

SPECIFICATION

Liquid crystal alkyl bicyclo(2,2,2)octyl phenyl or biphenyl nitrile compounds and liquid crystal materials and devices containing them

The present invention relates to liquid crystal alkyl bicyclo(2,2,2)octyl phenyl or biphenyl nitrile 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 incorporating 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 material; 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. The materials may be single compounds or mixtures of compounds.

According to the present invention there is provided a liquid crystal compound having the following molecular structure:



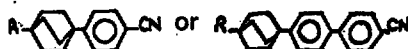
where R is an alkyl group,  is a bicyclo(2,2,2)octane ring  is a phenyl ring,

CN is a cyano group and n is 1 or 2.

A compound (or compounds) having molecular structure (I) will be referred to as a compound (or compounds), as defined.

The alkyl group R preferably contains less than eighteen carbon atoms, e.g. one to ten carbon atoms, and may be normal or branched. If R is branched it may contain a chiral centre in which case the compound is optically active.

The compound according to the present invention is thus either:



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

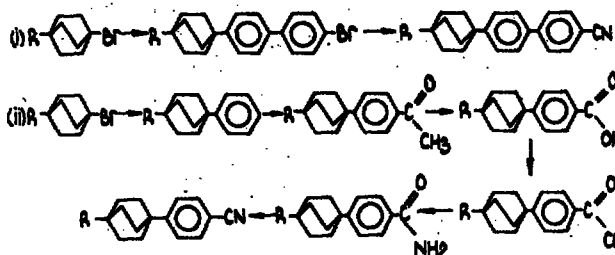
Compounds in category (ii) might for example be usefully dissolved in other liquid crystal compounds to extend or vary the liquid crystal temperature ranges of the compounds or to vary the molecular helical pitch (in the case of 'cholesteric' liquid crystals).

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'.

The liquid crystal phase exhibited by the material as defined may be nematic, smectic, or cholesteric.

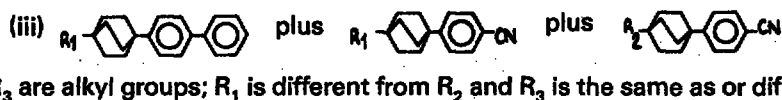
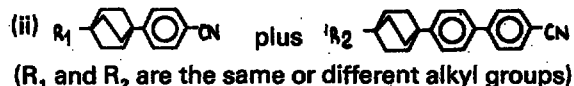
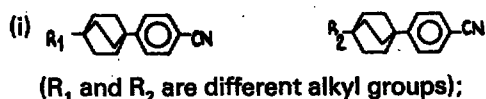
For a nematic phase the compound as defined should have a normal alkyl group R whilst for a cholesteric phase the compound as defined should have a branched alkyl group R containing a chiral centre.

Preferably compounds as defined are prepared from the intermediate bromo compound  eg by one of the following routes:



A compound as defined may be mixed with one or more other compounds as defined to enhance its liquid crystal properties, e.g. to extend its liquid crystal temperature range.

For example the following are examples of such mixtures:



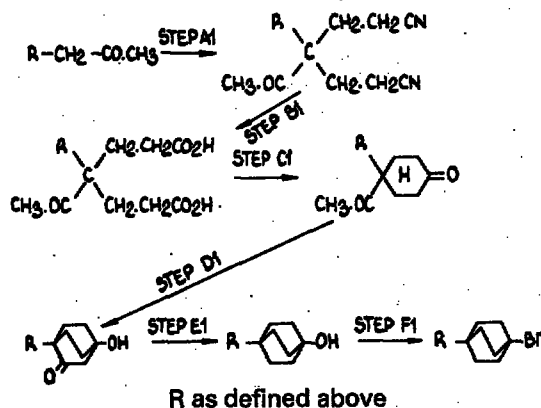
According to another aspect of the invention, an electro-optic liquid crystal device includes two adjacent substrates at least one of which is optically transparent, a layer of liquid crystal material contained in the space between the substrates wherein the liquid crystal material is in the material as defined above, and deposited on the inner facing surfaces of the substrates, 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. The device may be of known 'twisted nematic' effect or '(cholesteric-to-nematic) phase change' effect types.

Examples (Examples 2 and 3) of methods of preparing compounds as defined will now be described below. Example 1 as follows describes the preparation of an appropriate intermediate used in Examples 2 and 3.

In these examples 'MP' represents melting-point, C—N represents crystalline to nematic liquid crystal transition temperature and 'N—I' represents nematic liquid crystal to isotropic liquid transition temperature.

20 EXAMPLE 1

The intermediate compound 1-bromo-4-alkyl substituted bicyclo(2,2,2)octane which is used in the preparations described below may be prepared by the following route:



STEP A1: The production of 3-acetyl-1,5-dicyano-3 substituted pentane.

25 STEP B1: The production of 3-acetyl-3-substituted pentane-1,5-dicarboxylic acid.

STEP C1: The production of 4-acetyl-4-substituted cyclohexanone.

STEP D1: The production of 4-hydroxy-1-substituted bicyclo(2.2.2)octan-2-one.

STEP E1: The production of 1-hydroxy-4-substituted bicyclo(2.2.2)octane.

STEP F1: The production of 1-bromo-4-substituted-bicyclo[2.2.2]octane.

30 All six of these steps may be carried out by methods essentially analogous to those for R = methyl and ethyl described by H D Holtz and L M Stock in the Preparation of 1-Carboxy-4-Substituted Bicyclo [2.2.2] Octanes, J. Am. Chem. Soc, 86, 5183 (1964).

EXAMPLE 2

The production of 4-alkyl substituted 1-(4'-cyano-4''-biphenyl) bicyclo [2.2.2] octane by the following route:



5 STEP A2: The production of 1-(4'-bromo-4''-biphenyl)-4-substituted bicyclo [2.2.2] octane. 5

A solution of 1-bromo-4-substituted bicyclo [2.2.2] octane (0.0039 mole) in dry nitrobenzene (15 cm³) is added dropwise over a period of thirty minutes to a well stirred solution of crushed anhydrous aluminium chloride (0.0016 mol) and 4-bromobiphenyl (0.0116 mole) in dry nitrobenzene (25 cm³) maintained at 80°C under anhydrous conditions. The mixture is kept at this temperature for five hours.

- 10 It is then left stirring at room temperature, e.g. overnight. It is then added to a small amount of a hydrochloric acid/ice/water mixture and stirred for about twenty minutes. The organic layer is separated off and steam distilled to remove the solvent and 4-bromobiphenyl. The residue is dissolved in toluene and the solution so formed is dried over magnesium sulphate. It is then filtered and evaporated to dryness under vacuum. The solid residue is crystallised from ethanol and toluene. When R = pentyl, the 15 product of this step has C—N = 192.0°C and N—I = 231.2°C.

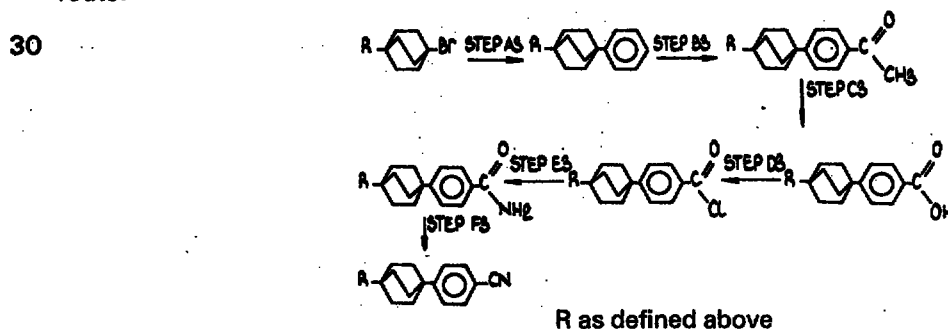
STEP B2: The production of 1-(4'-cyano-4''-biphenyl)-4-substituted bicyclo [2.2.2] octane.

A solution of 1-(4'-bromo-4''-biphenyl)-4-substituted bicyclo [2.2.2] octane (0.0019 mole) in dry 1-methyl-2-pyrrolidinone (5 cm³) is heated at 180°C with anhydrous copper (I) cyanide (0.0039 mole) for two hours under anhydrous conditions. The mixture is allowed to cool and then added to a 20 solution of anhydrous iron (III) chloride (0.35 g) in water (5 cm³) with concentrated hydrochloric acid (0.5 cm³). This is stirred for twenty minutes at 50°C and then water is added (50 cm³). This mixture is shaken several times with ether and then the combined organic layers are dried over magnesium sulphate. The solution is filtered and evaporated to dryness under vacuum. The product is purified by 25 column chromatography using silica-gel with a chloroform/hexane mixture as eluent. It is finally crystallised from 2-methoxy-ethanol.

An example of such a product is: $n\text{-C}_5\text{H}_{11}$ C—N = 159.7°C
N—I = 269.3°C. See also Table 2 below.

EXAMPLE 3

The production of 1-[4'-cyanophenyl]-4-alkyl substituted bicyclo [2.2.2] octane by the following route:



STEP A3: The production of 1-phenyl-4-substituted bicyclo [2.2.2] octane may be carried out by a reaction which is analogous to that described by S Sotheeswara, Ph D Thesis, Hull University Library 1967. When R = pentyl the product of this step has M.P. = 37°C.

STEP B3: The production of 4'-(4-substituted 1-bicyclo [2.2.2] octyl)acetophenone.

- 35 A solution of acetyl chloride (0.0077 mole) in dry nitrobenzene (3 cm³) is added dropwise to a well stirred solution of 4-substituted 1-phenyl bicyclo [2.2.2] octane (0.007 mole) and crushed anhydrous aluminium chloride (0.0082 mole) in dry nitrobenzene (7 cm³) at 0°C. This solution is left stirring, e.g. overnight, at room temperature. It is then added to a small amount of a hydrochloric acid/ice/water mixture and stirred for 30 minutes. The organic layer is separated off and steam distilled. The solid 40 residue is taken up in chloroform and the resultant solution dried over magnesium sulphate. It is then filtered and evaporated to dryness under vacuum to give a solid. This is crystallised from a methanol/ethanol mixture. When R = pentyl the product of this step has M.P. = 81°C.

STEP C3: The production of 4'-(4-substituted 1-bicyclo [2.2.2] octyl) benzoic acid.

A solution of sodium hypobromite, prepared by dissolving bromine (0.0168 mole) in a solution of

sodium hydroxide (0.0570 mole) in water (15 cm³) at 0°C, is added to a well stirred solution of 4'-(4-substituted 1-bicyclo [2.2.2] octyl)acetophenone, prepared in step B3, in dioxan (15 cm³). Throughout the addition and for thirty minutes afterwards the temperature is maintained at 35—40°C. The excess of sodium hypobromite is destroyed by adding a solution of sodium metabisulphite in water. More water is added and bromoform distilled from the reaction mixture. On cooling, the solution is acidified with concentrated hydrochloric acid and the precipitated product filtered off and washed with water.

The product was crystallised from a methanol/ethanol mixture. When R = pentyl the product of this step has C—N = 226.7°C; N—I = 288.7°C.

STEP D3: The production of 4'-(4-substituted 1-bicyclo [2.2.2] octyl) benzoylchloride.

A solution of 4'-(4-substituted-1-bicyclo [2.2.2] octyl) benzoic acid prepared in Step C3 (0.0017 mole) in dry toluene (10 cm³) is heated under reflux with thionyl chloride (1 cm³) for one hour under anhydrous conditions and then allowed to cool. The mixture is evaporated to dryness and then more dry toluene (10 cm³) is added. The resultant solution is again evaporated to dryness under vacuum. The acid chloride residue is used in the step E3 without further purification.

STEP E3: The production of 4'-(4-substituted 1-bicyclo [2.2.2] octyl) benzamide.

A solution of the acid chloride prepared in step D3, in dry benzene (10 cm³) is added dropwise to a well stirred ammonia solution (10 cm³ d = 0.88). The resultant precipitate is collected (with some difficulty) and washed with water. It is crystallised from a water/ethanol mixture at 0°C. When R = pentyl the product of this step has M.P. = 247.3°C.

STEP F3: The production of 1-(4'-(4-substituted 1-bicyclo [2.2.2] octyl) benzamide.

A solution of 4'-(4-substituted 1-bicyclo [2.2.2] octyl) benzamide (0.0010 mole) in chloroform (18 cm³) is stirred for one hour with a solution of sodium hydroxide (0.0750 mole) in water (3 cm³) and 0.02 g of benzyltriethylammonium hydroxide. The mixture is gently heated for fifteen minutes in a warm water bath and then allowed to cool. Ether (40 cm³) and water (40 cm³) are added. The organic layer is separated off, washed with water and then dried over magnesium sulphate. The solution is filtered and evaporated to dryness under vacuum. The solid residue is purified by column chromatography using silica gel with chloroform as eluent. It is then crystallised from light petroleum (b.p. 40—60).

An example of the product of this step is $n\text{-C}_5\text{H}_{11}$  which has C—N = 62°C,

N—I = 100°C. (See also Table 1 below).

The following tables give examples of the liquid crystalline temperature ranges of compounds and mixtures embodying the invention. In the tables R represents a normal alkyl group having the stated composition, C—N represents solid crystal to nematic liquid crystal transition temperature (°C), C—I represents solid crystal to isotropic liquid transition temperature (°C) and N—I represents nematic to isotropic liquid transition temperature (°C).

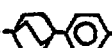
Table 1 — Compounds having the formula 

R	C—N or I	N—I
CH ₃	93 (C—I)	(-35)*
C ₂ H ₅	62.5 (C—I)	(17)*
n-C ₃ H ₇	66.5 (C—N)	88
n-C ₄ H ₉	75.5 (C—N)	85
n-C ₅ H ₁₁	62 (C—N)	100
n-C ₆ H ₁₃	72 (C—N)	86
n-C ₇ H ₁₅	61 (C—N)	95

(*) represents a monotropic 'virtual' transition temperature obtained by studying suitable binary mixtures of each compound with a standard material.

Further examples are $n\text{-C}_9\text{H}_{17}$ -, $n\text{-C}_9\text{H}_{19}$ -, $n\text{-C}_{10}\text{H}_{21}$ -.

Optically active analogues, e.g. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ --CN may be prepared by an analogous route.

Table 2 — Compounds having the formula R -

	R	C—N or I	N—I	
5	CH_3	198 (C—I)	(170)*	5
	R	C—N or I	N—I	
	C_2H_5	188 (C—N)	221	
	$n\text{-C}_3\text{H}_7$	180.5 (C—N)	276	
	$n\text{-C}_4\text{H}_9$	173 (C—N)	271.5	
10	$n\text{-C}_5\text{H}_{11}$	159 (C—N)	269	10
	$n\text{-C}_6\text{H}_{13}$	133 (C—N)	259	
	$n\text{-C}_7\text{H}_{15}$	141 (C—N)	250.5	

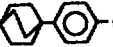
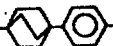
(*) represents a monotropic 'virtual' transition temperature obtained by studying suitable binary mixtures of each compound with a standard material.

15 Further examples are $n\text{-C}_9\text{H}_{17}$ -, $n\text{-C}_9\text{H}_{19}$ - and $n\text{-C}_{10}\text{H}_{21}$ --CN 15

Optically active analogues e.g. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ --CN may be prepared by an analogous route.

20 Although departures from ideality are known, examples of eutectic or nearly eutectic mixtures embodying the invention are quoted (Tables 3—6) as exemplifying the application of the above compounds in Tables 1 and 2. 20

Table 3 — The following mixture:

Mixture Constituent	Mole %	C—N
$n\text{-C}_9\text{H}_{17}$ -  -CN	51.0)	33.3
$n\text{-C}_5\text{H}_{11}$ -  -CN	49.0)	

25

Table 4 — The following mixture:

25

Mixture Constituent	Mole %	C—N
$n\text{-C}_9\text{H}_{17}$ -  -CN	38.0)	20.8
$n\text{-C}_5\text{H}_{11}$ -  -CN	34.9)	
$n\text{-C}_6\text{H}_{13}$ -  -CN	27.1)	

Table 5 — The following mixture:

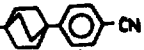
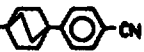
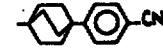
Mixture Constituent	Mole %	C—N
$n\text{-C}_3\text{H}_7$ 	37.9)	20.6
$n\text{-C}_5\text{H}_{11}$ 	34.4)	
$n\text{-C}_6\text{H}_{13}$ 	27.0)	
$n\text{-C}_4\text{H}_9$ 	0.7)	

Table 6 — The following mixture:

Mixture Constituent	Mole %	C—N
$n\text{-C}_3\text{H}_7$ 	19.9)	-3.5
$n\text{-C}_5\text{H}_{11}$ 	16.2)	
$n\text{-C}_6\text{H}_{13}$ 	12.3)	
$n\text{-C}_5\text{H}_{11}$ 	51.6)	

In addition the bicyclo-octane compounds embodying the invention may be mixed with any of the compounds in one or more of the other classes listed above.

A liquid crystal device embodying the invention will now be described by way of example only with reference to the accompanying drawings of which:

Figure 1 is an exploded view of a twisted nematic display;

Figure 2 is a front view of a watch having a twisted nematic crystal display constructed as shown in Figure 1; and,

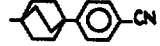
Figure 3 is a sectional view of the display part of the watch in Figure 2 but drawn to an enlarged scale.

As shown in Figure 1, a 'twisted nematic' type display includes a polariser 1 arranged with its polarisation axis 2 vertical. A liquid crystal cell 3 comprises two glass slides 4, 5 containing a layer of liquid crystal 6, consisting basically of a nematic material which may contain a small porportion (e.g. 1%) of a cholesteric compound. Electrodes 7, 8 e.g. of tin oxide, are arranged on the inner faces of the slides 4, 5. Behind the cell 3 is an analyser or second polariser 11 arranged with its polarisation axis 12 horizontal. A brushed aluminium reflector 27 is behind the analyser 11. Reference numeral 14 indicates the axis 12 projected onto the slide 5.

Prior to assembling the cell the slides 4, 5 are coated on their inner faces with silicon monoxide or magnesium fluoride. This coating is formed by evaporating a stream of e.g. silicon monoxide onto the slide at an angle of about 5° to the surface as for example described in UK Patent Specification No 1,454,296. On assembly the slides are arranged with the evaporation direction on the two slides 4, 5 at 90° to one another. With such a coating liquid crystal molecules at the coated surface lie in a single direction (parallel to the evaporation direction) and at an angle of about 25° to 35°, typically about 30° to the slide surface. As a result the liquid crystal molecules progressively twist from one slide 4 to the other slide 5. Thus the plane of plane polarised light is rotated through 90° on passing through the cell 3 providing the direction 13 of the molecules at the surface of the slide 4, 5 is parallel (or perpendicular) to the polarisers axis 2, 12.

Liquid crystal compounds and mixtures embodying the invention may also be used in known phase change effect devices in which an optically active material is normally mixed with a nematic material to give a long helical Pitch cholesteric material which may be switched to a nematic state by the action of an electric field applied in a way similar to that described above in relation to the twisted nematic device. An example of a phase change effect device is described in UK Patent No 1,433,130. The compounds or mixtures embodying the invention may comprise either the nematic material (if R is n-alkyl) or the optically material (if R is a chiral alkyl group) or both to form the long pitch cholesteric material. The material may be dyed with any known suitable pleochroic dye to give enhanced contrast. Compounds and mixtures embodying the invention are particularly suitable in phase change devices in view of their low birefringence.

The following mixtures are further examples demonstrating the usefulness of the compounds and mixtures embodying the invention in twisted nematic and cholesteric-to-nematic phase change effect devices.

	Mixture 1	wt%	N—I	
5	$n\text{-C}_3\text{H}_7$ 	30		5
	$n\text{-C}_5\text{H}_{11}$ 	40	92.7°C	
	$n\text{-C}_7\text{H}_{15}$ 	30		

Physical Properties of Mixture 1

10	Birefringence (Δn) at 20°C = 0.14			10
	Dielectric Anisotropy ($\Delta\epsilon$) at 20°C = 13.3			

Twisted Nematic Properties of Mixture 1

	(i) Measurements made in a 7 μm , rubbed polymer aligned cell at 20°C.			
	V90 (45°) = 1.35 V rms 32 Hz			
15	V50 (10°) = 1.89 V rms 32 Hz			15
	V10 (10°) = 2.66 V rms 32 Hz			

Key: Vx (y) x = % Transmission, y = angle of incidence.

$$\frac{dv}{dt} (10^\circ - 80^\circ\text{C}) = 13.4 \text{ mv}/^\circ\text{C}$$

(ii) Response Times

$$\left. \begin{array}{l} T_{\text{Rise}} 347 \text{ msec} \\ T_{\text{Decay}} 101 \text{ msec} \end{array} \right\} 3 \text{ V rms at } 20^\circ\text{C}$$

20	Mixture 2	Wt%	N—I	20
	$n\text{-C}_3\text{H}_7$ 	15	transition	
	$n\text{-C}_5\text{H}_{11}$ 	20	66°C	
	$n\text{-C}_7\text{H}_{15}$ 	15		
25	The benzoate ester mixture ZLI 1052 (Trade Mark) (produced by E. Merck Co)	50		25

Physical Properties of Mixture 2

Birefringence (Δn) at 20°C = 0.14

Twisted Nematic Properties of Mixture 2

	(i) Measurements made in a 7 μm , rubbed polymer aligned cell at 20°C:			
30	V90 (45°) = 1.30 V rms at 32 Hz			30
	V50 (10°) = 1.73 V rms at 32 Hz			
	V10 (10°) = 2.28 V rms at 32 Hz			

V90, V50 and V10 are the voltages for 90, 50 and 10% transmission respectively. The figures in brackets are the angles between the axis of measurement and the normal to the twisted nematic cell.

35	The rate of change of voltage with temperature			35
	$\frac{dv}{dt} 0-40^\circ\text{C} = 10.3 \text{ mV}/^\circ\text{C}.$			

(ii) Response Times

$$\left. \begin{array}{l} T_{\text{Rise}} 172 \text{ ms} \\ T_{\text{Decay}} 92 \text{ ms} \end{array} \right\} 3 \text{ V rms at } 20^\circ\text{C}$$

Mixture 3
(Long Pitch Cholesteric)

wt% Ch—I

Mixture 1

96.4 transition



3.6

97°C

5

Ch = cholesteric, I = Isotropic liquid, Pitch length = 5 μm .

Phase Change Properties

(i) Von = 7.8 V rms 12 μm cell with homeotropic boundary conditions, measured at 23°C.

(ii) Response Times

$\left. \begin{array}{l} T_{\text{Rise}} 450 \text{ ms} \\ T_{\text{Decay}} 400 \text{ ms} \end{array} \right\} \text{at } 10 \text{ V, } 23^\circ\text{C}$

10 CLAIMS

1. A liquid crystal compound having a molecular structure $\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$

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where R is an alkyl group and  is a bicyclo (2.2.2) octane ring, n being 1 or 2.

2. A liquid crystal compound as claimed in claim 1 and wherein R is an n-alkyl group having not more than 18 carbon atoms.

15 3. A liquid crystal compound as claimed in claim 1 and wherein R is a branched alkyl group having not more than 18 carbon atoms and containing a chiral centre.

4. A liquid crystal compound as claimed in claim 1 and wherein the integer n is one, the compound being a 1-4'-cyanophenyl-4-alkyl substituted bicyclo (2,2,2) octane.

20 5. A liquid crystal compound as claimed in claim 1 and wherein the integer n is two, the compound being a 1-4'-cyano-4''-biphenyl-4-alkyl substituted bicyclo (2,2,2) octane.

6. A liquid crystal compound as claimed in claim 4 and wherein R is an n-alkyl group having from 1 to 10 carbon atoms.

7. A liquid crystal compound as claimed in claim 4 and wherein R is an alkyl group having from four to 10 carbon atoms and containing a chiral centre.

25 8. A liquid crystal compound as claimed in claim 5 and wherein R is an n-alkyl group having from 1 to 10 carbon atoms.

9. A liquid crystal compound as claimed in claim 5 and wherein R is an alkyl group having from four to ten carbon atoms and containing a chiral centre.

10. A liquid crystal compound as claimed in claim 6 and wherein the compound is



30 11. A liquid crystal compound as claimed in claim 6 and wherein the compound is

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12. A liquid crystal compound as claimed in claim 6 and wherein the compound is



13. A liquid crystal compound as claimed in claim 6 and wherein the compound is



14. A liquid crystal compound as claimed in claim 6 and wherein the compound is

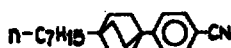


15. A liquid crystal compound as claimed in claim 6 and wherein the compound is



35 16. A liquid crystal compound as claimed in claim 6 and wherein the compound is

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Mixture 3
(Long Pitch Cholesteric)

wt% Ch—I
96.4 transition

Mixture 1



3.6 97°C

5

Ch = cholesteric, I = Isotropic liquid, Pitch length = 5 μm .

Phase Change Properties

(i) Von = 7.8 V rms 12 μm cell with homeotropic boundary conditions, measured at 23°C.

(ii) Response Times

$\left. \begin{array}{l} T_{\text{Rise}} 450 \text{ ms} \\ T_{\text{Decay}} 400 \text{ ms} \end{array} \right\} \text{at } 10 \text{ V, } 23^\circ\text{C}$

10 CLAIMS

10

1. A liquid crystal compound having a molecular structure $\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ where R is an alkyl group and C_6H_4 is a bicyclo (2,2,2) octane ring, n being 1 or 2.

2. A liquid crystal compound as claimed in claim 1 and wherein R is an n-alkyl group having not more than 18 carbon atoms.

15 3. A liquid crystal compound as claimed in claim 1 and wherein R is a branched alkyl group having not more than 18 carbon atoms and containing a chiral centre.

4. A liquid crystal compound as claimed in claim 1 and wherein the integer n is one, the compound being a 1-4'-cyanophenyl-4-alkyl substituted bicyclo (2,2,2) octane.

20 5. A liquid crystal compound as claimed in claim 1 and wherein the integer n is two, the compound being a 1-4'-cyano-4''-biphenyl-4-alkyl substituted bicyclo (2,2,2) octane.

6. A liquid crystal compound as claimed in claim 4 and wherein R is an n-alkyl group having from 1 to 10 carbon atoms.

7. A liquid crystal compound as claimed in claim 4 and wherein R is an alkyl group having from four to 10 carbon atoms and containing a chiral centre.

25 8. A liquid crystal compound as claimed in claim 5 and wherein R is an n-alkyl group having from 1 to 10 carbon atoms.

9. A liquid crystal compound as claimed in claim 5 and wherein R is an alkyl group having from four to ten carbon atoms and containing a chiral centre.

10. A liquid crystal compound as claimed in claim 6 and wherein the compound is



30 11. A liquid crystal compound as claimed in claim 6 and wherein the compound is



30

12. A liquid crystal compound as claimed in claim 6 and wherein the compound is



13. A liquid crystal compound as claimed in claim 6 and wherein the compound is



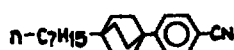
14. A liquid crystal compound as claimed in claim 6 and wherein the compound is



15. A liquid crystal compound as claimed in claim 6 and wherein the compound is



35 16. A liquid crystal compound as claimed in claim 6 and wherein the compound is



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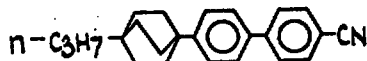
17. A liquid crystal compound as claimed in claim 8 and wherein the compound is



18. A liquid crystal compound as claimed in claim 8 and wherein the compound is



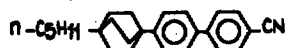
19. A liquid crystal compound as claimed in claim 8 and wherein the compound is



20. A liquid crystal compound as claimed in claim 8 and wherein the compound is



5 21. A liquid crystal compound as claimed in claim 8 and wherein the compound is 5



22. A liquid crystal compound as claimed in claim 8 and wherein the compound is



23. A liquid crystal compound as claimed in claim 8 and wherein the compound is



24. A liquid crystal material comprising a mixture of compounds at least one of which is a compound as claimed in claim 1.

10 25. A liquid crystal material comprising a mixture of compounds at least two of which are compounds as claimed in claim 1. 10

26. A liquid crystal material as claimed in claim 24 or claim 25 and wherein the mixture contains at least one compound of the form



and at least one compound of the form R_2 C1=CC=C(C=C1)C2=CC=CC=C2C3=CC=CC=C3C#N where R_1 and R_2 are n-alkyl groups.

15 27. A liquid crystal material as claimed in claim 24 and wherein the mixture contains at least one compound of the form 15



where R_3 is an alkyl or alkoxy group.

20 28. An electro-optic liquid crystal device including two adjacent substrates at least one of which is optically transparent, a layer of liquid crystal material contained in the space between the substrates and, deposited on the inner facing surfaces of the substrates, a film of conducting material to allow an electric field to be applied across the layer and characterised in that the liquid crystal material includes a compound as claimed in claim 1. 20

29. A device as claimed in claim 28 and wherein the liquid crystal device is a twisted nematic effect device.

25 30. A device as claimed in claim 28 and wherein the liquid crystal device is a cholesteric-to-nematic phase change effect device. 25