned with the blue phases and therefore the structure of these phases will not be discussed further. The blue phases have recently been reviewed by Crooker[54] and Seidman.[55]

1.5 MOLECULAR STRUCTURE AND THE THERMAL STABILITY OF MESOPHASES

Structural studies of liquid crystals are important for an understanding of the phase changes in molecular terms. As discussed earlier, two structural features are necessary for the formation of thermotropic mesophases. These are anisotropy of the intermolecular forces and anisotropy of molecular shape.

Non-amphiphilic liquid crystals of the calamitic type possess a characteristic molecular shape (described as being rod-like or lath-like) which gives rise to anisotropic intermolecular forces. A schematic representation is shown below,



where **A** and **B** are terminal groups which extend the molecule along its long molecular axis, rectangles represent rigid polarisable groups, usually aromatic rings, and **X** indicates a central linking group which provides rigidity and linearity.

Depending on the nature of these groups, the thermal stability, i.e. temperature of transition: nematic to isotropic (N-I), smectic to isotropic (S-I) or smectic to nematic (S-N), of any mesophase may be increased, decreased or completely lost.

The relationship between molecular structure and liquid crystal behaviour is of great academic and commercial interest and has been the subject of several review articles,[56,57] e.g. that by Toyne,[58] which provides an excellent insight into this topic.

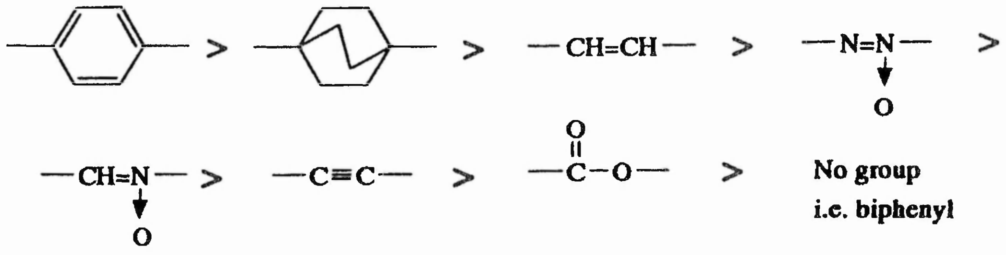
Although a detailed treatment is beyond the scope of this thesis, a brief summary of some of the effects on liquid crystal behaviour of altering molecular structure is appropriate and is given below.

The melting point of a compound marks the temperature at which the three-dimensional ordered, geometrical arrangement of molecules suddenly collapses and gives rise to the disordered liquid. However, mesomorphic compounds may pass through one or more ordered intermediate states before increasing thermal agitations give rise to the isotropic liquid. Such changes are usually associated with relatively low energy demands and any deviation of the molecular structure away from the highly polarisable, rigid, lath-like arrangement will affect these transitions.

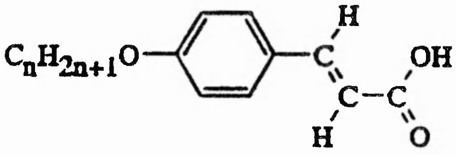
When more than one mesophase occurs upon heating, not only is the presence of polar interactions important but their direction is important. Smectic states are usually stabilised by multiple dipoles acting across the molecular axis (lateral attractions), whilst terminal attractions appear to be more important in determining the nematic stability. It is important to note that there is no similar, simple correlation between the melting point of a compound and its molecular structure.[59]

1.5.1 INFLUENCE OF THE CENTRAL LINKING GROUPS

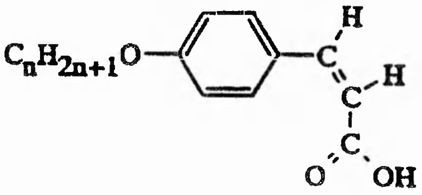
Generally, the central linking group extends the rigidity and linearity of the molecule. Gray[60] recognised a *central group efficiency order* (showing the effect of various groups on T_{N-I}) from which it can be seen that a single bond between two benzene rings is the least effective in promoting nematic thermal stability.



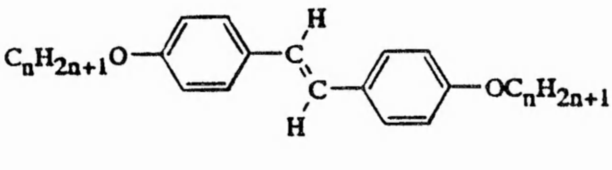
The effect of divergence from the necessary elongated molecular geometry on mesophase thermal stability is evidenced by comparison of the *trans*-4-n-alkoxycinnamic acids (**7**) and *trans*-stilbenes (**8**) with their corresponding *cis*-isomers (**7a** and **8a**, respectively).[61] The *trans*-isomers have the required molecular shape and form liquid crystals, but the *cis*-isomers are non-linear and show no mesomorphic properties.



(7)



(7a)



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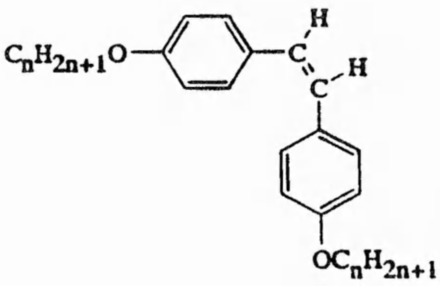


(8a)

In addition, if the conjugation of the central linking group is extended, e.g. by incorporation of -CH=N-N=CH- , the lath-like nature of the molecule will also be extended, i.e. the geometrical anisotropy will be increased, resulting in higher mesophase to isotropic transition temperatures.

More recently, saturated linking groups which are flexible and do not permit extended conjugation such as dimethylene, $-CH_2CH_2-$, have become more widely investigated in the search for room temperature mesogens.[62,63]

1.5.2 INFLUENCE OF TERMINAL GROUPS

Many terminal groups have been studied, e.g.

$CH_3(CH_2)_n$; $n\text{-}C_nH_{2n+1}O-$; -Halogen ; -CN ; $-NO_2$

and the nature of the group determines which type of mesophase will be observed.

If a terminal substituent in a mesogen extends the molecular axis, the anisotropy of molecular polarisability ($\Delta\alpha$) will increase. This normally results in an increase in the $T_{N\text{-}I}$ relative to hydrogen, provided that the substituent does not increase molecular breadth. The ability of terminal substituents to promote nematic or cholesteric mesophases has been quoted in an *average group efficiency order*,[57] as follows:

$$Ph > NHCOCH_3 > CN > OCH_3 > NO_2 > Cl > Br > N(CH_3)_2 > CH_3 > F > H$$

However, this order for the effect on mesophase stability is not always rigorously applicable because of associated complicating effects that a terminal substituent may have, such as:

1. attractive or repulsive effects on substituents of adjacent molecules;
2. increased lateral attractions;
3. an influence on the polarisability of an aromatic ring to which it is attached.

When the terminal alkyl chains are attached to ring systems (aliphatic or aromatic) either directly or via an oxygen atom as part of an alkoxy group, the liquid crystal transition temperatures show regular trends as the alkyl chain is extended in an homologous series. This may be seen by plotting the mesomorphic transition temperatures against the number of carbon atoms, n, in the alkyl chain. ***Figure 19*** shows such a plot for the 4′-n-alkoxybiphenyl-4-carboxylic acids.[64]

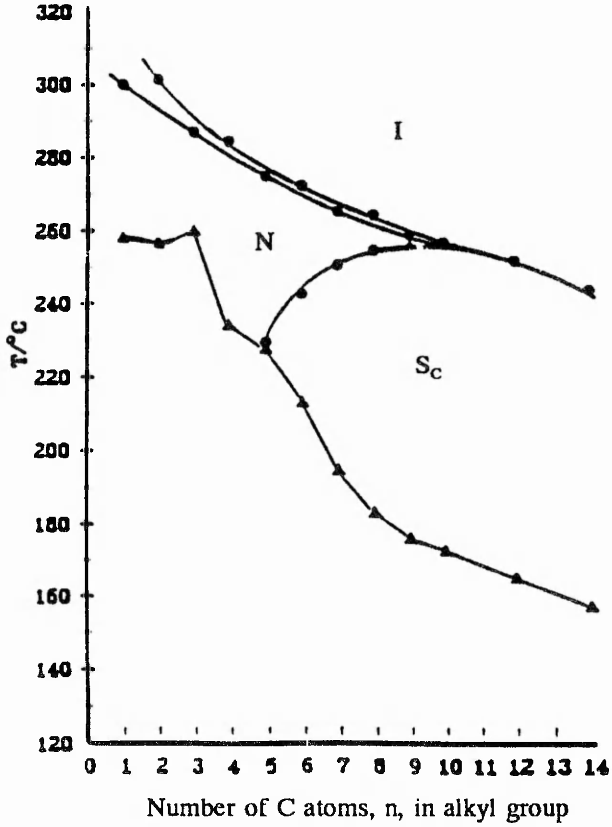
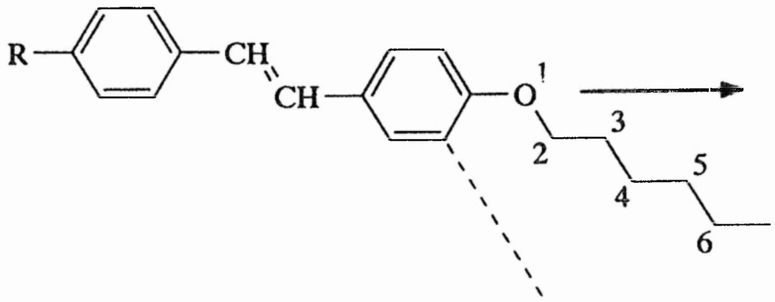


Figure 19. Plot of transition temperatures for an homologous series of 4-n-alkoxybiphenyl-4-carboxylic acids.

From this and other similar plots, several conclusions can be drawn, namely:

1. The nematic to isotropic transition temperatures usually fall with increasing chain length.
2. When both smectic and nematic properties occur, the early members normally show only a nematic phase, and the smectic phase(s) do not appear until an alkyl chain length of C-5 to C-8 is reached. Thereafter, for each successive member the smectic thermal stability increases as the alkyl chain length increases until it is the same as the nematic thermal stability. At this point nematic properties disappear and the smectic thermal stability then gradually decreases as the chain length increases.
3. Usually the transition temperatures for compounds with an odd number of carbon atoms in the chain are correlated by one smooth curve, while homologues with an even number of carbon atoms fit another smooth curve (even-n members above odd-n for alkoxy groups and odd-n above even-n for alkyl groups). The alternation in simple cases is thought to be related to the change in anisotropy of molecular polarisability as the chain length increases.

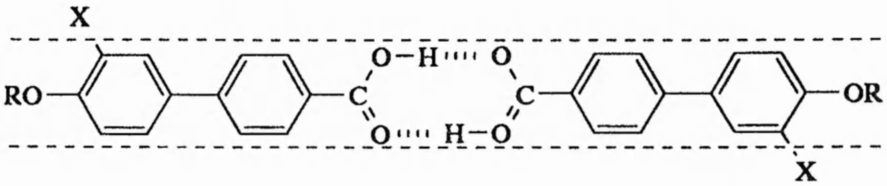


For an alkoxy group, lengthening the chain from 2 to 3, 4 to 5, etc, creates the new bond parallel to the axis of the *p*-substituted benzene ring, whereas it is formed at an angle to the axis when the chain is extended from 1 to 2, 3 to 4, etc. Thus there is a greater increase in the anisotropy of molecular polarisability in the former instance. Hence for a terminal alkoxy group there are more C-C bonds directed along the molecular axis when the number of carbon atoms is even and the transition temperature curve lies above that for odd members.[65] The reverse is true for an n-alkyl chain in a terminal position because the oxygen atom of the alkoxy group is replaced by a carbon atom.

1.5.3 INFLUENCE OF LATERAL SUBSTITUENTS

The introduction of a lateral substituent increases the separation of the long axes of molecules in mesophases. Such an increase in molecular breadth has an important effect on mesophase thermal stability which depends upon the size and position of the lateral substituent.[66]

Molecular breadth may be defined as the diameter of the smallest cylinder through which the molecule may pass, assuming no interference by alkyl chains, i.e. the cylinder of revolution of the molecule about the molecular long axis. Any increase in molecular breadth tends to reduce the geometrical anisotropy and the increase in intermolecular separation brought about by the introduction of the substituent reduces the intermolecular attractive forces and lowers the liquid crystal thermal stability. Studies by Gray and Worrall[67] on the dimeric 3′-substituted 4′-n-alkoxybiphenyl-4-carboxylic acids (**9**) showed that as X increases in size, the

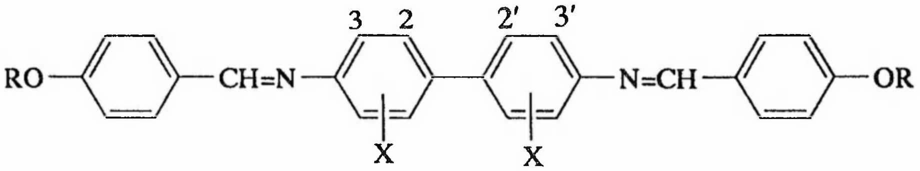


(9)

stability of both nematic and smectic mesophases is depressed, the latter to a greater extent than the former. This is a generally observed effect.

In biphenyl systems, the introduction of a substituent *ortho* to the ring junction causes twisting of the rings giving rise to an additional effect (which has been described by Gray as molecular 'thickening') superimposed on molecular broadening which further reduces mesophase thermal stability. Thus, the position of substitution within a molecule is extremely important. For example, in compound **(10)**[68] for the substituent X = Cl the stability of the nematic phase is markedly reduced in the following order:

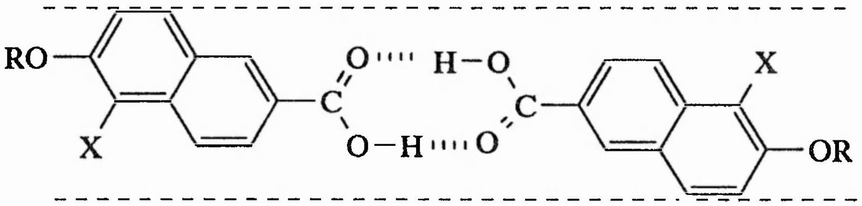
$$3 > 2 > 3,3' > 2,3' > 2,5 > 2,6 > 2,2' > 2,2',6 >> 2,2',6,6'$$



(10)

The reductions in nematic thermal stability are particularly pronounced when substitution is *ortho* to the ring junction. This is presumed to be due to severe twisting of the biphenyl system in these instances. Also, increased substitution seems to have an additive effect and mesomorphism completely disappears with 2,2′,6,6′-tetra-substitution. Smectic properties are only observed with the 3,3′-dichloro-derivatives.

In some cases, the position of substitution is such that the substituent is shielded, partly or completely, by the molecular structure. The first example of molecular shielding was observed in the 6-n-alkoxy-5-halogeno-2-naphthoic acids (11).[69]



(11)

A small substituent can be easily accommodated within the molecular perimeter. In such cases an increase in mesophase thermal stability, relative to the unsubstituted acids, occurs because the introduction of the substituent increases molecular polarisability. If the substituent is dipolar, such as chloro-, the lateral cohesive forces are substantially increased so that the thermal stability of the smectic phase is increased more than that of the nematic phase. Large 5-substituents, such as iodo- and nitro-, protrude outside the molecular perimeter and the breadth increasing effect of the substituent then results in a reduction in nematic thermal stability.

Surprisingly, Weissflog et al.[70] have recently shown that even in severe cases of lateral broadening, where lateral groups are n-alkyl chains, the compounds are still mesomorphic. In such cases it is probable that for alkyl groups with long alkyl chains a conformation is adopted along the molecular axis which preserves a high length to breadth ratio. Thus the increase in molecular breadth caused by a methyl or ethyl group is not significantly changed for substituents with longer alkyl chains.

1.6 THE PHYSICAL REQUIREMENTS OF NEMATIC MESOGENS IN ELECTRO-OPTIC DISPLAYS

Commercial liquid crystal materials usually contain approximately 4-10 individual compounds, mostly mesogens, mixed in certain proportions to satisfy various display requirements. Present-day commercial devices are mainly based on the Twisted Nematic Mode (TN Mode)[71] for which the following physical characteristics of a liquid crystal material are important.

1.6.1 ORDER PARAMETER

This is a measure of the extent of alignment about the director, $\tilde{n}$, in the mesophase, and is expressed as

$$S = \tfrac{1}{2} \{ 3\cos^2\theta - 1 \}$$

where θ is the angle between the molecular axis and the director. The order parameter for a mesophase lies between 1 (for an ideal mesophase) and 0 (for the isotropic liquid) and decreases with temperature. The value of S varies between 0.3 - 0.4 near the N-I transition temperature and may be as high as 0.9 for ordered smectogens.

1.6.2 REFRACTIVE INDEX

The refractive indices of the ordinary and extra-ordinary rays of a liquid crystal are determined by the polarisability of the molecules at visible light frequencies and therefore, to a large extent, they are dependent on the conjugation within the molecule,[72] i.e. the presence of aromatic rings and unsaturated linkages containing π-electrons.

Birefringence, Δn , is expressed as the difference between the refractive index of the extra-ordinary ray (n_e) and ordinary ray (n_o) when viewed between the prisms of an

Abbé refractometer. Birefringence is directly proportional to the order parameter, S, and is temperature dependent. All nematic and most smectic phases show a positive birefringence ($n_e > n_o$). The S_D phase, which is optically isotropic, has $\Delta n = 0$, and chiral smectic phases and cholesteric phases have a negative birefringence.

For liquid crystal materials used in display devices, values of Δn usually range between 0 and 0.4. Low values of Δn allow a wider angle of view. The birefringence of a mesophase influences the textural characteristics when observed under a polarising microscope.

1.6.3 DIELECTRIC CONSTANT

The dielectric anisotropy, $\Delta\varepsilon$, provides a measure of the strength of interaction between a liquid crystal and an applied field. It is usually expressed as

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants measured parallel and perpendicular to the major axis, respectively.

In an electric field the director orients to minimise the free energy of the system. Thus the sign of the dielectric anisotropy determines the alignment of the director of a liquid crystal material in a strong electric field, the alignment being in the direction of the larger constant. This is dependent on the molecular polarisabilities and the value and angular position of permanent dipoles. The TN display usually employs mixtures with large positive values of $\Delta\varepsilon$ hence reducing the driving voltage. Cyano-groups, which have a large dipole moment ($\mu CN=4.05$ D), give rise to a large positive $\Delta\varepsilon$ (with $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ having typical values of approximately 16 and 6, respectively) when situated in a terminal position of a mesogen.[73,74] However, large values of $\Delta\varepsilon$ usually result in loss of clarity and contrast which are dependent upon low values of $\Delta\varepsilon/\varepsilon_{\perp}$.[74,75]

As the frequency of the electric field increases, materials with a positive $\Delta\varepsilon$ experience a change in sign of this parameter and hence a reversal of orientation in the field. This property is made use of in *dual frequency switching* displays.[76]

1.6.4 VISCOSITY

A nematic liquid may be characterised by different viscosities and their theory is rather complex and not appropriate for discussion in the present context. Liquid crystal materials are usually characterised by a bulk, capillary flow, intrinsic viscosity the significance of which is not well understood in molecular terms. Nevertheless, the dynamic response of a liquid crystal display generally correlates well with such viscosity values.[77]

The viscosity of a nematic liquid crystal is lower than that of the isotropic liquid immediately formed from it, because the alignment of the lath-like molecules in the mesophase permits movement in the flow direction. As the temperature increases in the pre-transitional region there is a sharp increase in viscosity as the molecular order is lost. With change of temperature, away from the N-I transition, the viscosity is given by

$$\eta = \eta_o e^{-Ea/RT}$$

where η_o is the viscosity at absolute zero

E_a is the activation energy for relative motion

Materials with low η and E_a are normally required for use in display devices as low viscosity affords a short response time, and a low E_a corresponds to a low rate of increase in viscosity with increasing temperature. The viscosity of any system may be lowered by incorporating compounds with short terminal groups, no lateral substitution and low polarity and polarisability.[78]

1.6.5 ELASTIC CONSTANTS

The nematic state possesses three elastic constants, K_{11} , K_{22} , K_{33} (*Figure 20*). These elastic constants are associated with the restoring torques opposing splay, twist, and bend of the director, respectively.

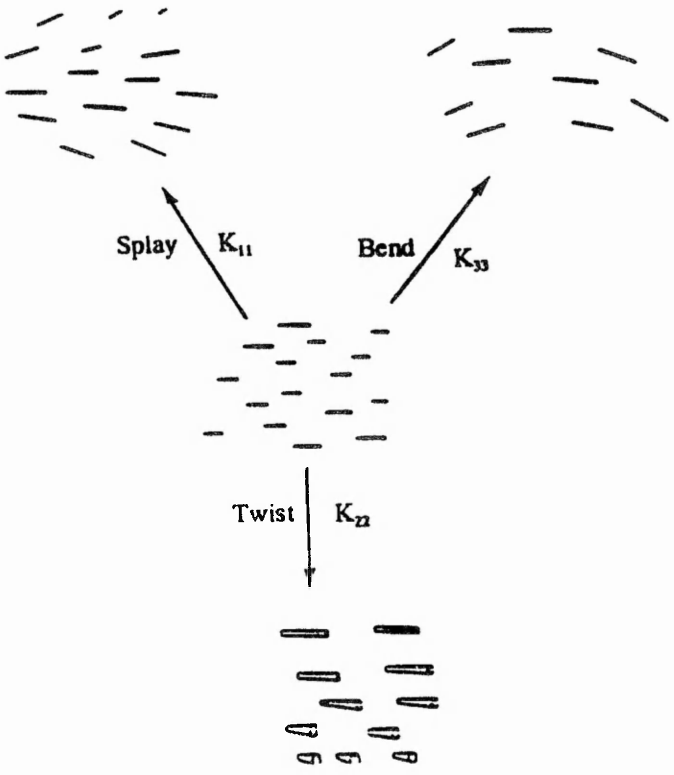


Figure 20. The three fundamental elastic distortions of nematic fluids

Molecules of a true liquid would immediately flow out of an applied mechanical shear by re-orientation, but molecules in a liquid crystal phase can sustain, to a certain degree, imposed elastic curvatures. Nevertheless, liquid crystal materials have relatively weak elastic behaviour (low K values) and they are very sensitive to perturbation by electric and magnetic fields. The relaxation response of materials in display devices is determined by elastic constants, e.g. the elastic distortion free energy, F_d , for a nematic liquid crystal is given by

$$F_d = \tfrac{1}{2} \left\{ AK_{11} + BK_{22} + CK_{33} \right\}$$

where A, B, C are energy terms.

However, it is the ratio of the elastic constants,[79] particularly K_{33}/K_{11}, which is related to the electro-optical switching characteristics of a display. To achieve high contrast the ratio, K_{33}/K_{11} should be as low as possible and this can best be attained by using materials containing aromatic and heterocyclic ring systems (which increase the width to length ratio of the centeral core of the molecule), high members of the homologous series, and excluding lateral substituents. However, a balance must be achieved as other properties may be affected adversely (such as viscosity, the occurrence of smectic phases, and a lowering of nematic thermal stability).

1.7 PROPERTIES OF FLUORINATED LIQUID CRYSTALS

During the last decade, the introduction of lateral fluoro-substituents into mesogenic compounds has been thoroughly investigated in an attempt to improve existing materials and to extend the commercial applications of other liquid crystal systems.[63,80-87] As was stated in the earlier discussion, in general, lateral substituents tend to increase the molecular breadth of a molecule thus reducing the geometrical anisotropy. Although the dipolarity of a lateral substituent also has an effect, nevertheless, it is the size of the substituent and the consequent increase in molecular breadth that disrupts the efficiency of the packing arrangement of the molecules in the mesophase resulting in substantial or, in some cases, complete loss of mesomorphic properties. Smectic phases are affected more than nematic phases by lateral substitution of a mesogen.

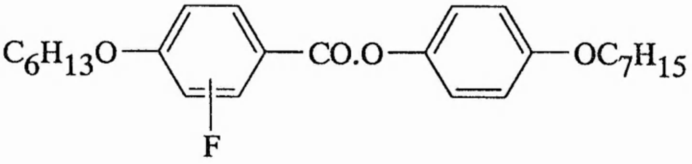
The properties of compounds with lateral fluoro-substitution have been extensively investigated because of the following characteristics of fluorine:

1. Small size. The van der Waals radius of a fluoro-substituent is approximately 12.5% greater than that of hydrogen. The slight increase in molecular breadth this causes is sufficient to maintain a favourable packing arrangement of molecules suitable for mesomorphic properties.
2. Moderate *ortho*-effect on the interplanar angle of biphenyl. A fluoro-substituent located *ortho* to the inter-ring bond in biphenyl causes the rings to twist around this bond resulting in a torsional angle of approximately 51°.[88] In comparison with biphenyl itself (with no *ortho*-substituents), where the torsional angle is approximately 32°, it appears that *ortho*-fluoro-substitution

does not disrupt the intermolecular cohesive forces sufficiently to prevent the formation of a mesomorphic compound.

3. High electronegativity. Fluorine is the most electronegative element (4.0 units as measured on the Pauling electronegativity scale) and when a lateral fluoro-substituent is introduced into the mesogen the resulting moderately polar bond is directed across the molecular axis. The presence of this dipole has been utilised as a means of reducing anti-parallel correlations in terminal cyano-compounds and, depending upon the position of the lateral fluoro-substituent within the molecular core, increasing $+\Delta\varepsilon$ values and reducing smectic properties.[82,89]

With regard to this latter effect, Osman[66] has reviewed the influence of lateral substituents on mesomorphic properties, especially the effect of fluorine, and has concluded that mesomorphic properties are greatly affected by the number of lateral fluoro-substituents and by the position (and direction of orientation) of the lateral fluoro-substituent within the molecular core. For example, in compound **(12)**,[80] the introduction of a fluoro-substituent into the 2-position (lateral-central site) strongly depresses or completely eliminates smectic phases whilst the thermal stability of the nematic phase is only slightly reduced compared with the parent compound. However, when the fluoro-substituent is introduced into the 3-position (lateral-terminal site)



(12)

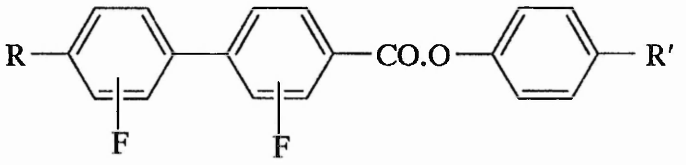
smectic phase thermal stability is not significantly reduced, and, in some cases, is enhanced at the expense of the nematic phase stability.[84]

The ability of laterally fluorinated compounds to depress or eliminate smectic phases at the expense of the nematic phase is of particular importance in the field of electro-optic display devices.[63] As mentioned earlier, the most widely used display device is based on the TN mode which requires a wide nematic range and large positive dielectric anisotropy. The latter requirement is achieved by using compounds containing a terminal cyano-substituent, for example, the 4-alkyl- and 4-alkoxy-4'-cyanobiphenyls (the K and M series). However, the dielectric anisotropy of these compounds is lower than expected because of anti-parallel correlations between the dipole moments of terminally situated polar cyano-groups. This causes an increase in the dielectric constant perpendicular to the major axis, thus reducing the overall dielectric anisotropy. McDonnell et al.[90,91] have shown that the presence of a lateral fluoro-substituent at the 2- or 2'-position in the K series reduces the extent of anti-parallel dipole ordering and hence gives rise to an increase in $+\Delta\varepsilon$ values.

A common problem that arises in many liquid crystal mixtures is the occurrence of injected smectic phases.[92] This is particularly evident when polar compounds are mixed with non-polar compounds, e.g. esters. Knowing that lateral fluorination depresses the smectic state, many researchers, notably Chan et al.,[93] have concentrated their work on preparing binary mixtures where one or both compounds contain a lateral fluoro-substituent. In some cases lateral fluorination has been found to reduce the occurrence of injected smectic phases, but this is not a general effect and lateral fluorination of one or both components of such mixtures does not necessarily give mixtures free from injected smectic phases.

More recently, use has been made of the fact that lateral fluorination can enhance S_C properties.[84,87,94] This is of particular interest for the ferroelectric display mode which primarily requires chiral smectic C (S_C^*) compounds possessing a large negative dielectric anisotropy. The main advantages of the ferroelectric mode over the TN mode are the very high speed switching of the display (micro-seconds compared with milli-seconds for the TN mode) and its bistability.

Laterally fluorinated phenyl biphenyl-4-carboxylates (**13**) have been shown to be low melting compounds exhibiting either a wide ranging S_C or S_A or both of these phases.[95]



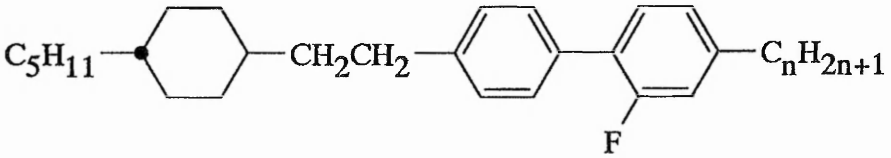
(13)

Also, as the number of lateral fluoro-substituents in the molecule is increased, the dielectric anisotropy becomes more negative. Hence, the compounds readily meet the requirements of the ferroelectric display mode.

AIMS

2. AIMS OF THE PRESENT RESEARCH

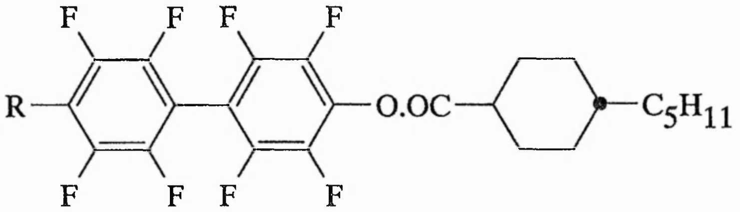
Following initial investigations by Byron, Lacey and Wilson[96] of the steric effect of a lateral fluoro-substituent by the investigation of the liquid crystal behaviour of 2-fluoro- and 2-chloro-biphenyl-4-yl 4-n-alkoxybenzoates, the interest at Trent in lateral fluorination was re-aroused following the syntheses by Balkwill et al.[63] of the *I - compounds* **(14)**



(14)

The *I-compounds* are hydrocarbon nematogens which show excellent physical properties necessary for the TN mode, for example, low viscosity, wide nematic range and moderate birefringence.

In an attempt to assess the effect of extensive fluoro-substitution Byron and co-workers[97] carried out initial work on symmetrically polyfluoro-substituted biphenyl esters **(15)**, **(16)** of the following type.

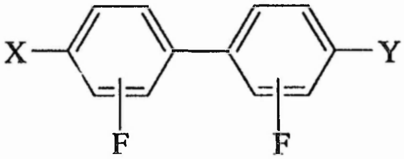


$R = C_5H_{11}O$ **(15)**

$= C_4H_9$ **(16)**

Contrary to expectation, an increase in lateral fluorination coupled with quite severe twisting of the biphenyl ring system (approximately 60°)[88] did not prevent the formation of mesomorphic compounds. These compounds possess moderate birefringence and low refractive index (similar to that of glass) making them potentially suitable for use in integrated optics. However, unfortunately, because of the extent of lateral substitution, these compounds have a rather high viscosity.

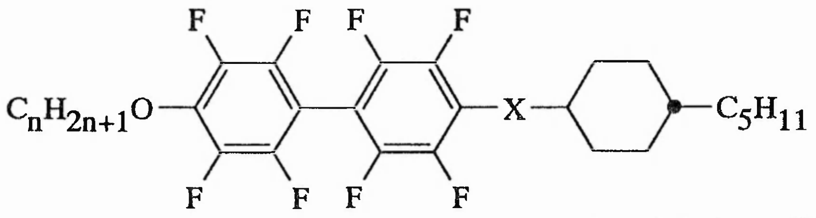
In view of these encouraging properties, the aim of the present research was to investigate the effect of the incorporation of 4,4′-disubstituted polyfluorobiphenyl systems **(17)** into other mesogens in order to discover the potential of such core units as sources of novel liquid crystalline compounds for use in liquid crystal display devices.



(17)

The initial synthetic work was centered on the preparation of a range of esters derived from 4-n-butyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl and 4-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluoro-4′-n-pentyloxybiphenyl.

Knowing that the above esters were likely to have a moderate to high viscosity, subsequent work was to be focussed on the synthesis of compounds **(18a)**, **(18b)** analogous to the *I-compounds*. It was envisaged, that replacement of the ester linkage by an ethane linkage would reduce the viscosity whilst maintaining or even improving the mesomorphic properties.



X = CH=CH **(18a)**
= CH_2CH_2 **(18b)**

The physical properties of these compounds were to be measured at Merck Ltd. as mixtures in a suitable host.

In addition to these studies of mesogens containing the octafluorobiphenyl core, it was planned to investigate a variety of 4,4′-disubstituted tetrafluorobiphenyls and hexafluorobiphenyls, with the fluoro-substituents situated symmetrically across the molecular axis, in order to study the effect of a systematic increase in lateral fluorination on liquid crystal and other physical properties.

DISCUSSION

3. DISCUSSION

This section conveniently divides into two parts.

Part A - Esters derived from 4-n-butyl-4′-hydroxyoctafluorobiphenyl and 4-n-alkoxy-4′-hydroxyoctafluorobiphenyl.

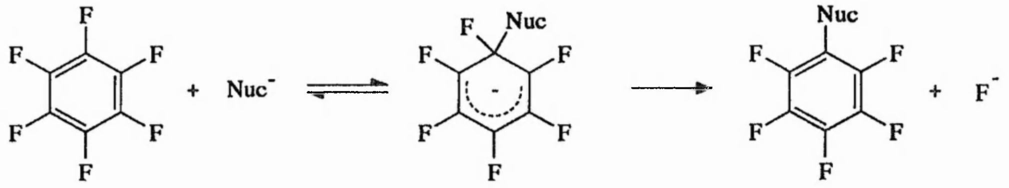
Part B - Alkylarylethenes and alkylarylethanes derived from polyfluoroaromatic aldehydes and *trans*-4-n-pentylcyclohexyl-1-methylphosphonium bromide.

In each part, following an initial consideration of the synthetic procedures, a discussion of liquid crystalline properties of the relevant compounds is given.

The majority of reactions carried out during the synthetic work involved nucleophilic attack on polyfluoroaromatic compounds. Hence, before attempting to discuss the results of this work it is appropriate at the outset briefly to review the mechanism of nucleophilic fluoroaromatic substitution ($S_{N(Ar)}$) reactions.

Polyfluoroaromatic compounds readily undergo aromatic nucleophilic substitution.[98-100] Recently, Rodinov et al.[101] reviewed the kinetics of the mechanism involving polyfluoro*benzenes* but data regarding mechanistic studies on polyfluorinated *biphenyls* is still rather limited. However, it is reasonable to assume that these are analogous systems with regard to the mechanism of nucleophilic aromatic substitution of a fluoro-substituent.

The proposed mechanism for nucleophilic substitution of a polyfluorobenzene follows a two-step process involving a short-lived σ-complex intermediate. Cacase et al.[102] investigated the isotopic exchange between radioactive $^{18}F^-$ and selected polyfluorinated benzenes, e.g. C_6F_6, C_6HF_5 in DMSO. Their kinetic studies provided results consistent with a $S_{N(Ar)}$ two-step mechanism and suggest an intermediate analogous to that for aromatic electrophilic substitution.



The retained fluoro-substituents stabilise the σ-complex by delocalising the negative charge. When partially or completely fluorinated biphenyls are considered the reactions generally proceed with substitution of the fluorine atom in the 4-position of the fluorinated ring. This is due to a direct consequence of a greater number of, and more energetically favourable, resonance structures contributing to the Wheland intermediate for 4-substitution.

Fluorine is highly electronegative and the introduction of several fluoro-substituents into the ring essentially increases the positive charge on the ring carbon atoms making them more susceptible to nucleophilic attack.[103] However, this *additive effect* does not always hold true because of other complicating factors such as substituent type and medium polarity.[101]

1. Substituent type. Substituents which tend to withdraw electron density away from the fluorinated ring will promote the rate of reaction and be *ortho:para*-directing towards nucleophilic substitution, whilst substituents which tend to donate electron density to the fluorinated ring will retard the rate of reaction and be *meta*-directing. n-Alkyl groups have been shown to be *para*-directing.

2. Medium polarity. The polarity of the reaction medium is particularly important during reactions involving attack by metal alkoxides. These reactions usually proceed in alcoholic solvents which readily solvate both anions and cations. However the reaction can be accelerated upon the addition of aprotic bipolar solvents, such as DMSO, DMF and sulpholane, which desolvate the reagent anion. Furthermore, alcoholic solvents tend to complicate the matter by forming side products. These are fomed as a direct result of the alcohol competing with the reagent (metal alkoxide) as a nucleophile in the reaction.

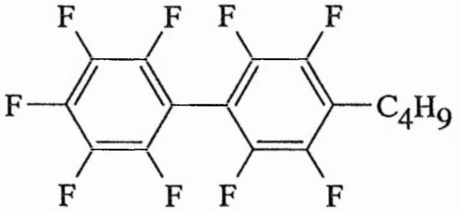
3.1 PART A - ESTERS DERIVED FROM 4-n-BUTYL-4'-HYDROXY-2,2',3,3',5,5',6,6'-OCTAFLUOROBIPHENYL AND 4-n-ALKOXY-4'-HYDROXY-2,2',3,3',5,5',6,6'-OCTAFLUOROBIPHENYL

The esters derived from 4-n-butyl-4'-hydroxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl (**20**) and 4-n-alkoxy-4'-hydroxy-2,2',3,3',5,5',6,6'-octafluorobiphenyls (**22**) were synthesised as shown in *Scheme 1* (p. 115) and *Scheme 2* (p. 116), respectively. Several disadvantages are associated with *Scheme 1* and these are now discussed.

Decafluorobiphenyl readily reacts with commercial 1.6M butyllithium (BuLi) at -20°C affording the desired 4-n-butylnonafluorobiphenyl (**19**), however a significant amount of 4,4'-di-n-butyloctafluorobiphenyl (30%) is also formed and a substantial quantity of starting material remains unchanged. Examination of the reaction mixture by t.l.c. revealed the R_f value of the starting material and the desired product to be extremely close and thus separation by column chromatography was not possible. Nevertheless separation was necessary as even the presence of a trace amount of decafluorobiphenyl is undesirable at the next stage of the synthesis. In addition, the formation of 4,4'-di-n-butyloctafluorobiphenyl consumes expensive starting material.

In an attempt to overcome these problems an alternative synthetic route to compound (**20**) was devised. This is shown in *Scheme 3* (p. 117). Decafluorobiphenyl was reacted with sodium methoxide to yield 4-methoxynonafluorobiphenyl (**35**) and again a considerable amount (40%) of 4,4'-dimethoxyoctafluorobiphenyl (**35a**) was obtained. Fortunately, the two components were separated easily by column chromatography on silica gel and the dimethoxy-compound **(35a)** was demethylated to give the corresponding dihydroxy-compound **(21)** which could be utilised as an intermediate in *Scheme 2*.

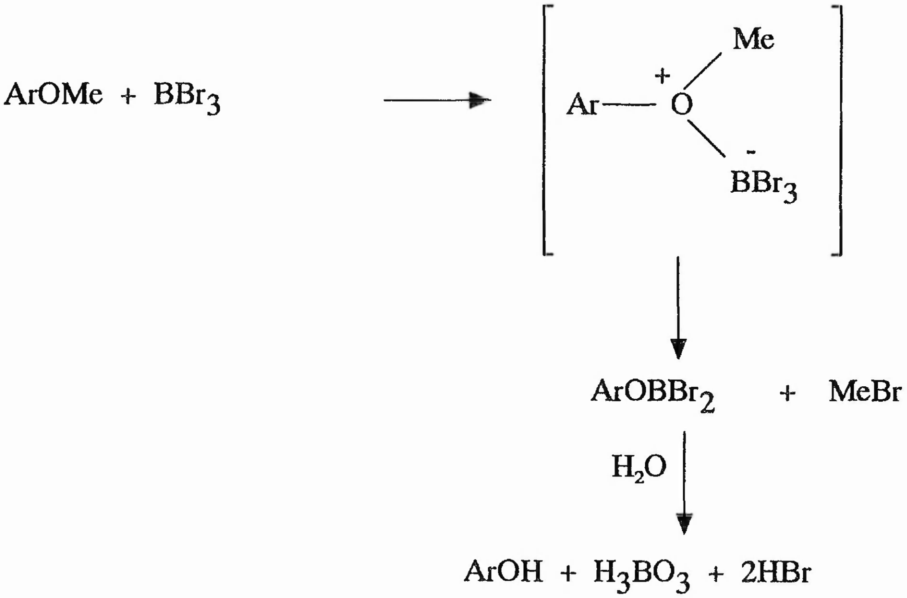
Subsequent reaction of 4-methoxynonafluorobiphenyl **(35)** with commercial 1.6M BuLi afforded a mixture of products. Examination of the mixture by t.l.c. indicated two fractions, one of which was close to the solvent front and another which had a similar R_f value as the starting material. Isolation and spectral identification (^1H n.m.r.) of the fractions revealed that the latter component was the desired 4-n-butyl-4'-methoxy-compound **(36)**. The proton n.m.r. spectrum of the former component revealed the absence of a singlet (actually a sharp, very narrow triplet due the interaction of the methoxy group with the *ortho*-fluoro-substituents)[105,106] corresponding to the methoxy group, and the presence of a downfield triplet characteristic of a methylene group attached to a fluorinated ring. Although a full spectral and elemental characterisation of this compound has not been carried out, one possible structure might be compound **(19)** suggesting replacement of the methoxy group by the n-butyl moeity.



(19)

Another possible alternative may be 4,4'-n-dibutyloctafluorobiphenyl, although this is unlikely because the 4,4'-n-dibutyl-compound distils at a considerably higher temperature (150°C/0.5mm Hg) than the 4-n-butyl-compound **(19)**.

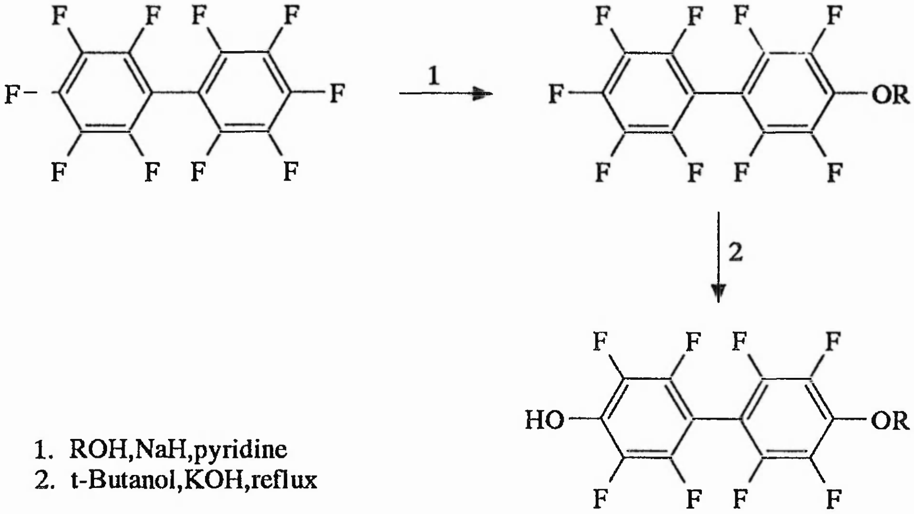
It was found that the 4-n-butyl-4'-methoxynonafluorobiphenyl **(36)** was readily demethylated with BBr_3 yielding the desired 4-n-butyl-4′-hydroxy-compound (**20**). Demethylation of alkoxyaryl ethers can be effected by a variety of reagents but it is usually necessary to employ fairly high temperatures, e.g. by boiling the compound with a solution of hydrogen bromide in acetic acid. A much milder reagent is boron tribromide (BBr_3) which McOmie et al.[104] have reported cleaves alkoxyaryl ethers in excellent yields at room temperature. The reaction probably proceeds as shown via a complex formed between the reagent and the oxygen atom of the ether.



On balance, *Scheme 3* (p. 117) proved a less satisfactory route than *Scheme 1* and thus subsequent preparation of the desired 4-n-butyl-4′-hydroxy-compound (**20**) was carried out via the original *Scheme 1* (p. 115).

The synthesis of 4-n-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyls (**22**) as shown in *Scheme 2* (p. 116) posed fewer problems. Decafluorobiphenyl readily undergoes nucleophilic hydroxylation at the 4- and 4′-positions[101] when heated under reflux with potassium hydroxide in *tert*-butanol. However, an unexpectedly poor yield (50%) of 4,4'-dihydroxyoctafluorobiphenyl **(21)** was obtained, since, under the conditions employed, a significant amount of the solvent is converted into potassium *tert*-butoxide and the *t*-butoxide anion then competes with the hydroxide anion as a nucleophilic species thus reducing the amount of 4,4'-dihydroxy-compound **(21)** formed.

Alkylation of the 4,4'-dihydroxy-compound afforded a mixture of the 4-n-alkoxy- **(22)** and 4,4'-di-n-alkoxy-compounds. These can be partially separated by column chromatography. The following alternative route was used if a large quantity of a specific 4-n-alkoxy-4'-hydroxyoctafluorobiphenyl was required.

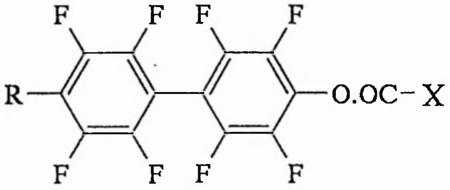


(22)

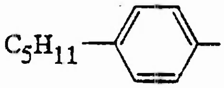
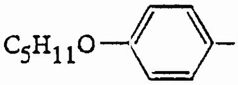
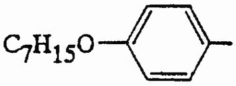
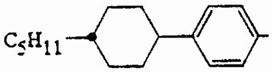
1. ROH,NaH,pyridine
2. t-Butanol,KOH,reflux

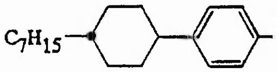
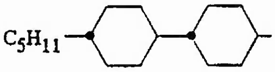
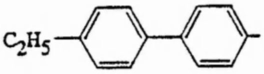
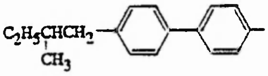
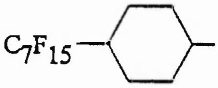
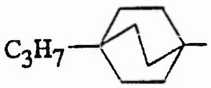
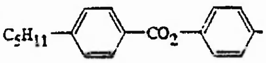
A variety of esters, e.g. **(23a)** and **(23b)** were synthesised by reaction of appropriate carboxylic acids with 4-n-butyl- and 4-n-pentyloxy-4'-hydroxyoctafluorobiphenyl, respectively, in the presence of dicyclohexylcarbodiimide (DCC)[107] and their transition temperatures are shown in ***Table 1.***

Table 1. Transition temperatures for esters derived from 4-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluoro-4′-n-pentyloxybiphenyl (e.g. **22**) and 4-n-butyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**20**)



R = $C_5H_{11}O$ (a)
C_4H_9 (b)

No.	X	C-N/S_A/I	S_A-N	N-I	comments
23a		63	-	(60.4)	monotropic
23b		101.7	-	-	
24a		51.7	-	89.8	
24b		91.9	-	(59.2)	monotropic
25a		63.0	-	84.1	
25b		73.9	-	(66.2)	monotropic
26a		90.1	-	222.9	
26b		125.9	-	206.4	

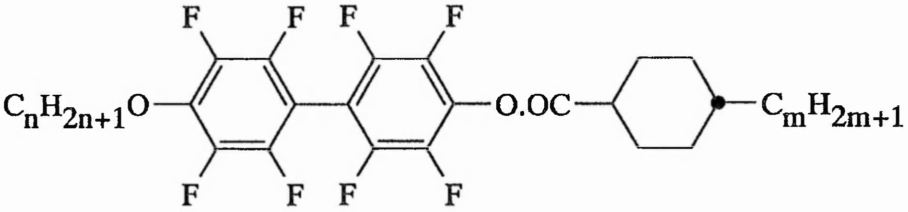
27a		87.7	-	208.1	
27b		100.5	-	206.4	
28a		63.7	117.9	252.1	
28b		96.7	-	248	
29a		127.3	-	228.5	
29b		132.2	-	207.8	
30a		86.5	-	188.9	
30b		152.5	-	170.3	
31a		98.9	156.7	160.2	monotropic S_A-S_B 93.7
31b		103.4	147.9	150.2	
32a		85.9	-	151.4	
32b		112	-	126.9	
33a		96.7	-	222.4	
33b		128-130	-	219	decomposes

The results listed in ***Table 1*** show that the majority of compounds are purely nematogenic. The nematic to isotropic (N-I) range is extremely wide, approximately of the order of 100°C. Similar behaviour has also been reported by Vauchier et al.[108] for esters derived from 2,2′-difluoro-4-n-alkoxy-4′-hydroxybiphenyls. Some compounds also exhibit smectic phases and in these cases only S_A and S_B are observed. Comparing the effect of the 4-n-butyl group with that of the 4-n-pentyloxy-group it is apparent that in the former case:

1. The crystal to mesophase transition temperatures are always higher. This might be due to the presence of the shorter less flexible, i.e. more rigid, alkyl chain, but as there are very few cases known where the crystal to mesophase transitions can be correlated with molecular structure[59,109] this observation may have no structural significance.
2. The nematic to isotropic transition temperatures ($T_{N\text{-}I}$) are always lower, i.e. the compounds give rise to thermally less stable nematic phases.

A comparison of the liquid crystalline properties of esters derived from 4-n-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyls **(22)** and *trans*-4-n-alkylcyclohexane carboxylic acids was also carried out. Four members (n=5,8,9,10) of each homologous series **(34a)**, **(34b)** and **(34c)** were prepared. The compounds are nematogens and their liquid crystal transition temperatures are shown in ***Table 2*** and presented graphically in ***Figures 21a, 21b, 21c*** as a plot against n, the number of carbon atoms in the alkyl chain.

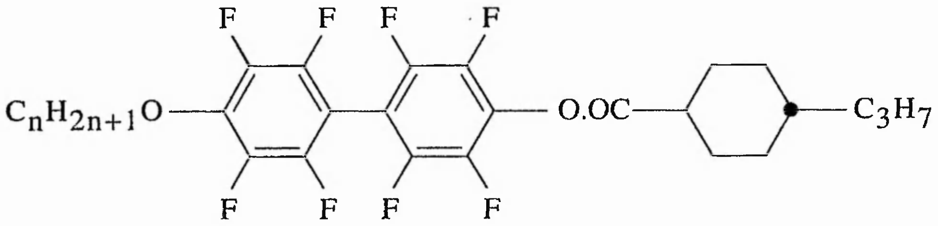
Table 2. Liquid crystal transition temperatures for 4-n-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl *trans*-4-n-alkylcyclohexane-1-carboxylates **(34a)**, **(34b)** and **(34c)**



	m = 3 **(34a)**		*m* = 5 **(34b)**		*m* = 7 **(34c)**	
n-Alkyl group	*C-N*	*N-I*	*C-N*	*N-I*	*C-N*	*N-I*
C_5H_{11}	*58*	*105*	*43*	*112*	*58*	*102*
C_8H_{17}	*54*	*94*	*54*	*99*	*57*	*95*
C_9H_{19}	*52*	*87*	*53*	*93*	*55*	*92*
$C_{10}H_{21}$	*50*	*84*	*53*	*91*	*59*	*91*

The points for the N-I transition temperatures show an odd/even alternation and lie on two curves which fall as n increases, with the points for the even-n homologues lying on the upper curve.

Alternatively, when n is fixed and m is varied (m=3,5,7) as shown in ***Figure 21d***, the points for the N-I transition temperatures, for any given value of n, lie on a smooth curve which rises at first then gradually falls peaking at the m=5 homologue.



(34a)

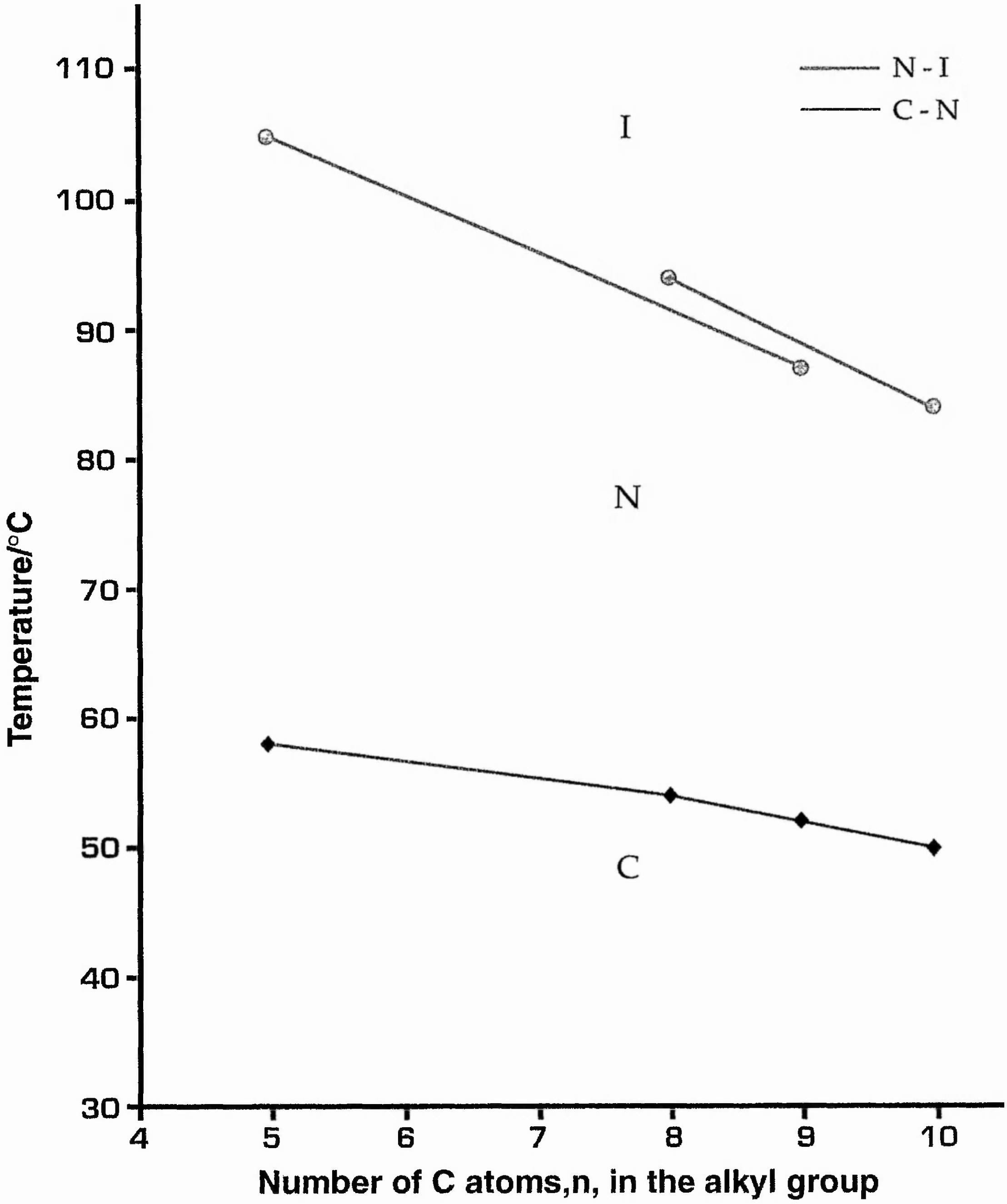
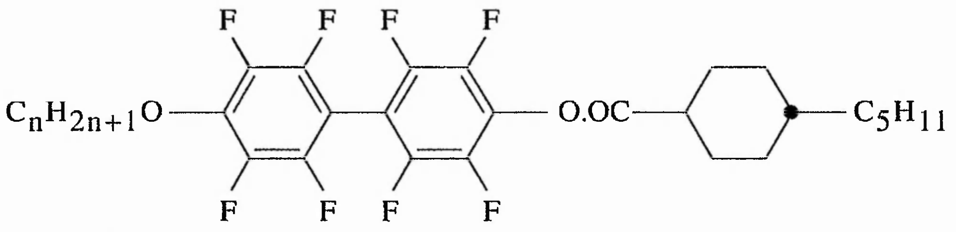


Figure 21a. Plot of transition temperatures for certain 4'-n-alkoxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-yl *trans*-4-n-propylcyclohexane-1-carboxylates (**34a**)



(**34b**)

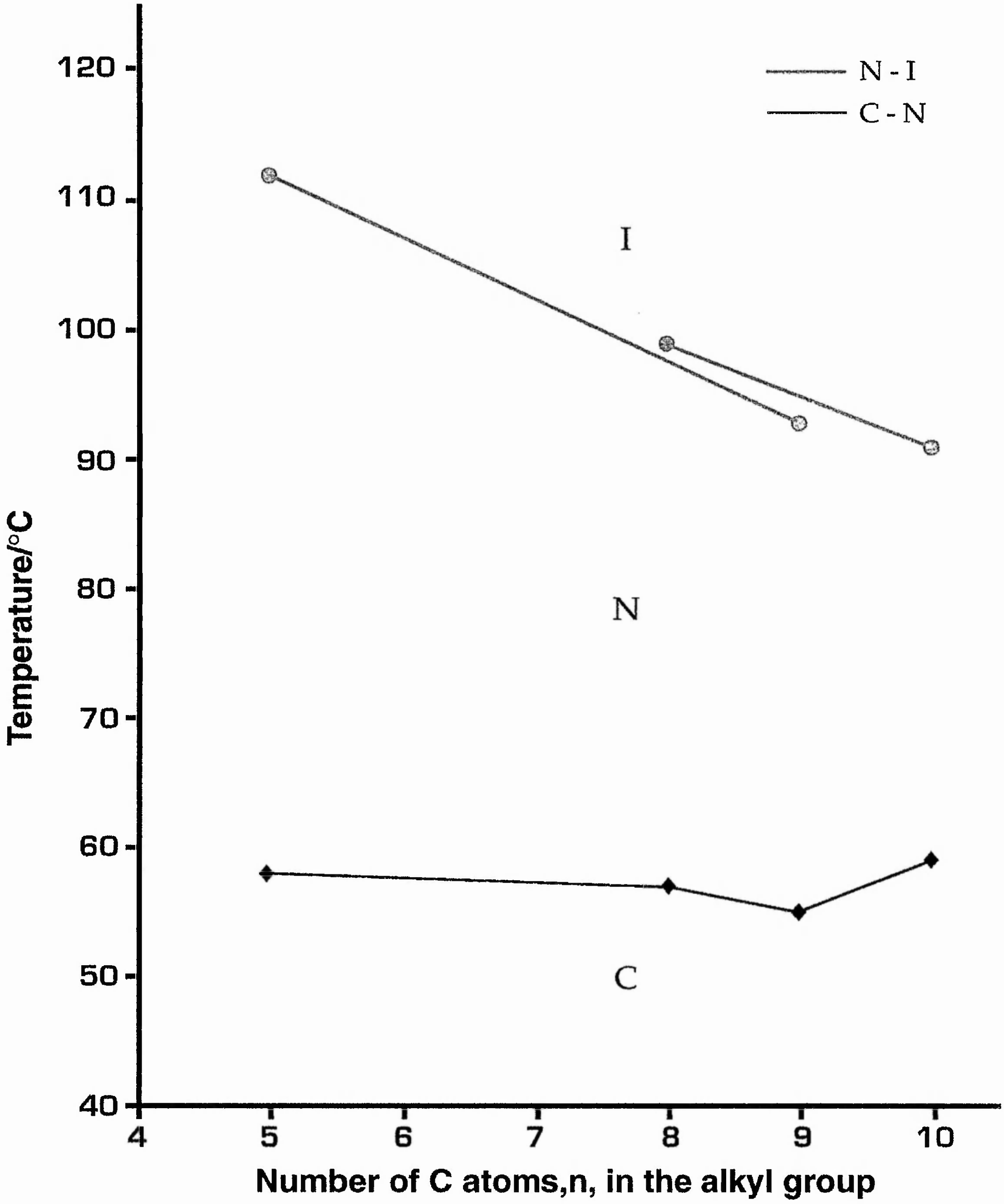
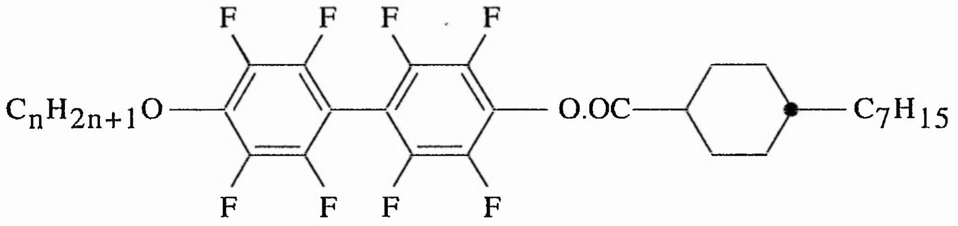


Figure 21b. Plot of transition temperatures for certain 4'-n-alkoxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-yl *trans*-4-n-pentylcyclohexane-1-carboxylates (**34b**)



(34c)

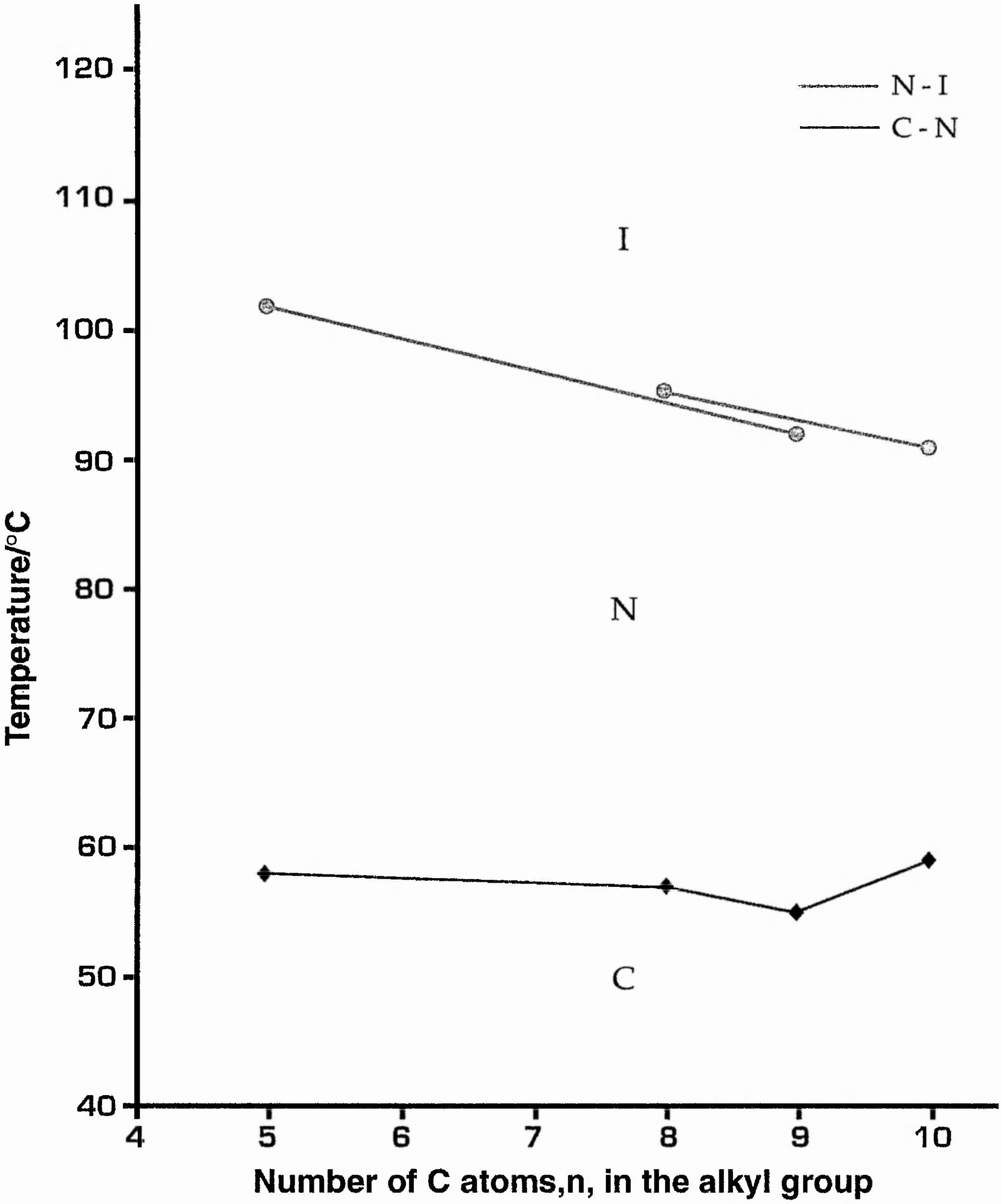


Figure 21c. Plot of transition temperatures for certain 4'-n-alkoxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-yl *trans*-4-n-heptylcyclohexane-1-carboxylates (**34c**)

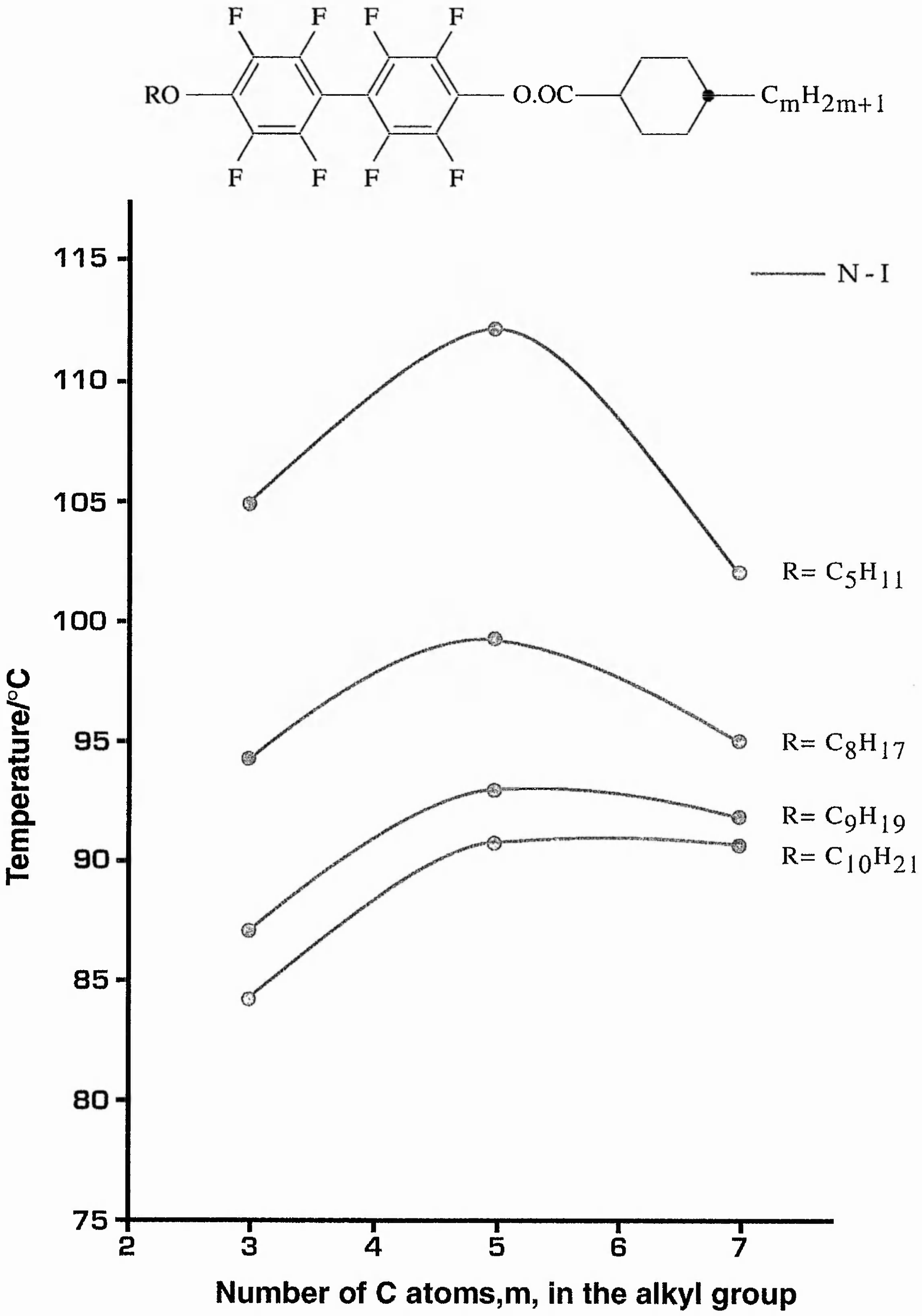
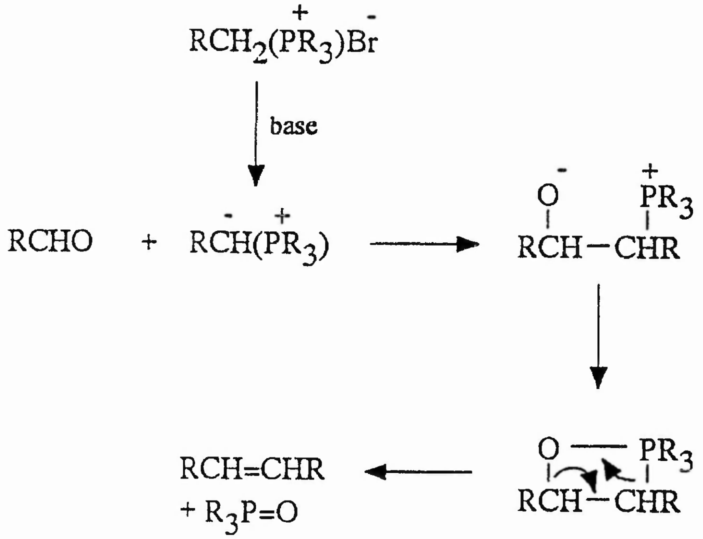


Figure 21d. Plot of transition temperatures for certain 4'-n-alkoxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-yl *trans*-4-n-alkylcyclohexane-1-carboxylates

3.2 PART B - SYNTHESIS AND PHYSICAL PROPERTIES OF ALKYLARYLETHENES AND ALKYLARYLETHANES DERIVED FROM POLYFLUOROAROMATIC ALDEHYDES AND *trans*-4-n-PENTYLCYCLOHEXYL-1-METHYLTRIPHENYLPHOSPHONIUM BROMIDE

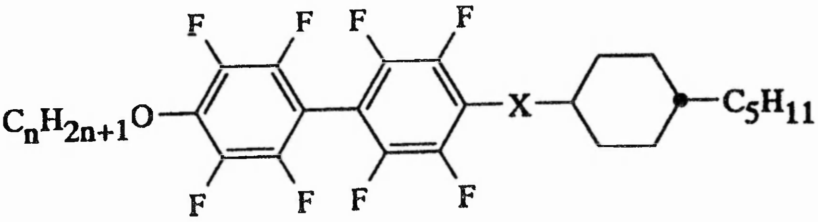
The alkylarylethanes were obtained by reduction of the corresponding alkylarylethenes. The preparation of alkenes by the Wittig reaction is very well documented.[110,111] The Wittig reaction takes place between an aldehyde and a phosphonium salt, in the presence of base, to yield an alkene as shown below.



The advantage of the Wittig reaction is that the carbonyl group is replaced by a carbon-carbon double bond without the formation of isomeric alkenes. However, the stereochemistry of the double bond formed, i.e. *cis* or *trans* configuration, is sometimes difficult to control.

Several alkylarylethanes were prepared via the synthetic route shown in *Scheme 4* (p. 118). The main difficulty was the synthesis of the appropriate fluorinated biphenyl. This and other associated problems are now discussed.

1. Synthesis of 1-(4′-n-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans* -4-n-pentylcyclohexyl)-ethenes (**18a**) and -ethanes (**18b**).



X = CH=CH **(18a)**
= CH_2CH_2 **(18b)**

Scheme 4 (p. 118), which includes the initial synthesis of nonafluorobiphenyl (e.g. **38**) was followed. This compound was obtained by Holland et al.[112] in an 80% yield via reduction of the corresponding 4-hydrazinononafluoro-biphenyl (e.g. **37**) with aqueous copper(II) sulphate. The reduction reaction is believed to proceed via oxidation of 4-hydrazinononafluorobiphenyl (e.g. **37**) to the intermediate diazo-compound (X):

$$\begin{tikzcd} \underset{\text{(e.g. }\mathbf{37}\text{)}}{C_{12}F_9NHNH_2} \arrow[r, "Cu^{2+}"] & C_{12}F_9\dot{N}NH_2 \arrow[r, "Cu^{2+}"] & \underset{\text{(X)}}{C_{12}F_9N{=}NH} \arrow[d] \\ & & \underset{\text{(e.g. }\mathbf{38}\text{)}}{C_{12}F_9H + N_2} \end{tikzcd}$$

which then eliminates nitrogen to yield the desired nonafluorobiphenyl (e.g. **38**).

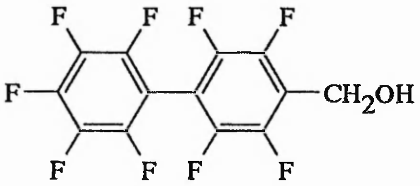
When this method was attempted a mixture of mono- , di- and poly-substituted hydrazino-compounds was obtained. Separation of these compounds was difficult and lengthy to accomplish. The overall yield of the monohydrazino-compound (e.g. **37**) was only approximately 50% and was not always reproducible. As Wall et al.[113] have reported a 'one-pot' synthesis of pentafluorobenzene from hexafluorobenzene in the presence of lithium aluminium hydride, the same method was applied to decafluorobiphenyl. A mixture of mono- and di-hydro-compounds, i.e. 2,2′,3,3′,4′, 5,5′,6,6′-nonafluoro- and 2,2′,3,3′,5,5′,6,6′-octafluoro-biphenyls, and some unreacted starting material in the ratio 5:2:3 was obtained. This was especially encouraging because of the ease of carrying out the reaction and the extremely short reaction time (8h. compared with a minimum of 1 week for the hydrazine method).

However, recently, following a personal communication with Dr. J.Burdon[114] regarding the work carried out by Holland et al., a modification of the reaction conditions by isolation of the hydrazino-compound (e.g. **37**) as the hydrochloride prior to reduction with copper(II) sulphate, was tried. This modification has been successfully employed giving yields of up to 70% of the monohydro-compound (e.g. **38**).

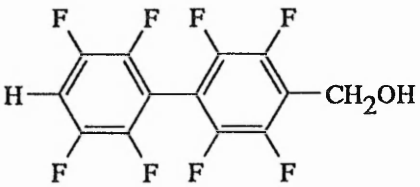
Nonafluorobiphenyl-4-carboxylic acid (e.g. **39**) was prepared by treating nonafluorobiphenyl (e.g. **38**) with commercial 1.6M BuLi followed by carbonation with solid carbon dioxide. The yield in this reaction is very solvent dependent, although this is not stated in the literature,[115] and when lithiations were attempted either in dry ether or dry tetrahydrofuran yields were poor (<50%), but in a mixture of dry 1:1 ether : hexane the desired carboxylic acid (e.g. **39**) was obtained in a yield in excess of 90%.

Initially, the carboxylic acid (e.g. **39**) was reduced to the alcohol (e.g. **40**) with $LiAlH_4$.[116] Examination of the product by t.l.c. in 4:1 light petroleum (60-80°C) :

ethyl acetate showed only a single spot. However, repeated development of the t.l.c. plate revealed that the 'single spot' was actually due to two very closely running components. As it is known that under forcing conditions LiAlH$_4$ can substitute one or more fluoro-substituents,[113] it was assumed that the two products were (e.g. **40**) and (**40a**), the latter formed by nucleophilic substitution of the 4'-F substituent by the hydride ion derived from LiAlH$_4$.

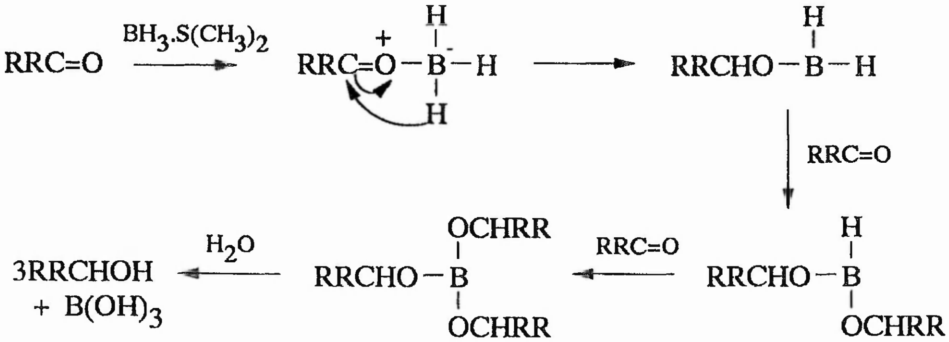


(e.g. **40**)

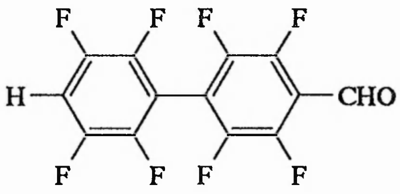


(**40a**)

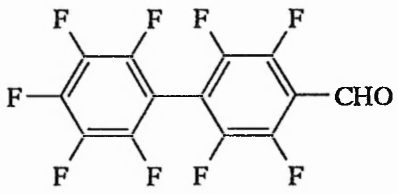
To resolve this problem, borane dimethyl sulphide (BMS),[117] which is a reducing agent of an electrophilic type, was employed instead of LiAlH$_4$. The mechanism of the reduction by boranes is shown and involves attack at that part of the organic molecule which has a free electron pair, i.e. at the carbonyl oxygen atom.



Pyridinium chlorochromate (PCC)[118] was used to oxidise the alcohol (e.g. **40**) obtained by this method to the corresponding aldehyde (e.g. **41**). At this stage very unusual behaviour was observed. Starting from the nonafluorobiphenyl obtained by the method of Holland et al.,[112] and carrying out the subsequent synthetic procedures, examination of the resulting aldehydic product by t.l.c. revealed two fractions. The faster running spot was labelled A1 (19%) and the other A2 (77%). Although not entirely consistent with the spectroscopic data, the following structures for A1 and A2 seemed most likely.



(A1)



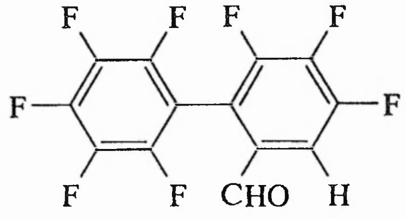
(A2)

The proton n.m.r. spectrum of A1 suggested the presence of a hydrogen atom associated with a fluorinated biphenyl ring, as indicated by a complex multiplet centered at 7 p.p.m. The aldehyde absorption occurred at 11.1 p.p.m. not as a singlet but as a very sharp, narrow doublet (J approximately 2-3 Hz), with lines of approximately equal intensity, which is not usual for aromatic aldehydes, e.g. benzaldehyde, tolualdehyde. In contrast, the proton n.m.r. spectrum of A2 showed a sharp singlet at 11.1 p.p.m. characteristic of the aldehydic proton with no coupling in the region of aromatic absorption. Mass spectral analysis of A1 gave a molecular weight of 326 consistent with the proposed structure of A1. HPLC analysis showed that the A1 aldehyde was 95% pure, the 5% impurity possibly being due to autoxidation to the acid.

In order to elucidate the proposed structures of A1 and A2 unambiguous syntheses were attempted. The reactions shown in *Scheme 5* (p. 119) were carried out in an attempt to establish the proposed structure of A1. 4,4′-Dihydro-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**48**) was obtained by heating decafluorobiphenyl with $LiAlH_4$ under reflux in ether for 72h. After treatment with 1.6M BuLi, followed by carbonation, the monocarboxylic acid (**49**) was separated from the dicarboxylic acid by recrystallisation from a large volume of hexane. The mono-acid (**49**) was reduced with BMS to the alcohol (**50**), which was then oxidised to the aldehyde using PCC. Examination of the aldehyde by t.l.c. and comparison with the behaviour of A1 and A2 revealed that it had a very similar R_f to A2 showing that the proposed structure for A1 was *incorrect.*

The reactions shown in *Scheme 6* (p. 120) established that the proposed structure of A2 was correct. Unambiguous proof was fairly straightforward by preparation via another route of the alkylaryl-ethenes (**18a**) and -ethanes (**18b**) derived from the aldehyde A2. It was necessary to introduce the alkoxy group into the biphenyl system intially so as to substitute the 4-position and leave the 4′-position open for later attack. The derived alkylarylethanes (**18b**) had the same transition temperatures as the compounds prepared from the aldehyde A2.

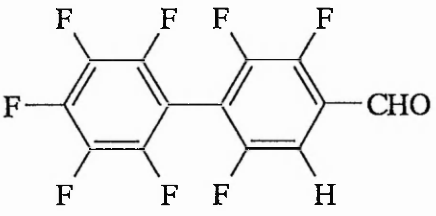
The problem of the structure of the aldehyde A1 remained and was of particular interest because an alkylarylethane derived from A1 was liquid crystalline (with transition temperatures: C-N 19°C, N-I 39°C). Hence, a sample of A1 was sent to the Dyson-Perrins Laboratory at Oxford University for investigation by ^{19}F n.m.r. spectroscopy. The results suggested the following structure (**41c**) as a possibility, but



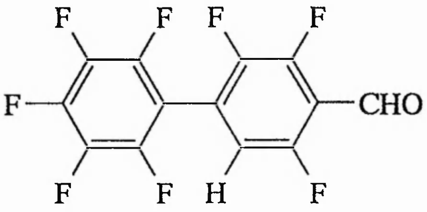
(**41c**)

this is not consistent with the formation of a linear, lath-like alkylarylethane from A1.

However, after further consultation with the Oxford group regarding the mesogenic properties of the derived alkylarylethane, it was concluded that either of the following structures **(41d)**, **(41e)** for A1 was consistent with the rather complex ^{19}F n.m.r. spectrum observed.



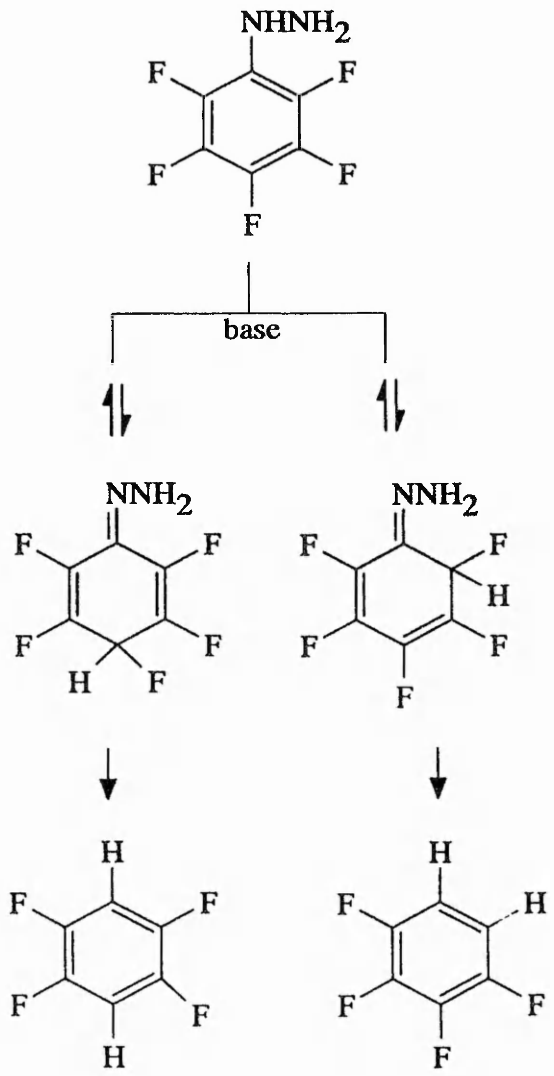
(41d)



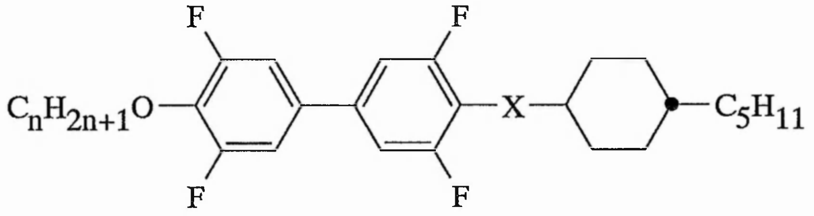
(41e)

With regard to the ^{1}H n.m.r. doublet observed for the aldehydic proton of A1, personal communication with Dr.J.Burdon[114] confirmed that this was likely if there was rotation about the ring-CHO bond. This would result in long-range through-space coupling of the aldehydic proton with the hydrogen atom located *ortho-* to the aldehyde group. Hence, taking into account all the available evidence, **(41d)** is the most likely structure for A1. It is possible, however, that the doublet observed for the aldehydic proton of A1 was due to a mixture of equal amounts of two closely similar isomeric aldehydes, inseparable by t.l.c. and HPLC, being present in the sample A1.

At this stage it should be stressed that A1 was only a minor product that might have resulted from some kind of oxidation-reduction occurring at the reduction stage with copper(II) sulphate. Holland et al.[119] reported that the reaction of hydrazine with pentafluorophenylhydrazine yielded the desired substitution product, 1,4-dihydrohydrazinotetrafluorobenzene, together with 1,2,4,5-tetrafluorobenzene. The latter was attributed to a competing reaction due to the action of hydrazine acting as a base. On reaction with strong base, the hydrazine function is subsequently lost as nitrogen and a substituent is displaced from either the *ortho-* or *para-*position. There is evidence to indicate that this is an internal oxidation-reduction reaction, as shown, that proceeds through quinoid tautomerism.



2. Synthesis of 1-(4′-n-alkoxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**55a**) and -ethanes (**55b**).



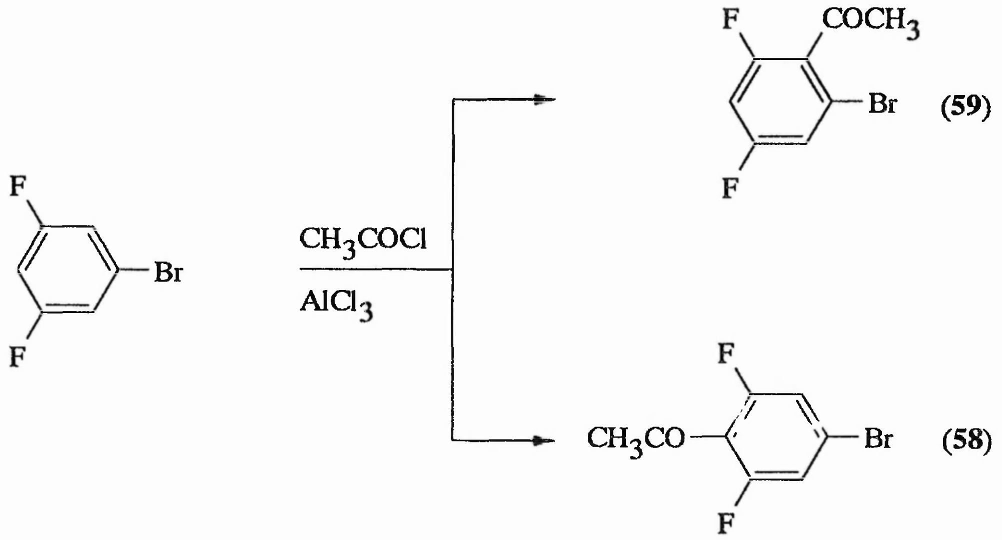
X = CH=CH (**55a**)
= CH_2CH_2 (**55b**)

At the time the synthetic work was begun, neither the appropriate fluorinated biphenyl nor a simple precursor to the biphenyl were commercially available. Hence attempts were made to synthesise 3,3′,5,5′-tetrafluorobiphenyl (**56**) and to utilise it as an intermediate in *Scheme 7* (p. 121) proposed for the preparation of the desired alkoxy- (**55a**), (**55b**) and alkyl- compounds.

Several methods for homo-coupling 1-bromo-3,5-difluorobenzene were attempted and the best overall yield (50-60%) was obtained using a method reported by Cohen et al.[120] Friedel-Crafts acylation was attempted on the resulting 3,3′,5,5′-tetrafluorobiphenyl (**56**) but gave a mixture of products which could not be separated. Hence this route was abandoned.

An alternative approach, shown in *Scheme 8* (p. 122), which involved Friedel-Crafts acylation of 1-bromo-3,5-difluorobenzene, was then attempted. Examination of the reaction mixture by t.l.c. revealed two very closely running spots. The two components were partially separated by column chromatography on silica gel and characterised by proton n.m.r. spectroscopy. The first fraction appeared to be

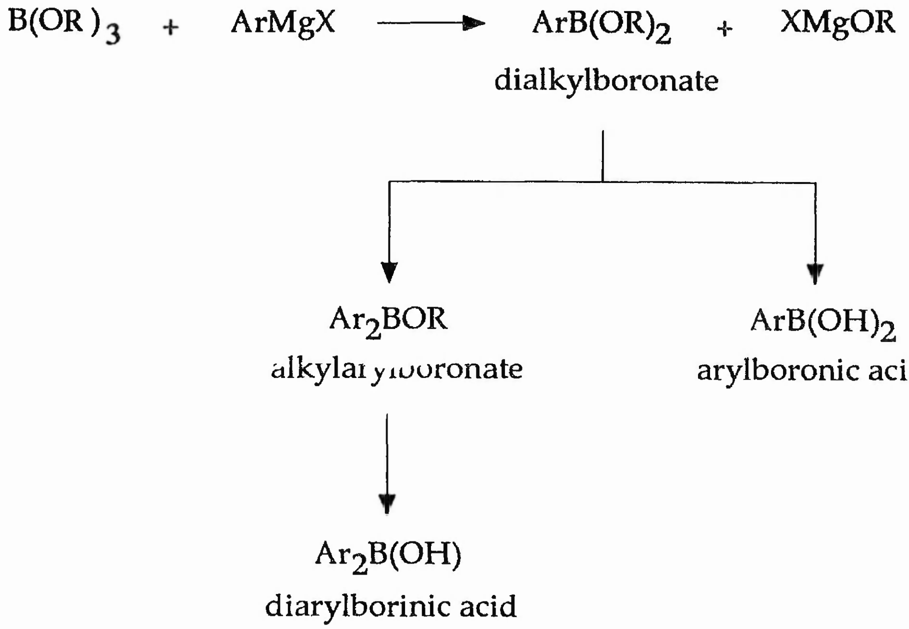
2-acetyl-1-bromo-3,5-difluorobenzene **(59)** and the second was the desired 4-acetyl-1-bromo-3,5-difluorobenzene **(58)**. Hence, contrary to expectation, acylation had occured both *ortho-* and *para-* to the bromo-substituent giving rise to approximately equal amounts of the two isomers. The overall yield (35%) was poor and this route was also abandoned.



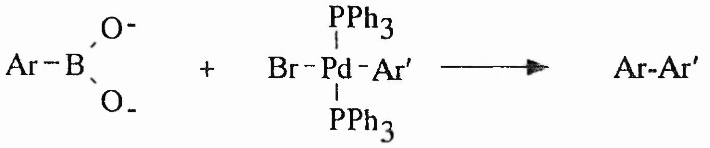
However, shortly afterwards, a synthetically useful intermediate, 1-bromo-3,4,5-trifluorobenzene, became commercially available. Utilising this compound it was proposed to synthesise 3,3',4,5,5'-pentafluorobiphenyl **(61)**, as shown in *Scheme 9* (p. 123), via a palladium(0)-catalysed cross-coupling of an arylboronic acid e.g. **(60)**.[121-123] This would then enable the same series of reactions, leading to the desired alkylaryl-ethenes **(55a)** and -ethanes **(55b)** to be performed as shown in *Scheme 4* (p. 118).

The Grignard reagent derived from 1-bromo-3,5-difluorobenzene was prepared in the usual way and added to an excess of trimethyl borate (TMB) at -78°C. The resulting pure 3,5-difluorophenylboronic acid **(60)** was then coupled with 1-bromo-3,4,5-trifluorobenzene in the presence of tetrakis(triphenylphosphine)-palladium(0) ($Pd(PPh_3)_4$)[124] catalyst affording the desired 3,3′,4,5,5′-pentafluorobiphenyl **(61)**.

As indicated in the following scheme, the synthesis of arylboronic acids commonly give rise to diarylborinic acids,[125] as by-products. With regard to the



mechanism, during the coupling reaction, Thompson et al.[126] suggest that the arylboronate dianion (*I*) acts as the reactive organometallic intermediate which attacks the arylpalladium bromide complex (*II*). Hence arylboronic acid anhydrides which are formed by the dehydration of the respective boronic acids can also be used effectively in the cross-coupling reaction.

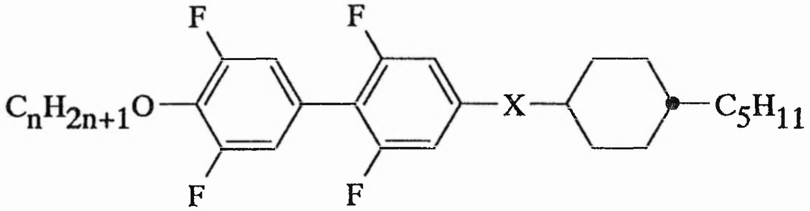


reactive organometallic intermediate (*I*)

arylpalladium bromide complex (*II*)

The 3,3′,4,5,5′-Pentafluorobiphenyl (**61**) obtained by this method was then treated with butyllithium and converted into 3,3′,4′,5,5′-pentafluorobiphenyl-4-carbaldehyde (e.g. **41**) by the route shown in *Scheme 4* (p. 118). The aldehyde then subjected to the Wittig reaction to obtain the corresponding alkylaryl-ethenes (**55a**) and -ethanes (**55b**).

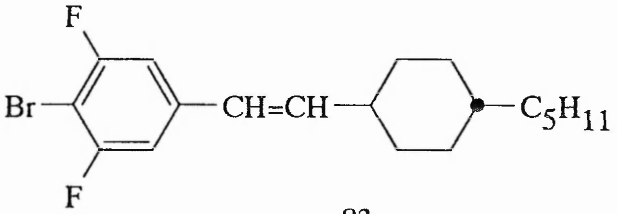
3. Synthesis of 1-(4′-n-alkoxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**62a**) and -ethanes (**62b**).



X = $CH{=}CH$ (**62a**)
= CH_2CH_2 (**62b**)

The preparation of 2′,3,4,5,6′-pentafluorobiphenyl by Pd(0)-catalysed cross-coupling of an arylboronic acid with an arylhalide was not synthetically feasible due to the lack of appropriate starting materials. Hence a new strategy was adopted for synthesising the desired alkylaryl-ethenes (**62a**) and -ethanes (**62b**) as shown in *Scheme 10* (p. 124).

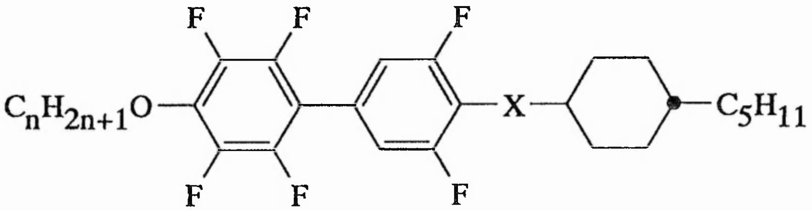
The carbonyl group of 3,5-difluorobenzaldehyde was first protected by conversion to the cyclic acetal with ethylene glycol[127] and the product (**63**) then brominated, via lithiation at the 4-position, to afford 4-bromo-3,5-difluorobenzaldehyde (**65**). The Wittig reaction was carried out on this compound to yield the alkene (**67**)



(67)

which was cross-coupled with 3,4,5-trifluorophenylboronic acid **(66)** and, the product then alkylated to give the desired alkylaryl-ethenes **(62a)** which were reduced to the corresponding -ethanes **(62b)**.

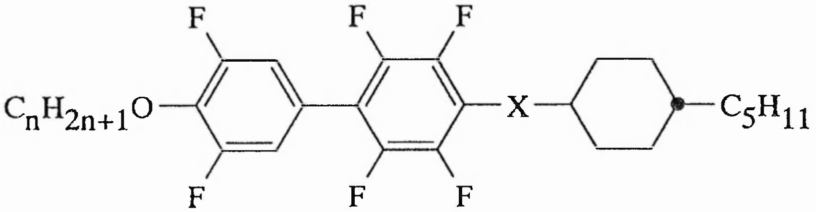
4. Synthesis of 1-(4′-n-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes **(68a)** and -ethanes **(68b)**.



X = CH=CH **(68a)**
= CH_2CH_2 **(68b)**

3,5-Difluorophenylboronic acid **(60)**, *Scheme 9* (p. 123), was readily coupled with bromopentafluorobenzene to yield 2,3,3′,4,5,5′,6-heptafluorobiphenyl (e.g. **38**), *Scheme 4* (p. 118). Following treatment of this compound with butyllithium and conversion into 2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-carbaldehyde (e.g. **41**), the corresponding alkylaryl-ethenes **(68a)** and -ethanes **(68b)** were then prepared via the Wittig reaction as indicated in *Scheme 4* (p. 118).

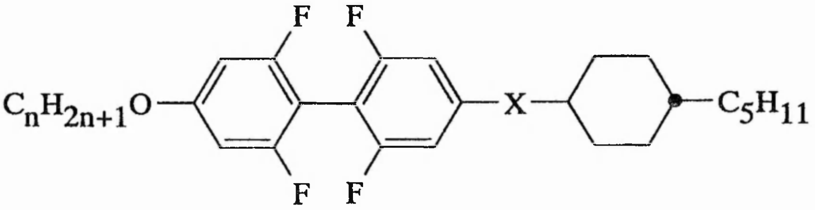
5. Synthesis of 1-(4′-n-alkoxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes **(69a)** and -ethanes **(69b)**.



X = CH=CH **(69a)**
= CH_2CH_2 **(69b)**

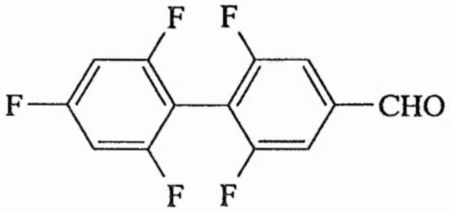
2,3,3′,4′,5,5′,6-Heptafluorobiphenyl (e.g. **38**), *Scheme 4* (p. 118), was synthesised by cross-coupling 3,4,5-trifluorophenylboronic acid (**66**) with 4-bromo-2,3,5,6-tetrafluorobenzene. The heptafluorobiphenyl was converted into 2,3,3′,4′,5,5′,6-heptafluorobiphenyl-4-carbaldehyde (e.g. **41**) from which the desired alkylaryl-ethenes (**69a**) and corresponding -ethanes (**69b**) were prepared utilising the Wittig reaction as shown in *Scheme 4* (p. 118).

6. Attempted synthesis of 1-(4-n-alkoxy-2,2′,6,6′-tetrafluorobiphenyl-4′-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**70a**) and -ethanes (**70b**).



X = CH=CH (**70a**)
= CH_2CH_2 (**70b**)

The synthesis of these alkylarylethanes (**70b**) was of particular interest because the fluoro-substituents located in the 2,2′ and 6,6′ positions cause an appreciable twisting of the biphenyl system. In a recent review by Sneickus,[128] there are many examples of the formation of sterically hindered biphenyl derivatives by the boronic acid coupling method. Hence, via such a reaction, initial attempts were made to synthesise 2,2′,4′,6,6′-pentafluorobiphenyl-4-carbaldehyde (**71**) which could be converted into the required compounds by the Wittig route.



(**71**)

a. Coupling with 2,4,6-trifluorophenylboronic acid (**72**)

1-Bromo-2,4,6-trifluorobenzene was lithiated in the customary manner and treated with an excess of trimethyl borate at -78°C affording the desired boronic acid (**72**). The formation of the boronic acid via a Grignard synthesis gave extremely poor results (10-15%). This was thought to be due mainly to side reactions resulting from the formation of an aryne intermediate.[129]

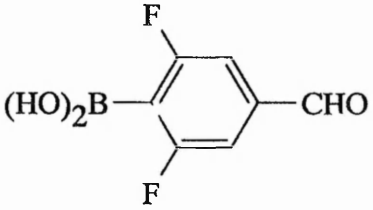
Several attempts were made to couple the 2,4,6-trifluorophenylboronic acid with 4-bromo-3,5-difluorobenzaldehyde under various reaction conditions as indicated in ***Table 3***. The reactions were monitored by t.l.c., but the results indicated that none of the reactions gave biphenyl products even under forcing conditions. If the coupling reaction had succeeded, the intention was to react 2,2′,4′,6,6′-pentafluorobiphenyl-4-carbaldehyde with *trans*-4-n-pentylcyclohexyl-1-methylphosphonium bromide, via the Wittig reaction, to afford the desired alkylaryl-ethenes (**70a**) and -ethanes (**70b**).

Table 3. Reaction conditions for the reaction between 4-bromo-3,5-difluorobenzaldehyde (**65**) and 2,4,6-trifluorophenylboronic acid (**72**)

Solvent system/cm^3			reactant/mol.equiv.			time/h	yield/%
2M Na_2CO_3	benzene	ethanol	$R(BOH)_2$	R′Br	$Pd(PPh_3)_4$		
30	30	10	1.1	1	0.03	24	0
60	30	10	1.1	1	0.3	24	0
60	30	10	1.1	1	3	48	0

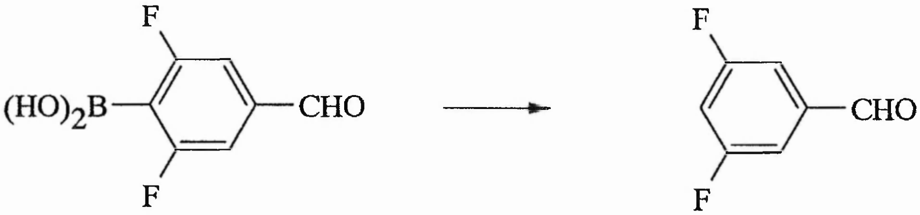
b. Coupling with 2,6-difluoro-4-formylphenylboronic acid (**73**).

The carbonyl group of 3,5-difluorobenzaldehyde was initially protected by conversion into the cyclic acetal with ethylene glycol, and the boronic acid group introduced into the 4-position in the usual way via lithiation with butyllithium. The resultant boronic acid (**73**) was then coupled with 1-bromo-2,4,6-trifluorobenzene and the reaction monitored by t.l.c. After heating the reaction mixture under gentle reflux for 10 min. examination of the reaction mixture by t.l.c.



(**73**)

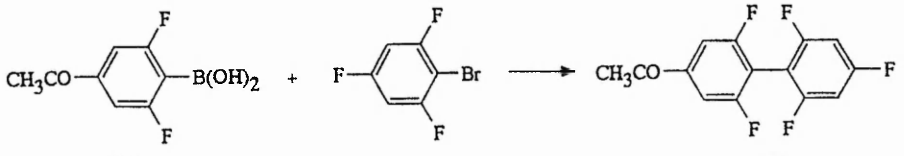
revealed partial consumption of the boronic acid and the formation of a new component. This was isolated by column chromatography on silica gel and its melting point determined and proton n.m.r. spectrum recorded. The results showed that this compound was actually 3,5-difluorobenzaldehyde suggesting that protodeboronation[86,125,130] of the boronic acid moiety had occurred, i.e.



(**73**)

c. Coupling with 4-acetyl-2,6-difluorophenylboronic acid (**74**).

It was envisaged that coupling of 4-acetyl-2,6-difluorophenylboronic acid (**74**) with 1-bromo-2,4,6-trifluorobenzene would afford 4-acetyl-2,2′,4′,6,6′-pentafluorobiphenyl (**75**) which could then be converted into the corresponding acid via the haloform reaction.[131]



(74) (75)

After carrying out the coupling procedure, and examination of the reaction mixture by t.l.c., a new component was observed which was thought to be the desired product. However, mass spectral analysis of the compound revealed a fragment at $^{m}/_{e}$ 157, consistent with the relative molecular weight of 3,5-difluoroacetophenone and a mixed melting point determination of the product with an authentic sample of 3,5-difluoroacetophenone revealed no depression of the melting point, confirming that the compound was 3,5-difluoroacetophenone. Thus protodeboronation had again occurred. In view of this result, the stability of the boronic acid in the reaction medium was investigated on a qualitative basis.

4-Acetyl-2,6-difluorophenylboronic acid **(74)** was added to solvent mixtures both in the presence and absence of the Pd(0) catalyst but in each case with 1-bromo-2,4,6-trifluorobenzene excluded. The reaction mixtures were stirred at room temperature and monitored by t.l.c. The results are listed in *Table 4* and

Table 4. Effect of various solvent systems on 4-acetyl-2,6-difluorophenylboronic acid **(74)**

Solvent system	$Pd(PPh_3)_4$	t.l.c.-no. of spots
benzene	absent	1
benzene/ethanol	absent	1
benzene/ethanol/Na_2CO_3	present	3

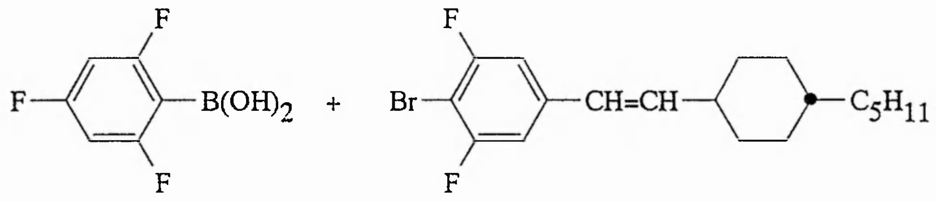
dimethylformamide/piperidine	present	3
dimethylformamide/thallium carbonate	present	3
dimethylformamide/triethylamine	present	3

show that the breakdown of the boronic acid **(74)** readily occurs only in the presence of the catalyst and aqueous 2M Na_2CO_3. Hence, the effects of other bases, such as thallium carbonate, triethylamine and piperidine in dry dimethylformamide,[130] in the absence of water, were investigated but again the reactions failed to work.

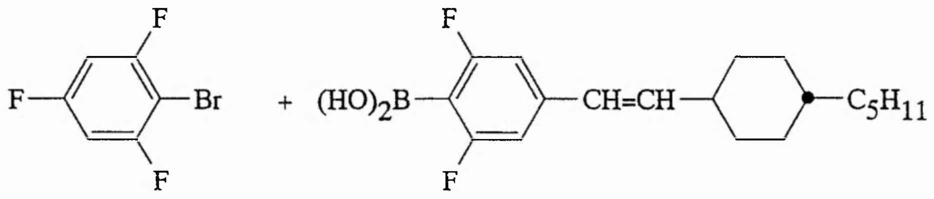
d. Miscellaneous boronic acid couplings

Other coupling reaction types were also attempted as follows:

1.

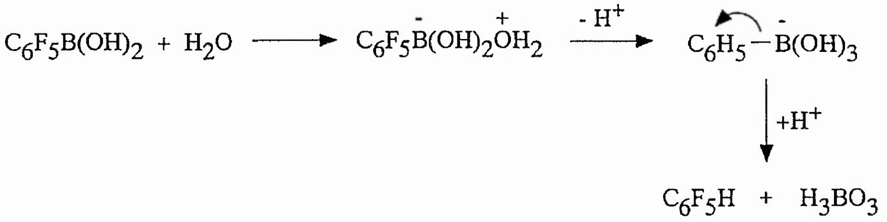


2.



However these reactions were also unsuccessful.

The activity of a boronic acid moiety is markedly affected by the presence of a single *ortho*-fluoro-substituent. Chambers et al.[132] reported that when two *ortho*-fluoro-substituents are present, compounds such as pentafluorophenylboronic acid, which is analogous with the 2,6 difluorophenylboronic acid discussed above, have markedly increased susceptibility to nucleophilic cleavage, as indicated.



$$\begin{tikzcd} C_6F_5B(OH)_2 + H_2O \arrow[r] & C_6F_5\overset{-}{B}(OH)_2\overset{+}{O}H_2 \arrow[r, "- H^+"] & C_6H_5-\overset{-}{B}(OH)_3 \arrow[d, "+H^+"] \\ & & C_6F_5H + H_3BO_3 \end{tikzcd}$$

At this stage, the Pd(0)-catalysed cross-coupling reactions of the arylboronic acid were abandoned in favour of a new approach to the synthesis of the 2,2′,6,6′-tetrafluorobiphenyl system. Initially, classical methods for homo-coupling were reviewed[133] in an attempt to synthesise a compound with suitable functional groups in the 4- and 4′-positions of 2,2′,6,6′-tetrafluorobiphenyl.

The benzidine rearrangement[134] of 3,3′,5,5′-tetrafluorohydrazobenzene **(76)** was considered as this would afford 2,2′,6,6′-tetrafluorobenzidine (77) which may have been utilised as a outlined in *Scheme 11* (p. 125). However due to the carcinogenic nature of the benzidines, the reactions of *Scheme 11* were not attempted.

The Ullmann reaction[135] was also reviewed with the aim of synthesising 4,4′-diacetyl-2,2′,6,6′-tetrafluorobiphenyl **(80)** from the corresponding 3,5-difluoro-4-iodoacetophenone **(79a)**. The copper-catalysed homo-coupling of **(79a)** shown in *Scheme 12* (p. 126) proceeded both in the presence and absence of solvent (dimethylformamide) but gave rather poor yields (20-30%) due to de-iodination of the 3,5-difluoro-4-iodoacetophenone. The Baeyer-Villiger[136] oxidation of one acetyl group was attempted by treatment of the 4,4′-diacetyl-compound **(80)** with sodium perborate and trifluoroacetic acid, with the aim of obtaining 4-acetyl-4′-hydroxy-2,2′,6,6′-

tetrafluorobiphenyl (**82**). However the reaction was difficult to control and examination of the reaction mixture by t.l.c. revealed a variety of components which were inseparable by column chromatography. This route was therefore abandoned.

Gokel et al.[137] recently reported a modified Gomberg-Hey reaction[138] involving cross-coupling between halogenobenzenediazonium tetrafluoroborates and benzene, catalysed by crown ethers and potassium acetate, in high yield (>90%). Potassium acetate, phase transferred into non-polar solution by the presence of 18-crown-6, reacts with aryldiazonium ion, apparently forming a diazoanhydride. Decomposition of the diazoanhydride in the presence of arenes leads to the coupling products between aryl radicals and the arene.

$$\overset{+}{\mathrm{ArN_2}}\overset{-}{\mathrm{BF_4}} \;+\; \overset{+}{\mathrm{K}}\overset{-}{\mathrm{OAc}} \;\rightleftharpoons\; \mathrm{KBF_4} \;+\; \mathrm{Ar\text{-}N{=}N\text{-}OAc}$$

$$\mathrm{Ar\text{-}N{=}N\text{-}OAc} \;+\; \mathrm{AcO^-} \;\longrightarrow\; \mathrm{Ar\text{-}N{=}N\text{-}O^-} \;+\; \mathrm{Ac_2O}$$

$$\mathrm{Ar\text{-}N{=}N\text{-}O^-} \;+\; \mathrm{ArN_2^+} \;\longrightarrow\; \mathrm{Ar\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ar}$$

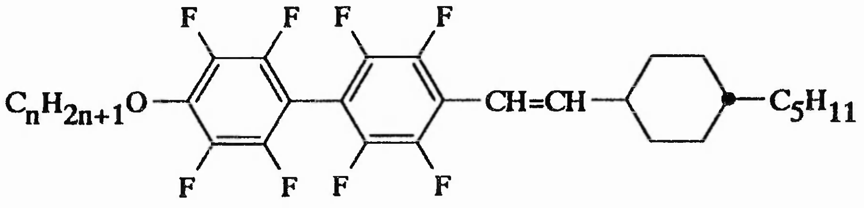
$$\mathrm{Ar\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ar} \;\longrightarrow\; \mathrm{Ar\text{-}N{=}N\text{-}O\cdot} \;+\; \mathrm{Ar^{\cdot}} \;+\; \mathrm{N_2}$$

$$\mathrm{Ar^{\cdot}} \;+\; \mathrm{C_6H_6} \;\longrightarrow\; \mathrm{ArC_6H_5}$$

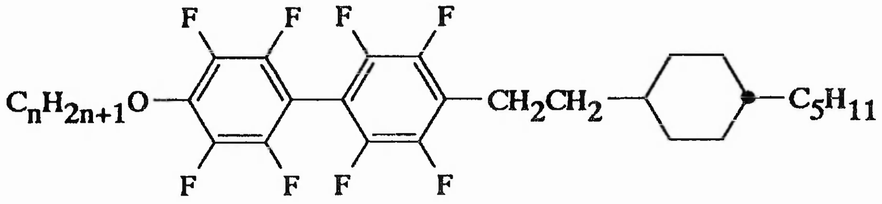
If coupling by this method could have been achieved, the reaction sequence shown in *Scheme 13* (p. 127) resulting in the formation of 4′-bromo-2,2′,6,6′-pentafluorobiphenyl (**85**) as a synthetically useful intermediate could have been attempted. However, although the coupling reaction mixture was stirred for one week at room temperature and monitored by t.l.c., again, there was no indication that any reaction had occurred.

3.2.1 LIQUID CRYSTALLINE PROPERTIES OF ALKYLARYL-ETHENES AND -ETHANES

1. 1-(4′-n-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes **(18a)** and -ethanes **(18b)**



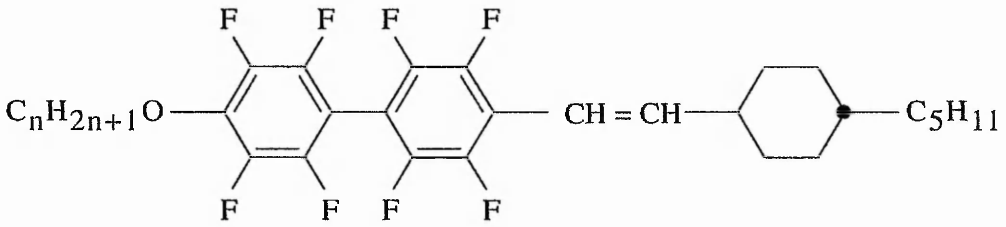
(18a)



(18b)

The liquid crystalline transition temperatures for the homologous series of alkylaryl-ethenes **(18a)** and the corresponding -ethanes **(18b)** derived from A2 are shown in ***Table 5***, and represented graphically in ***Figure 22a*** and ***22b***, as a plot against n, the number of carbon atoms in the alkyl chain.

Table 5 :	Alkylarylethenes **(18a)**		Alkylarylethanes **(18b)**		
n-Alkyl group	*C-N*	*N-I*	*C-I*	*C-N*	*N-I*
C_3H_7	*91*	*135*		*59*	*60.5*
C_4H_9	*74*	*134*	*66*		*(63.5)*
C_5H_{11}	*65*	*125*	*59*		*(54)*
C_6H_{13}	*62*	*123*		*53.5*	*56.5*
C_7H_{15}	*68*	*118*		*51*	*52*
C_8H_{17}	*71*	*115*		*41.5*	*52*
C_9H_{19}	*73*	*113*		*39.5*	*50.5*
$C_{10}H_{21}$	*76*	*112*		*40*	*50*



(18a)

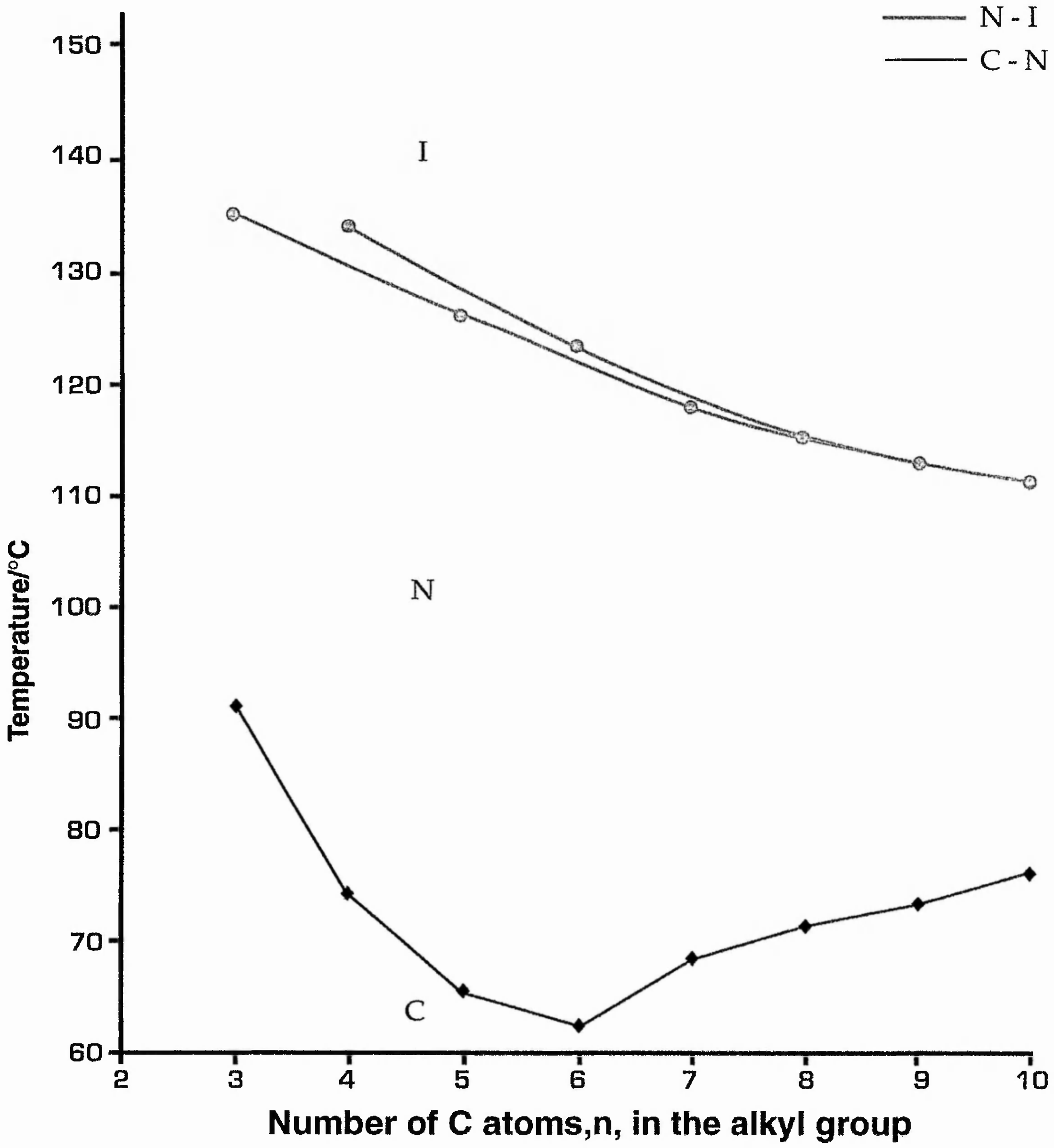
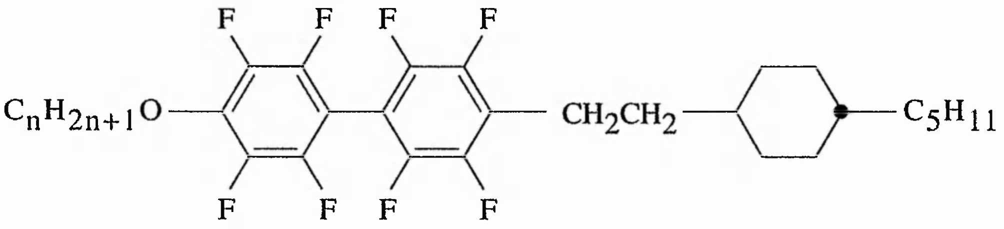


Figure 22a. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes (**18a**)



(18b)

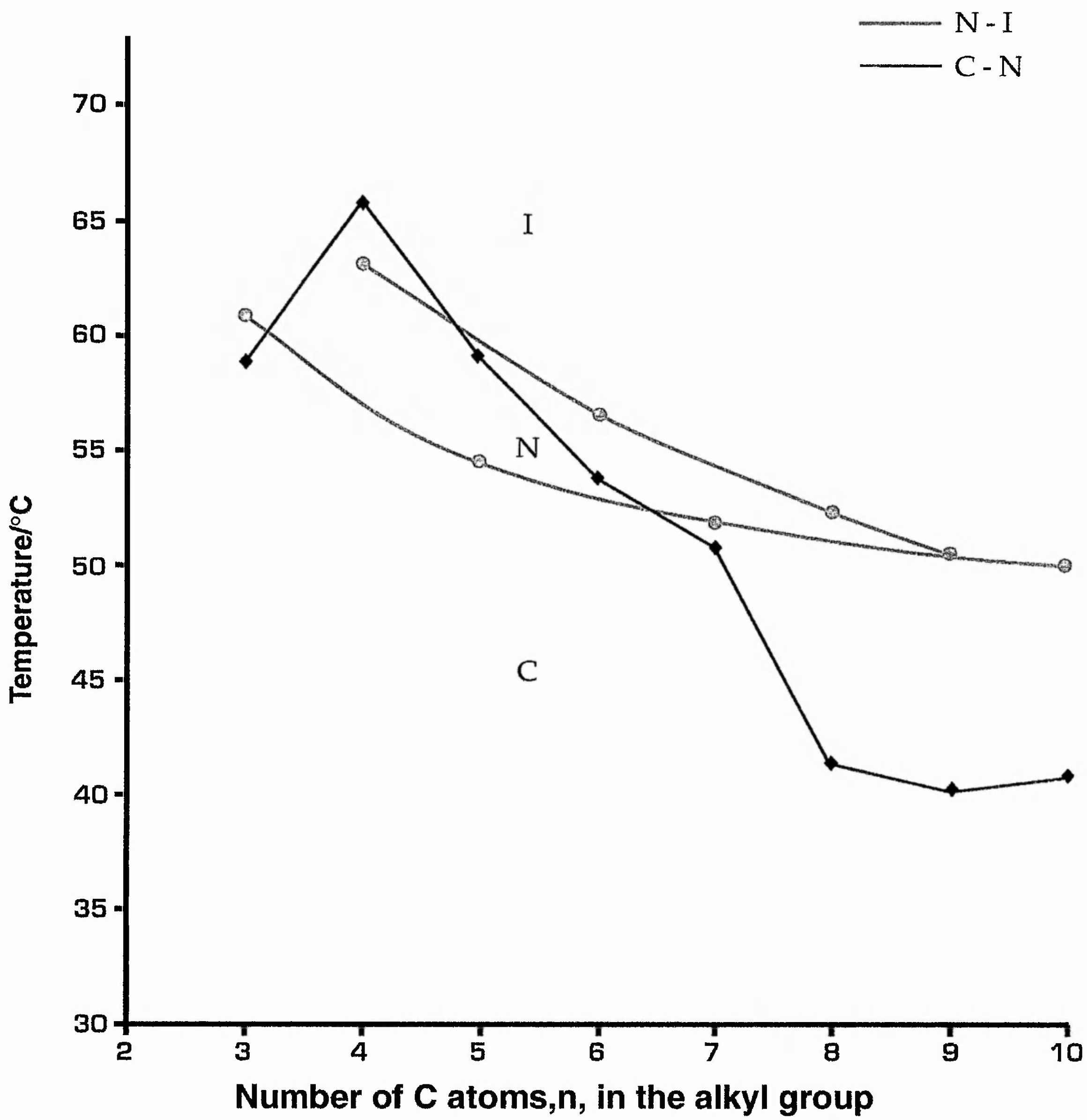
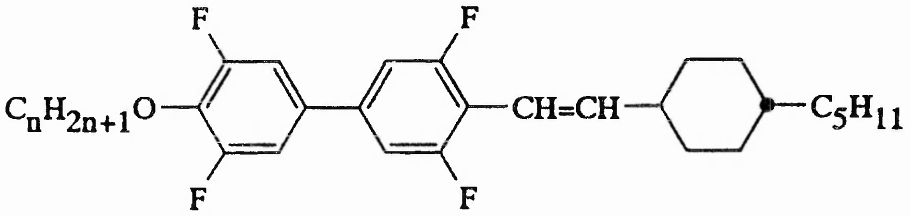
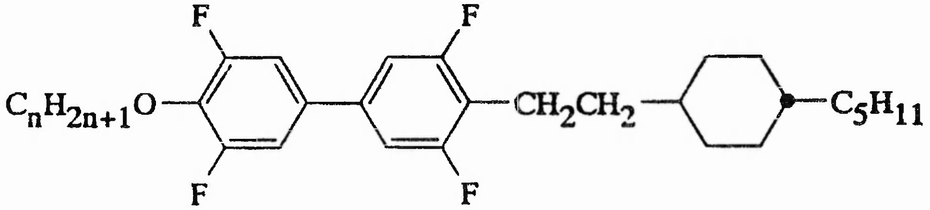


Figure 22b. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2,2',3,3',5,5',6,6'-octafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes (**18b**)

2. 1-(4′-n-alkoxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**55a**) and -ethanes (**55b**)



(55a)

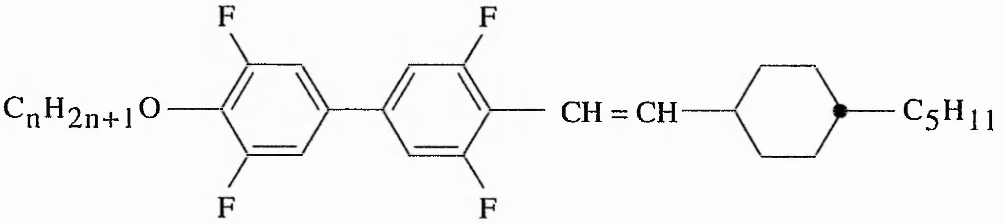


(55b)

The liquid crystalline transition temperatures for the homologous series of alkylaryl-ethenes (**55a**) and the corresponding -ethanes (**55b**) are shown in ***Table 6***, and represented graphically in ***Figure 23a*** and ***23b***, as a plot against n, the number of carbon atoms in the alkyl chain.

Table 6 :

	Alkylaryletheres (**55a**)			Alkylarylethanes (**55b**)			
n-Alkyl group	*C-S_A*	*S_A-N*	*N-I*	*C-N*	*C-S_A*	*S_A-N*	*N-I*
C_3H_7	32	118	178	57		(45)	97
C_4H_9	33	125	177	-	-	-	-
C_5H_{11}	31	132	168		38	73	88
C_6H_{13}	32	137	165		35	77	91
C_7H_{15}	34	136	157		32	77	85
C_8H_{17}	-	-	-		33	77.4	86



(55a)

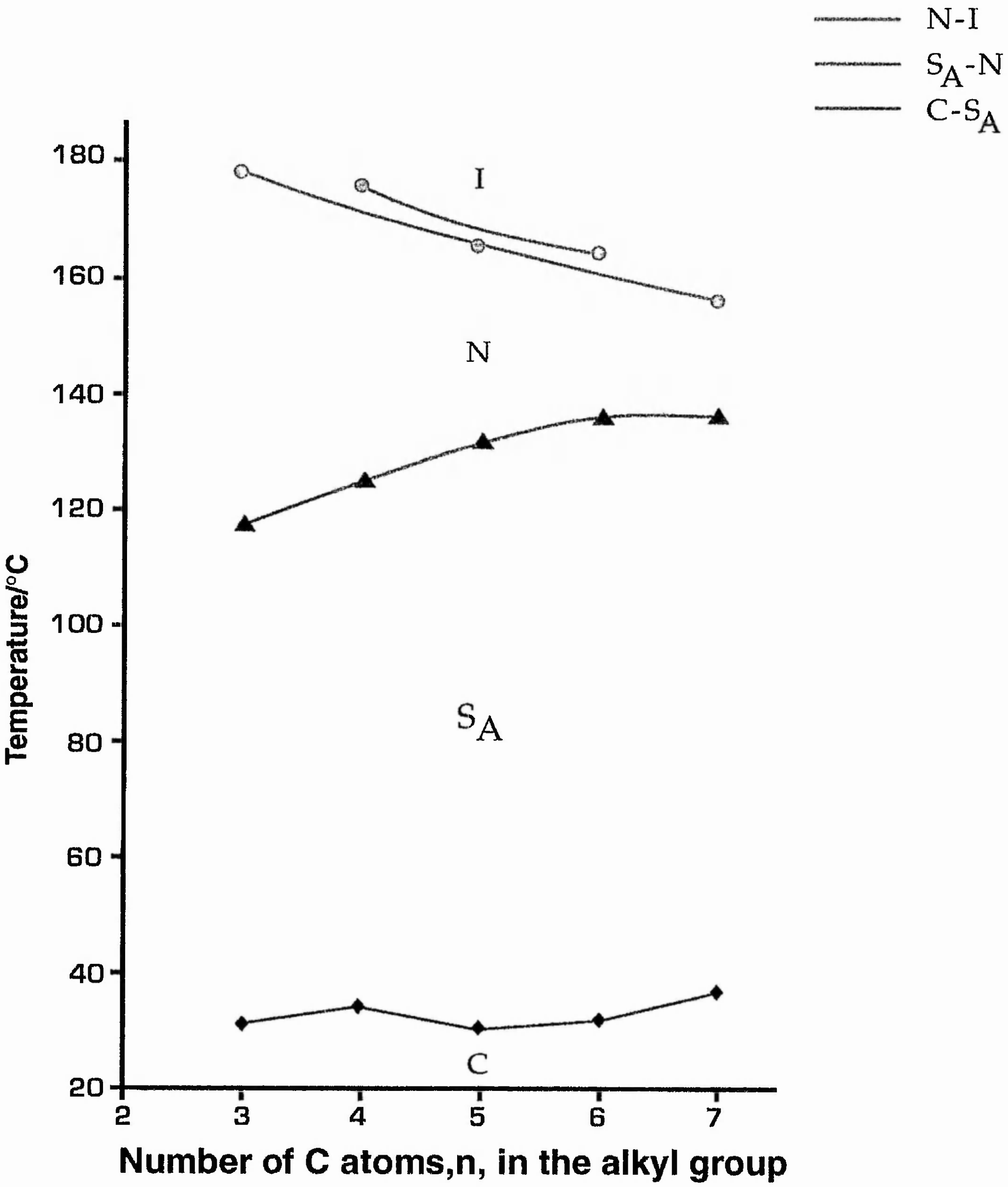
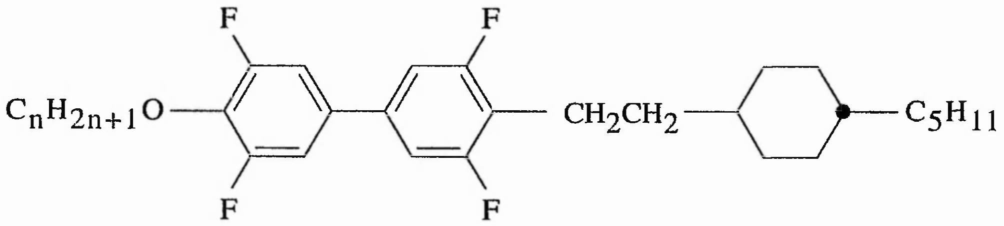


Figure 23a. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 3,3',5,5'-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes (**55a**)



(55b)

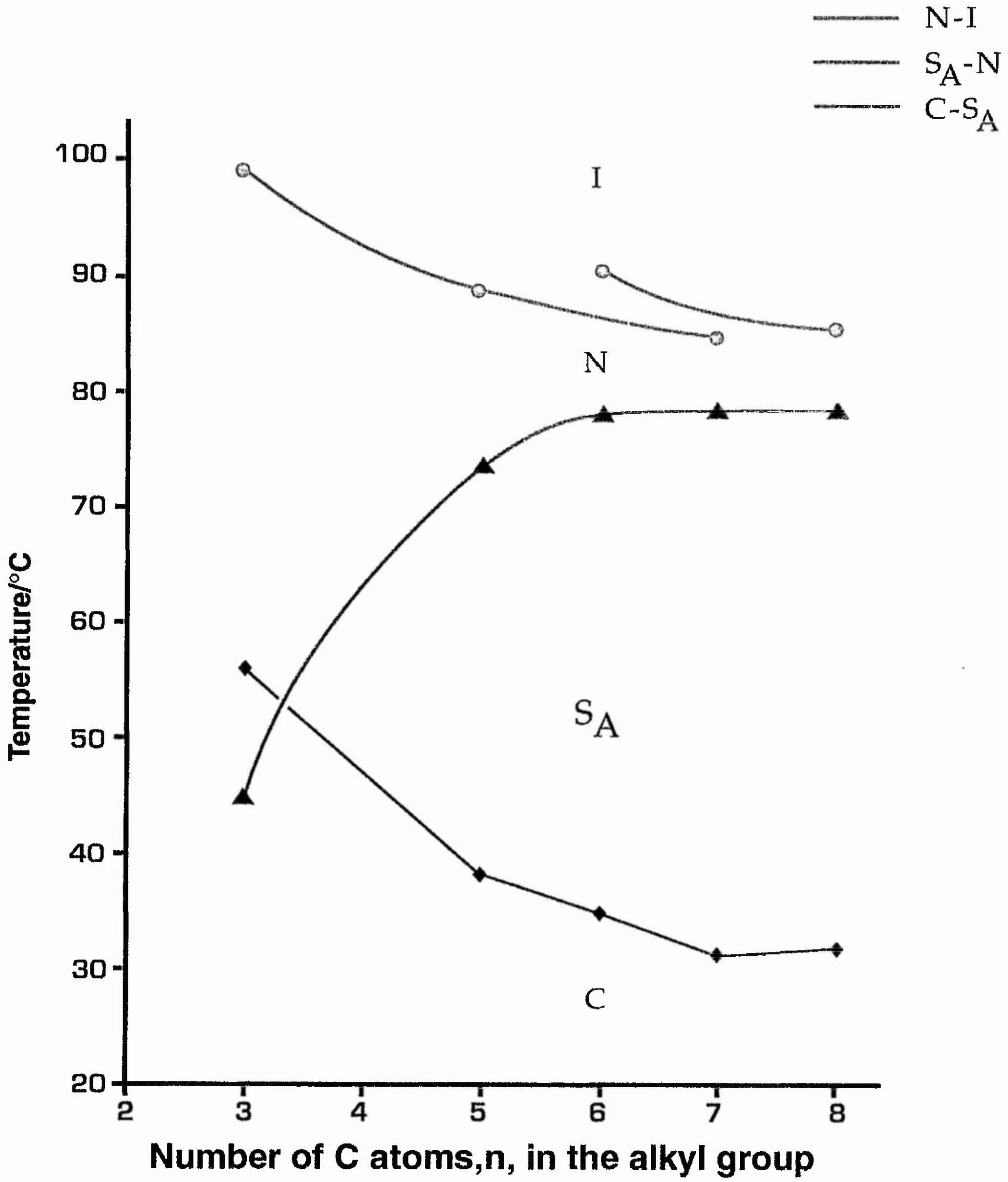
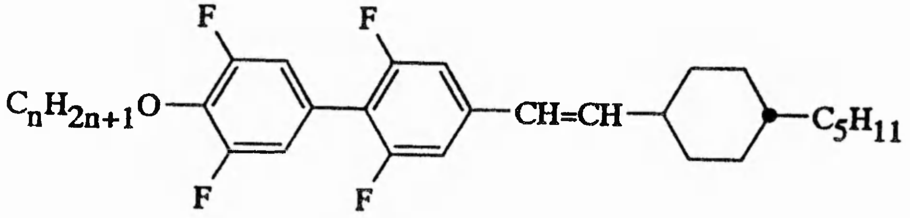
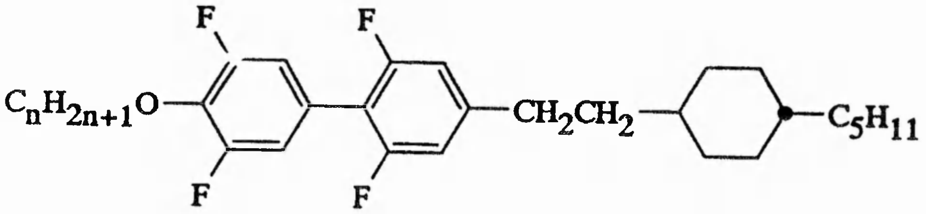


Figure 23b. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 3,3',5,5'-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes (**55b**)

3. 1-(4'-n-alkoxy-2,3',5',6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**62a**) and -ethanes (**62b**)



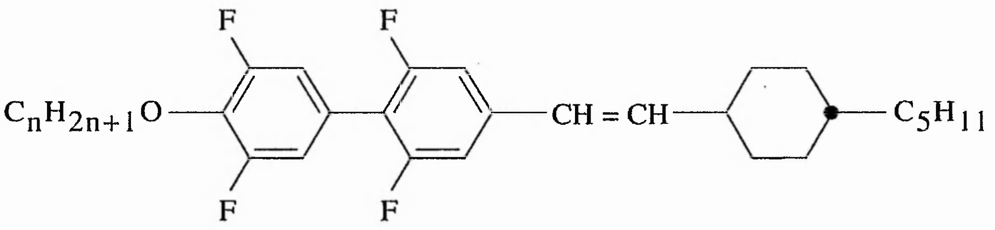
(62a)



(62b)

The liquid crystalline transition temperatures for the homologous series of alkylaryl-ethenes (**62a**) and the corresponding -ethanes (**62b**) are shown in ***Table 7***, and represented graphically in ***Figure 24a*** and ***24b***, as a plot against n, the number of carbon atoms in the alkyl chain.

Table 7 :	Alkylarylethenes (**62a**)			Alkylarylethanes (**62b**)		
n-Alkyl group	*C-S_A*	*S_A-N*	*N-I*	*C-S_A*	*S_A-N*	*N-I*
C_5H_{11}	78	112	138	31	65	81
C_6H_{13}	70	110	129	31	79	80
C_7H_{15}	72	106	123	30	75	73
C_8H_{17}	69	107	122	31	68	76
C_9H_{19}	71	101	105			
$C_{10}H_{21}$	68	104	118			



(62a)

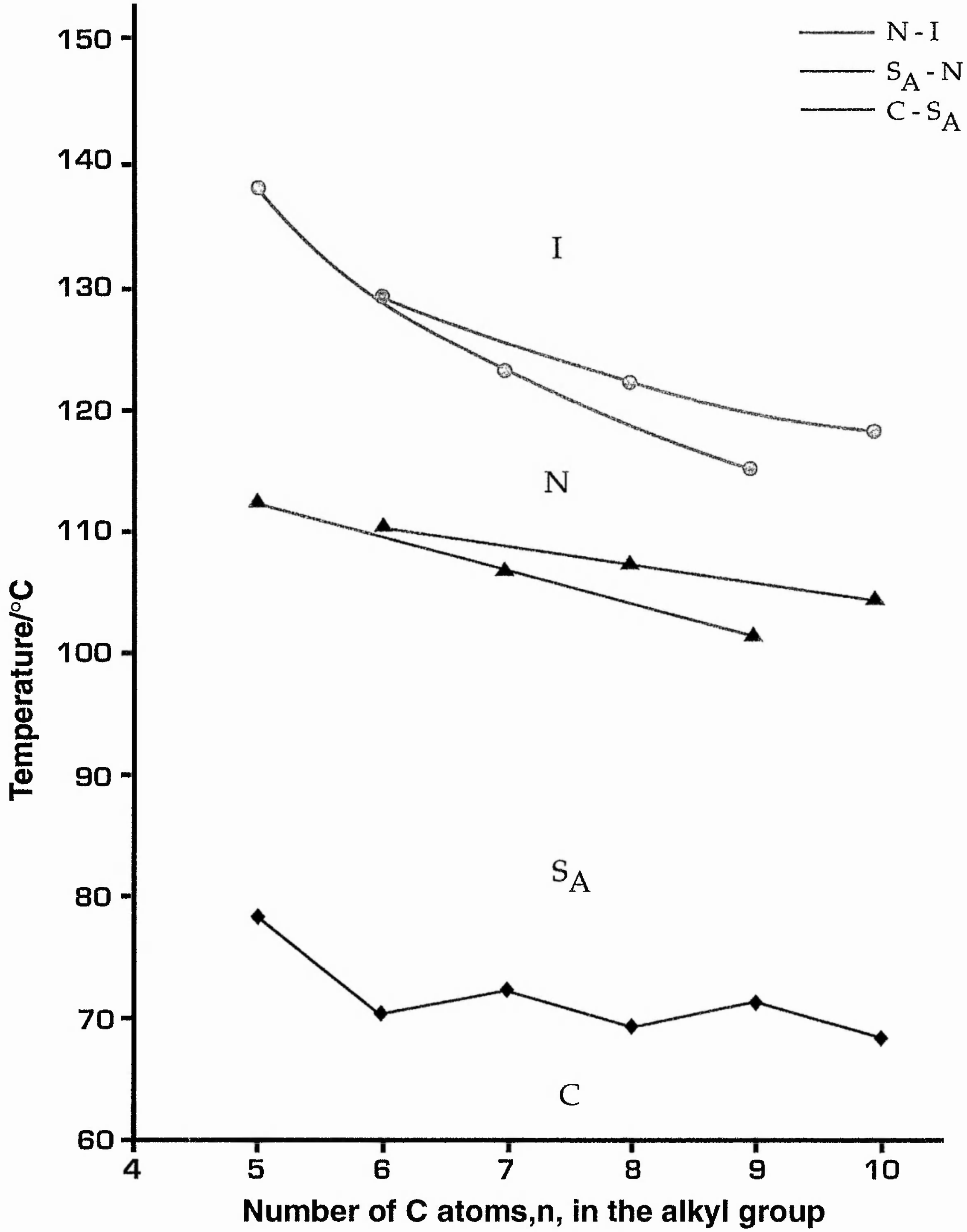
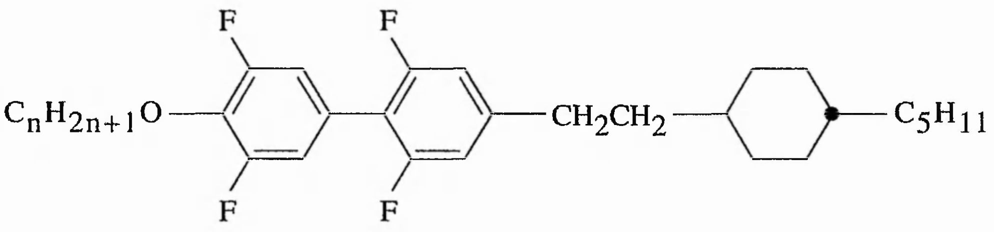


Figure 24a. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2,3',5',6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes (**62a**)



(62b)

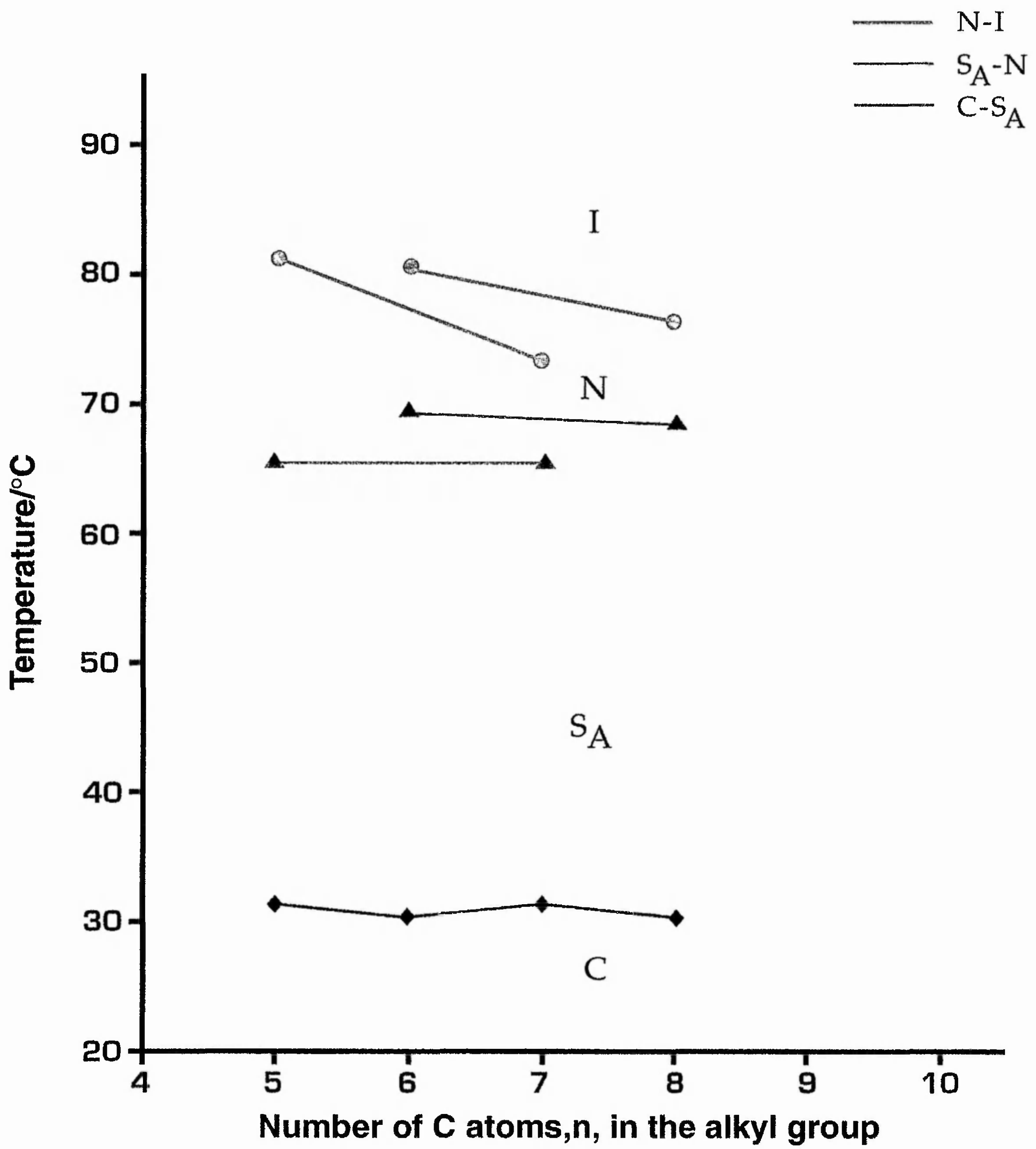
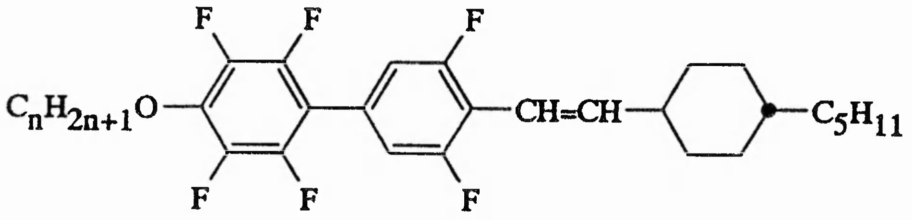
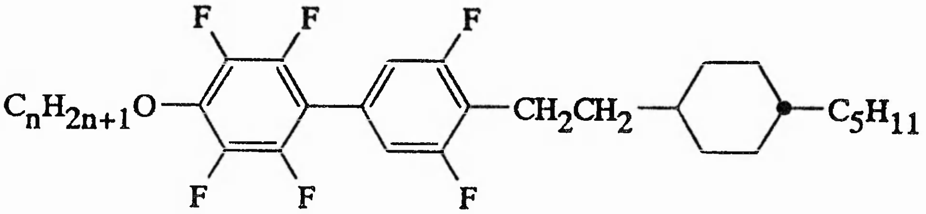


Figure 24b. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2,3',5',6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes (**62b**)

4. 1-(4′-n-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**68a**) and -ethanes (**68b**)



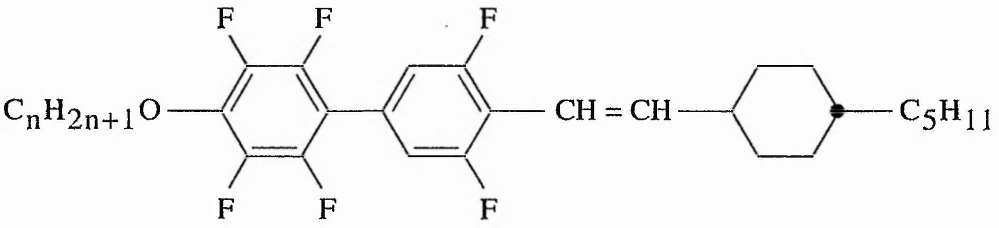
(68a)



(68b)

The liquid crystalline transition temperatures for the homologous series of alkylaryl-ethenes (**68a**) and the corresponding -ethanes (**68b**) are shown in ***Table 8***, and represented graphically in ***Figure 25a*** and ***25b***, as a plot against n, the number of carbon atoms in the alkyl chain.

Table 8 :	Alkylarylethenes (**68a**)		Alkylarylethanes (**68b**)		
n-Alkyl group	*C-N*	*N-I*	*C-I*	*C-N*	*N-I*
C_5H_{11}	*85*	*136*	*69*		*(65)*
C_6H_{13}	*77*	*136*		*55*	*65.5*
C_7H_{15}	*69*	*121*		*53.5*	*61.5*
C_8H_{17}	*67*	*123*		*59*	*63*
C_9H_{19}	*74*	*118*		*60*	*61*
$C_{10}H_{21}$	*59*	*118*		*59*	*62*



(68a)

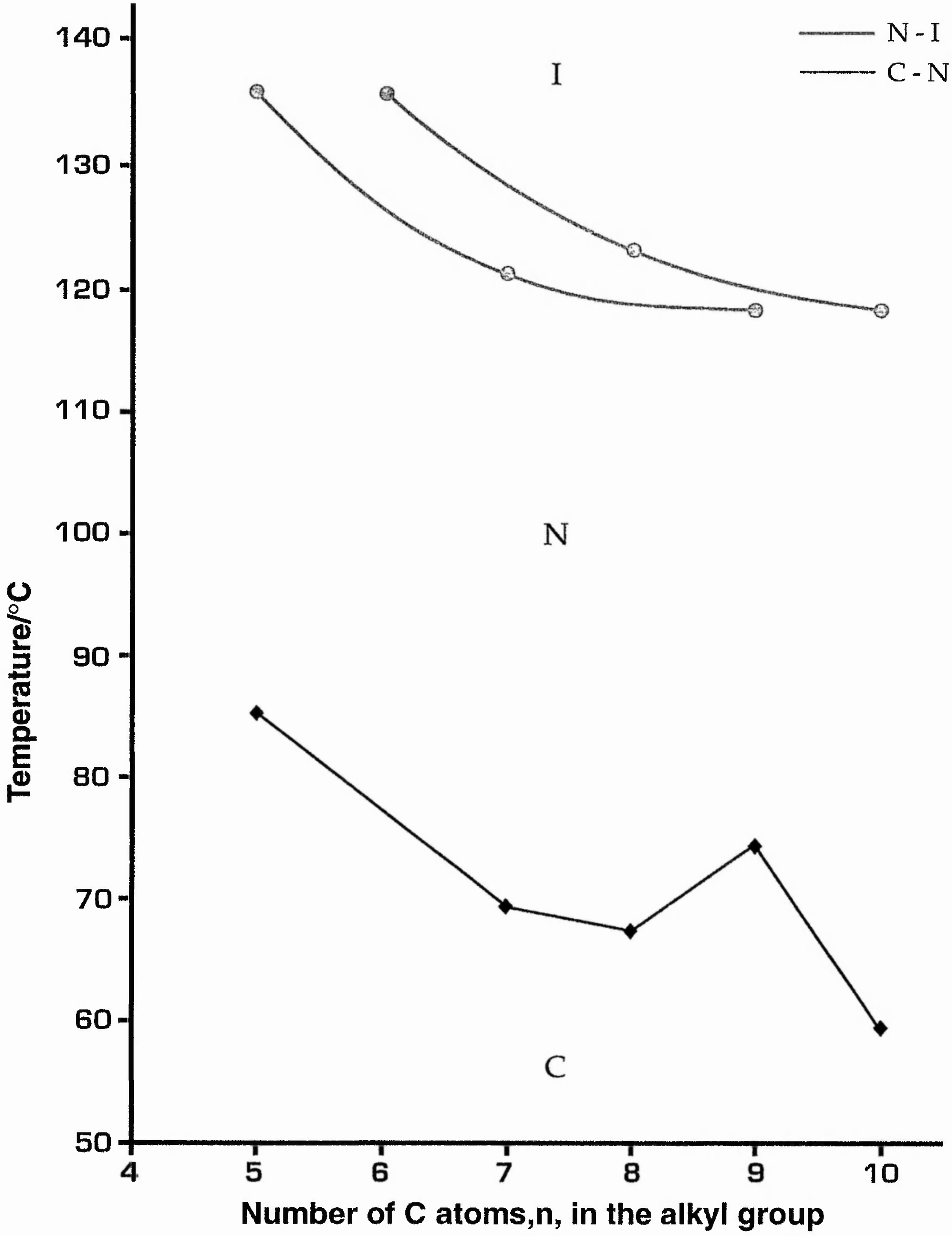
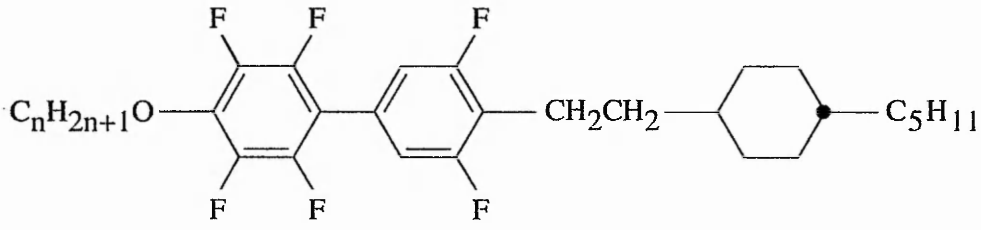


Figure 25a . Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2',3,3',5,5',6'-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes (**68a**)



(68b)

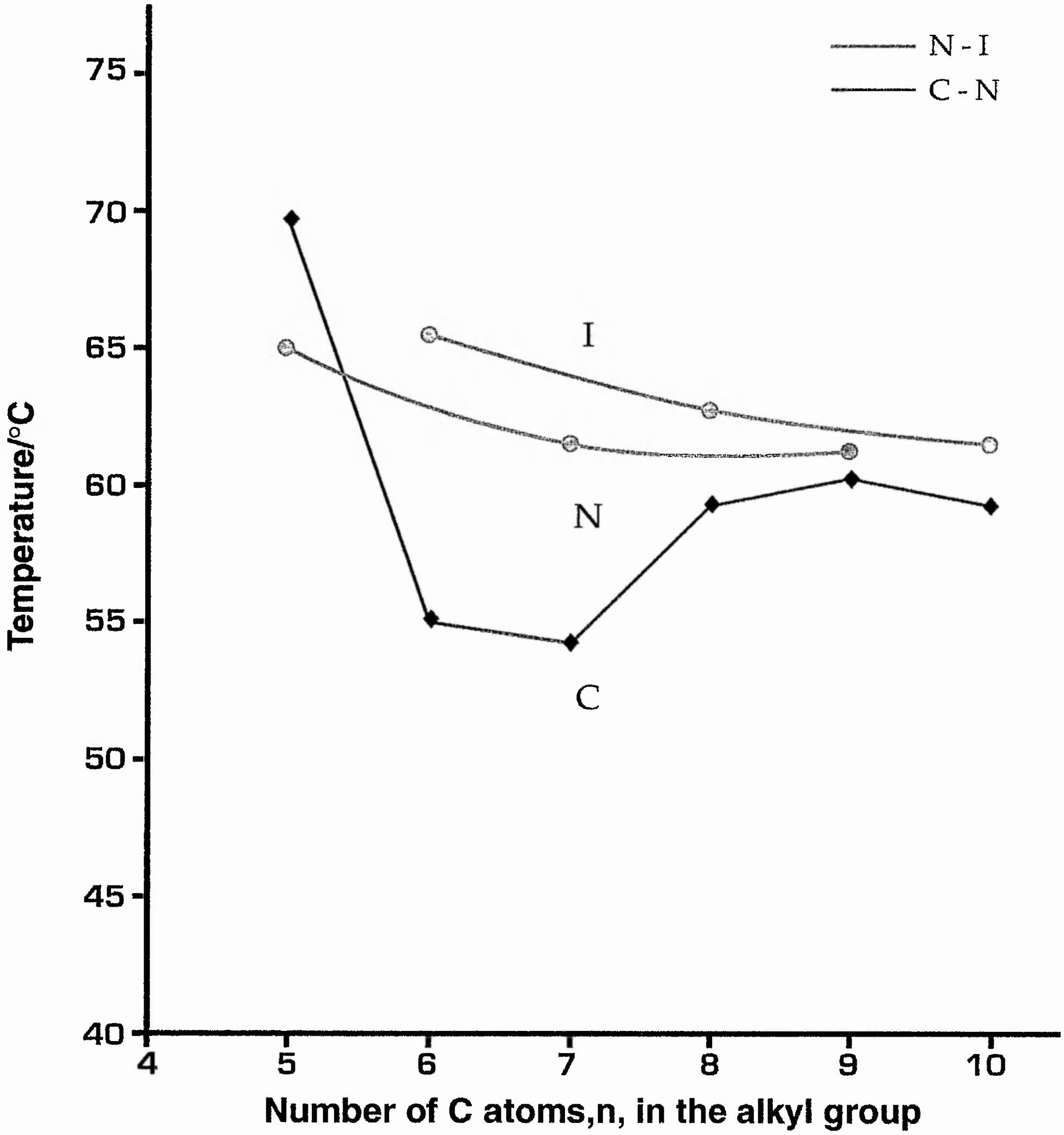
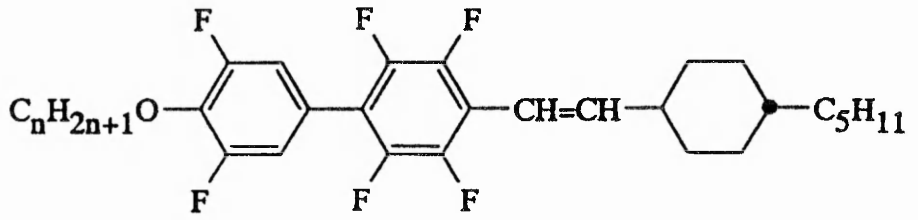
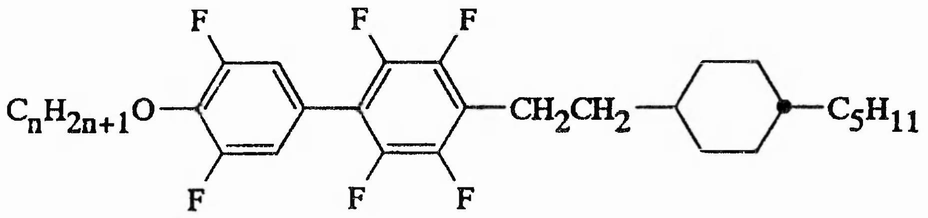


Figure 1. Plot of transition temperatures for certain 1-(4'-n-alkoxy-2',3,3',5,5',6'-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes (**68b**)

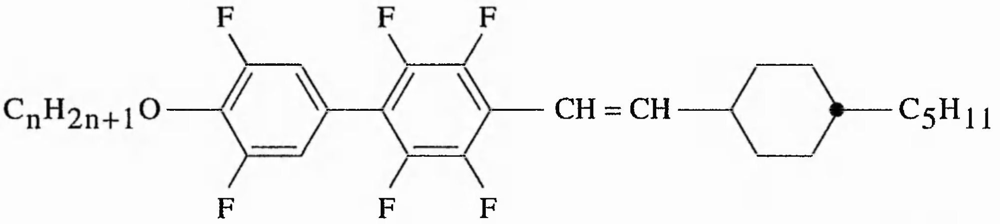
5. 1-(4′-n-alkoxy-2,3,3′,5.5′,6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (**69a**) and -ethanes (**69b**)


(69a)


(69b)

The liquid crystalline transition temperatures for the homologous series of alkylaryl-ethenes (**69a**) and the corresponding -ethanes (**69b**) shown in ***Table 9***, are represented graphically in ***Figure 26a*** and ***26b***, as a plot against n, the number of carbon atoms in the alkyl chain.

Table 9 :	Alkylarylethenes (**69a**)			alkylarylethanes (**69b**)		
n-Alkyl group	*C-S_A*	*S_A-N*	*N-I*	*C-I*	*C-N*	*N-I*
C_5H_{11}	*54*	*112*	*142*		*64.5*	*69*
C_7H_{15}	*57*	*104*	*129*	*63*		*(60)*
C_8H_{17}	*58*	*105*	*129*		*59.5*	*66*
C_9H_{19}	*54*	*97*	*119*	*64.5*		*(59.5)*
$C_{10}H_{21}$	*58*	*101*	*122*	*64*		*(63.5)*



(69a)

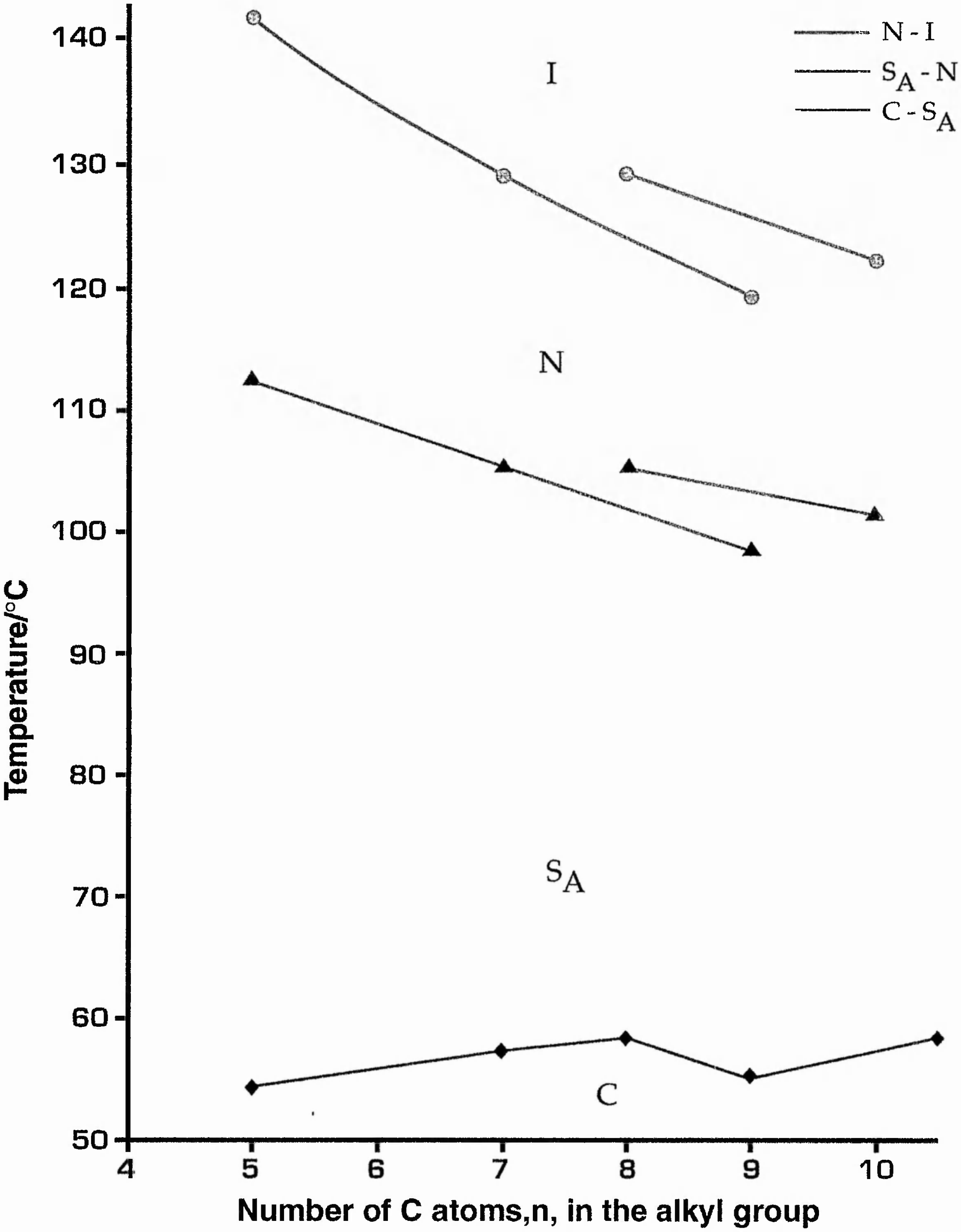
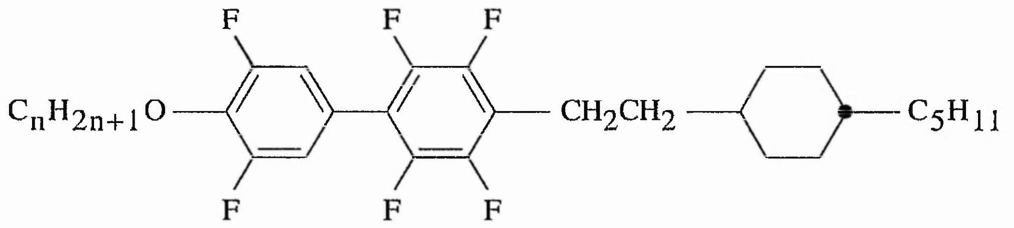


Figure 26a . Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2,3,3',5,5',6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes (**69a**)



(69b)

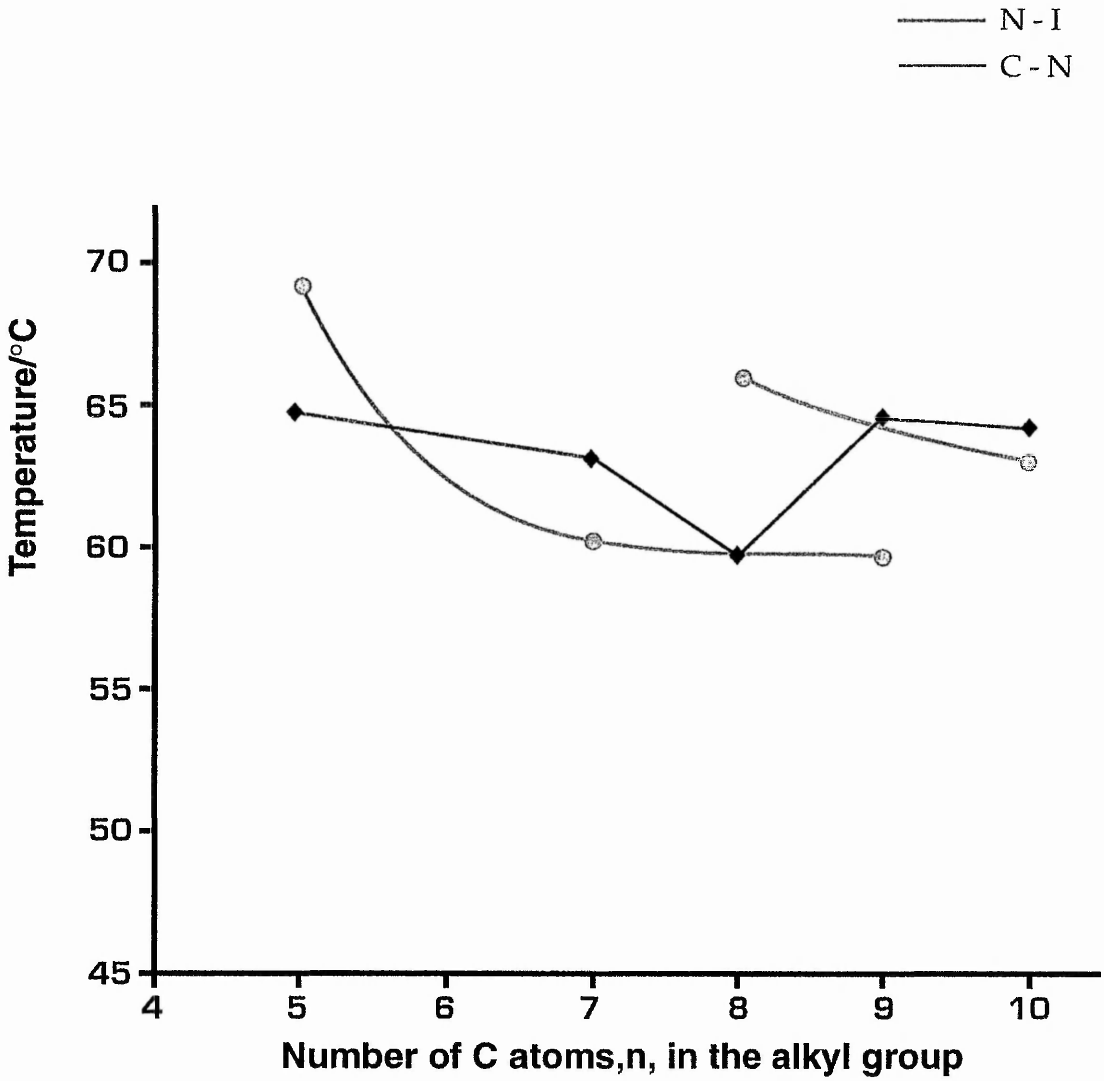


Figure 26b. Plot of transition temperatures for certain 1-(4'-n-alkoxy - 2,3,3',5,5',6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes (**69b**)

In general the members of the homologous series **(18a)**,**(18b)**, **(68a)**,**(68b)** and **(69b)** are nematogens and the points for the N-I transition temperatures alternate and lie on two curves which fall as n increases, with points for the even-n homologues on the uppermost curve. The curves tend to become convergent at the higher homologues ($n > 8$) except for homologous series **(69b)**.

However, members of the homologous series **(55a)**,**(55b)**, **(62a)**,**(62b)** and **(69a)** give rise to following sequence of phases on heating.

$$C - S_A - N - I$$

The points for the N-I transition temperatures lie on two curves and show the usual odd/even-n alternation. In homologous series **(62a)** the alternation begins after the n=6 homologue.

A similar trend is also observed for the points for the S_A-N transition temperatures which alternate and lie on two curves. However for homologous series **(55a)** and **(55b)**, the points for the S_A-N transition temperatures lie on a smooth curve which initially rises and then gradually decreases peaking at the n=6 and 7 homologues.

3.2.2 COMPARISON OF THE LIQUID CRYSTALLINE PROPERTIES OF ALKYLARYL-ETHENES AND -ETHANES DERIVED FROM A POLY-FLUORINATED BIPHENYL SYSTEM CARRYING FOUR, SIX, OR EIGHT FLUORO-SUBSTISTUENTS

The average S_A-N and N-I transition temperatures for each of the homologous series (n=5,6,7,8) are shown in ***Table 10.*** In general, the results listed in ***Table 10*** show that for corresponding pairs of homologous series, replacement of the ethene linkage, -CH=CH- , by the ethane linkage, $-CH_2CH_2-$, results in the following two effects:

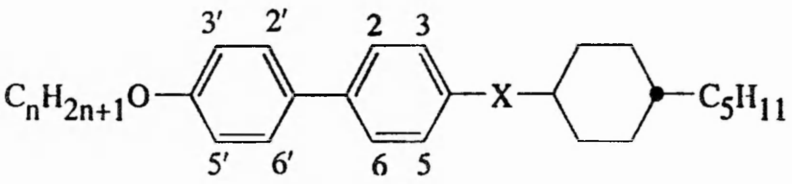
1. A reduction in the crystal to mesophase transition temperature.
2. A reduction in the S_A-N and the N-I transition temperatures (the alkylarylethenes give more thermally stable mesophases).

On increasing the number of fluoro-substituents (from four, to six, to eight) in either the alkylaryl-ethenes or -ethanes, the average S_A-N and N-I transition temperatures decrease. The alkylarylethenes are more severely affected and the extent of the reduction in mesophase thermal stability is dependent upon both the number and position of fluoro-substituents present.

Gray, Hird and Toyne[86] have rationalised the effect of fluoro-substitution on mesophase type and transition temperatures. They identified three major factors which influence the type and the thermal stability of the mesophases obtained:

1. Broadening of the molecule;
2. twisting about the inter-annular bond, and;
3. the presence of *inner* or *outer* fluoro-substituents.

Table 10. Influence of the position and number of fluoro-substituents on the average liquid crystalline transition temperatures of certain alkylaryl-ethenes and -ethanes containing a polyfluorinated biphenyl unit



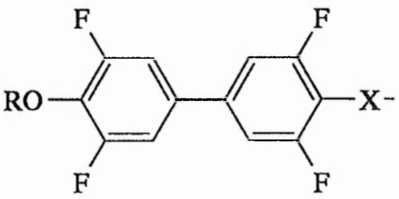
	X = -CH=CH-				X = -CH_2CH_2-		
Position of fluoro-substituents	homologous series	average S_A-N	average N-I		homologous series	average S_A-N	average N-I
3′,2′, 2,3 5′,6′, 6,5	**(18a)**	-	120		**(18b)**	-	53.6
3′,2′, 3 5′,6′, 5	**(68a)**	-	129		**(68b)**	-	63.5
3′ 2,3 5′ 6,5	**(69a)**	107	134		**(69b)**	-	66
3′ 3 5′ 5	**(55a)**	133	163		**(55b)**	76	87
3′ 2 5′ 6	**(62a)**	108	128		**(62b)**	67	77

The influence of these factors is considered in the following discussion in which the alkylaryl-ethenes and -ethanes are sub-divided in terms of the number of fluoro-substituents present.

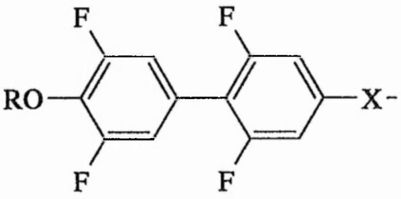
1. Four fluoro-substituents

When four fluoro-substituents are located in the positions indicated in **(55a)**, **(55b)** and **(62a)**, **(62b)** both the ethene and the ethane series of compounds give rise to the following sequence of transitions

$$C - S_A - N - I$$



(55b)
(55a)

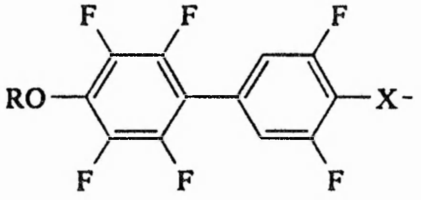


(62a)
(62b)

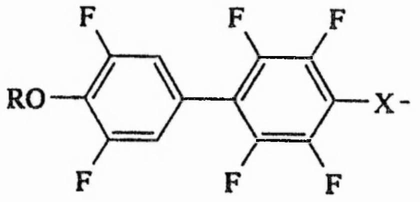
However, the average N-I and S_A-N transition temperatures are greater for compounds containing the 3,3′,5,5′-tetrafluorobiphenyl unit **(55a)**, **(55b)** than for compounds with the isomeric 2,3′,5′,6-tetrafluorobiphenyl unit **(62a)**, **(62b)**. With the latter disposition of substituents, the two fluoro-substituents located *ortho-* to the ring junction cause substantial twisting of the fluorinated biphenyl system about the inter-ring bond (resulting in the planes of the rings being inclined at approx. 57°). This steric twisting effectively increases the molecular breadth or thickness and disrupts the efficiency of the lath-like packing arrangement of the molecules in the mesophase and results in a lowering of the mesophase thermal stability. The steric twisting will also interfere with inter-ring conjugation hence reducing the overall molecular polarisability.

2. Six fluoro-substituents

The presence of four fluoro-substituents located on the right hand, centrally disposed ring of the biphenyl unit **(69a)** gives rise to compounds possessing both S_A and nematic mesophases. In the isomeric series, when four fluoro-substituents are located on the left hand terminal ring **(68a)**, **(68b)** the compounds of both the ethene and ethane series exhibit only a nematic phase.



(68a)
(68b)



(69a)
(69b)

A possible explanation may be associated with the direction in which the electronegative fluoro-substituents are oriented. In the unit **(69a)** the 3- and 5′- and 3′- and 5- fluoro-substituents point in opposite directions and therefore their effects cancel each other out. This leaves the 2- and 6-substituents to point outwards, away from the central core, towards the terminal alkoxy-group. In this situation, the smectic properties are retained. In contrast, in the unit **(68a)**, **(68b)** the 3,3′- and 5,5′- fluoro-substituents again have their effects cancelled out leaving the 2′- and 6′- fluoro-substituents pointing inwards towards the central linking group. With this substitution pattern the smectic properties are lost but the nematic character is maintained.

3.2.3 PHYSICAL PROPERTIES OF MEMBERS OF THE HOMOLOGOUS SERIES (18b)

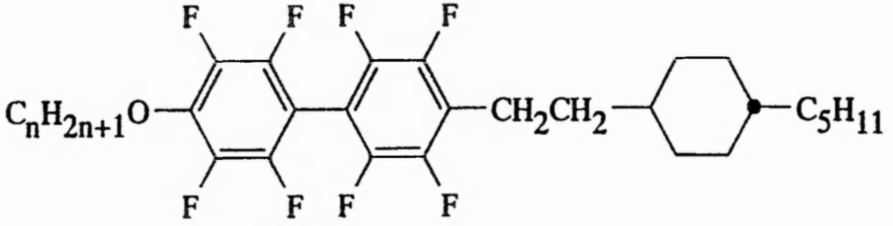
In order to gain a brief insight into the various techniques employed to determine some of the physical properties of a liquid crystalline material, a period of one week was spent at Merck Ltd. The physical properties of the members of the homologous series **(18b)** were investigated and ***Table 11*** lists the results of the measurements made.

In general, to determine the physical properties of a nematic liquid crystal it has to be incorporated into a suitable host. Many guest-host combinations, for example those between non-polar and highly polar compounds, are complicated by the occurrence of injected smectic phases which are undesirable. Another important criterion is miscibility as it is essential that the components are miscible in each other.

The compounds under investigation were incorporated into a non-polar liquid crystalline host ZLi-3086 which consists of a mixture of phenylcyclohexanes. To ensure complete miscibility the compounds were mixed with ZLi-3086 at a 10% loading. The physical properties were measured and then extrapolated for the pure compound.

The results shown in ***Table 11***, clearly reveal that ZLI-3086 is not a suitable host . For example, the extrapolated N-I values are totally inaccurate. The large variation between the extrapolated N-I values with respect to the actual N-I values (***Table 5***, p. 92) for members of the homologous series **(18b)** infers extreme non-ideal

Table 11. Physical properties of certain 1-(4′-n-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethanes (**18b**)



(18b)

n=	Δn	η/cSt	N-I	Δε	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon/\varepsilon_{\perp}$
3	0.097		-2.7	5.64	2.55	-3.09	-1.82
4	0.094		-5.6	2.19	3.70	1.51	1.45
5	0.077	72	4.1	0.39	4.19	3.80	0.10
6	0.093		36.6	-3.50	-0.98	2.52	-1.38
7	0.074	89	-20.0	-0.69	1.80	2.49	-0.28
8	0.05		-5.6	-0.32	2.51	2.83	-0.11
9	0.04		-2.1	-2.51	-0.11	2.40	-1.04
10	0.086	81					

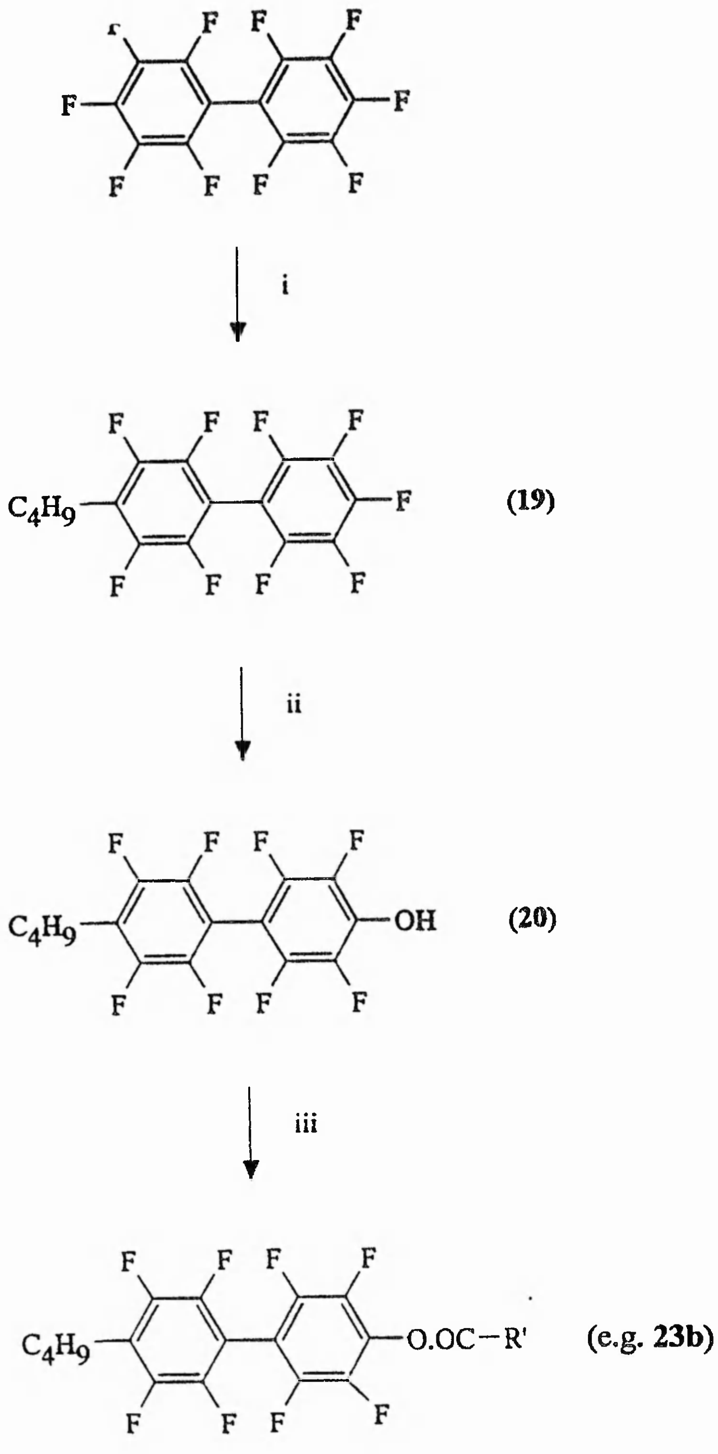
behaviour of the mixture. In addition, the *negative* values obtained for the dielectric anisotropy of certain members appear to be anomalous and indicative of a structure containing strong lateral dipoles. However, this is inconsistent with the symmetrical structure of the octafluorobiphenyl core, in which the opposing transverse dipoles cancel out each other so that the dielectric anisotropy should be approximately equal to zero. Whether or not the negative values for the dielectric anisotropy can be attributed to the extreme non-ideality of the mixture or to errors in measuring the capacitance of the cell or even a combination of both factors is not clear.

Other results listed in ***Table 11***, which may not be too inaccurate due to the unsuitability of the host, indicate that:

1. The compounds have a moderate viscosity, values of which range from 70-90 cSt;
2. the compounds possess very low birefringence (Δn approx. 0.1)

The results obtained in ZLI-3086 are clearly unreliable and, in some cases, meaningless, and it is evident that the host-dependent effect needs further investigation. However, due to the limited time available at Merck Ltd., other more appropriate hosts, i.e. those containing fluorinated compounds, were not tried. It is envisaged that the incorporation of members of the homologous series (**18b**) into a suitable fluorinated host would result in more ideal behaviour of the mixture and enable less anomalous results to be obtained.

REACTION SCHEMES



(19)

(20)

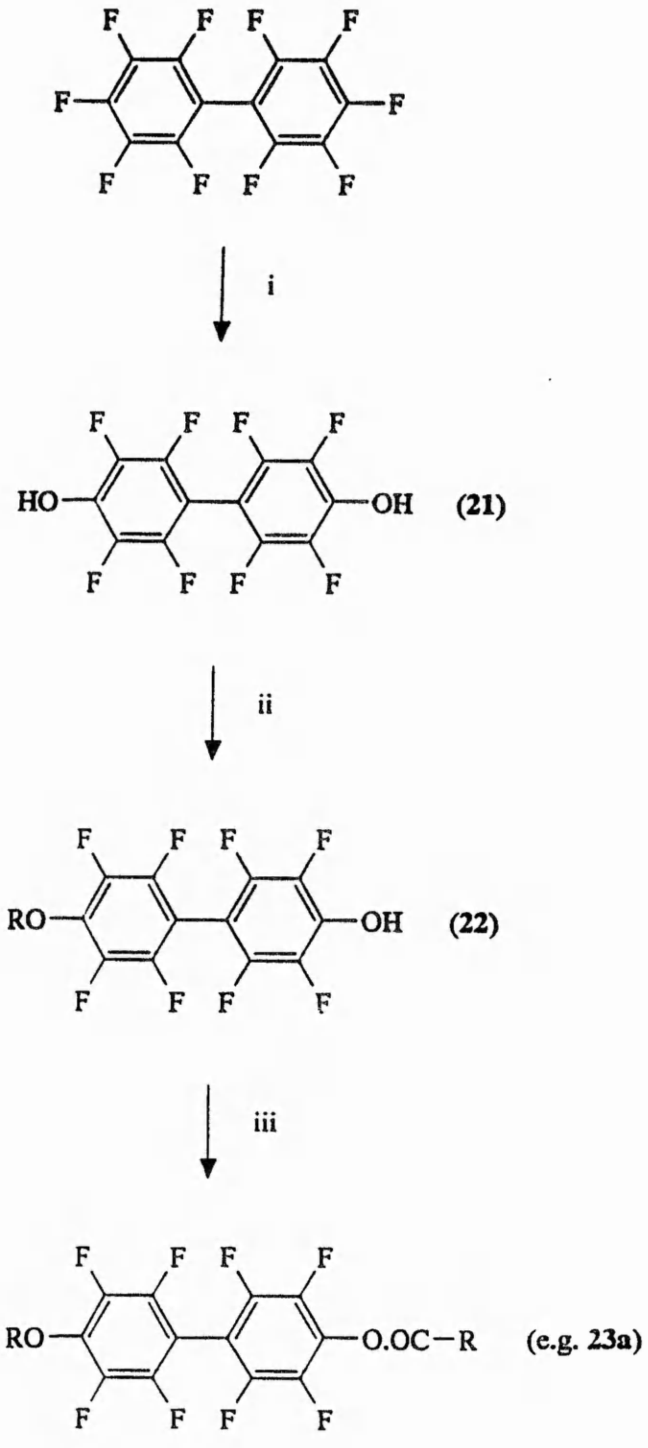
(e.g. **23b**)

i. 1.6M BuLi, N_2, -20°C

ii. KOH, *tert*-BuOH, reflux

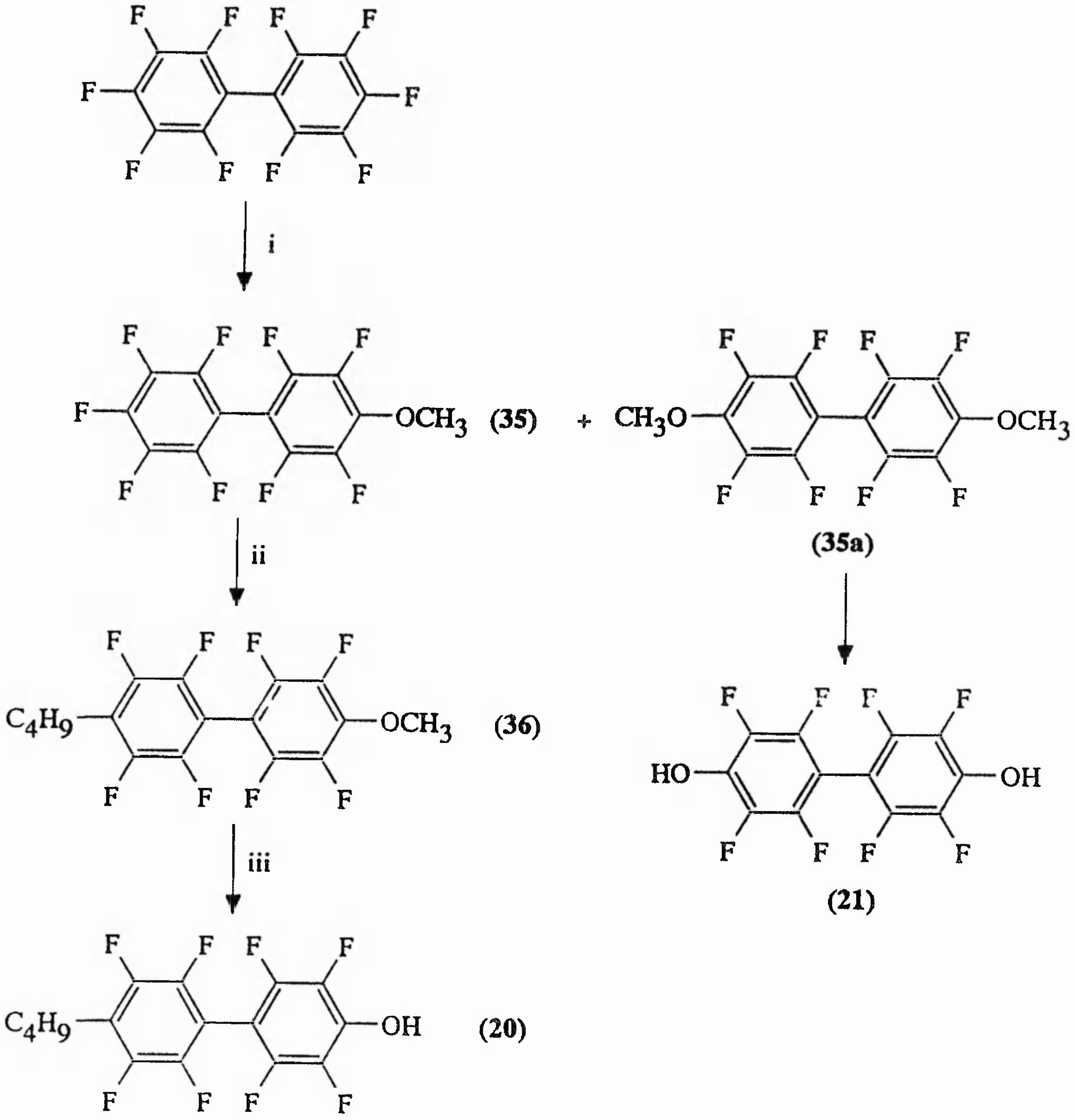
iii. R'CO_2H, DCC, DCM, room temp.

Scheme 1



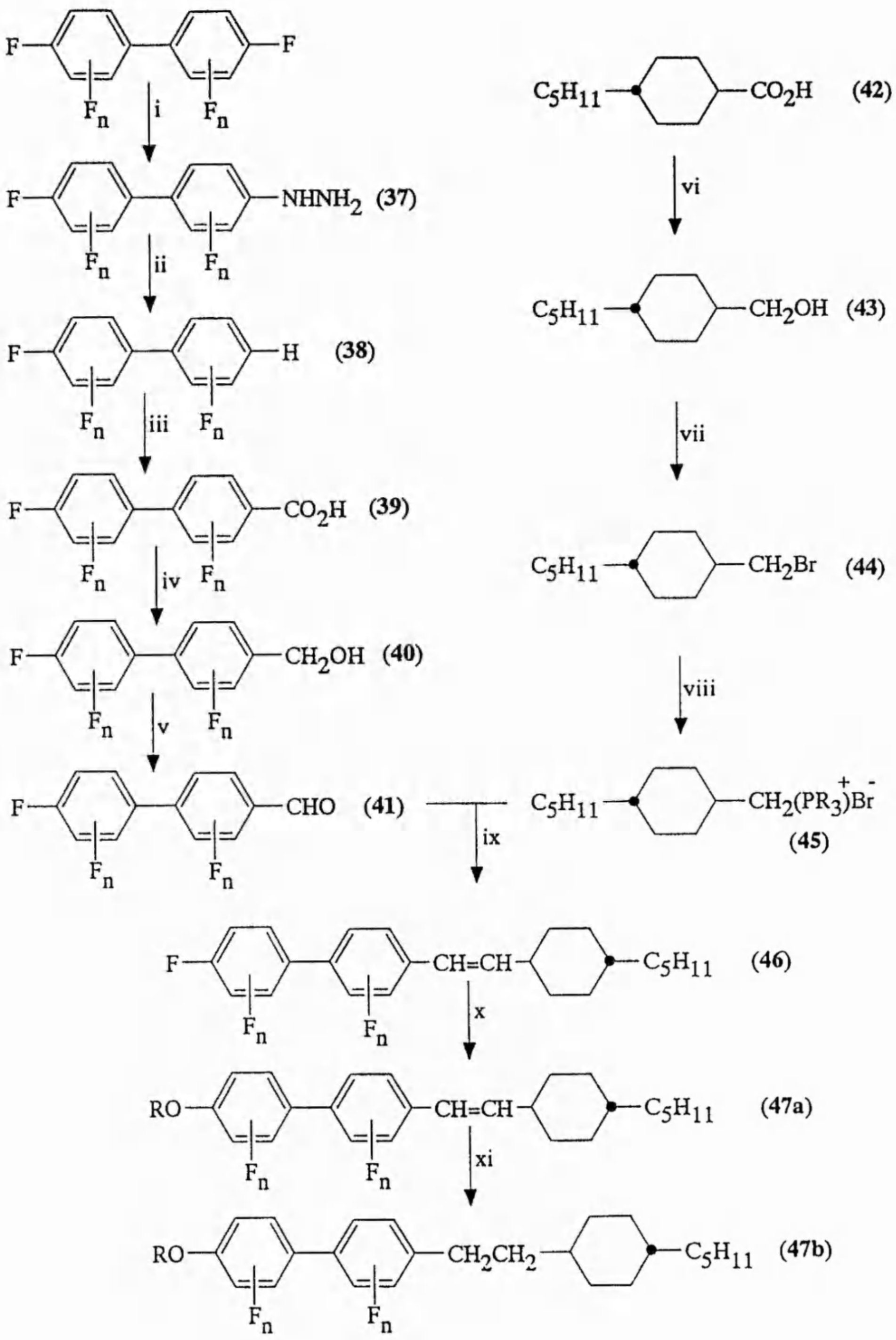
- i. KOH, *tert*-BuOH, reflux
- ii. RBr, KOH, EtOH, reflux
- iii. R′CO_2H, DCC, DCM, room temp.

Scheme 2



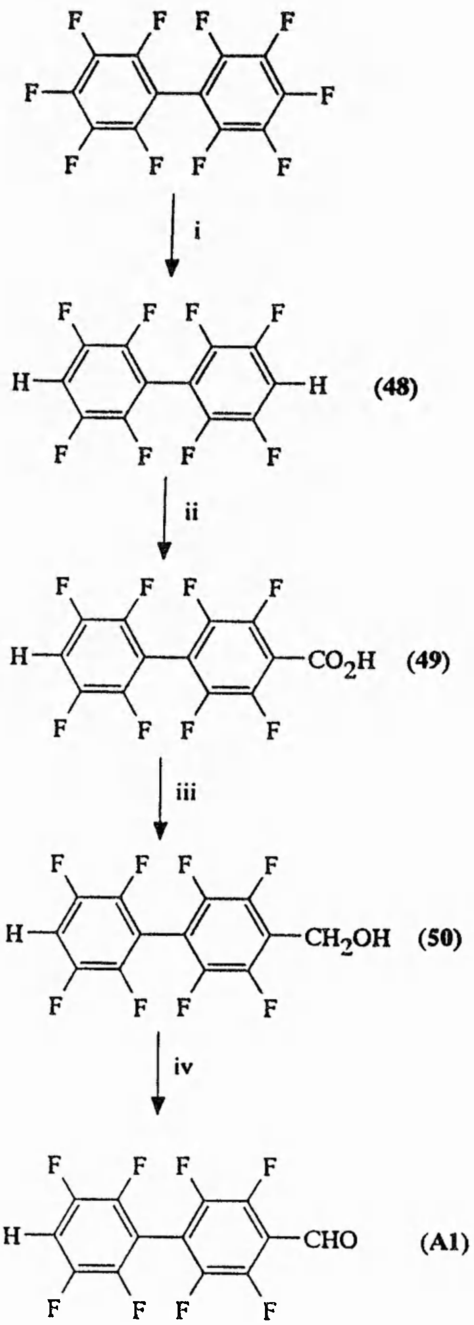
i. NaH, MeOH, pyridine
ii. 1.6M BuLi, -20°C
iii. BBr_3, DCM, -20°C to room temp.

Scheme 3



i.	NH_2NH_2, dioxane, reflux	vii.	H_2SO_4,/HBr, reflux
ii.	$CuSO_4$, EtOH, reflux	viii.	P(Ph_3), heat
iii.	1.6M BuLi, -78°C, CO_2	ix.	1.6M BuLi, -10°C, N_2
iv.	BMS, ether, N_2	x.	NaH, ROH, pyridine
v.	PCC, DCM, room temp.	xi.	H_2, 5%Pd/C, EtOH, room temp.
vi.	$LiAlH_4$, ether, reflux		

Scheme 4



(48)

(49)

(50)

(A1)

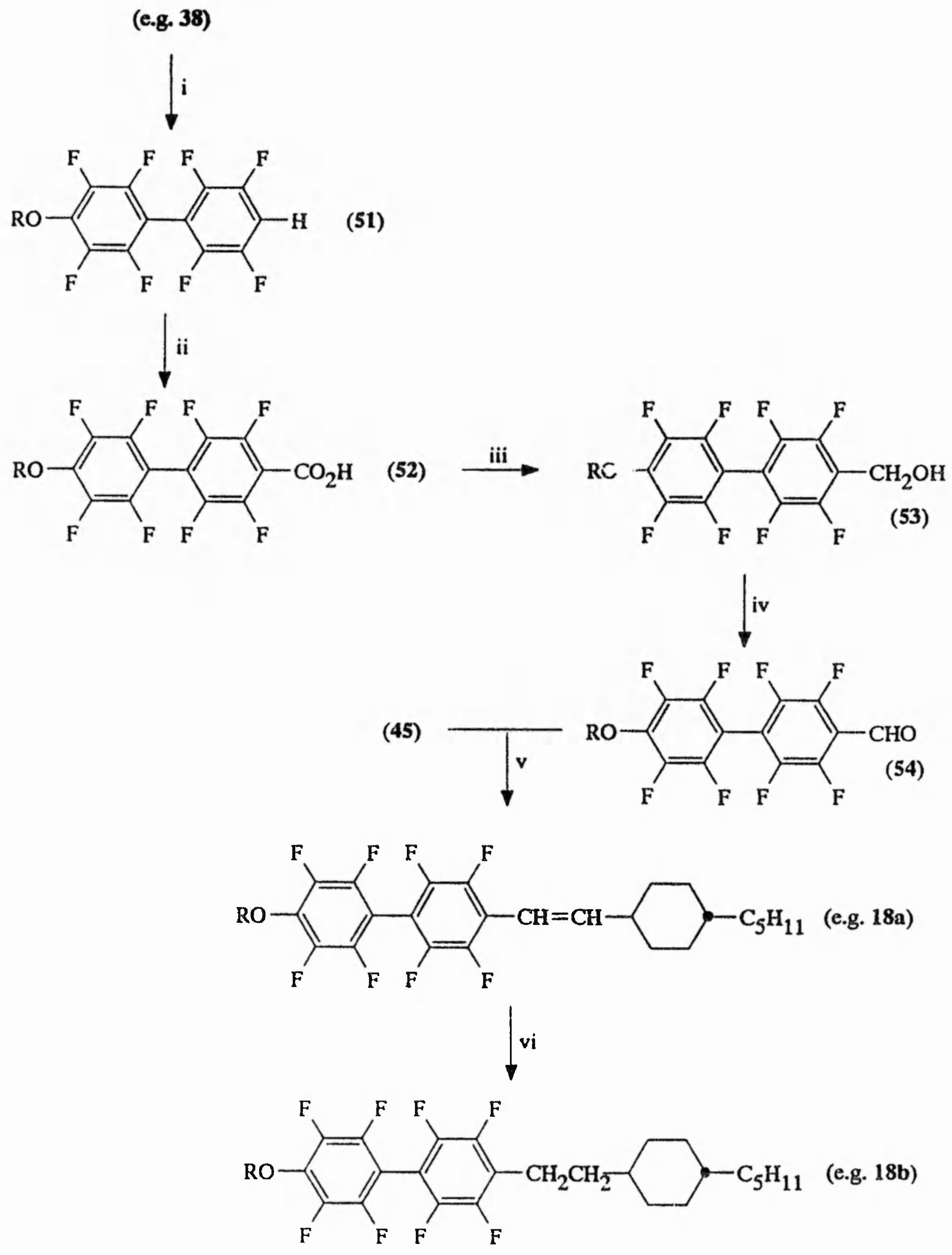
i. LiAlH$_4$, ether, reflux

ii. 1.6M BuLi, -78°C, CO$_2$

iii. BMS, ether, N$_2$

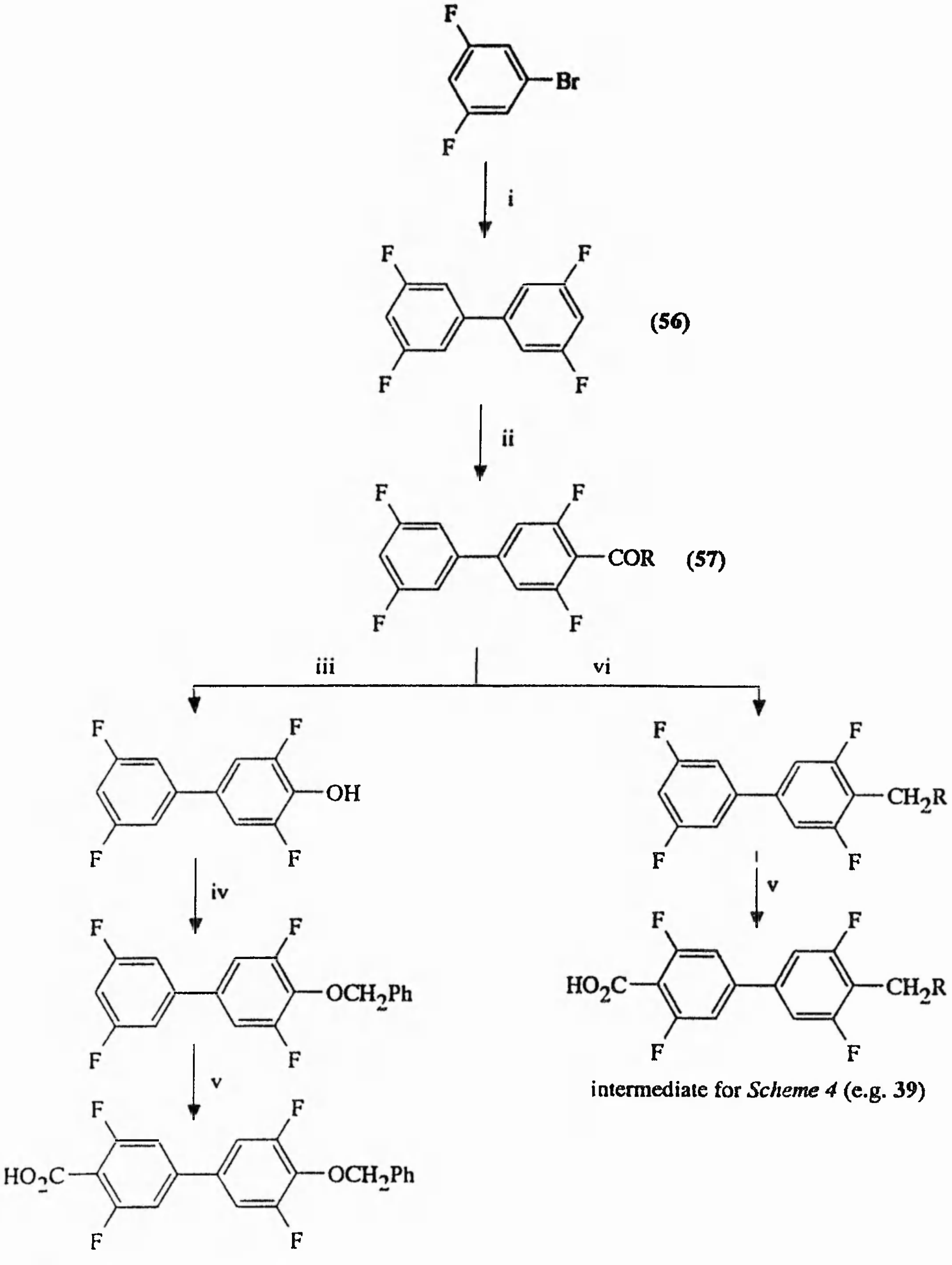
iv. PCC, DCM, room temp.

Scheme 5



i. NaH, ROH, pyridine
ii. 1.6M BuLi, -78°C, CO_2
iii. BMS, ether, N_2
iv. PCC, DCM, room temp.
v. 1.6M BuLi, -10°C, THF
vi. H_2, 5%Pd/C, EtOH, room temp.

Scheme 6

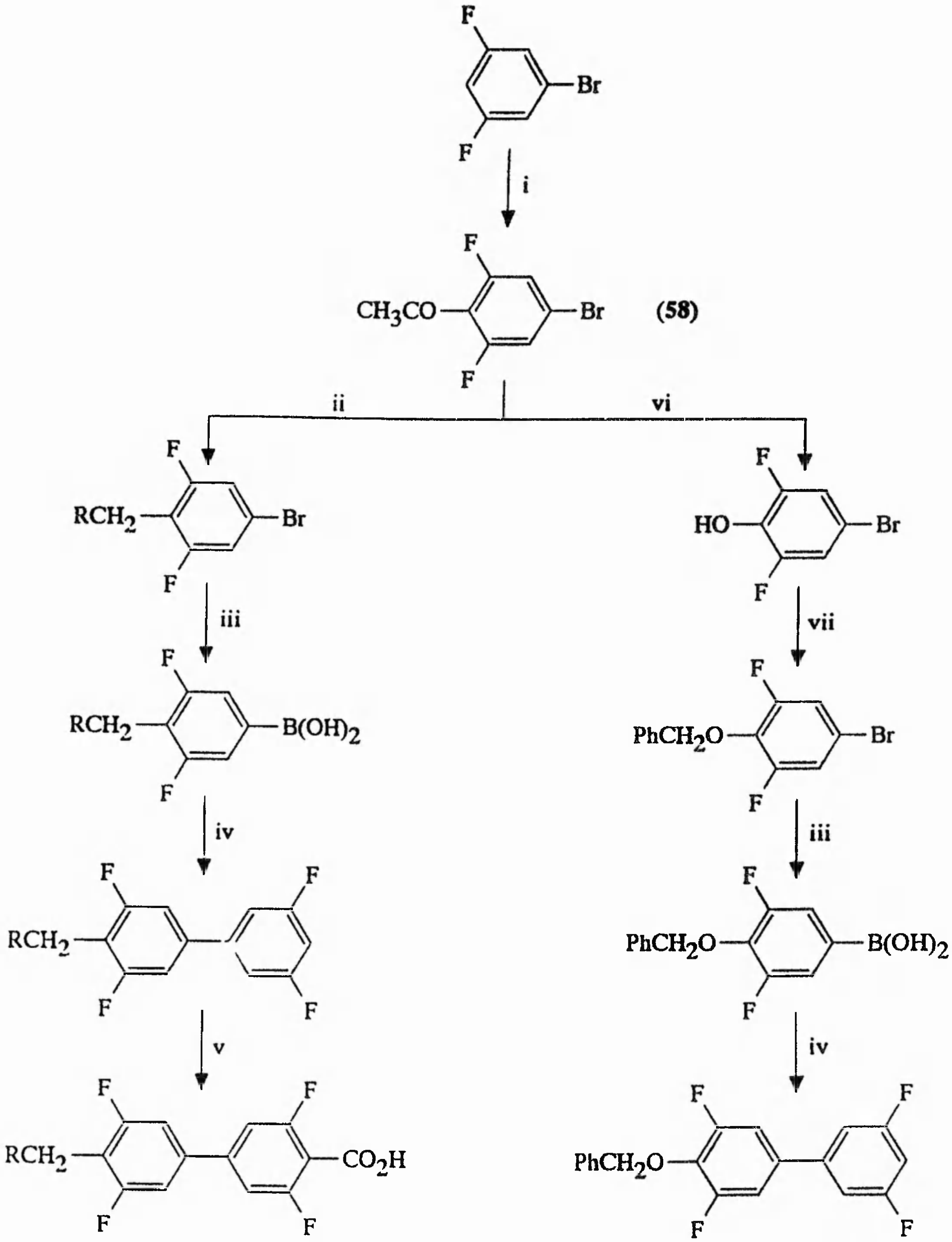


intermediate for *Scheme 4* (e.g. **39**)

intermediate for *Scheme 4* (e.g. **39**)

- i. 1.6M BuLi, $TiCl_4$, -78°C to room temp.
- ii. RCOCl, $AlCl_3$, DCM
- iii. m-$ClC_6H_5CO_3H$, KOH, EtOH
- iv. $PhCH_2Br$, K_2CO_3, acetone, reflux
- v. 1.6M BuLi, -78°C, CO_2
- vi. $Si(C_2H_5)_3H$, TFA, room temp.

Scheme 7



intermediate for *Scheme 4* (e.g. **39**)

intermediate for *Scheme 4* (e.g. **38**)

i. CH_3COCl, $AlCl_3$, DCM

ii. $Si(C_2H_5)_3H$, TFA, room temp.

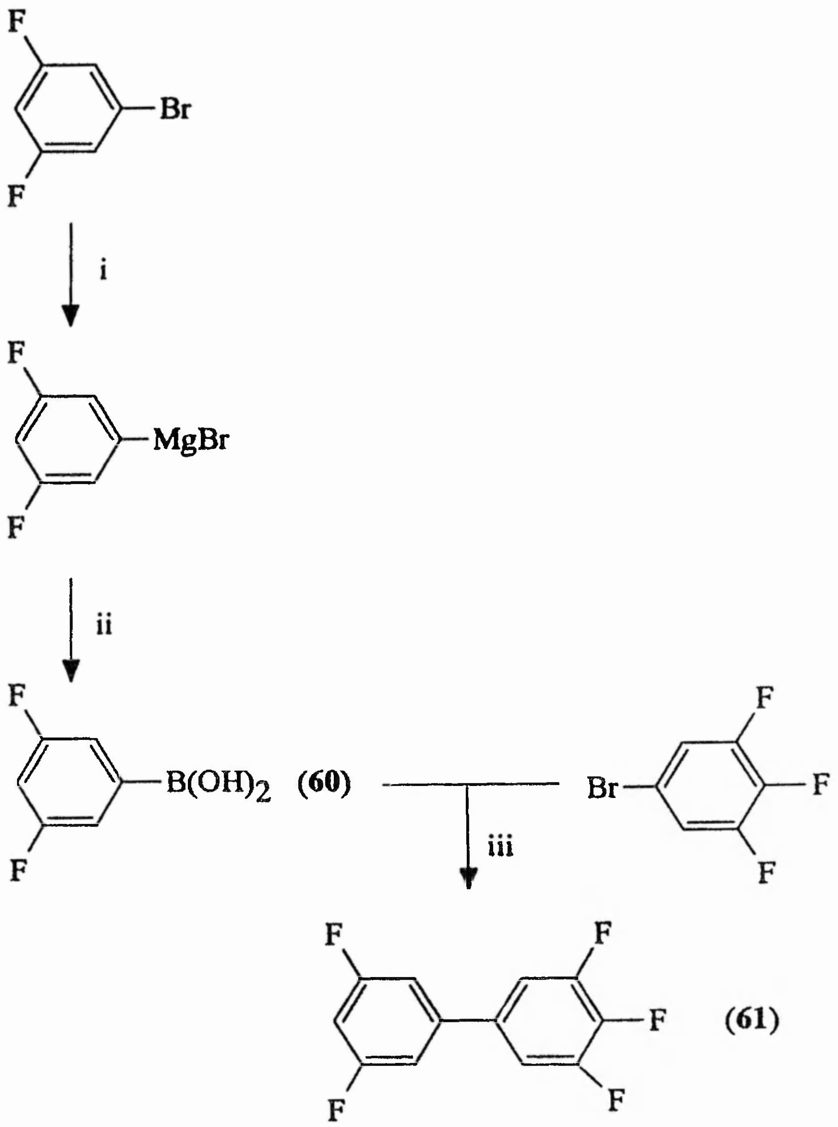
iii. Mg, TMB, -78°C, N_2

iv. 1-Bromo-3,5-difluorobenzene, $Pd(PPh_3)_4$, Na_2CO_3, benzene, EtOH, reflux

v. 1.6M BuLi, -78°C, CO_2

vi. *m*-$ClC_6H_5CO_3H$, KOH, EtOH

Scheme 8

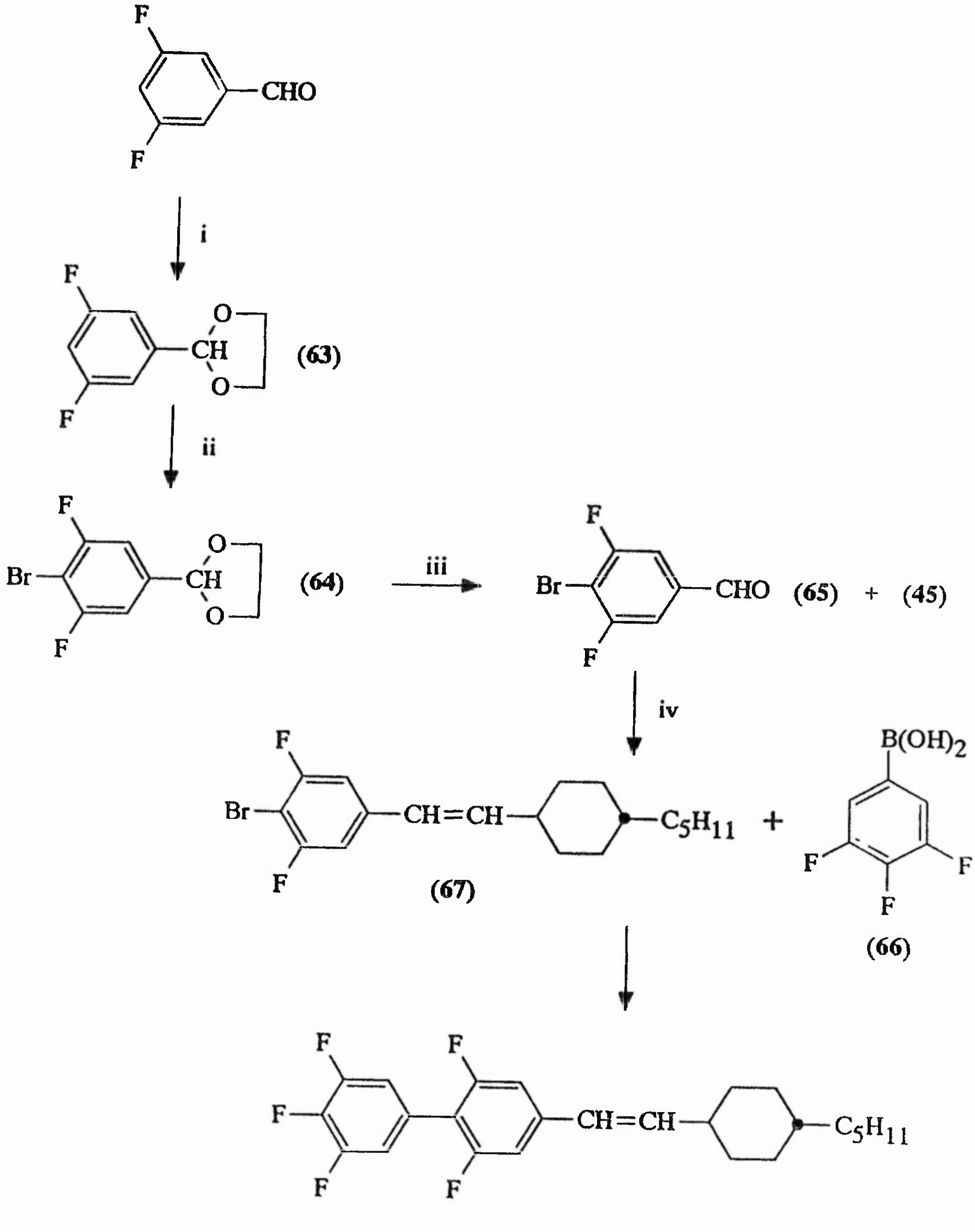


i. Mg/I$_2$, ether, reflux

ii. TMB, THF, -78°C, N$_2$

iii. Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, benzene, EtOH, reflux

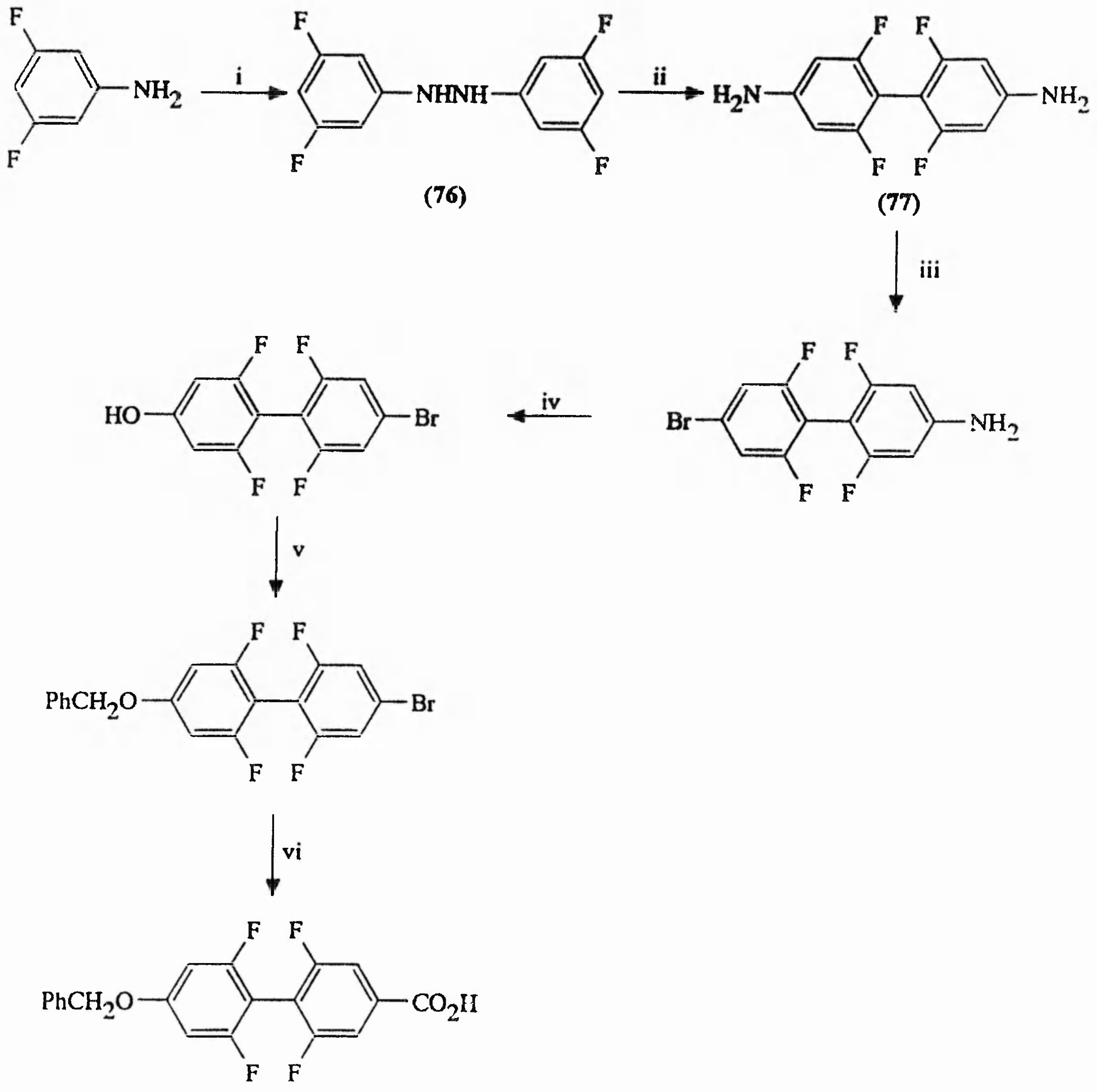
Scheme 9



intermediate for *Scheme 4* (e.g. **46**)

i. $HOCH_2CH_2OH$, *p*TSA, reflux
ii. 1.6M BuLi, Br_2, -78°C, N_2
iii. HCl, dioxane, reflux
iv. 1.6M BuLi, -10°C, THF
v. $Pd(PPh_3)_4$, Na_2CO_3, benzene, EtOH, reflux

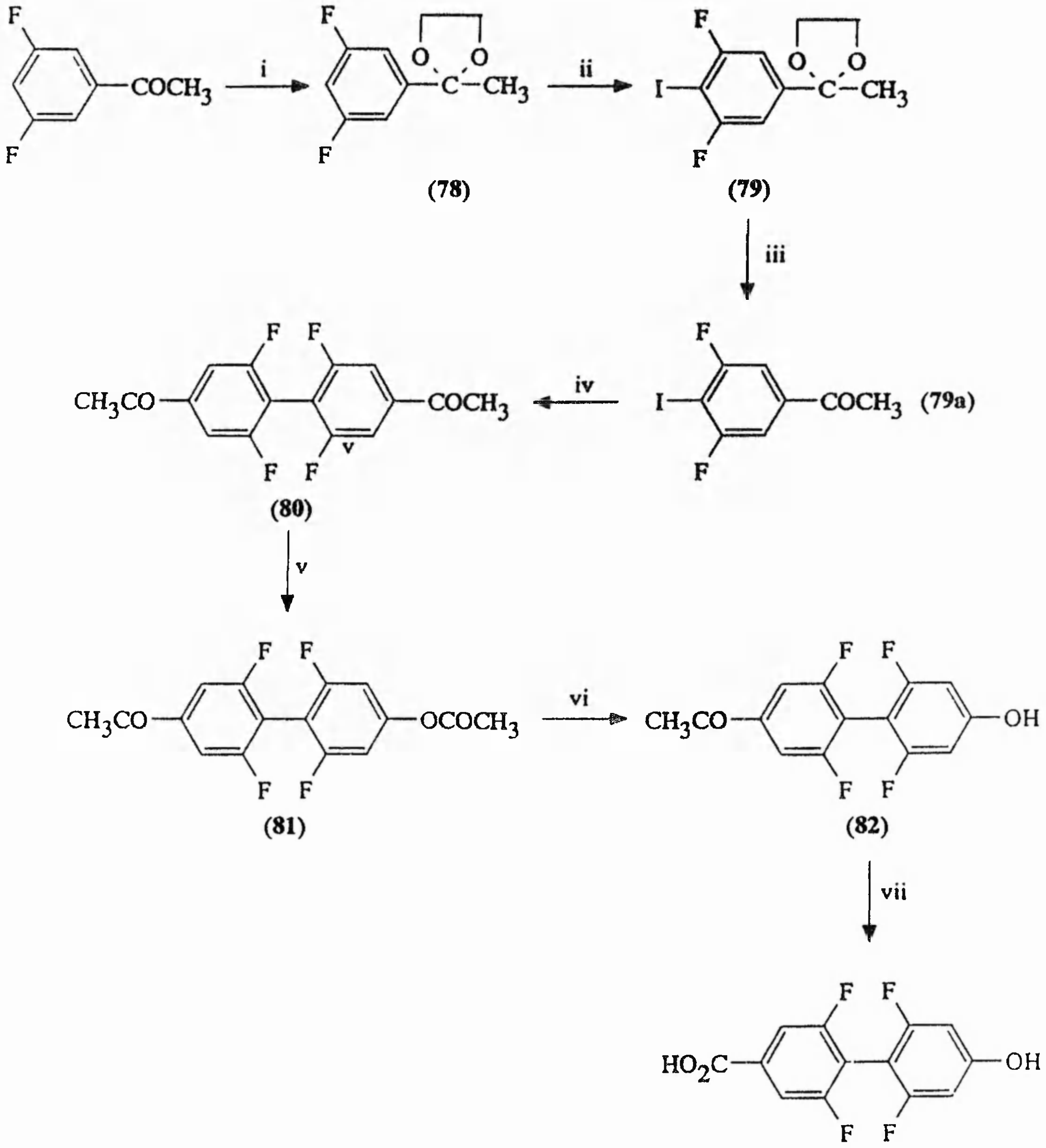
Scheme 10



intermediate for *Scheme 4* (e.g. **39**)

- i. Zn/aq. NaOH
- ii. HCl/EtOH
- iii. $NaNO_2$, HCl, CuBr
- iv. Mg, TMB, -78°C, H_2O_2
- v. $PhCH_2Br$, K_2CO_3, acetone, reflux

Scheme 11



intermediate for *Scheme 4* (e.g. 39)

i. $HOCH_2CH_2OH$, *p*TSA, reflux

ii. 1.6M BuLi, I_2, -78°C, N_2

iii. HCl, dioxane, reflux

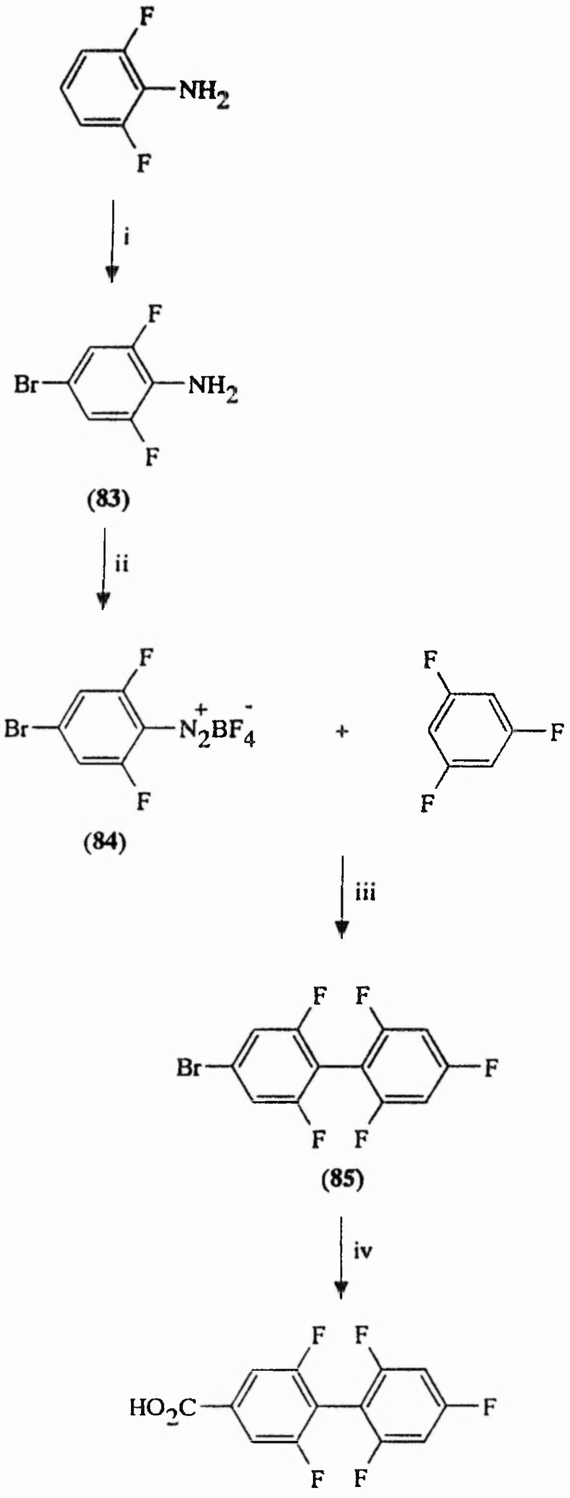
iv. Cu powder, 220°C, sealed tube

v. Sodium perborate, TFA

vi. KOH, EtOH, reflux

vii. Br_2, NaOH, dioxane

Scheme 12



intermediate for *Scheme 4* (e.g. 39)

i. CH_3CO_2H, Br_2
ii. $NaNO_2$, HCl, $NaBF_4$, 0-5°C
iii. 1,3,5-trifluorobenzene, 18-Crown-6, KOAc, stir, room temp.
iv. Mg, CO_2

Scheme 13

EXPERIMENTAL

5. EXPERIMENTAL

Common reagents and techniques employed during the synthetic work.

1. Lithiations were carried out using commercial 1.6M n-butyllithium in hexane obtained from Aldrich Chemical Company Ltd.
2. *Trans*-4-n-alkylcyclohexanecarboxylic acids were kindly donated by Merck Ltd., Poole, Dorset.
3. Fluorinated chemicals were obtained from Aldrich Chemical Company Ltd.
4. Dry hexane and dry ether were obtained by storing the appropriate solvent over freshly pressed sodium wire for 24h.
5. Dry tetrahydrofuran was prepared by continuously heating under reflux, tetrahydrofuran, sodium metal and benzophenone. A blue colouration of the solution was indicative of dry tetrahydrofuran.
6. The progress of reactions was monitored by t.l.c. using silica gel coated on aluminium plates (Art. 5554, Merck, Darmstadt).
7. Column chromatography was employed using silica gel (60-120 mesh size), whilst flash chromatography utilised silica gel (40-63μm). Both were obtained from Merck Ltd., Poole, Dorset.

4-n-Butyl-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl **(19)** (*Scheme 1*)

Decafluorobiphenyl (20 g, 0.06 mol) was dissolved in dry ether (100 cm^3) contained in a 250 cm^3 3-necked round-bottomed flask equipped with a nitrogen inlet, rubber septum, alcohol thermometer and a suitable stirrer. The flask was purged with nitrogen and cooled to -20°C using a 'Cardice'/acetone bath. To the cold, stirred solution, commercial butyllithium (37.5 cm^3, 0.06 mol) was added, dropwise via the rubber septum ensuring that the temperature did not exceed -15°C . On completion of the addition, the reaction mixture was maintained at -20°C for an additional 1h. Water (50 cm^3) was added and the ether layer was separated, dried over anhydrous magnesium sulphate, and the solvent removed under reduced pressure to give a clear oil. Examination of the crude product by t.l.c. revealed that the product and starting material had closely similar R_f values and hence purification via column chromatography was not possible. However, purification was achieved by vacuum sublimation of the starting material from the crude product followed by vacuum distillation (Kugelrohr) of the residue. The desired 4-n-butyl-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl, 10 g (45%), b.p. 103°C/ 0.5mm Hg, was obtained as a clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.7(3H,t,CH_3), 1.3(4H,m,CH_2CH_2), 2.6(2H,t,CH_2)

i.r. ν_{max} (film) 3600,3300,2950,2900,1660,1530,1500,1480,1160,725 cm^{-1}

4-n-Butyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl **(20)** (*Scheme 1)* Method 1

4-n-Butyl-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (10 g, 0.023 mol), potassium hydroxide (5 g, 0.09 mol) and *tert*-butanol (150 cm^3) were placed in 500 cm^3 round-bottomed flask and heated under reflux. After 3h. the reaction mixture was poured into water (300 cm^3), and transferred to a separating funnel. The aqueous layer was washed with ether (2x100 cm^3) to remove unchanged starting material, acidified with 4M-aqueous hydrochloric acid and extracted with ether (2x100 cm^3). The ether extracts were combined, dried ($MgSO_4$), and the solvent removed under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with 5:1 light petroleum (b.p. 60-80°C) : ethyl acetate then by vacuum distillation (Kugelrohr) affording the pure 4-n-butyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 8 g (94%), b.p. 196°C/0.7mm Hg, as a clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 1.1(3H,t,CH_3), 1.5(4H,m,CH_2CH_2), 2.8(2H,t, CH_2), 6.0(1H,s,OH)

i.r. ν_{max} (film) 3600,3300,2900,1660,1530,1500,1480,1160,725 cm^{-1}

This compound was also prepared by method 2 (p. 134).

4,4′-Dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl **(21)** (*Scheme 2*)

Decafluorobiphenyl (20 g, 0.06 mol), potassium hydroxide (30 g, 0.52 mol) and *tert*-butanol (250 cm^3) were heated under reflux. The procedure (p. 129) described for the synthesis of 4-n-butyl-2,2′,3,3′5,5′,6,6′-nonafluorobiphenyl **(20)** was then followed. The crude residue was purified by recrystallisation from toluene affording the 4,4′-dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 10 g (50%), m.p. 210-211°C (lit.[139] 198.5-199.5°C), as white needles.

4-n-Alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyls (e.g. **22**) (*Scheme 2*)

4,4′-Dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (5 g, 0.0015 mol), ethanol (10 cm^3) and the appropriate n-alkylbromide (mol. equiv.) were gently heated under reflux, with stirring. Potassium hydroxide (2.8 g, 0.05 mol) in water (10 cm^3) was added dropwise to the reaction mixture over 1h. On completion of the addition, heating under reflux was continued for a further 3h. The reaction mixture was cooled, acidified (4M HCl), and extracted with ether (2x50 cm^3). The extracts were combined, dried ($MgSO_4$), and the solvent removed under reduced pressure. The resulting amber coloured oil was purified by flash chromatography on silica gel eluting with 2:1 light petroleum (b.p. 60-80°C) : ethyl acetate, then distilled under vacuum (Kugelrohr) to give the desired 4-n-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (35-40%) as a clear oil which solidified on cooling.

n-Alkoxy group	b.p.°C/mm Hg
C_5H_{11}	160/0.04
C_8H_{17}	169/0.04
C_9H_{19}	195/0.08
$C_{10}H_{21}$	200/0.08

The following proton n.m.r. and i.r. spectra of 4-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluoro-4′-n-pentyloxybiphenyl are representative of the series.

^1H n.m.r. δ($CDCl_3$,TMS) 1.1 (3H,t,CH_3), 1.3 (6H,m,$(CH_2)_3$), 4.5 (2H,t, OCH_2), 5.2 (1H,s,OH)

i.r. ν_{max} (film) 3300,2950,2900,1720,1660,1530,1500,1480,1100,725 cm^{-1}

Carboxylate esters derived from 4-n-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyls (e.g. **23a**) (*Schemes 1* and *2*)

Dicyclohexylcarbodiimide (1.1 mol) and the appropriate 4-n-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (1 mol) and carboxylic acid (1.1 mol) were added to dry dichloromethane (20 cm^3). 4-(N-Pyrollidino)pyridine (0.001 mol), as catalyst, was added and the reaction mixture was then stirred overnight. After checking the course of the reaction by t.l.c., the white precipitate (dicyclohexyl urea) was filtered off and the filtrate evaporated in vacuo to give the crude ester. The pure product was obtained by column chromatography on silica gel eluting with chloroform, followed by several recrystallisations from ethanol to give the pure ester (>90%), as a white crystalline solid. The liquid crystal transition temperatures of the esters prepared by this method are listed in ***Tables 1*** (p. 64) and 2 (p. 67) in the discussion section.

4-n-Alkoxy-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyls (e.g. **35**) (*Scheme 3*)

The appropriate sodium alkoxide (0.03 mol), prepared from the alcohol by the addition of the necessary amount of sodium hydride, was added dropwise, with stirring, to decafluorobiphenyl (10 g, 0.03 mol) dissolved in dry pyridine (30 cm^3) at -10°C. The reaction mixture was maintained at -10°C for 1h., and then acidified (4M HCl). The product was extracted with ether (3x50 cm^3), the ether extracts were dried ($MgSO_4$), and the solvent removed under reduced pressure. The resulting clear oil was purified by column chromatography on silica gel eluting with light petroleum (b.p. 60-80°C) affording the 4-n-alkoxy-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (55-60%) either as a white crystalline solid or as a clear oil depending upon the alkyl chain length.

n-Alkoxy group	m.p./b.p. °C
CH_3	74-75
C_5H_{11}	120/0.01mm Hg
$C_{10}H_{21}$	151/0.01mm Hg

The following proton n.m.r. and i.r. spectra for 2,2′,3,3′,4′,5,5′,6,6′-nonafluoro-4-n-pentyloxybiphenyl are representative of the series.

^{1}H n.m.r. δ($CDCl_3$,TMS) 1.0(3H,t,CH_3), 1.3(6H, m,$(CH_2)_3$), 4.2(2H,t,OCH_2)

i.r. ν_{max} (film) 2950,2900,1720,1660,1530,1500,1480,1160,725 cm^{-1}

4-n-Butyl-4′-methoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**36**) (*Scheme 3)*

4-Methoxy-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (3 g, 0.01 mol) was treated with commercial 1.6M BuLi (6.8 cm^3, 0.011 mol) as described in the method given on p. 129. Examination of the crude product by t.l.c. revealed two components, one of which was close to the solvent front and another which had the same R_f as the starting material. The components were separated by column chromatography on silica gel eluting with light petroleum (b.p. 60-80°C). The first fraction which gave a clear oil, 1.5 g (43%), b.p.110°C/0.6mm Hg, was not the required product (as indicated by the ^{1}H n.m.r. spectrum). The second fraction afforded the desired 4-n-butyl-4′-methoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 1.3 g (37%), b.p. 136°C/mm Hg, as a clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.2(4H,m,CH_2CH_2), 2.7(2H,t,CH_2), 4.2(3H,s,OCH_3)

i.r. ν_{max} (film) 2975,1660,1530,1500,1200,1140,725 cm^{-1}

4-n-Butyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**20**) Method 2 (*Scheme 3*)

Boron tribromide (1.6 cm^3, 0.015 mol) was added dropwise, with rapid stirring to 4-n-butyl-4′-methoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (2 g, 0.0005 mol) in dry dichloromethane (20 cm^3) at -20°C. On completion of the addition, the reaction mixture was allowed to warm to room temperature. After standing overnight, the reaction mixture was then poured into water (50 cm^3) and extracted with ether (2x50 cm^3). The extracts were combined, washed with water (2x50 cm^3), dried (MgSO$_4$), and the solvent removed in vacuo. The resulting amber coloured oil was purified by vacuum distillation (Kugelrohr) affording the product, 1.5 g (80%), b.p. 196°C/0.7mm Hg, as a clear oil.

Spectral characteristics are listed under method 1 (p. 130)

4-Hydrazino-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (e.g. **37**) (*Scheme 4*)

To decafluorobiphenyl (20 g, 0.06 mol) in ethanol (150 cm^3), 96% hydrazine hydrate (3.25 g, 0.06 mol) was added, dropwise, under reflux. The reaction mixture was maintained under reflux for an additional 1h., then poured into water (500 cm^3) and allowed to stand overnight. The resulting solid was filtered off, dissolved in ether (100 cm^3), dried (MgSO$_4$), and the solvent removed in vacuo. Examination of the crude product by t.l.c. revealed a mixture containing unchanged starting material, mono-substituted decafluorobiphenyl and polysubstituted decafluorobiphenyls. The starting material was removed by sublimation (70°C/20mm Hg) and the residue left behind was then purified by fractional crystallisation from hexane. Insoluble material was removed by hot filtration and the solution set aside. The initial batch of crystals was poly-substituted material whilst the second fraction corresponded with the desired 4-hydrazino-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl, 13 g (65%), m.p. 132-135°C (lit.[112] 132-133.5°C).

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl (e.g. **38**) (*Scheme 4*) Method 1

Copper(II) sulphate (30 g, 0.04 mol) was added to a solution of 4-hydrazino-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (13 g, 0.04 mol) dissolved in 1:1 ethanol: water. The reaction mixture was gently heated under reflux for several hours. As the reaction proceeded, nitrogen gas was evolved and copper was deposited. On completion, the mixture was filtered through a funnel loosely packed with glass wool to remove suspended solids. The resulting solution was extracted with ether (3x200 cm^3), and the combined extracts were washed with water (3x100 cm^3), dried ($MgSO_4$), and the solvent removed under reduced pressure. Sublimation of the resulting solid gave the pure 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl, 9 g (71%), m.p. 83-84°C (lit.[140] 81-82°C), as white needles.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.5(1H,m,ArH)

i.r. ν_{max} (KBr) 3150,1660,1600,1530,1500,1480,1220,740,705 cm^{-1}

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl (e.g. **38**) Method 2

In an atmosphere of nitrogen, a slurry of $LiAlH_4$ (0.31 g, 0.008 mol) in dry ether (20 cm^3) was added, dropwise, to a rapidly stirred solution of decafluorobiphenyl (3.6 g, 0.011 mol) in dry ether (30 cm^3) at such a rate that the ether boiled gently. On completion of the addition, the reaction was heated under reflux for an additional 8h. and then allowed to cool. The excess of $LiAlH_4$ was hydrolysed by the addition of moist ether, ethyl acetate, water (1-2 cm^3) and finally

4M-aqueous hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether (2x50 cm^3). The combined ethereal extracts were dried ($MgSO_4$), and the solvent removed in vacuo. Examination of the residue by t.l.c. revealed a mixture containing unchanged starting material and the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl.

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl-4-carboxylic acid (e.g. **39**) (*Scheme 4*)

Commercial butyllithium (20.6 cm^3, 0.033 mol) was added dropwise to a rapidly stirred solution of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (9.5 g, 0.03 mol) in dry 1:1 ether:hexane (150 cm^3) maintained at -78°C to -65°C throughout the addition which took 2h. to complete. The reaction mixture was then maintained at -78°C for an additional 1h. after which it was poured onto powdered solid carbon dioxide and allowed to warm to room temperature. The mixture was acidified (4M HCl) and the resulting acid extracted into ether (2x100 cm^3). The combined ether extracts were dried ($MgSO_4$), and the solvent removed under reduced pressure. Recrystallisation of the off-white solid from hexane afforded the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carboxylic acid, 10 g (88%), m.p. 170-172°C (lit.[141] 175-176°C), as a white crystalline solid.

^1H n.m.r. δ($CDCl_3$/DMSO,TMS) 12.3(1H,s,CO_2H)

i.r. ν_{max} (KBr) 3500,3300-2750,1720,1660,1530,1500,1480,1260,1000,725 cm^{-1}

Other polyfluorobiphenyl-4-carboxylic acids were also obtained by this method, as detailed below.

2,2',3,3',5,5',6,6'-Octafluorobiphenyl-4-carboxylic acid (**49**) (*Scheme 5*)

Quantities: 2,2',3,3',5,5',6,6'-octafluorobiphenyl (4 g, 0.013 mol),

1.6M BuLi (9 cm^3, 0.014 mol).

Yield 3.6 g (81%), m.p. 194-197°C.

^{1}H n.m.r. δ(CDCl$_3$/DMSO,TMS) 7.3(1H,m,ArH), 11.5(1H,s,CO$_2$H).

i.r. ν_{max} (KBr) 3500,3300-2600,1710,1520,1480,1000,725 cm^{-1}

4'-n-Decyloxy-2,2',3,3',5,5',6,6'-Octafluorobiphenyl-4-carboxylic acid (e.g. **52**) (*Scheme 6*)

Quantities: 4-n-Decyloxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl (2 g, 0.004 mol),

1.6M BuLi (3 cm^3, 0.005 mol).

Yield 2 g (93%), m.p. (C-I), 112.5-113.2 ; (I-N), 111.8-111.4°C.

^{1}H n.m.r. δ(CDCl$_3$/DMSO,TMS) 0.9(3H,t,CH$_3$), 1.4(16H,br s,alkyl), 4.3(2H,t,OCH$_3$), 9.2(1H,s,CO$_2$H)

i.r. ν_{max} (KBr) 3420-2850,1720,1660,1520,1500,1480,1000,725 cm^{-1}

3,3',4',5,5'-Pentafluorobiphenyl-4-carboxylic acid (e.g. **39**) (*Scheme 4*)

Quantities: 3,3',4',5,5'-Pentafluorobiphenyl (5 g, 0.02 mol), 1.6M BuLi

(14 cm^3, 0.022 mol).

Yield 5.4 g (94%), m.p. 170-172.5°C.

^{1}H n.m.r. δ(CDCl$_3$/DMSO,TMS) 7.2(4H,m,ArH), 12.1(1H,s,CO$_2$H).

i.r. ν_{max} (KBr) 3500,3300-2750,1705,1640,1580,1400,1000,850 cm^{-1}

2,3,3',4',5,5',6-Heptafluorobiphenyl-4-carboxylic acid (e.g. **39**) (*Scheme 4*)

Quantities: 2,3,3',4',5,5',6-Heptafluorobiphenyl (5 g, 0.017 mol), 1.6M BuLi

(12.2 cm^3, 0.019 mol).

Yield 5.3 g (96%), m.p. 177-179°C.

^{1}H n.m.r. δ($CDCl_3$/DMSO,TMS) 7.2(2H,t,ArH), 12.0(1H,s,CO_2H).

i.r. ν_{max} (KBr) 3500,3300-2800,1705,1640,1580,1400,1050,1000, 850 cm^{-1}

2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carboxylic acid (e.g. **39**) (*Scheme 4*)

Quantities: 2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl (5 g, 0.018 mol), 1.6M BuLi (12.2 cm^3, 0.019 mol).

Yield 5 g (86%), m.p. 195-200°C.

^{1}H n.m.r. δ($CDCl_3$/DMSO,TMS) 7.3(2H,t,ArH), 10.2 (1H,br s, CO_2H).

i.r. ν_{max} (KBr) 3500,3300-2800,1710,1640,1580,1500,1400,1050, 1000,850 cm^{-1}

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl-4-ylmethanol (e.g. **40**) (*Scheme 4*) Method 1

In an atmosphere of nitrogen, 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carboxylic acid (10 g, 0.027 mol) in dry ether (100 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (1.2 g, 0.03 mol), contained in 2-necked round-bottomed flask equipped with reflux condenser, calcium chloride guard tube and pressure equalising funnel, at such a rate that the ether boiled gently. On completion of the addition, the reaction mixture was heated under reflux for an additional 3h. and then allowed to cool. The excess of lithium aluminium hydride was hydrolysed by carefully adding moist ether, ethyl acetate and finally 1-2 drops of water. The reaction mixture was then transferred to a separating funnel and acidified with 4M-aqueous hydrochloric acid (100 cm^3). The ether layer was separated and the aqueous layer was extracted with ether (2x100 cm^3). The combined ether extracts were washed with water (2x100 cm^3), dried ($MgSO_4$), and the solvent removed in vacuo. Purification of the product was achieved by flash chromatography on silica gel eluting with 3:1 light petroleum (b.p. 60-80°C) : ethyl acetate followed recrystallisation from hexane, yielding the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-ylmethanol, 8.7 g (93%), m.p. 78-80°C, as a white crystalline solid.

^1H n.m.r. $\delta(CDCl_3,TMS)$ 2.5(1H,s,OH), 4.9(2H,s,CH_2)

i.r. ν_{max} (KBr) 3500-3300,2975,1660,1530,1500,1480,10000,725 cm^{-1}

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl-4-ylmethanol (e.g. **40**) (*Scheme 4*) Method 2

In an atmosphere of nitrogen, borane dimethylsulphide (4.2 cm^3, 0.044 mol) was added dropwise to a solution of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carboxylic acid (5 g, 0.014 mol) in dry ether (50 cm^3) causing vigorous effervesence and the ether to boil. On completion of the addition, the mixture was heated under reflux for 2h. The reaction mixture was then poured into cold methanol (200 cm^3) and allowed to stand overnight before removal of the solvent in vacuo. The resulting off-white solid was recrystallised from from hexane affording the pure 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-ylmethanol 4.8 g (100%), m.p. 78-80°C, as a white crystalline solid.

The following polyfluorobiphenyl-4-yl-methanols were similarly prepared. Only in the first case was the product isolated, otherwise the compounds were converted directly into the corresponding aldehyde, without purification.

2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl-4-ylmethanol **(50)** (*Scheme 5*)

Quantities: 2,2′,3,3′,4′,5,5′,6,6′-octafluorobiphenyl-4-carboxylic acid (2.5 g, 0.006 mol), BMS (4.75 cm^3, 0.05 mol).

Yield 1.7 g (86%), m.p. 116-117°C.

^{1}H n.m.r. δ(CDCl$_3$/DMSO,TMS) 4.7(1H,s,OH), 4.9(2H,s,CH$_2$), 7.3(1H,m,ArH).

i.r. ν_{max} (KBr) 3300,2950,1530,1480,1120,925,725 cm^{-1}

4′-n-Decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-ylmethanol (e.g. **53**) (*Scheme 6*)

Quantities: 4′-n-Decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-carboxylic acid (1.5 g, 0.003 mol), BMS (0.85 cm^3, 0.009 mol).

3,3′,4′,5,5′-Pentafluorobiphenyl-4-ylmethanol (e.g. **40**) (*Scheme 4*)

Quantities: 3,3′,4′,5,5′-Pentafluorobiphenyl-4-carboxylic acid (5 g, 0.017 mol), BMS (4.75 cm^3, 0.05 mol).

2′,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-ylmethanol (e.g. **40**) (*Scheme 4*)

Quantities: 2′,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-carboxylic acid (5 g, 0.015 mol), BMS (4.75 cm^3, 0.05 mol).

2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-ylmethanol (e.g. **40**) (*Scheme 4*)

Quantities: 2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carboxylic acid (5 g, 0.015 mol), BMS (4.75 cm^3, 0.05 mol).

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl-4-carbaldehyde (e.g. **41**) (*Scheme 4*)

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl-4-ylmethanol (5 g, 0.014 mol) in dry dichloromethane (10 cm^3) was added to a rapidly stirred suspension of pyridinium chlorochromate (6 g, 0.027 mol) in dry dichloromethane (100 cm^3). The reaction was monitored by t.l.c. and, on completion, dry ether (100 cm^3) was added. The supernatant liquid was decanted from the black gum which was washed with more dry ether (2x100 cm^3). The ether solutions were combined, filtered through 'Hyflo-supercel' and the solvent removed under reduced pressure. The resulting dark brown oil was purified by flash chromatography on silica gel eluting with 3:1 light petroleum (b.p. 60-80°C) : chloroform, followed by recrystallisation from hexane affording the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carbaldehyde, 3.7 g (77%), m.p. 75-76°C, as a white crystalline solid.

^{1}H n.m.r. δ($CDCl_3$,TMS) 10.4(1H,s,CHO)

i.r. ν_{max} (KBr) 2950,2850,1710,1660,1530,1500,1480,1000,725 cm^{-1}

Five other polyfluorobiphenyl-4-carbaldehydes were prepared by this route, as described below.

2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl-4-carbaldehyde (A1) (*Scheme 5*)

Quantities: 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl-4-ylmethanol (1.7 g, 0.005 mol), PCC (2 g, 0.01 mol).

Yield 1.2 g (74%), m.p. 114-116°C.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.4(1H,m,ArH), 10.3(1H,s,CHO).

i.r. ν_{max} (KBr) 2950,1710,1530,1480,1000,925,720 cm^{-1}

4′-n-Decyloxy-2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl-4-carbaldehyde (e.g. **54**) (*Scheme 6*)

Quantities: 4′-n-Decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-carboxylic acid (1.5 g, 0.003 mol), BMS (0.85 cm^3, 0.009 mol) and PCC (2 g, 0.009 mol).

Yield 1 g (69%), m.p. 63.5-65°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.4(16H,br s,alkyl), 4.3 (2H,t,OCH_3), 10.4(1H,s,CHO)

i.r ν_{max} (KBr) 2950,2900,2850,1710,1660,1550,1500,950,725 cm^{-1}

3,3′,4′,5,5′-Pentafluorobiphenyl-4-carbaldehyde (e.g. 41) (*Scheme 4*)

Quantities: 3,3′,4′,5,5′-Pentafluorobiphenyl-4-carboxylic acid (5 g, 0.017 mol), BMS (4.75 cm^3, 0.05 mol) and PCC (6.3 g, 0.03 mol).

Yield 2.9 g (63%), m.p. 153-154.5°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.3(4H,m,ArH), 10.5(1H,s,CHO)

i.r. ν_{max} (KBr) 2950,2850,1705,1640,1550.1050,850,785 cm^{-1}

2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carbaldehyde (e.g. **41**) (*Scheme 4*)

Quantities: 2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carboxylic acid (5 g, 0.017 mol), BMS (4.75 cm^3, 0.05 mol) and PCC (6.3 g,0.03 mol).

Yield 2.5 g (54%), m.p. 109-110°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.2(2H,m,ArH), 10.4(1H,s,CHO)

i.r. ν_{max} (KBr) 3050,2950,2850,1705,1640,1550,1000,840,810 cm^{-1}

2,3,3',4',5,5',6-Heptafluorobiphenyl-4-carbaldehyde (e.g. **41**) (*Scheme 4*)

Quantities: 2,3,3',4',5,5',6-Heptafluorobiphenyl-4-carboxylic acid (5 g, 0.017 mol), BMS (4.75 cm^3, 0.05 mol) and PCC (6.5 g, 0.03 mol).

Yield 3.8 g (82%), m.p. 101-103°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.2(2H,m,ArH), 10.3(1H,s,CHO)

i.r. ν_{max} (KBr) 3050,2950,2850,1705,1640,1550,1000,840,810 cm^{-1}

General method : 1-(polyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethenes (e.g. **46**) (*Scheme 4*)

In an atmosphere of nitrogen, commercial butyllithium (1.1 mol) was added dropwise to a rapidly stirred suspension of *trans*-4-n-pentylcyclohexyl-1-methyl triphenylphosphonium bromide (1 mol) in dry tetrahydrofuran (50 cm^3) cooled to -10°C. On completion of the addition, the dark orange-brown solution was stirred for 1h. at 0°C. The appropriate aldehyde (1 mol), dissolved in dry tetrahydrofuran (10 cm^3), was added and the reaction mixture then stirred at 5°C for 1h. at 0°C. Water (50 cm^3) was added and the reaction mixture extracted with ether (3x50 cm^3). The extracts were combined, washed with water (2x75 cm^3), dried ($MgSO_4$), and the solvent removed in vacuo. The crude residue was purified by column chromatography on silica gel eluting with light petroleum (b.p. 60-80°C). The desired fractions were collected and the solvent removed in vacuo to yield a clear oil, which on addition of cold ethanol (10-20 cm^3) afforded the desired alkylarylethene, (60-70%), as white flakes.

The following 1-(polyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes were also prepared via this route, as described below.

1-(3,3′,4′,5,5′-Pentafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene (e.g. **46**) (*Scheme 4*)

Quantities: 3,3′,4′,5,5′-Pentafluorobiphenyl-4-carbaldehyde (2.5 g, 0.009 mol), *trans*-4-n-pentylcyclohexyl-1-methyltriphenylphosphonium bromide(7.2 g, 0.015 mol) and 1.6M BuLi (9.6 cm^3, 0.015 mol).

Yield 1 g (26%), m.p. (C-N), 71.8-72.9 : N-I, 106.7-109°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.3(17,m,alkyl), 1.8(1H,m, alkyl), 6.3(2H,m,CH=CH), 7.1(4H,m,ArH)

i.r. ν_{max} (KBr) 2950,2850,1620,1550,1480,1050,840 cm^{-1}

1-(2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene (e.g. **46**) (*Scheme 4*)

Quantities: 2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carbaldehyde (2.5 g, 0.008 mol), *trans*-4-n-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (6.2 g, 0.012 mol) and 1.6M BuLi (8 cm^3, 0.013 mol).

Yield 1.5 g (41%), m.p. (C-N), 68-69 ; N-I, 107-108.7°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.3(17H,br s,alkyl), 1.8 (1H,s,cyclohexyl-H), 6.5(2H,m,-CH=CH-) 7.0(2H,m,ArH)

i.r ν_{max} (KBr) 2950,2875,1620,1550,1480,1050,840 cm^{-1}

1-(2,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene (e.g. **46**) (*Scheme 4*)

Quantities: 2,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-carbaldehyde (3.1 g, 0.009 mol), *trans*-4-n-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (7.5 g, 0.015 mol) and 1.6M BuLi (10 cm^3, 0.016 mol).

Yield 1.5 g (41%), m.p. (C-I), 71-72 : (I-N), 61-60.2°C

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.3(17H,br s,alkyl), 1.8
(1H,m,cyclohexyl-H), 6.4(2H,m,-CH=CH-),
7.1(2H,t,ArH)

i.r. ν_{max} (KBr) 2950,2875,1610,1550,1480,1055,1000,840 cm^{-1}

1-(4-Bromo-3,5-difluorophenyl)-2-(*trans*-4-n-pentylcyclohexyl)ethene (**67**) (*Scheme 10*)

Quantities: 4-Bromo-3,5-difluorobenzaldehyde (5 g, 0.02 mol), *trans*-4-n-pentyl cyclohexyl-1-methyltriphenylphosphonium bromide (15 g, 0.03 mol) and 1.6M BuLi (19 cm^3, 0.033 mol).

Yield 3.5 g (43%), b.p. 160°C/0.05mm Hg.

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.2(17H,br s,alkyl), 1.8
(1H,m,cyclohexyl-H), 6.0(2H,m,CH=CH),
7.1 (2H,m,ArH)

i.r. ν_{max} (film) 3050,2950,2850,1610,1490,1100,1050,950,850 cm^{-1}

General method: 1-(4'-n-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes (e.g. **47a**) (*Scheme 4*)

The appropriate sodium alkoxide (1.1 mol), prepared from the alcohol by the addition of the necessary quantity of sodium hydride, was added dropwise, with stirring, to the appropriate 1-(polyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene (1 mol) in dry pyridine at -10°C. The progress of the reaction was monitored by t.l.c. at 10 min. intervals as the mixture was slowly allowed to warm to room temperature. The overall reaction time was determined either by the complete consumption of the 1-(polyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene or by the formation of undesirable side-products. The reaction mixture was then acidified (4M HCl/ice) and the aqueous layer was extracted with ether (2x50 cm^3). The ether extracts were combined, washed with water (50 cm^3), dried ($MgSO_4$), and the solvent removed in vacuo. The resulting pale yellow liquid was purified by flash chromatography on silica gel eluting with light petroleum (b.p. 60-80°C). The desired fractions were collected and the solvent removed in vacuo. The residue was recrystallised from ethanol to give the pure 1-(4′-n-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene as a white crystalline solid. The yield of the product was normally greater than 90%. The liquid crystalline transition temperatures for the substituted alkylarylethenes are listed in ***Tables 5*** (p. 92), ***6*** (p. 95), ***7*** (p. 98), ***8*** (p. 101) and ***9*** (p. 104) in the discussion section.

The following proton n.m.r. and i.r. spectra for 1-(4′-n-decyloxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene are representative of the series.

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(6H,t,2xCH_3), 1.3(33H,br s,alkyl), 1.8(1H,m,
cyclohexyl-H), 4.2(2H,t,OCH_3), 6.5(2H,m,CH=CH),
7.0(4H,m,ArH)

i.r. ν_{max} (KBr) 2950,2850,1540,1480,1150,1050,880 cm^{-1}

General method: 1-(4′-n-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes (e.g. **47b**) (*Scheme 4*)

1-(4′-n-Alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethene (0.5 g) was added to a stirred suspension of 5% Pd/C (150 mg) in ethanol (20 cm^3) and hydrogenated at room temperature and atmospheric presure. After uptake of the appropriate amount of hydrogen (approximately 1h.) the catalyst was filtered off and the filtrate evaporated to dryness. The residue was dissolved in hot ethanol, insoluble material was removed by hot filtration, and the solution then set aside to cool when the pure 1-(4′-n-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-n-pentyl-cyclohexyl)ethane (100%) crystallised out as white flakes.

The liquid crystal transition temperatures for the substituted alkylarylethanes are shown in ***Tables 5*** (p. 92), ***6*** (p. 95), ***7*** (p. 98), ***8*** (p. 101) and ***9*** (p. 104) in the discussion section.

The following proton n.m.r. and i.r. spectra for 1-(4′-n-decyloxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethane are representative of the series.

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(6H,t,2xCH_3), 1.3(33H,br s ,alkyl), 1.8(1H,m, cyclohexyl-H), 4.2(2H,t,OCH_3), 7.0(4H,m,ArH)

i.r. ν_{max} (KBr) 2950,2850,1540,1480,1150,1050,880 cm^{-1}

Trans-4-n-pentylcyclohexyl-1-methanol **(43)** (*Scheme 4*)

Trans-4-n-pentylcyclohexanecarboxylic acid (20 g, 0.1 mol) was treated with borane dimethyl sulphide (28 cm^3, 0.3 mol) as described in the method given on p. 139. Vacuum distillation of the resulting oil afforded the pure *trans*-4-n-pentylcyclohexyl-1-methanol, 18 g (97%), b.p. 100°C/0.5mm Hg (lit.[142] 99°C/ 0.1mm Hg), as a clear oil.

Trans-4-n-pentylcyclohexyl-1-methylbromide **(44)** (*Scheme 4*)

Trans-4-n-pentylcyclohexyl-1-methanol (30 g, 0.16 mol) was added to 3:1 (vol.) 47% hydrobromic acid : conc. sulphuric acid (50 cm^3). The reaction mixture was heated under reflux for 5h. and then poured into ice/water (300 cm^3). The aqueous layer was extracted with ether (4x100 cm^3) and the extracts were washed with conc. hydrochloric acid (30 cm^3), water (2x100 cm^3), saturated sodium bicarbonate solution (2x100 cm^3), water (100 cm^3), then dried ($MgSO_4$), and the solvent removed in vacuo. Vacuum distillation of the resulting dark residue afforded the pure alkyl bromide, 37 g (95%), b.p. 90°C/0.1mm Hg (lit.[142] 155°C/15mm Hg), as a clear oil.

Trans-4-n-pentylcyclohexyl-1-methyltriphenylphosphonium bromide **(45)** (*Scheme 4*)

Triphenylphosphine (47 g, 0.18 mol) and *trans*-4-n-pentylcyclohexyl-1-methylbromide (30 g, 0.12 mol) were heated under vigorous reflux for 0.5h. Upon cooling, the reaction mixture was poured into dry ether (200 cm^3). The resulting solid was filtered off, washed several times with dry ether in order to remove any unchanged triphenylphosphine, and dried in an oven at 100°C. The pure phosphonium salt, 40 g (63%), m.p. 177-181°C, was stored in a vacuum desiccator.

^{1}H n.m.r. δ($CDCl_3$/DMSO,TMS) 0.8(3H,t,CH_3), 1.2(9H,br s,alkyl), 1.6(9H, m,alkyl), 3.6(2H,m,CH_2), 7.1(15H,m,ArH)

i.r. ν_{max} (KBr) 3100,3000,2950,1605,1550,1400,825 cm^{-1}

2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl **(48)** (*Scheme 5*)

Decafluorobiphenyl (5 g, 0.01 mol) was treated with $LiAlH_4$ (1.9 g, 0.05 mol) as described in the method given on p. 135. However, in this instance, the reaction mixture was heated under reflux for 3 days. The crude product was purified by column chromatography on silica gel eluting with light petroleum (b.p. 60-80°C). The desired fractions were collected and the solvent removed in vacuo affording the pure 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 4 g (90%), m.p. 79-81°C (lit.[120] 81-83°C), as a white crystalline solid.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.3(2H,m,ArH)

i.r. ν_{max} (KBr) 3150,1660,1600,1530,1500,1480,1220,740,725 cm^{-1}

4-n-Decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (e.g. **51**) (*Scheme 6*)

2,2′,3,3′,4′,5,5′,6,6′-Nonafluorobiphenyl (2 g, 0.006 mol) was treated with sodium decoxide (0.008 mol) as described in the method given on p. 132. The crude product was purified by column chromatography on silica gel eluting with light petroleum (b.p. 60-80°C), followed by vacuum distillation, affording the desired 4-n-decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 2.7 g (96%), b.p. 121°C/ 0.01mm Hg, as a clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 1.0(3H,t,CH_3), 1.3(16H,m,alkyl), 4.2(2H,t,OCH_3), 7.3(1H,m,ArH)

i.r. ν_{max} (film) 2950,2900,1660,1520,1500,1480,1120,740 cm^{-1}

3,3′,5,5′-Tetrafluorobiphenyl (**56**) (*Scheme 7*): Method 1, using $TiCl_4$

In an atmosphere of nitrogen, commercial 1.6M BuLi (31 cm^3, 0.05 mol) was added dropwise to a rapidly stirred solution of 1-bromo-3,5-difluorobenzene (10 g, 0.05 mol) in dry ether (100 cm^3) cooled to -78°C. Titanium tetrachloride (5.5 cm^3, 0.05 mol) was then added dropwise. Stirring was continued overnight as the reaction mixture was allowed to warm to room temperature. The mixture was then poured into ice/4M-aqueous hydrochloric acid (100 cm^3) and the ether layer separated. The aqueous layer was extracted with ether (2x50 cm^3), and the ether solutions combined, dried ($MgSO_4$), and the solvent removed in vacuo. The resulting dark oil was purified by column chromatography on silica gel eluting with light petroleum (b.p. 60-80°C) affording the desired 3,3′,5,5′-tetrafluorobiphenyl, 3.2 g (56%), m.p. 81-83°C, as a white crystalline solid.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.0(6H,m,ArH)

i.r. ν_{max} (KBr) 2950,1610,1580,1500,1420,1000,900,720 cm^{-1}

3,3′,5,5′-Tetrafluorobiphenyl **(56)** (*Scheme 7*): Method 2, via the Ullmann reaction

1-Bromo-3,5-difluorobenzene (20 g, 0.1 mol) and copper powder (20 g, 0.3 mol) were placed in a special glass tube which was heat sealed. The glass tube was then introduced into an oven and heated at 220°C for 24h. The tube was cooled, carefully opened and the contents continuously extracted (Soxhlet) with chloroform for 24h. The solvent was removed in vacuo yielding a dark oil which was shown to contain several components by t.l.c. Purification by flash chromatography on silica gel, eluting with light petroleum (b.p. 60-80°C), afforded the desired product, 3 g (27%), m.p. 81-83°C, as a white crystalline solid.

3,3′,5,5′-Tetrafluorobiphenyl **(56)** (*Scheme 7*): Method 3, using a nickel catalyst

A mixture of zinc dust, triphenylphosphine, nickel *bis*(triphenylphosphino)-dichloride, and potassium iodide in the molar ratio 1:0.4:0.05:0.05 was added to dry dimethylformamide (200 cm^3) contained in round-bottomed flask purged with nitrogen. The reaction mixture was stirred at room temperature, during which time the colour changed from green to dark brown, after which 1-bromo-3,5-difluorobenzene (1 mol) was added. The progress of the reaction was monitored by t.l.c., and after stirring for 5h. the reaction mixture was treated with 4M-aqueous hydrochloric acid (100 cm^3), then extracted with ether (2x100 cm^3), and the combined extracts washed with water (100 cm^3), dried ($MgSO_4$), and the solvent removed in vacuo. Purification was achieved by flash chromatography on silica gel, eluting with light petroleum (b.p. 60-80°C), affording the desired 3,3′,5,5′-tetrafluorobiphenyl (40%), m.p. 81-83°C, as a white crystalline solid.

Attempted synthesis of 4-acetyl-3,3′,5,5′-tetrafluorobiphenyl **(57)** (*Scheme 7*)

A solution of 3,3′,5,5′-tetrafluorobiphenyl (5 g, 0.02 mol) in dry dichloromethane (20 cm^3) was added dropwise, over 1h., to a rapidly stirred mixture of acetyl chloride (1.7 g, 0.02 mol) and powdered anhydrous aluminium chloride (4 g, 0.03 mol) maintained at 0°C. On completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for a further 5h. The reaction mixture was then poured into 4M-aqueous hydochloric acid/ice (100 cm^3), stirred for 1h., and then extracted with dichloromethane (2x50 cm^3). The combined extracts were dried ($MgSO_4$), and the solvent removed in vacuo, whereafter examination of the crude residue by t.l.c. revealed a mixture of components which could not be separated by column chromatography.

4-Bromo-2,6-difluoroacetophenone (**58**) (*Scheme 8*)

1-Bromo-3,5-difluorobenzene (5 g, 0.026 mol) was added over a period of 1h. to a stirred mixture of freshly distilled acetyl chloride (2.02 g, 0.026 mol) and dry aluminium chloride (4.2 g, 0.032 mol) maintained at 0°C. After completion of the addition the reaction mixture was stirred at room temperature for 5h., then poured into ice/4M-aqueous hydrochloric acid (300 cm^3), stirred for 1h., and extracted with dichloromethane (2x100 cm^3). The extracts were combined, washed with water (2x50 cm^3), dried ($MgSO_4$), and the solvent removed in vacuo. Examination of the resulting amber coloured oil by t.l.c. revealed a mixture of two components (discussed on p.80-81) which were partially separated by flash chromatography on silica gel, eluting with 4:1 light petroleum (b.p. 60-80°C) : chloroform. The solvent was removed in vacuo from the desired fractions affording the 4-bromo-2,6-difluoroacetophenone, 1.8 g (35%), b.p. 100°C/ 0.9mm Hg, as a clear oil.

^{1}H n.m.r. $\delta(CDCl_3,TMS)$ 2.5(3H,s,CH_3), 7.1(2H,d,ArH)

i.r. ν_{max} (film) 3050,2950,2850,1700,1605,1560,1400,1050 cm^{-1}

3,5-Difluorophenylboronic acid (**60**) (*Scheme 9*)

In an atmosphere of nitrogen, the Grignard reagent prepared from 1-bromo-3,5-difluorobenzene (10 g, 0.05 mol) and magnesium turnings (1.43 g, 0.06 mol) in dry ether (100 cm^3) was added, with stirring, dropwise to trimethylborate (16 cm^3, 0.15 mol) in dry tetrahydrofuran (100 cm^3) at -78°C. The reaction mixture was allowed to warm to room temperature, stirred overnight, and then 10% aqueous hydrochloric acid (100 cm^3) was added. The product was extracted into ether

($3x100$ cm^3) and the solution then stirred with 4M-aqueous sodium hydroxide (100 cm^3) for 1h. The ether layer was separated and discarded whilst the aqueous layer was acidified (4M HCl) and extracted with ether ($3x100$ cm^3). The combined extracts were washed with water ($2x100$ cm^3), dried ($MgSO_4$), and the solvent removed in vacuo yielding the desired 3,5-difluorophenylboronic acid, 6.5 g (82%), m.p. 180-185°C, as a light brown solid.

^{1}H n.m.r. δ($CDCl_3$/DMSO,TMS) 6.8(3H,m,ArH), 6.7(2H,s,OH)

i.r. ν_{max} (KBr) 3500-3100,2950,2850,1640,1600,1480,1000,850 cm^{-1}

The following polyfluorophenylboronic acid was synthesised in an analogous manner.

3,4,5-Trifluorophenylboronic acid **(66)** (*Scheme 10*)

Quantities: 1-Bromo-3,4,5-trifluorobenzene (10 g, 0.05 mol), magnesium (1.4g, 0.06 mol) and trimethylborate (16 cm^3, 0.015 mol).

Yield 6.5 g (78%), m.p. 285-289°C.

^{1}H n.m.r. δ($CDCl_3$/DMSO,TMS) 7.5(4H,m,ArH and 2xOH)

i.r. ν_{max} (KBr) 3500-3300,1650,1590,1480,1000,850 cm^{-1}

In cases where the Grignard reagent was likely to result in the formation of an aryne, the following polyfluorophenylboronic acids were synthesised via an organolithium intermediate at -78°C as detailed below.

2,4,6-Trifluorophenylboronic acid **(72)** p. 86

In an atmosphere of nitrogen, commercial 1.6M BuLi (32 cm^3, 0.05 mol) was added dropwise, over 1h., to a stirred solution of 1-bromo-2,4,6-trifluorobenzene (10 g, 0.047 mol) in dry tetrahydrofuran (100 cm^3) maintained at -78°C. On completion of the addition, the reaction mixture was maintained at -78°C for an additional 1h. and then transferred via a double-tipped needle into another flask (purged with nitrogen) containing trimethylborate (16 cm^3, 0.15 mol) in dry tetrahydrofuran at -78°C. The reaction mixture was allowed to warm to room temperature, stirred overnight, and then 10% aqueous hydrochloric acid added. The reaction mixture was stirred for 1h. and then extracted with ether (3x100 cm^3). The extracts were combined, washed with water (100 cm^3), dried ($MgSO_4$), and the solvent removed in vacuo yielding a pale yellow solid. Purification was achieved by washing the crude solid with hot light petroleum (b.p. 60-80°C) affording the desired 2,4,6-trifluorophenylboronic acid, 6.5 g (88%), m.p. 220-225°C, as a light brown solid.

^{1}H n.m.r δ($CDCl_3$/DMSO,TMS) 6.7(2H,s,2xOH), 6.9(2H,m,ArH)

i.r. ν_{max} (KBr) 3500-3300,1620,1520,1350,1040,750cm^{-1}

The following fluorophenylboronic acids were also prepared by this method.

2,6-Difluoro-4-formylphenylboronic acid (**73**) p. 87

Quantities: 2-(3,5-difluorophenyl)-1,3-dioxolane (10 g,0.05 mol), 1.6M BuLi (37 cm^3, 0.06 mol), and trimethylborate (16 cm^3, 0.15 mol).

Yield 4 g (43%), m.p. 151-153°C.

^{1}H n.m.r. δ($CDCl_3$/DMSO) 6.8(2H,s,2xOH), 7.4(2H,m,ArH), 9.9(1H,s,CHO)

i.r. ν_{max} (KBr) 3500-3300,2950,1710,1640,1580,1440,1000,800 cm^{-1}

4-Acetyl-2,6-difluorophenylboronic acid **(74)** p. 87

Quantities: 2-(3,5-difluorophenyl)-2-methyl-1,3-dioxolane (10 g, 0.05 mol), 1.6M BuLi (34 cm^3, 0.055 mol), and trimethylborate (16 cm^3, 0.15 mol).

Yield 4 g (40%), m.p. 181-185°C.

^{1}H n.m.r. δ($CDCl_3$/DMSO,TMS) 2.5(3H,s,CH_3), 7.4(4H,m,ArH and 2xOH)

i.r. ν_{max} (KBr) 3500,3300-2950,1700,1640,1580,1440,1000,875 cm^{-1}

3,3′,4,5,5′-Pentafluorobiphenyl. A general procedure for Pd(0)-catalysed cross-coupling reactions **(61)** (*Scheme 9*)

In an atmosphere of nitrogen, a solution of 3,5-difluorophenylboronic acid (5 g, 0.03 mol) in ethanol (10 cm^3) was added to a vigorously stirred mixture of 1-bromo-3,4,5-trifluorobenzene (5.7 g, 0.027 mol), tetrakis(triphenylphosphine)-palladium(0) (0.2 g, 0.0007 mol), 2M-aqueous sodium carbonate (30 cm^3) and benzene (30 cm^3). The stirred mixture was heated under reflux until the 1-bromo-3,4,5-trifluorobenzene had been completely consumed (as indicated by t.l.c.). The product was extracted into ether (2x100 cm^3), the extracts combined, dried ($MgSO_4$), and the solvent removed in vacuo. The resulting residue was purified by column chromatography on silica gel, eluting with light petroleum (b.p. 60-80°C), affording the desired 3,3′,4,5,5′-pentafluorobiphenyl, m.p. 76-78°C, as a white crystalline solid. The yield was normally greater than 90%.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.1(5H,m,ArH)

i.r. ν_{max} (KBr) 3100,1610,1590,1530,1400,1000,850,725 cm^{-1}

This method was successfully employed to prepare the following fluorinated biphenyls.

2,3,3',4,5,5',6-Heptafluorobiphenyl (e.g. **38**) (*Scheme 4*)

Quantities: Bromopentafluorobenzene (4 g, 0.025 mol), 3,5-difluorophenyl boronic acid (4.3 g, 0.025 mol), $PdP(Ph_3)_4$ (0.17 g, 0.00015 mol).

Yield 5 g (71%), m.p. 65-66°C.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.0(2H,m,ArH)

i.r. ν_{max} (KBr) 3000,2950,1620,1550,1430,1210,1000,850 cm^{-1}

2,3,3',4',5,5',6-Heptafluorobiphenyl (e.g. **38**) (*Scheme 4*)

Quantities: 4-Bromo-2,3,5,6-tetrafluorobenzene (5 g, 0.02 mol), 3,4,5-trifluorophenylboronic acid (4.2 g, 0.023 mol) and $PdP(Ph_3)_4$ (0.15 g, 0.00013 mol).

Yield 5.5 g (98%), m.p. 51.5-53°C.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.1(3H,m,ArH)

i.r. ν_{max} (KBr) 3000,2950,1620,1550,1430,1210,1000,850 cm^{-1}

1-(2,3',4',5',6-Pentafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)-ethene (e.g. **46**) (*Schemes 4* and *10*)

Quantities: 1-(Bromo-3,5-difluorophenyl)-2-(*trans*-4-n-pentylcyclohexyl)-ethene (3 g, 0.008 mol), 3,4,5-trifluorophenylboronic acid (1.6 g, 0.0088 mol) and $Pd(PPh_3)_4$ (0.1 g, 0.00008 mol).

Yield 0.9 g (27%), m.p. (C-I) 87-89 ; (I-N) 80-77.5°C

b.p. 185°C/0.2mm Hg.

^{1}H n.m.r. δ($CDCl_3$,TMS) 0.9(3H,t,CH_3), 1.3(17H,br s,alkyl), 1.8 (1H,m,cyclohexyl-H), 6.3(2H,m,CH=CH), 7.0(4H,m,ArH)

i.r. ν_{max} (KBr) 2950,2850,1540,1500,1480,1150,1050,880 cm^{-1}

2-(3,5-Difluorophenyl)-1,3-dioxolane **(63)** (*Scheme 10*)

3,5-Difluorobenzaldehyde (20 g, 0.14 mol), ethylene glycol (13 g, 0.21mol), toluene (100 cm^3) and *p*-toluenesulphonic acid (0.3 g) were placed in a 250 cm^3 round-bottommed flask fitted with a Dean-Stark trap and heated under reflux. The water formed during the ensuing reaction was continuously removed as an azeotrope with toluene and collected in the Dean-Stark trap. On completion of the reaction (which was followed by t.l.c.), the reaction mixture was poured into 10%-aqueous sodium bicarbonate (200 cm^3). The toluene layer was separated from the aqueous phase which was extracted with ether (2x50 cm^3). The organic phases were combined, dried ($MgSO_4$), and the solvent removed in vacuo affording the desired 2-(3,5-difluorophenyl)-1,3-dioxolane, 25 g (98%), b.p. 70°C/1.00mm Hg as a clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 3.9(4H,m,CH_2CH_2), 5.8(1H,s,CH), 6.9(3H,m,ArH)

i.r. ν_{max} (film) 3050,2950,2850,1620,1600,1310,1110,1000,840,725 cm^{-1}

2-(3,5-Difluorophenyl)-2-methyl-1,3-dioxolane **(78)** (*Scheme 12*) was also prepared in a similar manner.

Quantities: 3,5-Difluoroacetophenone (20 g, 0.13 mol), ethylene glycol (12 g, 0.19 mol) and *p*-toluenesulphonic acid (0.3 g).

Yield 25 g (96%), b.p. 75°C/4.0mm Hg. A clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 1.6(3H,s,CH_3), 4.0(4H,d,CH_2CH_2),
7.0(3H,m,ArH)

i.r. ν_{max} (film) 3050,2950,2850,1640,1600,1420,1050,1000,
860,700 cm^{-1}

2-(4-Bromo-3,5-difluorophenyl)-1,3-dioxolane (**64**) (*Scheme 10*)

In an atmosphere of nitrogen, commercial 1.6M BuLi (37 cm^3, 0.06 mol) was added, with stirring, dropwise, to 2-(3,5-difluorophenyl)-1,3-dioxolane (10 g, 0.05 mol) in dry tetrahydrofuran (100 cm^3) at -78°C. On completion of the addtion, the reaction mixture was maintained at -78°C for an additional 1h. after which bromine (5 cm^3, 0.1 mol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then poured into 4M-aqueous sodium hydroxide (100 cm^3). The organic layer was separated from the the aqueous phase which was extracted with ether (2x100 cm^3). The organic phases were combined, washed with aqueous sodium metabisulphite, water (2x100cm^3), dried ($MgSO_4$), and the solvent removed under reduced pressure. The desired 2-(4-bromo-3,5-difluorophenyl)-1,3-dioxolane, 11 g (82%), b.p. 97°C/0.5mm Hg remained as a clear oil.

^{1}H n.m.r. δ($CDCl_3$,TMS) 4.1(4H,m,CH_2CH_2), 5.8(1H,s,CH), 7.2(3H,m,ArH)

i.r. ν_{max} (film) 3050,2950,2850,1620,1600,1440,1650,840 cm^{-1}

4-Bromo-3,5-difluorobenzaldehyde (**65**) (*Scheme 10*)

2-(4-Bromo-3,5-difluorophenyl)-1,3-dioxolane (10 g, 0.04 mol), concentrated hydrochloric acid (5 cm^3) and dioxane (100 cm^3) were heated under reflux for 1h.

The reaction mixture was allowed to cool and then poured into water (200 cm^3). The product was extracted into ether (2x100 cm^3) and the extracts were combined, dried ($MgSO_4$), and the solvent removed in vacuo. The residue was recrystallised from hexane affording the desired 4-bromo-3,5-difluorobenzaldehyde, 8.8 g (100%), m.p. 83-85°C, as a white crystalline solid.

^{1}H n.m.r. δ($CDCl_3$,TMS) 7.4(2H,d,ArH), 10.0(1H,s,CHO)

i.r. ν_{max} (KBr) 3050,2950,2850,1700,1500,1440,1305,1000,850 cm^{-1}

Attempted preparation of 2,2′,4′,6,6′-pentafluorobiphenyl-4-carbaldehyde (71) (p. 85)

In an atmosphere of nitrogen, a solution of 2,4,6-trifluorophenylboronic acid (5 g, 0.028 mol) in ethanol (10 cm^3) was added to a vigorously stirred mixture of 4-bromo-3,5-difluorobenzaldehyde (5.5 g, 0.025 mol), 2M-aqueous sodium carbonate (30-60 cm^3), $Pd(PPh_3)_4$ (1.7 g, 0.005 mol) and benzene (30 cm^3). After heating under reflux for 24h., examination of the reaction mixture by t.l.c. indicated that no reaction had occurred.

3,5-Difluoro-4-iodoacetophenone (**79a**) (*Scheme 12*)

In an atmosphere of nitrogen, commercial 1.6M BuLi (34 cm^3, 0.055 mol) was added, dropwise, to a stirred solution of 2-(3,5-difluorophenyl)-2-methyl-1,3-dioxolane (10 g, 0.05 mol) in dry tetrahydrofuran (100 cm^3) at -78°C. On completion of the addition, the reaction mixture was maintained at -78°C for an additional 1h. and then a solution of iodine (19 g, 0.075 mol) in dry tetrahydrofuran (100 cm^3) was added dropwise. The reaction mixture was allowed to rise to 0°C while stirring and then poured into 4M-aqueous sodium hydroxide (200 cm^3). The product was extracted with ether (3x100 cm^3) and the combined ether extracts washed with aqueous sodium metabisulphite (twice), water (2x100 cm^3), then dried ($MgSO_4$) and the solvent removed in vacuo. The resulting crude residue was dissolved in dioxane (100 cm^3) and concentrated hydrochloric acid (5 cm^3) and the reaction mixture heated under reflux for 30 min. The reaction mixture was poured into water (200 cm^3) and extracted with ether (2x100 cm^3). The extracts were combined, dried ($MgSO_4$), and the solvent removed in vacuo yielding a pale yellow solid. Recrystallisation from hexane afforded the desired 3,5-difluoro-4-iodoacetophenone, 13 g (93%), m.p. 81-83°C, as golden needles.

^{1}H n.m.r. δ($CDCl_3$,TMS) 2.6(3H,s,CH_3), 7.4(2H,d,ArH)

i.r. ν_{max} (KBr) 3000,2950,1710,1605,1590,1400,1220,1105,825 cm^{-1}

<u>4,4′-Diacetyl-2,2′,6,6′-tetrafluorobiphenyl</u> **(80)** (*Scheme 12*)

3,5-Difluoro-4-iodoacetophenone (10 g, 0.035 mol) and copper bronze (4.5 g, 0.07 mol), contained in a 250 cm^3 round-bottomed flask fitted with an air condenser and thermometer, were heated to 200-210°C for 30min. and then poured into water (100 cm^3). Longer reaction times did not increase the yield. The suspended solids were filtered off and subjected to continuous extraction (Soxhlet) with chloroform for 24h., whilst the filtrate was extracted with ether (2x100 cm^3). The organic phases were combined, dried ($MgSO_4$), and the solvent removed in vacuo. Examination of the crude residue by t.l.c. revealed a mixture of components which were separated by flash chromatography on silica gel, eluting with 1:1 light petroleum (b.p. 60-80°C) : chloroform. Recrystallisation of the desired component from hexane afforded the pure 4,4′-diacetyl-2,2′,6,6′-tetrafluorobiphenyl, 1.9 g (37%), m.p. 95-96°C, as golden needles.

^{1}H n.m.r. δ($CDCl_3$,TMS) 2.6(6H,s,2xCH_3), 7.6(4H,m,ArH)

i.r. ν_{max} (KBr) 3100,2950,1710,1605,1590,1400,1200,1100,850 cm^{-1}

Attempted synthesis of 4′-acetyl-2,2′,6,6′-tetrafluorobiphenyl-4-yl ethanoate (**81**) (*Scheme 12*)

A solution of 3-chloroperbenzoic acid (4.2 g, 0.024 mol) in dry dichloromethane (20 cm^3) was added dropwise to a stirred solution of 4,4′-diacetyl-2,2′,6,6′-tetrafluorobiphenyl (5 g, 0.016 mol) in dry dichloromethane (20 cm^3) ensuring that the temperature did not exceed 5°C. The reaction mixture was stirred for 48h. at room temperature. Examination of the reaction mixture by t.l.c. revealed a number of components which had R_f values similar to the starting material. The precipitated 3-chlorobenzoic acid was filtered off and washed with dichloromethane (2x100 cm^3). The filtrate and washings were combined and treated successively with saturated aqueous sodium bicarbonate (2x50 cm^3), and water (2x50 cm^3), and finally dried ($MgSO_4$). After removal of the solvent, an attempt was made to purify the resulting crude residue by column chromatography on silica gel. However this was unsuccessful.

4-Bromo-2,6-difluoroaniline (**83**) (*Scheme 13*)

A solution of bromine (31 g, 0.19 mol) in glacial acetic acid (50 cm^3) was added drowise, with stirring, to 2,6-difluoroaniline (25 g, 0.019 mol) in glacial acetic acid (150 cm^3), maintaining the temperature below 25°C. The reaction mixture was stirred at room temperature for 2h., and then sodium thiosulphate (25 g), sodium acetate (50 g) and water (300 cm^3) were added in succession, and the mixture was allowed to stand in a refrigerator overnight. The product was filtered off, dissolved in ether, and the ether solution then washed with water (100 cm^3), 10% aqueous sodium hydroxide (50 cm^3), water (100 cm^3), and dried ($MgSO_4$). The solvent was removed in vacuo to yield a pale yellow solid which was sublimed (60°C/20mm Hg) affording the desired 4-bromo-2,6-difluoroaniline, 25 g (68%), m.p. 67-68°C (lit.[89] 67-68°C), as a white crystalline solid.

4-Bromo-2,6-difluorobenzenediazonium tetrafluoroborate (**84**) (*Scheme 13*)

4-Bromo-2,6-difluoroaniline (25 g, 0.12 mol) was dissolved in concentrated hydrochloric acid (32 cm^3) and water (32 cm^3). The solution was cooled rapidly to 5°C to obtain a fine suspension of the hydrochloride. An ice-cold solution of sodium nitrite (9 g, 0.13 mol) in water (50 cm^3) was then added, dropwise, to the stirred suspension, maintaining the temperature below 5°C throughout. On completion of the addition, a cold solution of sodium tetrafluoroborate (20 g, 0.18 mol) in water (50cm^3) was then added, in small portions with stirring. The resulting thick yellow precipitate was filtered off, washed with dry ether (50 cm^3) and allowed to dry in the air overnight, affording the desired 4-bromo-2,6-benzenediazonium tetrafluoroborate, 10 g (27%), as a yellow solid.

Attempted synthesis of 4′-bromo-2,2′,4,6,6′-pentafluorobiphenyl (**85**) (*Scheme 13*)

In an atmosphere of nitrogen, potassium acetate (3.3 g, 0.034 mol) was added to a stirred mixture of 4-bromo-2,6-difluorobenzenediazonium tetrafluoroborate (5 g, 0.017 mol) and 18-crown-6 (0.21 g, 0.0008 mol) and 1,3,5-trifluorobenzene ($50\ cm^3$) contained in a $100\ cm^3$ round-bottomed flask protected from the light. The reaction mixture was stirred at 20°C and the progress of the reaction was monitored by t.l.c. After stirring for 5 days, there was no indication of the formation of any coupling products.

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ABSTRACT

SYNTHESIS AND PROPERTIES OF SOME FLUORINATED BIPHENYL MESOGENS

Summary of a thesis to be submitted to the Council for
National Academic Awards for the degree of
Doctor of Philosophy
by
Avtar Singh Matharu

The initial aim of this work was to extend and complete an investigation into the liquid crystal properties of esters derived from compounds (1) and (2) containing a polyfluorinated biphenyl nucleus.

(1) 4-n-butyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl
(2) 4-n-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl

A range of esters derived from (1) and (2) was investigated. These compounds are generally quite low melting nematogens with an extremely wide nematic to isotropic range, but, unfortunately, because of the extensive lateral substitution, they have a rather high viscosity.

Due to the interest in the potential commercial applications of fluorinated liquid crystals generated by the synthesis of the *I-compounds*, members of the homologous series (3) and (4)(analogous to the *I-compounds*) were synthesised.

(3) 1-(4′-n-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes
(4) 1-(4′-n-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes

Replacement of the ester linkage by the ethane linkage (series (4)) resulted in lower melting nematogens possessing low birefringence and moderate viscosity.

The effect of systematically reducing the number of fluoro-substituents present on the biphenyl nucleus was also investigated. A number of polyfluorinated alkylaryl-ethenes and -ethanes were synthesised (series (5)-(12)), differing only in the number and position of the fluoro-substituents.

(5) 1-(4′-n-alkoxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes
(6) 1-(4′-n-alkoxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes
(7) 1-(4′-n-alkoxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes
(8) 1-(4′-n-alkoxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes
(9) 1-(4′-n-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes
(10) 1-(4′-n-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes
(11) 1-(4′-n-alkoxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethenes
(12) 1-(4′-n-alkoxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-n-pentylcyclohexyl)ethanes

All the compounds are low melting and mesogenic, and the type of mesophase formed is dependent upon the number and position of the fluoro-substituents. This work has resulted in a patent application.