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A new class of liquid crystals: methylene-1,4-dihydropyridines

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A group of liquid crystal materials which contain the novel methylene-1,4-dihydropyridine substructure were synthesized and their mesogenic properties examined. Three main classes of liquid crystal compounds which differ in the structure of the aromatic core group (phenyl, azobenzene and diphenylacetylene) attached to the nitrogen of the 1,4-dihydropyridine group were studied. The synthesis of the methylene-1,4-dihydropyridine group was accomplished in excellent yield by a Knoevenagel condensation of a 4-pyridone intermediate with an active methylene compound. The liquid crystal materials prepared thus far which contain this methylene-1,4-dihydropyridine structure all possess broad enantiotropic smectic A phases and one example also possesses a tilted smectic C phase. These mesogens may possess useful properties such as high birefringence.

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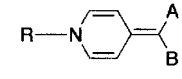
1. Introduction

Liquid crystals (LCs) with large birefringence are potentially useful for incorporation into electro-optic devices including a number of different display configurations. We are particularly interested in developing new LCs with large birefringence [1, 2] for application in flat panel liquid crystal displays which operate by a reflecting or scattering mechanism. Such displays often utilize polymer modified liquid crystal compositions, for example, polymer dispersed liquid crystals (PDLCs) or polymer stabilized cholesteric textures (PSCTs) [3–6]. Another potential application of high birefringence materials and possibly liquid crystals involves photorefractive organic thin films [7, 8]. Such applications benefit from compounds which exhibit a large anisotropy of linear polarizability. For a uniaxial LC phase such as the nematic or smectic A, the birefringence is defined as $\Delta n = n_{\parallel} - n_{\perp}$ where $n_{\parallel}$ and $n_{\perp}$ are the refractive indices parallel and perpendicular to the LC director axis respectively. A semi-empirical model for the molecular origins of birefringence in LCs has been developed by Wu and coworkers. While the predominant contribution to the observed refractive index comes from σ–σ^* transitions, the major contributor to birefringence is derived from π–π^* transitions. In addition, the order parameter mediates the Δn of the bulk material comprising these liquid crystal molecules. From a molecular design perspective Δn is optimized when conjugated π-bonds are incorporated into a rigid core, the electronic transitions are highly oriented relative to the core, and the molecules possess a high degree of axial order in the LC phase.

Recently, a monomeric glass-forming organic photorefractive material was described which incorporated molecules with the methylene-1,4-dihydropyridine structure [9]. Many of these molecules were prepared and evaluated, having different functional groups (see the figure: *R*, alkyl or aryl group; *A* and *B*, electron accepting groups) and additionally, for the sake of synthetic ease, methyl groups at both the 2 and 6 positions of the dihydropyridine ring. Amongst these compounds some



R = Aryl, Alkyl

A,B = Electron Withdrawing Groups

Figure. Structure of the methylene-1,4-dihydropyridine unit. Mesogens are created from this building block by appending a variety of substituents at the three different sites *R*, *A* and *B*. Depending on the identity of these groups this heterocycle may appear at the centre or towards either end of the mesogenic molecule in which it is contained. Known photorefractive glass chromophores from which these mesogens are derived also have methyl groups at both the 2- and 6-positions.

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were found to possess a glass phase, especially those in which the methylene group is substituted with cyano and ester groups. These compounds could be quenched from the melt to produce high optical quality glass samples. These monomeric glass photorefractive compositions function so well because the methylene-1,4-dihydropyridine chromophore possesses both a highly anisotropic linear polarizability and a large ground state dipole moment which, under the influence of an aligning electric field, yield a highly birefringent bulk material. It occurred to us that this structure unit ought to be amenable to further modification to permit incorporation into molecules with mesogenic behaviour. This was readily accomplished in modified systems where the *R* group is an aromatic ring (or combination of aromatic rings) and the 2,6-methyl groups (found in the photorefractive chromophores) are absent. Herein, we describe a new class of liquid crystal materials containing the methylene-1,4-dihydropyridine structural unit which has great versatility and can be utilized as a central or terminal unit depending on the manipulation of the three available functional groups.

2. Synthesis

Unless otherwise noted, the commercial starting materials were purchased from Aldrich and used as supplied. The synthesis of all these new LCs involves two common steps: creation of a 4-pyridone-containing molecule, and its conversion to a methylene-1,4-dihydropyridine. The progress of both of these reactions is easily followed by thin layer chromatography, and structures of all new compounds were confirmed by NMR. The subsequent discussion of the synthesis schemes is organized here primarily by the type of core group (phenyl, tolane or azobenzene) and then by the specific reaction sequence employed.

2.1. *General schemes of synthesis*

The synthesis of the 4-pyridone precursors was accomplished by two routes which involve either the

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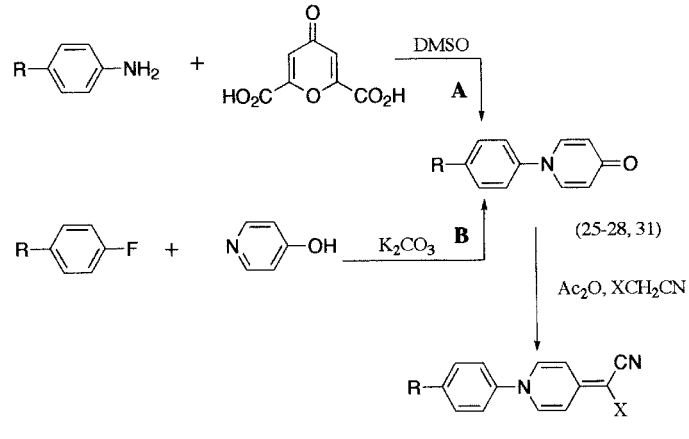
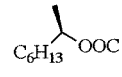
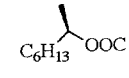


4-Pyridone	R	Method
(25)	C_6H_{13}	A
(26)	C_6F_{13}	B
(27)		B
(28)	H_5C_2OOC	B
(31)		B

Methylene Dihydropyridine	R	X
(8)	H_5C_2OOC	CN
(10)		CN
(11)	H_5C_2OOC	$COOC_8H_{17}$

Scheme 1. General synthetic sequence for 4-pyridone precursors and their methylene-1,4-dihydropyridine derivatives. If *R* is an activating group for aromatic nucleophilic substitution then route B can be very convenient for the preparation of the requisite 4-pyridone intermediates from an aryl fluoride and 4-hydroxypyridine. If *R* is not an activating group or the *R* substituted aniline happens to be more readily available, then the chelidonic acid route A is a useful alternative. As the final step in the LC synthesis the 4-pyridone is condensed with an active methylene compound to give the methylene-1,4-dihydropyridine by a Knoevenagel reaction.

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condensation of chelidonic acid with a 4-substituted aniline [10] (scheme 1, route A) or the nucleophilic substitution of an activated arylfluoride with 4-hydroxypyridine [11] (scheme 1, route B). The 4-*n*-hexylphenyl pyridone **25** was prepared by the conventional route A from chelidonic acid and the aniline derivative. This method was required because the hexyl group does not activate displacement of fluorine (for example, from 4-*n*-hexylfluorobenzene) to permit application of the aromatic nucleophilic substitution route B. However, all the other pyridones used in this study were prepared using route B as part of their synthesis. Activating groups for aromatic nucleophilic substitution employed here include perfluoroalkyl, ester and heterocycle-containing substituents; all these substituents are electron withdrawing by some combination of inductive or resonance processes. Typically these reactions were run with an excess of 4-hydroxypyridine in a dipolar aprotic solvent such as *N*-methylpyrrolidinone (NMP), with potassium carbonate as base. Reaction temperature and duration varied, and the better the activating group the more facile was the conversion (the preparation of the ester activated system **28** at 140° for 3 h being typical). The yields for some of these aromatic nucleophilic substitution reactions with 4-hydroxypyridine approached quantitative and no reaction with the opposing phenol group was evident.

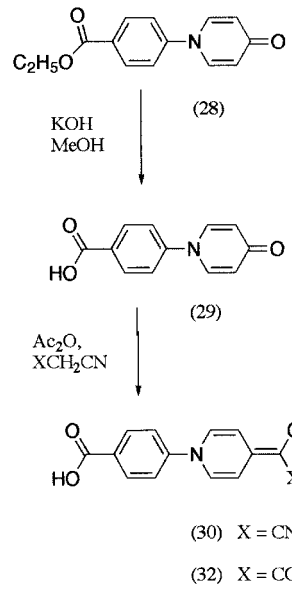
The pyridones were readily converted to methylene-1,4-dihydropyridines by the Knoevenagel condensation [12] in acetic anhydride. Reaction times varied between a few minutes and a few hours as a function of identity of reactants and temperature (between 100°C and boiling, 140°) and the yields usually ranged from 70 to 95%. In the case of ketone-containing activated methylene compounds (such as benzoylacetonitrile) which self-condense, an even larger excess may be required to bring the reaction to completion. Numerous other activated methylene compounds are also known to condense with pyridones and could also lead to liquid crystalline derivatives. The benzthiazole-containing pyridone **27** and methylene-1,4-dihydropyridine-containing LC **7** are included here as an indication of the potentially wide range of structures which can be pursued using this general synthetic approach.

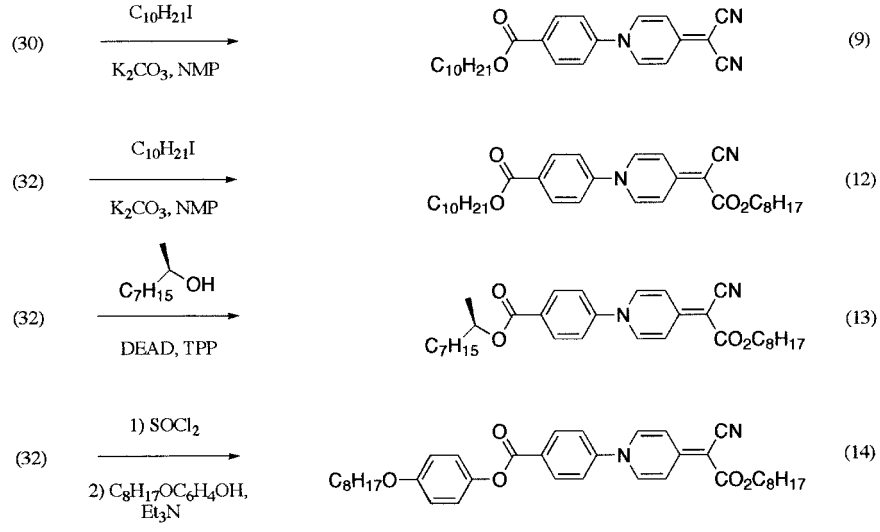
The preparation of the simple *N*-(4-*R*-phenyl)-substituted methylene-1,4-dihydropyridines (R = alkyl or perfluoroalkyl) and their corresponding 4-pyridone precursors are also described in scheme 1. In this sequence the complete *R*-substituent is already present at the pyridone stage and the last step of the synthesis creates the methylene-1,4-dihydropyridines via Knoevenagel condensation. Also depicted in scheme 1 are those ester-substituted systems ($R = COOC_2H_5$ and $COOCH(CH_3)C_6H_{13}$) for which the final LCs are prepared by this same sequence. Because of the multifunctional nature of these mesogens, in some cases the sequence of synthesis steps may be changed. This is demonstrated in scheme 2 for an additional set of ester-substituted *N*-(4-*R*-phenyl)-substituted methylene-1,4-dihydropyridines ($R = COOC_{10}H_{21}$, $COOCH(CH_3)C_7H_{15}$ and $COOC_6H_4OC_8H_{17}$) systems in which the methylene-1,4-dihydropyridine structure is introduced prior to the final complete elaboration of the *R*-substituent. A particularly important intermediate here is the benzoic acid-substituted pyridone **29** which is prepared by saponification of ester **28**. This pyridone can be converted to a methylene-1,4-dihydropyridine by reaction with an active methylene compound, such as malononitrile to give **30**, or octylcyanoacetate to give **32**. The carboxylic acid group in these methylene-1,4-dihydropyridine-containing intermediates can now be esterified by a variety of techniques: alkylation with an aliphatic iodide provides **9** and **12**, Mitsunobu reaction with an optically active secondary alcohol gives **13**, and formation of the acid chloride followed by reaction with a 4-alkoxyphenol gives **14**.

Scheme 3 depicts the synthesis of diphenylacetylene (tolane) and azobenzene pyridone-containing intermediates which were also described previously (it should be noted that many of these pyridones also possess interesting mesogenic properties) [11]. Standard transition metal mediated chemistry was used for the synthesis of the tolanes and standard azo coupling chemistry was used for the preparation of the azobenzenes. General reaction conditions for most of the Knoevenagel reactions are described below. Numerous other activated methylene compounds are also known to condense with pyridones and could also lead to liquid crystalline derivatives. Reaction progress is easily monitored by thin layer chromatography, and structures of all new compounds were confirmed by NMR.

2.2. *General procedure for the synthesis of methylene-1,4-dihydropyridines from 4-pyridones*

In a round-bottom flask with stir bar and reflux condenser was placed the 4-pyridone (4 mmol), activated methylene compound (20 mmol) and acetic anhydride (25–50 ml). The reaction mixture was heated between 100–140°C until TLC showed all pyridone was consumed (0·25–3·00 h) and was then allowed to cool to room temperature. The resulting crystalline solid was filtered off and washed with acetic anhydride. The crude product was usually >98% pure by NMR and could be recrystallized from a variety of solvents (usually 1-propanol or acetic anhydride).





Scheme 2. Alternative synthesis sequence for methylene-1,4-dihydropyridine derivatives. In some cases it is convenient to introduce the methylene-1,4-dihydropyridine group before elaboration of the full LC structure. In the case depicted the benzoic acid derivatives are readily converted to mesogenic esters by a variety of reactions.

2.2.1. *1-(4-n-Hexylphenyl)-4-(dicyanomethylene)-1,4-dihydropyridine* (**1**)

This compound was synthesized from **25** and malononitrile in 66% yield as yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·87 (t, 3H), 1·29 (m, 6H), 1·61 (m, 2H), 2·66 (t, 2H), 6·98 (d, 2H), 7·25 (d, 2H), 7·33 (d, 2H), 7·50 (d, 2H).

2.2.2. *1-(4-n-Perfluorohexylphenyl)-4-(dicyanomethylene)-1,4-dihydropyridine* (**2**)

This compound was synthesized from **26** and malononitrile in 74% yield as pale yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7·02 (d, 2H), 7·52 (m, 4H), 7·81 (d, 2H).

2.2.3. *1-(4-n-Hexylphenyl)-4-(ethyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**3**)

This compound was synthesized from **25** and ethyl cyanoacetate in 69% yield as yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·87 (t, 3H), 1·15–1·4 (m, 9H), 1·61 (m, 2H), 2·66 (t, 2H), 4·22 (q, 2H), 7·10 (dd, 2H), 7·20–7·40 (m, 4H), 7·50 (m, 2H), 8·44 (dd, 2H).

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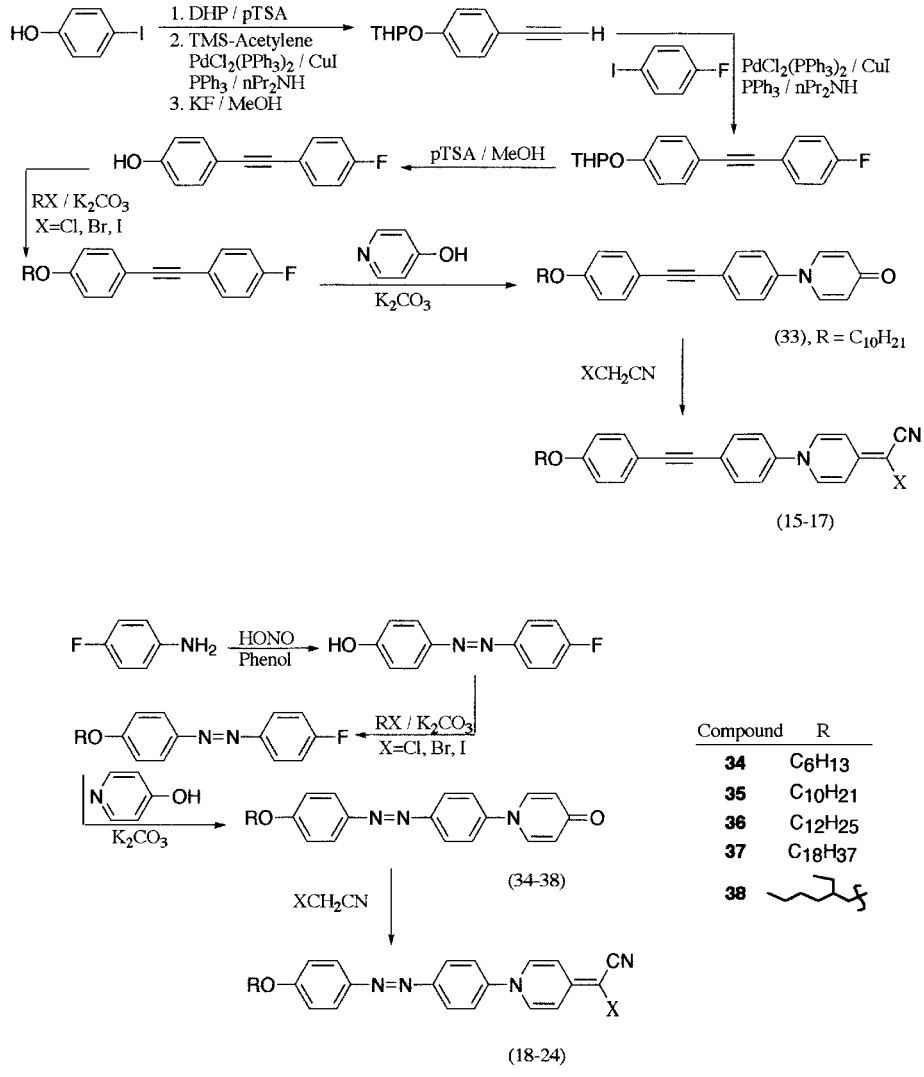

Scheme 3. Synthetic procedures for 4-pyridone intermediates with tolane and azobenzene cores. The unsaturated acetylene and azo bridge in these groups is sufficiently activating to permit preparation of the 4-pyridones by aromatic nucleophilic substitution. The 4-pyridones are subsequently converted to the methylene-1,4-dihydropyridine LCs by the general sequence.

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2.2.4. *1-(4-n-Perfluorohexylphenyl)-4-(ethyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**4**)

This compound was synthesized from **26** and ethyl cyanoacetate in 83% yield as yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1·32 (t, 3H), 4·21 (q, 2H), 7·12 (dd, 2H), 7·50 (m, 4H), 7·78 (d, 2H), 8·46 (dd, 2H).

2.2.5. *1-(4-n-Hexylphenyl)-4-(octyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**5**)

This compound was synthesized from **25** and octyl cyanoacetate in 83% yield as yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·87 (m, 6H), 1·29 (m, 16H), 1·65 (m, 4H), 2·66 (t, 2H), 4·13 (t, 2H), 7·09 (dd, 1H), 7·23 (d, 2H), 7·31 (d, 2H), 7·50 (t, 2H), 8·43 (dd, 1H).

2.2.6. *1-(4-n-Perfluorohexylphenyl)-4-(octyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**6**)

This compound was synthesized from **26** and octyl cyanoacetate in 83% yield as light yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·26 (m, 10H), 1·67 (m, 2H), 4·15 (t, 2H), 7·11 (dd, 1H), 7·50 (m, 4H), 7·78 (d, 2H), 8·46 (dd, 1H).

2.2.7. *1-(2-Benzthiazoyl)-4-(octyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**7**)

This compound was synthesized from **27** and octyl cyanoacetate in 62% yield as light yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·26 (m, 10H), 1·67 (m, 2H), 4·16 (t, 2H), 7·15 (dd, 1H), 7·35–7·65

(m, 6H), 7·90 (d, 1H), 8·07 (d, 1H), 8·25 (d, 2H), 8·47 (dd, 1H).

2.2.8. *4-(Dicyanomethylene)-4H-pyridin-1-ylbenzoic acid ethyl ester* (**8**)

This compound was synthesized from **28** and malononitrile in 77% yield as orange crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1·41 (t, 3H), 4·40 (q, 2H), 7·00 (d, 2H), 7·42 (d, 2H), 7·52 (d, 2H), 8·23 (d, 2H).

2.2.9. *4-(Dicyanomethylene-4H-pyridin-1-ylbenzoic acid decyl ester* (**9**)

1-Iododecane (1·037 g, 3·86 mmol), benzoic acid derivative **30** (339 mg, 1·29 mmol) and potassium carbonate (890 mg, 6·4 mmol) in 10 ml 1-methyl-2-pyrrolidinone were stirred for 12 h at 70°C. After cooling, a mixture of water and methanol was added with stirring to precipitate the crude product. After filtration this was dissolved in 1-methyl-2-pyrrolidinone (15 ml) and then warmed to about 40°C. To the stirred solution was added 15 ml methanol and then water, dropwise, until the precipitate persisted. The mixture was boiled until everything dissolved and was then allowed to cool to room temperature. The product was filtered and air dried to yield 325 mg (63%) of a yellow solid: R_F 0·46, 50:50 (hexanes:ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·24 (m, 14H), 1·79 (m, 2H), 4·34 (t, 2H), 7·00 (d, 2H), 7·42 (d, 2H), 7·52 (d, 2H), 8·22 (d, 2H).

2.2.10. *(R)-4-(Dicyanomethylene)-4H-pyridin-1-ylbenzoic acid (1-methylheptyl) ester* (**10**)

This was synthesized from **31** and malononitrile in 62% yield as orange crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·85 (t, 3H), 1·25 (m, 8H), 1·34 (d, 2H), 1·50–1·80 (m, 2H), 5·15 (m, 1H), 7·00 (d, 2H), 7·42 (d, 2H), 7·52 (d, 2H), 8·23 (d, 2H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 14·05, 20·03, 22·56, 25·39, 29·10, 31·71, 35·96, 52·18, 72·86, 113·80, 116·85, 122·38, 131·86, 131·96, 136·34, 145·18, 155·77, 164·48.

2.2.11. *4-(Ethyloxycarbonylcyanomethylene)-4H-pyridin-1-ylbenzoic acid ethyl ester* (**11**)

This was synthesized from **28** and ethyl cyanoacetate in 88% yield as yellow crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1·31 (t, 3H), 1·40 (t, 3H), 4·20 (q, 2H), 4·40 (q, 2H), 7·10 (dd, 1H), 7·40–7·60 (m, 4H), 8·20 (d, 2H), 8·45 (dd, 1H).

2.2.12. *4-(Octyloxycarbonylcyanomethylene)-4H-pyridin-1-ylbenzoic acid decyl ester* (**12**)

1-Iododecane (1·075 g, 4·0 mmol), acid **32** (395 mg, 1·0 mmol), and potassium carbonate (691 mg, 5·0 mmol) in 10 ml 1-methyl-2-pyrrolidinone were stirred for 3 h at 70°C. A solution of methanol and water (50:50) was added dropwise with stirring. The resulting solid was filtered and washed with methanol:water (75:25) to yield 442 mg (83%) of a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·83 (m, 6H), 1·23 (m, 24H), 1·60 (m, 2H), 1·75 (m, 2H), 4·08 (t, 2H), 4·31 (t, 2H), 7·07 (dd, 1H), 7·44 (d, 2H), 7·56 (m, 2H), 8·18 (d, 2H), 8·42 (dd, 1H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 14·10, 22·65, 25·94, 25·99, 28·65, 28·89, 29·20, 29·27, 29·52, 31·81, 31·87, 64·09, 65·82, 74·38, 114·40, 115·71, 120·27, 122·20, 130·93, 131·84, 135·30, 135·58, 145·53, 153·70, 165·03, 166·39.

2.2.13. *(R)-4-(Octyloxycarbonylcyanomethylene)-4H-pyridin-1-ylbenzoic acid (1-methyloctyl) ester* (**13**)

Diethylazodicarboxylate (123 mg, 0·71 mmol) was added to a solution of *S*-2-nonanol (90 mg, 0·622 mmol), acid **32** (223 mg, 0·566 mmol) and triphenylphosphine (185 mg, 0·71 mmol) in 8 ml anhydrous tetrahydrofuran. The reaction mixture was stirred overnight and was then adsorbed onto silica gel. The product was purified via flash chromatography over silica gel with gradual elutions from 80:20 to 50:50 (hexanes:ethyl acetate). The product was then recrystallized from methanol to yield 126 mg (43%) of a yellow solid: R_F 0·15, 80:20 (hexanes:ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·84 (m, 6H), 1·23 (m, 23H), 1·60 (m, 4H), 4·09 (t, 2H), 5·14 (m, 1H), 7·07 (dd, 1H), 7·44 (d, 2H), 7·56 (m, 2H), 8·18 (d, 2H), 8·42 (dd, 1H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 14·10, 20·03, 22·64, 25·43, 25·95, 28·89, 29·19, 29·28, 29·40, 31·76, 31·81, 35·97, 64·08, 72·73, 74·31, 114·41, 115·71, 120·30, 122·17, 131·34, 131·81, 135·33, 135·61, 145·47, 153·72, 164·58, 166·42.

2.2.14. *4-(Octyloxycarbonylcyanomethylene)-4H-pyridin-1-ylbenzoic acid 4-octyloxyphenyl ester* (**14**)

Carboxylic acid **32** (107 mg, 0·27 mmol) was stirred in 5 ml thionyl chloride for 4 h. Excess thionyl chloride was evaporated off and the crude acid chloride was taken up in 4 ml dichloromethane. To this solution 4-octyloxyphenol (66 mg, 0·298 mmol) was added quickly; this was followed by the slow addition of triethylamine (41 mg, 0·40 mmol) dissolved in 1 ml dichloromethane. The reaction mixture was stirred for 2 h and was then adsorbed onto silica gel. The crude product was purified by flash chromatography over silica gel with dichloromethane as eluent. Evaporation of the solvent yielded 129 mg (80%) of a yellow solid: R_F 0·29, (dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·81 (m, 6H), 1·23 (m, 20H), 1·67 (m, 4H), 3·90 (t, 2H), 4·11 (t, 2H), 6·87 (d, 2H), 7·05 (d, 2H), 7·08 (dd, 1H), 7·43 (d, 2H), 7·50 (m, 2H), 8·30 (d, 2H), 8·42 (dd, 1H).

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2.2.15. *1-[4-(4-Decyloxyphenylethynyl)phenyl]-4-(dicyanomethylene)-1,4-dihydropyridine* (**15**)

This product was synthesized according to the general procedure from **33** and malononitrile in 69% yield as an orange solid: R_F 0·53, 50:50 (hexanes:ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·85 (t, 3H), 1·15–1·50 (m, 14H), 1·78 (m, 2H), 3·96 (t, 2H), 6·87 (d, 2H), 7·01 (d, 2H), 7·30 (d, 2H), 7·44 (d, 2H), 7·51 (d, 2H), 7·65 (d, 2H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 14·03, 22·59, 25·91, 29·07, 29·26, 29·47, 29·55, 31·82, 51·50, 68·09, 85·99, 92·60, 113·65, 113·93, 114·61, 116·95, 122·44, 125·37, 133·14, 133·27, 136·36, 140·93, 155·62, 159·73.

2.2.16. *1-[4-(4-Decyloxyphenylethynyl)phenyl]-4-(ethyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**16**)

This product was synthesized according to the general procedure from **33** and ethyl cyanoacetate in 77% yield as a yellow solid: R_F 0·53, 50:50 (hexanes:ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·15–1·50 (m, 17H), 1·78 (m, 2H), 3·96 (t, 2H), 4·22 (q, 2H), 6·87 (d, 2H), 7·11 (dd, 1H), 7·30 (d, 2H), 7·44 (d, 2H), 7·51 (m, 2H), 7·65 (d, 2H), 8·45 (dd, 1H).

2.2.17. *1-[4-(4-Decyloxyphenylethynyl)phenyl]-4-(octyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**17**)

This product was synthesized according to the general procedure from **33** and octyl cyanoacetate in 91% yield as a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (m, 6H), 1·15–1·50 (m, 24H), 1·72 (m, 4H), 3·96 (t, 2H), 4·15 (t, 2H), 6·87 (d, 2H), 7·11 (dd, 1H), 7·30 (d, 2H), 7·44 (d, 2H), 7·50 (m, 2H), 7·64 (d, 2H), 8·45 (dd, 1H).

2.2.18. *1-[4-(4-Hexyloxyphenylazo)phenyl]-4-(dicyanomethylene)-1,4-dihydropyridine* (**18**)

This compound was synthesized according to the general procedure from **34** and malononitrile in 75% yield as an orange solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·90 (t, 3H), 1·25–1·55 (m, 6H), 1·80 (m, 2H), 4·04 (t, 2H), 7·00 (m, 4H), 7·46 (d, 2H), 7·55 (d, 2H), 7·92 (d, 2H), 8·05 (d, 2H).

2.2.19. *1-[4-(4-Decyloxyphenylazo)phenyl]-4-(dicyanomethylene)-1,4-dihydropyridine* (**19**)

This compound was synthesized according to the general procedure from **35** and malononitrile in 82% yield as an orange solid: ^{1}H NMR (250 MHz, THF-d8) δ 0·90 (t, 3H), 1·20–1·55 (m, 14H), 1·82 (m, 2H), 4·08 (t, 2H), 6·96 (d, 2H), 7·06 (d, 2H), 7·72 (d, 2H), 7·91 (d, 2H), 7·95 (d, 2H), 8·05 (d, 2H); ^{13}C NMR (250 MHz, THF-d8) δ 14·48, 23·60, 24·71, 25·02, 25·34, 25·68, 26·00, 27·00, 30·18, 30·33, 30·40, 30·59, 32·90, 51·60, 69·21, 113·65, 115·67, 117·12, 124·27, 124·87, 125·91, 138·25, 144·59, 147·67, 153·22, 156·40, 163·63.

2.2.20. *1-[4-(4-Octadecyloxyphenylazo)phenyl]-4-(dicyanomethylene)-1,4-dihydropyridine* (**20**)

This compound was synthesized according to the general procedure from **37** and malononitrile in 84% yield as an orange solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·15–1·55 (m, 30H), 1·86 (m, 2H), 4·04 (t, 2H), 6·99 (d, 2H), 7·03 (d, 2H), 7·46 (d, 2H), 7·50 (d, 2H), 7·92 (d, 2H), 8·03 (d, 2H).

2.2.21. *1-{4-[4-(2-Ethyl-hexyloxy)phenylazo]phenyl}-4-(dicyanomethylene)-1,4-dihydropyridine* (**21**)

This compound was synthesized according to the general procedure from **38** and malononitrile in 77% yield as an orange solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·90 (m, 6H), 1·20–1·55 (m, 7H), 1·70 (m, 2H), 3·92 (d, 2H), 7·00 (m, 4H), 7·46 (d, 2H), 7·57 (d, 2H), 7·92 (d, 2H), 8·03 (d, 2H).

2.2.22. *1-[4-(4-Decyloxyphenylazo)phenyl]-4-(ethyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**22**)

This compound was synthesized according to the general procedure from **35** and malononitrile in 91% yield as a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·15–1·55 (m, 17H), 1·80 (m, 2H), 4·02 (t, 2H), 4·19 (q, 2H), 6·99 (d, 2H), 7·08 (dd, 1H), 7·46 (d, 2H), 7·54 (m, 2H), 7·90 (d, 2H), 8·01 (d, 2H), 8·45 (dd, 1H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 14·12, 14·58, 22·68, 26·00, 29·16, 29·32, 29·38, 29·56, 31·89, 59·82, 68·50, 73·73, 114·40, 114·87, 115·71, 120·61, 123·06, 124·47, 125·23, 135·61, 135·84, 143·14, 146·61, 152·40, 153·80, 162·51, 166·51.

2.2.23. *1-[4-(4-Decyloxyphenylazo)phenyl]-4-(octyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**23**)

This compound was synthesized according to the general procedure from **35** and octylcyanoacetate in 89% yield as a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 6H), 1·15–1·50 (m, 24H), 1·65 (m, 2H), 1·80 (m, 2H), 4·03 (t, 2H), 4·12 (t, 2H), 6·99 (d, 2H), 7·08 (dd, 1H), 7·46 (d, 2H), 7·54 (m, 2H), 7·90 (d, 2H), 8·00 (d, 2H), 8·45 (dd, 1H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 14·12, 22·67, 25·99, 28·93, 29·16, 29·22, 29·32, 29·38, 29·56, 31·83, 31·89, 64·06, 68·50, 73·82, 114·39, 114·86, 115·69, 120·49, 123·05, 124·47, 125·23, 135·58, 135·80, 143·15, 146·61, 152·39, 153·76, 162·51, 166·59.

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2.2.24. *1-[4-(4-Dodecyloxyphenylazo)phenyl]-4-(phenylcarbonylcyanomethylene)-1,4-dihydropyridine* (**24**)

This product was synthesized by a modification of the general procedure (a total of 10 equivalents of active methylene compound was added in approximately five portions over 1 h) from **36** and benzoylacetonitrile in 76% yield as a light yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3H), 1·15–1·55 (m, 18H), 1·82 (m, 2H), 4·05 (t, 2H), 7·00 (d, 2H), 7·41 (m, 4H), 7·52 (d, 2H), 7·78 (m, 5H), 7·93 (d, 2H), 8·05 (d, 2H).

2.2.25. *4-n-Hexyl-(4-oxo-4H-pyridin-1-yl)benzene* (**25**), *4-n-perfluorohexyl-(4-oxo-4H-pyridin-1-yl)benzene* (**26**), *4-benzothiazoyl-(4-oxo-4H-pyridin-1-yl)benzene* (**27**)

The synthesis and characterization of these compounds will be described in detail in a subsequent publication concerned with the scope of aromatic nucleophilic substitution with 4-hydroxypyridine [13]. These three compounds were all prepared by the general reaction of 4-hydroxypyridine with the appropriate arylfluoride as described subsequently for the preparation of pyridone **28**.

2.2.26. *4-(4-Oxo-4H-pyridin-1-yl)benzoic acid ethyl ester* (**28**)

In a 500 ml round-bottom flask with stir bar was placed 4-fluorobenzoic acid ethyl ester (16·8 g, 100 mmol), 4-hydroxypyridine (14·26 g, 150 mmol), potassium carbonate (20·7 g, 150 mmol), and 1-methyl-2-pyrrolidinone (75 ml). This mixture was gradually warmed to 140°C and kept at this temperature for 3 h after which time all the starting aryl fluoride was consumed. The mixture was cooled to room temperature and, with stirring, ice and water was added in portions to bring the volume to 500 ml. The precipitated product was isolated by suction filtration, washed well with water and air dried. The first product, 21·0 g (86%), was very pure and was used without further purification: m.p. 178–180°C, lit. 178–179°C [14].

2.2.27. *4-(4-Oxo-4H-pyridin-1-yl)benzoic acid* (**29**)

Potassium hydroxide (6·92 g, 123 mmol) and **28** (10 g, 41·1 mmol) was stirred overnight in 250 ml methanol. The reaction mixture was acidified with concentrated HCl, filtered, and washed with water to yield 9·08 g (95%) of a white solid as the monohydrate. No NMR data could be obtained due to the insolubility of this substance in conventional solvents.

2.2.28. *1-(4-Benzoic acid)-4-(dicyanomethylene)-1,4-dihydropyridine* (**30**)

Malononitrile (1·173 g, 17·75 mmol) and **29** (1·034 g, 4·44 mmol) in 50 ml acetic anhydride was stirred at 110°C for 7 h. The reaction mixture was refrigerated for 72 h at which time the product precipitated from solution. The crude product was filtered and washed with acetic acid to yield 913 mg (78%) of a tan solid: R_F 0·07, 50:50 (hexanes:ethyl acetate); ^{1}H NMR (250 MHz, DMSO-d6) δ 6·92 (d, 2H), 7·76 (d, 2H), 8·12 (d, 2H), 8·26 (d, 2H).

2.2.29. *(R)-4-(4-Oxo-4H-pyridin-1-yl)benzoic acid 1-methylheptyl ester* (**31**)

In a 250 ml round-bottom flask with stir bar was placed dry pyridine (30 ml) and (*R*)-2-octanol (6·50 g, 50 mmol). This mixture was stirred in a cold water bath and 4-fluorobenzoyl chloride (8·52 g, 60 mmol) was added dropwise over about 15 min; it was then allowed to warm to room temperature and stirred for 8 h. After this time water (2 ml) was added and the mixture stirred overnight, and then transferred to a separatory funnel with hexane and water. The phases were separated and the hexane phase washed with water, dilute bicarbonate solution, water, 10% aqueous HCl and water. The hexane phase was then dried ($MgSO_4$), passed through a short column of silica gel, and the filtrate concentrated by rotary evaporation to give 11·0 g (85%) of the ester as a colourless liquid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·85 (t, 3H), 1·15–1·50 (m, 11H), 1·55–1·90 (m, 2H), 5·14 (m, 1H), 6·49 (d, 2H), 7·38 (d, 2H), 7·60 (d, 2H), 8·16 (d, 2H).

2.2.30. *1-(4-Carboxyphenyl)-4-(octyloxycarbonylcyanomethylene)-1,4-dihydropyridine* (**32**)

This product was synthesized according to the general procedure from **29** and octyl cyanoacetate in 85% yield as a yellow solid: ^{1}H NMR (250 MHz, DMSO-d6) δ 0·84 (t, 3H), 1·24 (m, 10H), 1·55 (m, 2H), 4·04 (t, 2H), 6·95 (dd, 1H), 7·76 (d, 2H), 8·10 (d, 2H), 8·26 (m, 3H).

The synthesis and characterization of some of the tolane 4-pyridone intermediate (**33**) and the azobenzene 4-pyridone intermediates (**34**–**38**) have been described elsewhere [11].

3. Liquid crystalline properties

Liquid crystal phase diagrams were characterized by polarized light microscopy using an Olympus BH-2 microscope fitted with a Mettler FP5 temperature controller and an FP52 hot stage and also by differential scanning calorimetry. Mesophases were identified by their characteristic textures on untreated glass slides and should be considered as preliminary until a more definitive study is undertaken. Only the smectic A (A) and smectic C (C) mesophases were observed in this set of 1,4-methylenedihydropyridines.

Table 1 describes a series of alkylphenyl methylene-1,4-dihydropyridines with both perfluoroalkyl and conventional hydrocarbon tails. Both

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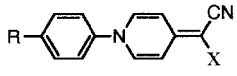
compounds **1** and **2** contain the dicyanomethylene terminal group, however only the perfluoro homologue **2** is a mesogen. In general, the substitution of a perfluoro tail in the place of a saturated hydrocarbon tail yields higher melting points and clearing points, and broader enantiotropic LC phase ranges in these compounds. This increase can be quite dramatic as illustrated by compounds cyanoesters **3** and **4**, where perfluoroalkyl tail-containing **4** melts at 248°C, an increase of nearly 100°C relative to the hydrocarbon derivative **3**. In addition, the A phase of perfluoro **4** is thermodynamically stable over a 67°C range, relative to only a 24°C enantiotropic range for hydrocarbon derivative **3**. Substitution of an ester group at the *X* position yielded mesogens where the hydrocarbon ester tail length had little effect on the LC phase behaviour in hydrocarbon tail-containing compounds **3** and **5**. In contrast, the LC phase behaviour of the perfluoro tail-containing homologues **4** and **6** proved quite sensitive to changes in the ester tail length. In particular, the lengthening of the tail from two to eight carbons in compound **6** resulted in a significant reduction in melting point (−71°C) and a modest reduction in the thermodynamic stability (−9°C) relative to compound **4**. Compound **7** with the benzthiazole functional group exhibited mesogenicity over a narrow range. This result suggests that a wide variety of functionalities may be substituted at the *R* and *X* positions as illustrated in table 1. Compound **7** is included amongst the alkylbenzenes due to its novelty, although it lacks an alkylbenzene tail.

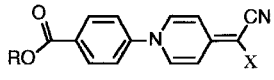
We next examined the mesogenic behaviour of compounds which incorporate the carboxyphenyl-substituted methylene-1,4-dihydropyridine core (table 2). None of the dicyanomethylene derivatives **8**–**10** exhibited any mesogenicity. However, substitution of an ester group for cyano (at position *X*) yielded LCs when

Table 1. Phase sequences of alkylphenyl- and perfluoroalkylphenyl-substituted methylene-1,4-dihydropyridine liquid crystal compounds.



Compound	*R*	*X*	Temperature/°C Cr		SmA		I
1	C_6H_{13}	CN	•	172	—		•
2	C_6F_{13}	CN	•	186	•	244	•
3	C_6H_{13}	$CO_2C_2H_5$	•	149	•	173	•
4	C_6F_{13}	$CO_2C_2H_5$	•	248	•	315	•
5	C_6H_{13}	$CO_2C_8H_{17}$	•	142	•	178	•
6	C_6F_{13}	$CO_2C_8H_{17}$	•	177	•	235	•
7		$CO_2C_8H_{17}$	•	243	•	253	•

Table 2. Phase sequences of carboxyphenyl-substituted methylene-1,4-dihydropyridine liquid crystal compounds.



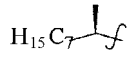
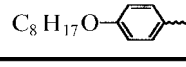
Compound	*R*	*X*	Temperature/°C Cr		SmA		I
8	C_2H_5	CN	•	290	—		•
9	$C_{10}H_{21}$	CN	•	226	—		•
10		CN	•	200	—		•
11	C_2H_5	$CO_2C_2H_5$	•	252	—		•
12	$C_{10}H_{21}$	$CO_2C_8H_{17}$	•	146	•	185	•
13		$CO_2C_8H_{17}$	•	104	•	132	•
14		$CO_2C_8H_{17}$	•	180	•	281	•

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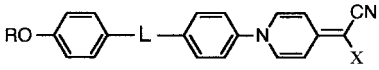
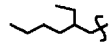
Table 3. Phase sequences of diphenylacetylene- and azobenzene-substituted methylene-1,4-dihydropyridine liquid crystal compounds.



Compound	*R*	*L*	*X*	Temperature/°C Cr		SmC		SmA		I
15	$C_{10}H_{21}$	C≡C	CN	•	189	—		•	262	•
16	$C_{10}H_{21}$	C≡C	$CO_2C_2H_5$	•	189	—		•	284	•
17	$C_{10}H_{21}$	C≡C	$CO_2C_8H_{17}$	•	149	—		•	279	•
18	C_6H_{13}	N=N	CN	•	277	—		—		•
19	$C_{10}H_{21}$	N=N	CN	•	191	—		•	245	•
20	$C_{18}H_{37}$	N=N	CN	•	125	•	176	•	272	•
21		N=N	CN	•	178	—		•	210	•
22	$C_{10}H_{21}$	N=N	$CO_2C_2H_5$	•	170	—		•	300	•
23	$C_{10}H_{21}$	N=N	$CO_2C_8H_{17}$	•	140	—		•	290	•
24	$C_{12}H_{25}$	N=N	COPh	•	200	—		•	>300	•

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both tails were sufficiently long (>2 carbons). Introduction of a chiral centre in **13** produced the example of a chiral smectic A material. Finally, the common phenylbenzoate LC core system was readily incorporated into the methylene-1,4-dihydropyridine LC, and compound **14** exhibits a relatively broad (>100°C) enantiotropic A phase. Thus, a variety of substituted carboxyphenyl functional groups may be attached to the methylene-1,4-dihydropyridine core in order to provide materials with LC behaviour.

Two common LC core structural units, the tolane and the azobenzene were also appended to the methylene-1,4-dihydropyridine group to provide the mesogens found in table 3. All the tolanes (**15**–**17**) exhibit broad enantiotropic (A) phases. The analogous azobenzene compounds **19**, **22** and **23** also exhibit (A) phases with transition temperatures very similar to the tolanes. For example, azo compound **23** possesses a broad A phase over 150°C which is similar to tolane **17** which exhibits mesogenicity over a 130°C range. Compounds **18**–**20** demonstrate that longer tails enhance mesogenicity in these systems. Compound **18** with a hexyloxy tail melts at 277°C and is not mesogenic, the decyloxy tail compound melts at 191°C has a LC range of 54°C while compound **20**, with an octadecyloxy tail, melts at 191°C and has a LC range of 147°C. In addition, **20** possesses a tilted smectic phase which we believe is a (C) phase and is the only example of any phase other than (A) detected thus far amongst this set of compounds. Branching of the tail also reduces the melting point, as demonstrated by **21** which exhibits a significant depression relative to **18** and **19**. Finally, compound **24** incorporates a carbonylphenyl group in the *X* position which suggests that a still expanded array of functionalities may be placed at this position yielding mesogenic properties.

4. Conclusion

A new class of liquid crystalline materials has been discovered which incorporates a substituted methylene-1,4-dihydropyridine structural array. These unique liquid crystals may offer useful applications involving high birefringence or photorefractivity. The synthesis method for the 1,4-dihydropyridines which has been developed is straightforward and will deliver a rich variety of functionalities into the LC core and tail structures. Evaluations of the electronic and optical properties of these materials are currently in progress.

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