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PATENT SPECIFICATION

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(54) SUBSTITUTED BIPHENYL AND POLYPHENYL
 COMPOUNDS AND LIQUID CRYSTAL MATERIALS AND
 DEVICES CONTAINING THEM

(71) I, SECRETARY OF STATE FOR DEFENCE, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

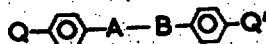
The present invention relates to substituted biphenyl and polyphenyl compounds and liquid crystal materials and devices containing them.

In the field of displays there is a requirement for electro-optic devices having a low power consumption. Devices made from liquid crystal materials have been shown to satisfy this requirement because they have an electrically switchable molecular arrangement and a very large electrical resistance, and at the present time a considerable amount of interest is being shown in such devices for these reasons.

There are many known liquid crystal materials; some have been known for many years. Liquid crystal materials are organic materials which exhibit a liquid crystal phase in which the molecules are arranged over limited spatial ranges in an ordered structure.

There are three known kinds of liquid crystal phase. One is known as a smectic mesophase in which the ordering of the molecules is of a lamellar kind. Another is known as a nematic mesophase in which a statistical ordering of the molecules exists parallel to the long axes of the molecules. The third is known as a cholesteric mesophase, in which the ordering of the molecules is of a helical kind.

Liquid crystal materials consist of compounds having a molecular structure which is elongated. For the liquid crystal compounds which have hitherto been used in devices the structure can be generalised and represented as follows:



where Q and Q' are terminal groups and A and B are linkage groups.

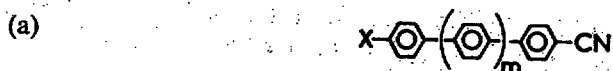
Except in the case of certain esters where the unit A—B includes the group CO.O the unit A—B generally includes a double or triple bond. For example the Schiff's bases which are widely used in commercial liquid crystal devices, such as para-methoxy-benzylidene-butylaniline (MBBA) or para-ethoxy-benzylidene-butylaniline (EBBA) are compounds containing the unit —C = N.

The presence of a double or triple bond in the unit A—B leads to a chemical

and/or photochemical instability of the material and is therefore undesirable for this reason. For example, Schiff's bases are readily hydrolysed, even by traces of water, yielding potentially toxic amines.

It has hitherto been supposed that the double or triple bond in the unit A—B is desirable to confer rigidity on the molecule and to provide a reasonably high liquid crystal to isotropic liquid transition temperature together with a reasonably low crystalline solid to liquid crystal transition temperature.

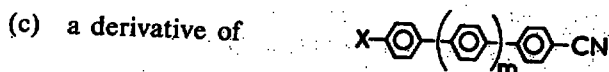
According to the present invention there is provided a liquid crystal substituted biphenyl or polyphenyl compound having one of the following molecular structures:



or



in which one of the phenyl rings of the structure is laterally substituted or



having a bridging group bridging any two adjacent ortho positions on adjacent rings of the structure, wherein

m is zero or an integer equal to one or more

X is an alkyl, alkoxy, alkanoyloxy or alkenyl group, and

CN is a cyano group.

A compound (or compounds) having one of these molecular structures will be referred to herein as a compound (or compounds) 'as defined'.

By a 'liquid crystal . . . compound' is meant a compound in one of the following two known categories:

(i) Compounds which normally exhibit a liquid crystal phase;

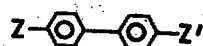
(ii) Compounds which do not normally exhibit a liquid crystal phase but which nevertheless usefully affect some aspect of liquid crystal behaviour when dissolved in other liquid crystal compounds.

Compounds in category (ii) show a 'virtual' liquid crystal to isotropic liquid transition at a temperature below the melting point of their solid phase. The virtual transition may be detected by rapid cooling of the liquid phase or by dissolving the compound in a material exhibiting a liquid crystal phase, observing change in the transition to the isotropic liquid phase of the material by the addition and calculating the virtual transition temperature by extrapolation.

Compounds in category (ii) might for example be usefully dissolved in other liquid crystal compounds to extend or vary the liquid crystal temperature ranges of the compounds or to vary the molecular helical pitch (in the case of cholesteric solutions).

Material which exhibits a liquid crystal phase and either consists of or contains a compound as defined above will be referred to herein as a material 'as defined'.

Certain biphenyl and polyphenyl compounds having a structure



have been known previously to exhibit liquid crystal phases. However in all of these known compounds the para-substituents Z and Z' have been of such a kind that these known compounds have exhibited their crystalline solid to liquid crystal transitions at very high temperatures; as a consequence these known compounds have not been used in known device applications.

By introducing the para-substituents X and CN in accordance with the invention to produce compounds as defined above reasonably low crystalline solid to liquid crystal and reasonably high liquid crystal to isotropic liquid transition temperatures can be obtained with the compounds either per se or mixed with one

or more other liquid crystal compounds; therefore compounds as defined are suitable for use in known device applications. Furthermore because a compound as defined does not contain a double or triple bond in the position corresponding to the unit A—B of the generalised liquid crystal molecular structure given above, its chemical and photochemical stability is potentially improved.

The liquid crystal phase (mesophase) exhibited by the material as defined may be nematic, smectic or cholesteric. In order for the phase to be cholesteric, the para-substituent X of the compound as defined may contain an asymmetric centre in a branched carbon chain, so that the compound is optically active.

It will be apparent to those skilled in the art that in order for the compound as defined to be a liquid crystal compound any lateral substituent or bridging group contained in its molecular structure must be simple, typically having four or less atoms.

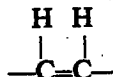
Examples of suitable lateral substituents are a methyl group and a halogen atom.

Examples of suitable bridging groups are as follows:

the group $>\text{CH}_2$ to form a fluorene;

the group $>\text{C}=\text{O}$ to form a fluorenone;

and the group



to form a phenanthrene.

According to another aspect of the present invention a liquid crystal device includes means for containing a region of liquid crystal material, a region of liquid crystal material contained in the containing means, wherein the liquid crystal material is material as defined above and means for applying an external stimulus to the material to alter the molecular arrangement in the material.

The means for applying an external stimulus may for example be means for applying an electric field to the region, means for applying a magnetic field to the region or means for applying a temperature change to the region.

The change in molecular arrangement produced by the external stimulus may be used to affect the transmission of electromagnetic radiation at any wavelength of the interest through the material, for example, by changing the transmissivity of the material or by changing the optical activity of the material, if it is optically active.

According to another aspect of the invention, an electro-optic liquid crystal device includes two adjacent plates at least one of which is optically transparent, a layer of liquid crystal material contained in the space between the plates wherein the liquid crystal material is the material as defined above, and deposited on the inner facing surfaces of the plates, a film of conducting material to allow an electric field to be applied across the layer. The electro-optic device may for example be a display device used, for instance, in an instrument such as a time watch or clock.

Embodiments of the present invention will be described by way of example, later with reference to the drawings filed with the Provisional Specification of Application No. 51698/72 (herein referred to as Figure 1) and the drawings filed with the Provisional Specification of Application No. 33709/73 (herein referred to as Figure 2 and 3) in which:

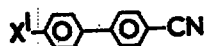
Figure 1 is a cross-sectional plan view (partly in circuit form) of an electro-optic device embodying the invention.

Figure 2 is a schematic diagram of a liquid crystal information storage device.

Figure 3 is a schematic diagram of a time clock or watch incorporating a liquid crystal display embodying the present invention.

It has been discovered in connection with the present invention that the materials as defined above may be synthesised and exhibit at least one liquid crystal phase (mesophase). The phase(s) may be cholesteric or nematic and/or smectic. The phase(s) may be exhibited at relatively low temperatures; this is a very desirable property of materials to be used in liquid crystal device applications.

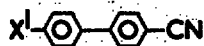
For example some compounds exhibiting a nematic liquid crystal phase are listed in Table 1 together with their crystal to nematic liquid crystal and nematic liquid crystal to isotropic liquid transition temperatures. Each compound is of the form



wherein X^1 represents an n-alkyl or an n-alkoxy group and is represented in Table 1 in an abbreviated form by its particular group X^1 .

TABLE 1

Transition temperatures for compounds



X^1	Crystal to Nematic transition temperature ($^{\circ}\text{C}$)	Nematic to Isotropic transition temperature ($^{\circ}\text{C}$)
n - C_5H_{11}	22.5	35
n - C_6H_{13}	13.5	27
n - C_7H_{15}	28.5	42
n - $\text{C}_5\text{H}_{11}\text{O}$	48	67.5
n - $\text{C}_6\text{H}_{13}\text{O}$	58	76.5
n - $\text{C}_7\text{H}_{15}\text{O}$	53.5	75

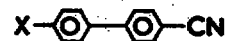
For example also some two-component mixtures exhibiting a nematic liquid crystal phase are listed in Table 2 together with their crystal to nematic liquid crystal and nematic liquid crystal to isotropic liquid transition temperatures. Each constituent compound in each mixture is of the form



where X^1 represents an n-alkyl group or an n-alkoxy group and is represented in Table 2 in an abbreviated form by its particular group X^1 . A suitable mole percentage for each constituent compound in each mixture is also listed.

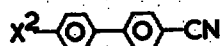
TABLE 2

Transition temperatures for binary mixtures of compounds



	Mole %	Crystal to Nematic transition temperature ($^{\circ}\text{C}$)	Nematic to Isotropic transition temperature ($^{\circ}\text{C}$)
<u>Mixture 1</u>			
n - C_7H_{15}	48.5	0.5	40
n - C_6H_{17}	51.5		
<u>Mixture 2</u>			
n - $\text{C}_5\text{H}_{11}\text{O}$	55	21	70.5
n - $\text{C}_7\text{H}_{15}\text{O}$	45		
<u>Mixture 3</u>			
n - C_5H_{11}	83.5	15	42
n - $\text{C}_6\text{H}_{13}\text{O}$	16.5		

For example also some mixtures exhibiting a cholesteric liquid crystal phase are listed in Table 3, together with their crystal to cholesteric liquid crystal and cholesteric liquid crystal to isotropic liquid transition temperatures. Each constituent compound in each mixture is of the form

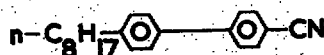


where X^2 represents an alkyl or alkoxy group which has either a normal or branched chain of carbon atoms; each constituent compound is represented in an abbreviated form by its particular group X^2 . A suitable mole percentage for each constituent compound is also listed.

TABLE 3

X^2	Mole %	Crystal to cholesteric transition temperature (°C)	Cholesteric to isotropic transition temperature (°C)
<u>Mixture 4</u>			
$n - C_5H_{11}O$	33	12.5	48
$n - C_7H_{15}O$	27		
$CH_3-CH_2-\underset{\substack{ \\ CH_3}}{C^*H}-CH_2O$	40		
<u>Mixture 5</u>			
$n - C_5H_{11}O$	21	11.5	53
$n - C_7H_{15}O$	17		
$n - C_8H_{17}O$	22		
$CH_3-CH_2-\underset{\substack{ \\ CH_3}}{C^*H}-CH_2O$	40		

In Mixtures 4 and 5 the asterisk (*) represents an asymmetric centre which causes the compound containing it to be optically active. For example also the compound



exhibits a smectic liquid crystal phase from 21°C to 32.5°C and a nematic liquid crystal phase from 32.5°C to 40°C.

Examples of methods of preparing compounds as defined above will now be described.

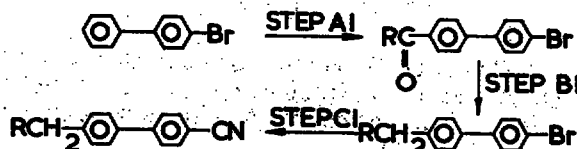
CAUTIONARY NOTICE.

Reference is made to the following description to the use of 4-nitrobiphenyl which is known to be a carcinogenic (cancer forming) substance and also to other related nitro and amino substances, eg 4-nitro-and-amino-4-bromobiphenyl, which may be carcinogenic. The industrial use of carcinogenic substances is regulated in the United Kingdom by the Carcinogenic Substances Regulations 1967. Reference is made in the following description to substances such as 4-nitrobiphenyl merely to illustrate preparation routes. In each case in question the use of the carcinogenic or possibly carcinogenic substance is merely given as one way of arriving at an intermediate product which may be a known compound, eg 4-hydroxy-4'-bromobiphenyl or a derivative thereof; it will be apparent to those

skilled in the art that other ways of arriving at the intermediate product in question which avoid the use of carcinogenic substances are known or possible.

EXAMPLE 1.

Preparation of 4'-alkyl-4-cyanobiphenyls by the following route:



where R is an alkyl group, for example an n-alkyl group.

STEP A1: The production of 4'-alkanoyl-4-bromobiphenyl (by Friedel-Crafts Acylation).

One example of a way of carrying out this step is as follows:

To commercially available 4-bromobiphenyl (0.08 mole) and anhydrous aluminium trichloride (0.1 mole) dissolved in dry "AnalaR" (Trade Mark) nitrobenzene (85 ml), the appropriate n-alkanoyl chloride (0.1 mole) is added in drops, the temperature being maintained below 20°C. The solution is stirred for about 18 hours at room temperature and poured onto a mixture of ice, water and concentrated hydrochloric acid. The mixture is then stirred for about 0.5 hour, and the nitrobenzene layer separated. The nitrobenzene is removed by steam distillation, and the residue is crystallised from absolute ethanol to constant melting point.

STEP B1: The production of 4'-n-alkyl-4-bromobiphenyl (by Huang Minlon Reduction).

One example of a way of carrying out this step is as follows:

To the appropriate bromoketone (0.037 mole) dissolved in a mixture of dry diethylene glycol (60 ml) by warming, a solution of (90%) hydrazine hydrate (0.08 mole) in dry diethylene glycol (20 ml) is added. Potassium hydroxide (0.09 mole) is added to the warm solution, and after heating at about 100°C until most of the solid is dissolved, the reaction mixture is heated under reflux for about 1 hour. The temperature is raised to about 180°C by distillation and maintained at about 180°C for 4 hours. On cooling, the reaction mixture is shaken with benzene and the extract is dried. The solvent is removed and the residue is crystallised from absolute ethanol to constant melting point.

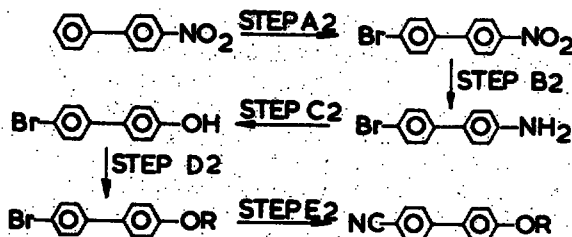
STEP C1: The production of 4'-n-alkyl-4-cyanobiphenyl.

One example of a way of carrying out this step is as follows:

A mixture of the 4'-n-alkyl-4-bromobiphenyl (0.021 mole) prepared by steps A and B and cuprous cyanide (0.031 mole) in dry dimethylformamide (75 ml) is heated under reflux for about 12 hours. On cooling the reaction mixture is poured onto a stirred mixture of ferric chloride, concentrated hydrochloric acid and water. After heating at about 60–70°C for 20 minutes the mixture is shaken with chloroform and the extract washed with 5N hydrochloric acid, water, 10% aqueous sodium hydroxide, water and then dried. The solvent is removed and the residue purified by column chromatography on silicic acid, followed by crystallisation from light petroleum (boiling point 40–60°C) at –78°C to constant melting point. Finally the produce is distilled under vacuum (0.5 mm Hg) at about 140–150°C.

EXAMPLE 2.

Preparation of 4-alkoxy-4'-cyanobiphenyls by the following route:



where R is an alkyl group, for example an n-alkyl group. The Cautionary Notice

given above applies here in respect of the production of the intermediate produce 4-bromo-4'-hydroxybiphenyl.

STEP A2: The production of 4-bromo-4'-nitrobiphenyl.

One example of a way of carrying out this step is as follows:

Commercially available 4-nitrobiphenyl is brominated by the method of Le Fevre and Turner (as described in J Chem Soc (1926), p.2045) to give 4'-bromo-4-nitrobiphenyl.

STEP B2: The production of 4-bromo-4'-aminobiphenyl.

One example of a way of carrying out this step is as follows:

Reduction of the nitro-compound produced by Step A2 (81 g) is achieved by stirring at 100°C for about 12 hours with a mixture of iron pin dust (58 g), ethanol (500 ml; 90%) and concentrated hydrochloric acid (29 ml). Sodium carbonate (22 g) is added and stirring is continued for 30 minutes whereupon a slight excess of dilute aqueous ammonia is added. On cooling, the amine formed is extracted into ether. The combined ether/alcohol extract of the amine is evaporated to remove the ether, and the residue is poured into water. The amine is precipitated, filtered off and dried.

STEP C2: The production of 4-Bromo-4'-hydroxybiphenyl.

One example of a way of carrying out this step is as follows:

4'-Amino-4-bromobiphenyl (60 g) produced by step B2 is dissolved in aqueous 95% acetic acid (360 ml) at 90°C, and to the solution vigorously stirred is added rapidly 40% w/w sulphuric acid (360 ml) preheated to 90°C. Stirring and rapid cooling to 0°C gives the finely divided amine sulphate, which is diazotised at 0°C ($\pm 1^\circ\text{C}$) by the slow addition of aqueous sodium nitrite (41.6 g) in water (100 ml). The excess of sodium nitrite is then destroyed with urea. 95% Acetic acid (400 ml) is then added to effect solution of the diazonium salt. The ice-cold solution of the diazonium sulphate is run immediately into a vigorously stirred and boiling solution of 40% w/w sulphuric acid (200 ml). The solution is added slowly at first, until suspended particles are visible in the mixture, after which the rate of addition is increased. The time required for the addition is about 30 minutes. The solution is then heated under reflux for about 15 minutes and cooled; dilution with an equal volume of water gives a solid which is digested with hot N-sodium hydroxide solution (3000 ml). After removal of insoluble material by filtration, the filtrate is acidified to give colourless 4-bromo-4'-hydroxybiphenyl.

STEP D2: The production of 4'-n-alkoxy-4-bromobiphenyls.

One example of a way of carrying out this step is as follows:

To a mixture of 4-bromo-4'-hydroxybiphenyl produced by step C2 (0.033 mole) and anhydrous potassium carbonate (0.132 mole) in cyclohexanone (70 ml), the appropriate n-alkyl bromide (0.053 mole) is added and the stirred mixture heated under reflux for about 4 hours. On cooling, the reaction mixture is filtered, and the solvent is removed from the filtrate. The residue is crystallised from a mixture of benzene and light petroleum (boiling point 40–60°C) to constant melting point.

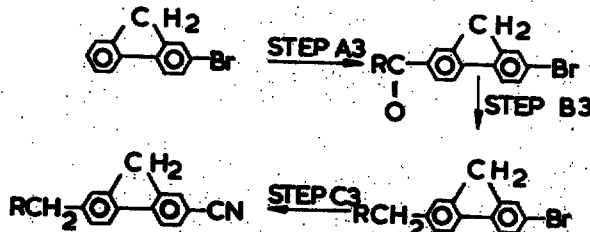
STEP E2: The production of 4'-n-alkoxy-4-cyanobiphenyls.

One example of a way of carrying out this step is as follows:

A mixture of 4'-n-alkoxy-4-bromobiphenyl (0.024 mole) produced by step D2 and cuprous cyanide (0.036 mole) in dry dimethylformamide (100 ml) is heated under reflux for about 12 hours. On cooling, the reaction mixture is poured onto a mixture of ferric chloride, concentrated hydrochloric acid and water. After heating at 60–70°C for about 20 minutes the mixture is shaken with chloroform and the extract washed with 5N hydrochloric acid, water, 20% aqueous sodium hydroxide, water and then dried. The solvent is removed and the residue purified by column chromatography on silicic acid, followed by crystallisation from light petroleum (boiling point 40–60°C) at –78°C to constant melting point. Finally the product is distilled under vacuum (0.5 mm Hg) at about 140°C.

EXAMPLE 3.

Preparation of 7-alkyl-2-cyanofluorenes by the following route:

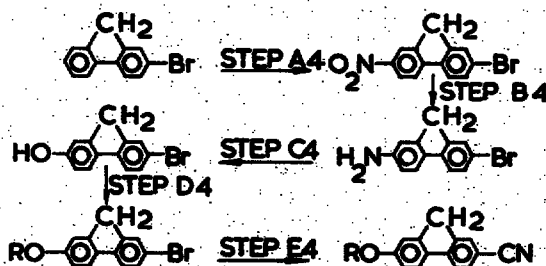


where R is an alkyl group, for example an n-alkyl group.

The starting material is 2-bromofluorene which is prepared by a conventional method. Steps A3, B3 and C3, may be carried out respectively in the same way as Steps A1, B1 and C1 described in Example 1, above.

EXAMPLE 4.

Preparation of 7-alkoxy-2-cyanofluorenes by the following route:



where R is for example an alkyl group, an n-alkyl group. The *Cautionary Notice* given above applies here in respect of the production of the intermediate product 7-hydroxy-2-bromofluorene.

STEP A4: Nitration of 2-bromofluorene.

One example of a way of carrying out this step is as follows:

2-Bromofluorene is converted into 7-nitro-2-bromofluorene by dissolving the 2-bromofluorene in glacial acetic acid at 60°C and adding a mixture of fuming nitric acid and concentrated nitric acid. The temperature is raised to 90°C for 1 hour to complete the reaction. The product is filtered off and purified by crystallisation.

STEP B4: Reduction of 7-amino-2-bromofluorene.

One example of a way of carrying out this step is as follows:

The reduction of 7-nitro-2-bromofluorene produced by step A4 is achieved by dissolving the 7-nitro-2-bromofluorene in hot glacial acetic acid and adding stannous chloride dissolved in concentrated hydrochloric acid. After heating under reflux, the amine hydrochloride so produced is filtered off and digested with warm aqueous sodium hydroxide. The product is purified by crystallisation.

STEP C4: The production of 7-hydroxy-2-bromofluorene.

One example of a way of carrying out this step is as follows:

The conversion of 7-amino-2-bromofluorene produced by step B4 into 7-hydroxy-2-bromofluorene is carried out in a similar manner to that described as an example of Step C2 above.

STEP D4: The production of 7-n-alkoxy-2-bromofluorene.

One example of a way of carrying out this step is as follows:

7-hydroxy-2-bromofluorene produced by Step C4 is alkylated in the same way as described in the example of Step D2 above to give 7-n-alkoxy-2-bromofluorene.

STEP E4: The production of 7-n-alkoxy-2-cyanofluorene.

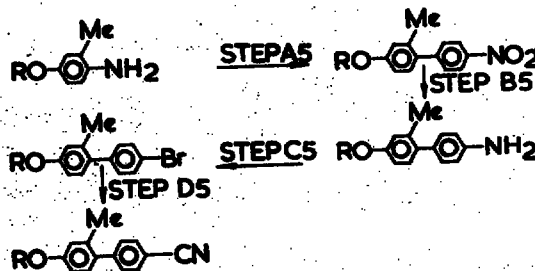
One example of a way of carrying out this step is as follows:

7-n-alkoxy-2-bromofluorene produced by Step D4 is converted into 7-n-

alkoxy-2-cyanofluorene by heating in dimethylformamide with cuprous cyanide in a way similar to the particular example of Step E2 described above.

EXAMPLE 5.

Preparation of a laterally methyl substituted 4'-alkoxy-4-cyanobiphenyl by the following route:



where R is an alkyl group for example, an n-alkyl group. The *Cautionary Notice* given above applies here in respect of the production of the intermediate product laterally methyl substituted 4'-alkoxy-4-bromobiphenyl.

STEP A5: The production of laterally methyl substituted 4'-n-alkoxy-4-nitro-biphenyl.

One example of a way of carrying out this step is as follows:

The appropriate 4-n-alkoxy-2-methylaniline is converted into laterally methyl substituted 4'-n-alkoxy-4-nitrobiphenyl by the Gomberg Reaction.

STEP B5: The production of laterally methyl substituted 4'-n-alkoxy-4-aminobiphenyl.

One example of a way of carrying out this step is as follows:

The laterally methyl substituted 4'-n-alkoxy-4-nitrobiphenyl produced by step A5 is reduced by iron pin dust reduction in a similar way to the particular example of Step B2 described above to produce laterally methyl substituted 4'-n-alkoxy-4-aminobiphenyl.

STEP C5: The production of laterally substituted 4'-n-alkoxy-4-bromobiphenyl.

One example of a way of carrying out this step is as follows:

The laterally methyl substituted 4'-n-alkoxy-4-aminobiphenyl produced by Step B5 is converted into the laterally substituted 4'-n-alkoxy-4-bromobiphenyl by diazotization in a way similar to the particular example of Step C2 described above. This is followed by the addition of cuprous bromide.

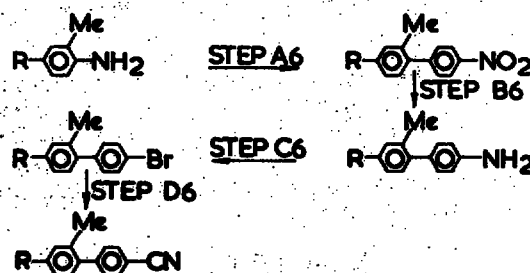
STEP D5: The production of laterally methyl substituted 4'-n-alkoxy-4-cyanobiphenyl.

One example of a way of carrying out this step is as follows:

The laterally methyl substituted 4'-n-alkoxy-4-bromobiphenyl produced by Step C5 is converted into the equivalent cyano-compound by reaction with cuprous cyanide in dimethylformamide in the same way as the particular example of Step E2 described above.

EXAMPLE 6.

The production of a laterally methyl substituted 4'-alkyl-4-cyanobiphenyl by the following route:



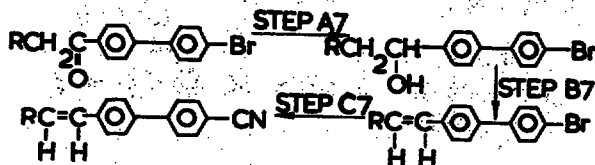
where R is an alkyl group for example, an n-alkyl group. The *Cautionary Notice*

given above applies here in respect of the production of the intermediate laterally substituted 4'-alkyl-4-bromobiphenyl.

The starting material is 4-alkyl-2-methylaniline which is produced in a known way. Steps A6, B6, C6 and D6 may be carried out in a similar way to Steps A5, B5, C5 and D5 respectively.

EXAMPLE 7.

The production of a 4'-alkenyl-4-cyanobiphenyl by the following route:



where R is an alkyl group for example, an n-alkyl group.

STEP A7: Reduction of the 4'-alkanol-4-bromobiphenyl.

One example of a way of carrying out this step is as follows:

The appropriate starting ketone, prepared from 4-bromobiphenyl by acylation in the same way as the particular example of Step A1 described above. The ketone is reduced by lithium aluminium hydride in dry ether to give the appropriate alcohol which is purified by crystallisation.

STEP B7: Dehydration of the alcohol produced by Step A9.

One example of this step is as follows:

4'-alkenyl-4-bromobiphenyl is prepared by dehydration of the alcohol produced by Step A7 by heating for 10 minutes in glacial acetic acid. The product is purified by crystallisation.

STEP C7: The production of 4'-alkenyl-4-cyanobiphenyl.

One example of a way of carrying out this step is as follows:

4'-alkenyl-4-cyanobiphenyl is prepared from the bromo-compound produced by Step B7 using cuprous cyanide in dimethylformamide in the same way as Step C1 described above. The product is purified by column chromatography and distillation.

EXAMPLE 8.

The production of 4"-alkyl-4-cyano-p-terphenyls.

The route used is similar to that used in Example 1; however in this example the appropriate terphenyl is used in each step instead of the corresponding biphenyl used in Example 1.

The starting material which is 4-bromo-p-terphenyl may be prepared by bromination of commercially available p-terphenyl by a known method.

EXAMPLE 9.

The production of 4"-alkoxy-4-cyano-p-terphenyls.

The route used is similar to that used in Example 2; however, in this example the appropriate terphenyl is used in each step instead of the corresponding biphenyl used in Example 2.

The *Cautionary Notice* given above applies here in respect of production of the intermediate product 4"-hydroxy-4-bromo-p-terphenyl.

The starting material which is 4"-nitro-p-terphenyl may be prepared by nitration of commercially available p-terphenyl by a known method.

EXAMPLE 10.

The production of di-ortho-substituted 4'-alkoxy-4-cyano-biphenyls.

The route used is similar to that used in Example 5; however in this case appropriately substituted nitrobenzene, for example, 1-methyl-2-nitrobenzene, is used as a reactant instead of the nitrobenzene used in step A5. The *Cautionary Notice* given above applies here in respect of the intermediate di-laterally substituted 4'-alkoxy-4-bromobiphenyl.

EXAMPLE 11.

The production of 4'-alkoxy-4-cyano-biphenyls having more than two ortho-substituents.

The route used is similar to that used in Example 5; however, in this case appropriately substituted compounds are used as starting reactants instead of the corresponding 4-n-alkoxy-2-methylaniline and nitrobenzene used in Step A5.

EXAMPLE 12.

5 The production of 4'-alkyl-4-cyano-biphenyls having at least two orthosubstituents.

The route used is similar to that used in Example 6; however, in this case either or both of the starting reactants 4-alkyl-2-methylaniline and nitrobenzene used in Step A6 has an appropriate substituent group.

EXAMPLE 13.

10 The production of 4"-alkyl-4-cyano-p-terphenyls having at least one ortho-substituent.

The route used is similar to that used in Examples 6 and 12; however, in this case the starting reactants are 4'-alkyl-4-aminobiphenyl prepared in a known way and nitrobenzene, at least one of which is appropriately substituted.

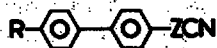
EXAMPLE 14.

The production of 4"-alkoxy-4-cyano-p-terphenyls having at least one ortho-substituent.

20 The route used is similar to that used in Examples 5, 10, and 11; however, in this case the starting reactants are 4'-alkoxy-4-aminobiphenyl prepared in a known way and nitrobenzene, at least one of which is appropriately substituted.

EXAMPLE 15.

The production of compounds having the formula

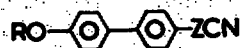


25 where R is an alkyl group, CN is a cyano group, and Z represents a plurality of directly para-linked benzene rings.

The route used is similar to that used in Example 1; however, in this example the appropriate multiphenyl is used in each step instead of the corresponding biphenyl used in Example 1.

EXAMPLE 16.

30 The production of compounds having the formula

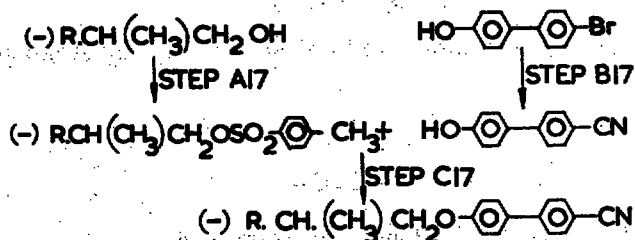


where R—O is an alkoxy group, CN is a cyano group and Z represents a plurality of directly para-linked benzene rings.

35 The route used is similar to that used in Example 2; however, in this example the appropriate multiphenyl is used in each step instead of the corresponding biphenyl used in Example 2.

EXAMPLE 17.

40 The production of optically active 4'-alkoxy-4-cyanobiphenyls by the following route:



where R is an alkyl group.

One example of Steps A17, B17, and C17, particularly for the case of the compound (-) 4'-(2"-methylbutyloxy)-4-cyano-biphenyl, is as follows:

STEP A17: The production of (-) 2-methyl-butyl-toluene-p-sulphonate.

One example of a way of carrying out this step is as follows:

To a solution of toluene-p-sulphonyl chloride (0.094 mole) in dry pyridine (75 ml) at -5°C, (-) 2-methyl butan-1-ol (0.085 mole) is added in one portion. The solution is maintained below 0°C and stirred for 2 hours. Water (15 ml) is added in portions of 1,1,1,2,5 and 5 ml at 5 minute intervals, the temperature being maintained below 5°C. The solution is diluted with water (75 ml). The oil so produced is extracted into chloroform and the extract washed successively with water, 2N sulphuric acid, water, 15% aqueous sodium bicarbonate and water, and finally dried over anhydrous sodium sulphate. The chloroform is removed by distillation under reduced pressure and the residual oil is distilled, the fraction being collected with a boiling point of 149°C at a pressure of 0.5 mm of mercury.

STEP B17: The production of 4'-hydroxy-4-cyanobiphenyl.

One example of a way of carrying out this step is as follows:

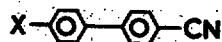
A mixture of 4'-hydroxy-4-bromobiphenyl (0.021 mole) and cuprous cyanide (0.031 mole) in dry dimethyl-formamide (75 ml) are heated under reflux for 6 hours. On cooling, the reaction mixture is poured onto a stirred mixture of ferric chloride, concentrated hydrochloric acid and water. After heating at about 60-70°C for 20 minutes the mixture is shaken with chloroform and the extract washed with 5N hydrochloric acid, water, 10% aqueous sodium bicarbonate, water and then dried. The solvent is removed and the residue is dissolved in the minimum volume of hot acetone, and the sufficient light petroleum (boiling point 40-60°C) is added to produce a slight turbidity. The solution is refrigerated and the crystals are filtered off. The material is further purified by sublimation at a bath temperature of 160°C at 0.3 mm; this yields a colourless solid.

STEP C17: The production of (-)4'-(2"-methyl-butyloxy)-4-cyanobiphenyl.

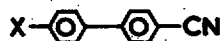
One example of a way of carrying out this step is as follows:

To 4'-hydroxy-4-cyanobiphenyl (0.01 mole), a solution of sodium (0.01 g atom) in dry ethanol (25 ml) is added and the mixture stirred until complete solution is obtained. The ethanol is removed by distillation under reduced pressure. To the sodium salt of the hydroxy compound so produced is added in dry dimethylformamide (55 ml) the tosylate (0.011 mole) prepared by step A17 and the mixture is heated and stirred at 110-130°C for 7 hours. After leaving to stand overnight, the reaction mixture is poured into water (100 ml) and the organic material is extracted into ether. The ethereal extract is washed successively with water, 15% aqueous sodium carbonate and water, and dried over anhydrous sodium carbonate. The ether is removed by distillation and the solid residue is purified by column chromatography on silicic acid using chloroform as the solvent. The product eluted from the column is crystallised from ethanol and finally distilled, the fraction being collected at a bath temperature of 130-135°C at a pressure of 0.3 mm of mercury.

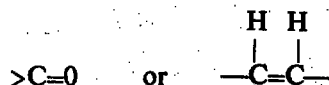
Other compounds as defined above which are ortho-substituted derivatives of



but in which the ortho-substituent(s) is (are) a halogen atom may be prepared by methods analogous to Example 5. Other compounds as defined above which are derivatives of



in which two of the ortho-positions are bridged by a bridging group and in which the bridging group is either



may be prepared by methods analogous to Example 4.

As taught in the Specification of Application No. 38449/75 divided from the present Specification alkanoyloxy groups may be introduced into a biphenyl or terphenyl structure as a para-substituent X by a conventional alkanoylation of the corresponding hydroxy compound. Thus it will be apparent to those skilled in the

art that compounds as defined above wherein X is an alkanoyloxy group may be prepared by routes analogous to those described above which involve alkylation of a hydroxy compound but the alkylation, eg step D2, of Example 2, being simply replaced by an alkanoylation.

Generally, compounds as defined above are potentially most useful when the number of carbon atoms in the para-substituent group X is 30 or less. If the compounds do not exhibit liquid crystal phases per se they may exhibit such phases when mixed with other materials such that the resultant materials constituting the mixtures exhibit liquid crystal phases.

Compounds having the formula



where R is an n-alkyl group, are particularly useful compounds exhibiting liquid crystal phases per se in the range where the n-alkyl group contains between 3 and 10 carbon atoms.

Generally, compounds mentioned in this specification may have a chain of carbon atoms in their para-substituent group X which chain is either normal (straight) or branched. Generally, compounds in which the para-substituent X has a branched carbon chain are potentially useful throughout roughly the same range of numbers of carbon atoms in the para-substituent X as those in which the para-substituent X has a normal carbon chain. However, some specific cases of the potentially most useful compounds in the various ranges are given in the following Table 4. This lists examples of compounds P having specific para-substituents Y and the potentially most useful ranges of the corresponding numbers N of carbon atoms in the para-substituent X for the compounds P. R represents an alkyl group in each case.

TABLE 4

P		N
$\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R Normal	3 to 24
$\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R branched	3 to 30
$\text{RO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R normal	3 to 30
$\text{RO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R branched	3 to 24
$\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R normal	2 to 24
$\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R branched	3 to 24
$\text{RO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R branched	3 to 24
$\text{RO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	R normal	2 to 24

The liquid crystal materials as defined above have a positive dielectric anisotropy (difference between the dielectric constant measured parallel to the long molecular axis and the dielectric constant measured perpendicular to this axis) owing to the presence of the cyano group.

Liquid crystal materials which are nematic and have a positive dielectric anisotropy may be used in devices employing the following known effects:

(i) the Schadt-Helfrich effect in which a twisted nematic liquid crystal (normally located between two transparent parallel plates such that the direction vector of the molecules is in the plane of the plates but varies over an angle of 90° from one plate to the other) located between an optical polariser and analyser exhibits an electric field dependent optical activity when an electric field is applied across the liquid crystal.

(ii) the Freedericks effect in which the direction vector of the molecules of a liquid crystal is changed from a first direction to a second direction perpendicular to the first direction by the action of an electric field applied in the second direction.

(iii) the phase-change effect in which the phase of a liquid crystal may be changed between cholesteric and field-induced nematic by the action of an electric field; in this effect the nematic material is mixed with an optically active material to produce a chloesteric material.

Liquid crystal materials which are cholesteric and have a positive dielectric anisotropy may be used in the phase change effect.

Examples of devices embodying the invention will now be described.

As an example of the use of a nematic liquid crystal material and a cholesteric liquid crystal material embodying the present invention a phase change effect device also embodying the invention will now be described. It is known that a method of producing cholesteric liquid crystal material suitable for use in a phase change effect device involves mixing an optically active liquid crystal material with a nematic liquid crystal material or a mixture of nematic liquid crystal materials. Using that method Mixture 4 of Mixture 5 (Table 3) defined above, may be provided as the basic material for a phase change effect device.

Figure 1 is a cross-sectional plan view, partly in circuit form, of an electro-optic liquid crystal phase change effect device embodying the invention. A thin layer 17 of Mixture 4 or Mixture 5 defined above is contained between a glass slide 19 and a glass slide 29. The glass slide 19 has on its surface in contact with the layer 17 a coating 23 of tin oxide. The glass slide 29 has on its surface in contact with the layer 17 a coating 25 of tin oxide. The glass slide 19 has a region overlapping the end of the glass slide 29 in order that an electrical connection 31 may be made to the tin oxide coating 23. Likewise the glass slide 29 has a region overlapping the end of the glass slide 19 in order that an electrical connection 33 may be made to the tin oxide coating 25. A battery 37 may be applied between the connection 31 and the connection 33 when a switch 35 in series with the battery 37 is closed. The battery 37 is such that the electric field strength obtained therefrom across the layer 17 is greater than the critical field strength for the phase change effect. The surface of the glass slide 19 not in contact with the layer 17 contains a silver coating mirror 39. The layer 17 may be sealed between the glass slides 19 and 29 by means of a ring 41 of Araldite (Trade Mark) or other suitable sealing material.

A dark screen S is located at an acute angle in front of the glass slide 19 in such a position that the reflection of the screen S can be seen in the mirror 39 by an eye E as indicated in the drawing when the layer 17 is transparent.

When the switch 35 is open the image seen in the mirror 39 is bright. This is because the layer 17 is opaque and reflects ambient light into the eye E. However, when the switch 35 is closed the image seen in the mirror is dark. This is because the layer 17 has become transparent and the image of the screen S is seen in the mirror 39. When the switch 35 is opened again the image seen is again bright because the layer 17 is opaque again.

A display device based on the device described with reference to Figure 1 may be made by forming the coatings 23 and 25 in a known way such that they are shaped in the form of localised characters or symbols. For such a display the switches connected to each character or symbol i.e. corresponding to the switch 35, may be electronically operated by control logic (not shown).

In an alternative device the electric field applied may be alternating (at a frequency of up to about 50 kHz) instead of direct.

Figure 2 is a schematic diagram of a liquid crystal information storage or display device of a known kind but incorporating novel material embodying the invention; the device illustrates use of either smectic or cholesteric material

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5 embodying the invention. A layer 63 of either cholesteric liquid crystal material containing a compound as defined above or of smectic liquid crystal material containing a compound as defined above, is contained between glass slides 65, 67 having conducting coatings 69, 68 on their respective inner faces. A laser 71 producing an output beam 73 in the infrared part of the spectrum is arranged so that the beam 73 can be scanned over the slide 65 and the coating 69 by a conventional laser deflector 75. The slide 65 is transparent to the beam 73, but the coating 69 absorbs the beam 73. A voltage source 77 providing an alternating output is electrically connected to the coating 68 and to the coating 69 through a switch 70.

10 The device operates in the following way. Information is written by the beam 73 on the coating 69, and on the layer 63 by thermal conduction from the coating 69. The heat conducted to the layer 63 is sufficient to raise the temperature of the selected localised areas of the layer 63 and to cause the phase of those areas to change. If the material of the layer 63 is originally in the cholesteric mesophase the phase is changed to the isotropic liquid phase. If the material is originally in the smectic mesophase the phase is changed to the nematic mesophase, if the material has one, or to the isotropic liquid phase. After the beam 73 has heated a given area of the coating 69 and of the layer 63 and has been deflected to another area the given area rapidly cools again; the material in that area returns to its original phase. However, it returns to a cloudy or scattering form of the original phase. Therefore if the areas of the layer 63 not scanned by the beam 73 are in the clear or non-scattering form of the original phase the areas scanned are distinguished from those not scanned by their optical scattering properties. Therefore if the layer 63 is observed visually through the slide 67 and the coating 68, either after the beam 73 has been removed or whilst it is in operation through an appropriate filter, the information written can be seen. The coatings 69, 68 are made optically transparent for this purpose.

25 Erasing stored or displayed information is carried out by scanning the layer 63 with the beam 73 whilst applying an electric field derived from the voltage source 77 across the layer 63 by closing the switch 70. The material of the layer 63 is again heated to change phase and cooled again to return to its original phase; however in this case the voltage causes the material to return to the clear form of the original phase.

30 Information can alternatively be erased by scanning the layer 63 with the beam 73 without using the applied electric field provided that an appropriately slow scanning rate is used for the beam 73.

35 Figure 3 is a schematic diagram of a time clock or watch; the clock or watch illustrates the use of a liquid crystal display embodying the invention. A quartz crystal oscillator 81 has an oscillation frequency of 32.168 kHz. An output signal from the oscillator at that frequency is divided in a count down unit 83 providing an output signal at a frequency of 64 Hz. The output signal is applied to a logic unit 85 which further divides the frequency by sixty four. The logic unit 85 generates a single pulse every second. It counts these second pulses and provides a minute pulse every time sixty of the second pulses have been counted. It also counts the minute pulses and provides an hour pulse every time sixty of the minute pulses have been counted.

40 The second, minute and hour pulses are fed to operate a gate (not shown) within the logic unit 85. The gate allows operating signals to be applied via selected members in a series of conductors 86 to a liquid crystal display 87. When a second, minute or hour pulse arrives at the gate of the unit 85 it causes the selected members of the conductors 86 to be changed appropriately.

45 The display 87 is a 3-section digital display. A first section 88 displays the appropriate second digits, a second section 89 displays the appropriate minute digits and a third section displays the appropriate hour digits. The gate of the logic unit 85 selects the appropriate digits to be operated in the sections 88, 89 and 90 by selecting the appropriate conductors 86 for applying operating signals. When it receives a second, minute or hour pulse the gate changes the selected members of the conductors 86 to those required for the next appropriate digits in chronological sequence.

50 The display 87 operates in any known way; for example its digits can be operated by the phase-change effect in the way described with reference to Figure 1. The liquid crystal material used for the display 87 is chosen to suit the method of operation. However the material which is in the nematic, cholesteric or smectic mesophase as appropriate contains at least one compound as defined above.

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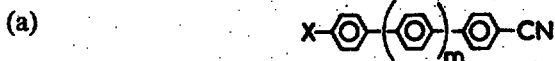
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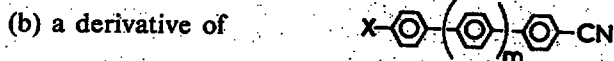
The count down unit 83 and the logic unit 85 can respectively be CMOS SCL 5423 (or 5425) and CMOS SCL 5424 (or 5428) digit/decoder driver manufactured by Solid Stage Scientific Inc.

WHAT I CLAIM IS:—

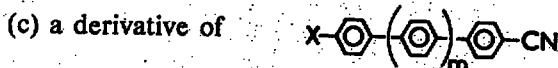
1. A liquid crystal substituted biphenyl or polyphenyl compound having one of the following molecular structures:



or



wherein one of the phenyl rings of the structure is laterally substituted or



having a bridging group bridging any two adjacent ortho positions on adjacent phenyl rings of the structure, wherein

m is zero or an integer equal to one or more

X is an alkyl, alkoxy, alkanoyloxy or alkenyl group and

CN is a cyano group.

2. A compound as claimed in claim 1 and wherein the compound is a laterally substituted derivative of



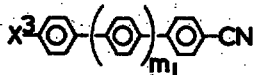
m₁ being 0 or 1, and has as a lateral substituent a methyl group.

3. A compound as claimed in claim 2 and having the following structural formula:



wherein X³ is an alkyl or alkoxy group and Me is a methyl group.

4. A compound as claimed in claim 1 and wherein the compound is a laterally substituted derivative of



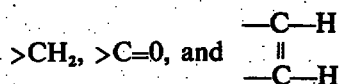
m₁ being 0 or 1, and has as a lateral substituent a halogen atom.

5. A compound as claimed in claim 1 and wherein the compound is a derivative of



m₁ being 0 or 1, having at least one bridging group bridging adjacent ortho positions on adjacent phenyl rings of its molecular structure.

6. A compound as claimed in claim 5 and wherein the bridging group is one of the following:



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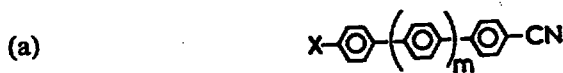
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The count down unit 83 and the logic unit 85 can respectively be CMOS SCL 5423 (or 5425) and CMOS SCL 5424 (or 5428) digit/decoder driver manufactured by Solid Stage Scientific Inc.

WHAT I CLAIM IS:—

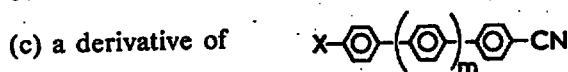
- 5 1. A liquid crystal substituted biphenyl or polyphenyl compound having one of the following molecular structures: 5



or

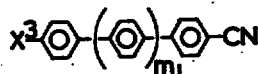


- 10 wherein one of the phenyl rings of the structure is laterally substituted or 10

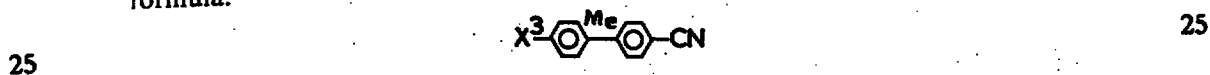


- 15 having a bridging group bridging any two adjacent ortho positions on adjacent phenyl rings of the structure, wherein 15
m is zero or an integer equal to one or more
X is an alkyl, alkoxy, alkanoyloxy or alkenyl group
and
CN is a cyano group.

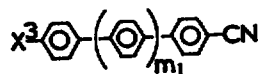
- 20 2. A compound as claimed in claim 1 and wherein the compound is a laterally substituted derivative of 20



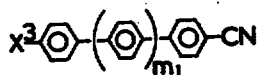
- m₁ being 0 or 1, and has as a lateral substituent a methyl group.
3. A compound as claimed in claim 2 and having the following structural formula:



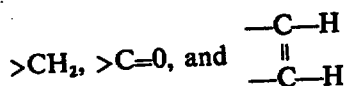
- wherein X³ is an alkyl or alkoxy group and Me is a methyl group.
4. A compound as claimed in claim 1 and wherein the compound is a laterally substituted derivative of



- 30 m₁ being 0 or 1, and has as a lateral substituent a halogen atom.
5. A compound as claimed in claim 1 and wherein the compound is a derivative of 30



- 35 m₁ being 0 or 1, having at least one bridging group bridging adjacent ortho positions on adjacent phenyl rings of its molecular structure.
6. A compound as claimed in claim 5 and wherein the bridging group is one of the following: 35





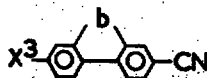
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17

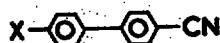
7. A compound as claimed in claim 6 and having the following structural formula:



wherein b is the bridging group and X³ is an alkyl or alkoxy group.

5

8. A compound as claimed in claim 1 and having the following structural formula:



wherein X is an alkyl, alkoxy, alkanoyloxy or alkenyl group.

10

9. A compound as claimed in claim 1 and having the following structural formula:

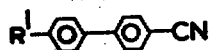


wherein X is an alkyl, alkoxy, alkanoyloxy or alkenyl group.

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10. A compound as claimed in any one of the preceding claims and wherein the para-substituent group X has 30 or less carbon atoms.

11. A compound as claimed in claim 10 and having the following structural formula:

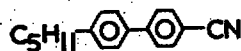


wherein R¹ is an n-alkyl group having at least 3 and at most 24 carbon atoms.

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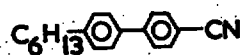
12. A compound as claimed in claim 11 and wherein the n-alkyl group has at least 3 and at most 10 carbon atoms.

13. A compound as claimed in claim 12 having the following structural formula:

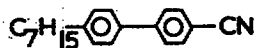


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14. A compound as claimed in claim 12 having the following structural formula:

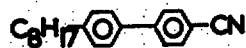


15. A compound as claimed in claim 12 and having the following structural formula:



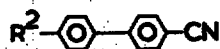
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16. A compound as claimed in claim 12 and having the following structural formula:



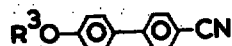
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17. A compound as claimed in claim 10 and having the following structural formula:



wherein R² is an asymmetrically branched alkyl group containing an optically active centre and having at least 3 carbon atoms.

18. A compound as claimed in claim 10 and having the following structural formula:



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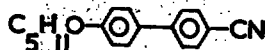
wherein R³O is an n-alkoxy group having at least 3 carbon atoms.

40

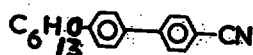


19. A compound as claimed in claim 18 and wherein the n-alkoxy group has at least 3 and at most 10 carbon atoms.

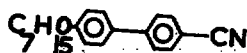
20. A compound as claimed in claim 19 and having the following structural formula:



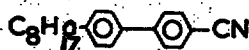
21. A compound as claimed in claim 19 and having the following structural formula:



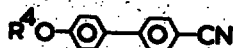
22. A compound as claimed in claim 19 and having the following structural formula:



23. A compound as claimed in claim 19 and having the following structural formula:

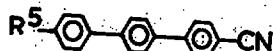


24. A compound as claimed in claim 10 and having the following structural formula



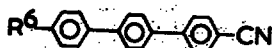
wherein R^4O is an asymmetrically branched alkoxy group containing an optically active centre and having at least 3 and at most 24 carbon atoms.

25. A compound as claimed in claim 10 and having the following structural formula:



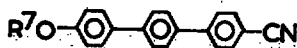
wherein R^5 is an n-alkyl group having at least 2 and at most 24 carbon atoms.

26. A compound as claimed in claim 10 and having the following structural formula:



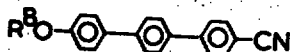
wherein R^6 is an asymmetrically branched alkyl group containing an optically active centre and having at least 3 and at most 24 carbon atoms.

27. A compound as claimed in claim 10 and having the following structural formula:



wherein R^7O is an n-alkoxy group having at least 2 and at most 24 carbon atoms.

28. A compound as claimed in claim 10 and having the following structural formula:



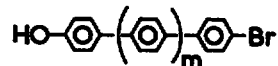
wherein R^8O is an asymmetrically branched alkoxy group containing an optically active centre and having at least 3 and at most 24 carbon atoms.

29. A method of preparing a compound as claimed in claim 1 having an alkyl group as the para-substituent group X wherein the method includes introducing the alkyl group by a Huang Minlon reduction of an alkanoyl compound and then introducing the cyano group by substitution of a bromo group in the alkylated compound.

30. A method of preparing a compound as claimed in claim 1 having an alkoxy group as the para-substituent group X wherein the method includes

28 27

introducing the alkoxy group by alkylation of the hydroxy group of a compound



or a derivative thereof, where m is as in claim 1, and then introducing the cyano group by substitution of the bromo group.

5 31. A method of preparing a compound as claimed in claim 1 the method being substantially the same as any one of Examples 1 to 17 described hereinbefore but excluding any steps quoted in those Examples to which the Cautionary Notice given hereinbefore applies. 5

10 32. A compound which is the product of the method claimed in any one of claims 29 to 31. 10

33. A liquid crystal material comprising a solution of at least two compounds at least one of which is a compound as claimed in any one of claims 1 to 28 or claim 32. 10

15 34. A liquid crystal device including means for containing a region of liquid crystal material, a region of liquid crystal material contained in the containing means, wherein the material consists of or includes a compound as claimed in any one of claims 1 to 28 or claim 32, and means for applying an external stimulus to the material to alter the molecular arrangement in the material. 15

20 35. A device as claimed in claim 34 and wherein the external stimulus is an electric field. 20

36. A device as claimed in claim 34 and wherein the external stimulus is a temperature change. 20

25 37. An electro-optic device according to claim 35 and wherein the containing means includes two adjacent plates at least one of which is optically transparent, the liquid crystal material being contained in the space between the plates and wherein the means for applying an electric field includes a film of conducting material forming an electrode deposited on the inner facing surfaces of the plates. 25

38. A device as claimed in claim 37 and wherein the plates are made of glass and the conducting films are made of tin oxide. 25

30 39. A device as claimed in claim 37 or 38 and wherein the device is an electro-optic display. 30

40. A device as claimed in claim 39 and wherein the electrodes have shapes therein corresponding to one or more characters or symbols. 30

35 41. A device as claimed in claim 39 or 40 and wherein the display is the indicator display of an instrument. 35

42. A device as claimed in claim 41 and wherein the indicator display is that of a time watch or clock. 35

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