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The forgotten liquid crystals of Daniel Vorländer: A new look at mesogenic 4-pyridones

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Three classes of 4-pyridone (1H-pyridin-4-one) terminated liquid crystals were synthesized and their mesogenic properties examined. These liquid crystal classes differ in the composition of the aromatic core group which vary among azobenzene, stilbene or tolane groups. The synthesis of the 4-pyridones was accomplished by aromatic nucleophilic substitution reaction of the appropriate activated aryl fluoride with 4-hydroxypyridine. These pyridone liquid crystals possess broad enantiotropic nematic and smectic A phases and may possess useful properties such as high birefringence and polarity including hydrogen bonding capability. The original report of a 4-pyridone containing liquid crystal due to Vorländer has been substantiated.

1. Introduction

In 1925 Daniel Vorländer, from the famous liquid crystal school at Halle, described the nitration of a series of compounds which included 1-phenyl-1H-pyridin-4-one. The resulting 1-(4-nitrophenyl)-1H-pyridin-4-one intermediate was further elaborated to a pair of azobenzene derivatives, one of which he reported exhibited a liquid crystalline phase [1]. The structures and physical properties of these compounds prepared by Vorländer are found in figure 1. Although there are several published accounts of mesogens which contain similar heterocyclic rings, namely 2-pyridones [2] and 3-phenylpyridazines [3], to our knowledge the 1H-pyridin-4-one structure has never been subsequently exploited as a structural unit in a liquid crystal.

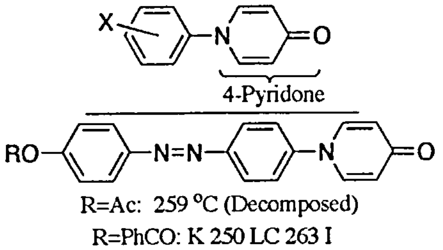

Figure 1. Structures of the original 4-pyridones described by Vorländer.

The 1H-pyridin-4-one (hereafter referred to as 4-pyridone) heterocycle should be highly polarizable and exhibit highly anisotropic polarizability. As such, introduction of this structure into a liquid crystal could yield high birefringence and therefore utility in many electrooptic applications including flat panel displays. The 4-pyridone group is very polar (for example, the dipole moment of 1-phenyl-1H-pyridin-4-one is 6·7 D) [4] and it is known to participate in complex formation and intermolecular hydrogen bonding [1, 5] and therefore may prove useful in the design of H-bonded liquid crystals and surface active agents. Herein we describe a new synthetic approach and the properties of a new series of liquid crystals which contain a 4-pyridone terminal group.

2. Synthesis

Three classes of 4-pyridone terminated liquid crystals which differ in the structure of the core group (azobenzene, Scheme 1; stilbene, Scheme 2; and tolane, Scheme 3) were synthesized and examined for mesogenic properties. All these syntheses rely on an aromatic nucleophilic substitution reaction in which displacement of an aryl fluoride by 4-hydroxypyridine is activated by the unsaturated bridge group. The use of 4-hydroxypyridine as a nucleophile in the aromatic nucleophilic substitution reaction has been described in only a few cases where conventional activating groups such as nitro were present [6]. The scope of activating groups which have

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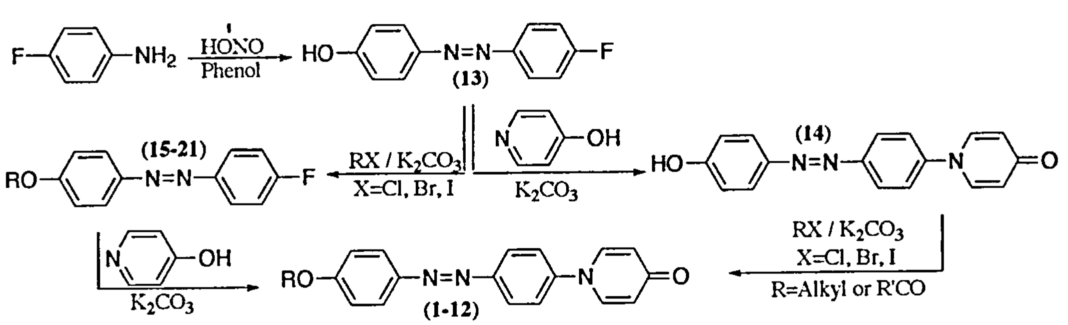
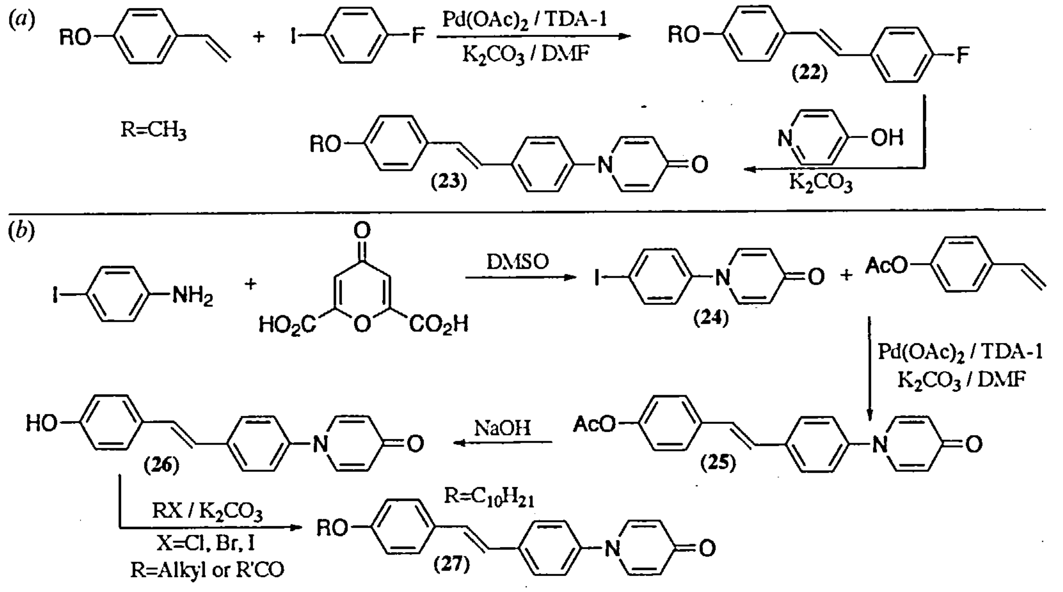
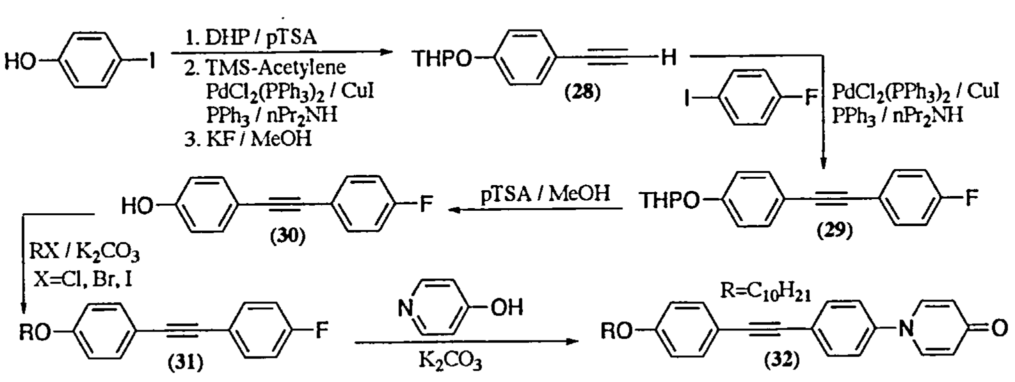


Scheme 1. Synthesis scheme employed for azobenzene core 4-pyridone liquid crystals.



Scheme 2. Synthesis schemes employed for stilbene core 4-pyridone liquid crystals. (*a*) The methoxy homologue (**23**) was synthesized in good yield but this approach did not give satisfactory results with carboxy or long chain alkyl derivatives. (*b*) An alternative synthesis method starting with iodoaniline and chelidonic acid was more effective for the synthesis of materials with longer alkyl tails and carboxy homologues.



Scheme 3. Synthesis scheme employed for tolan core 4-pyridone liquid crystals.

been utilized for aromatic nucleophilic substitution chemistry has recently grown appreciably, especially due to applications in thermoplastic polymer synthesis [7]. We have found that 4-hydroxypyridine is very reactive in this kind of aromatic nucleophilic substitution reaction and we have now extended the reaction to a wide array of substrates [8]. Typically we employed a molar excess of the 4-hydroxypyridine in a dipolar aprotic solvent such as 1-methyl-2-pyrrolidinone (NMP) and the reaction temperature was adjusted to bring about complete reaction in a convenient time. The relative reactivities of these systems towards aromatic nucleophilic substitution with 4-hydroxypyridine follow their substituent constants σ_p- (mechanism involves stabilization of negative charge from the reaction centre; PhN=N–, 0·45; PhC≡C–, 0·30; PhCH=CH–, 0·13) [9]. It should also be noted that 4-hydroxypyridine has been used previously in the synthesis of liquid crystals but these instances involve only its ester derivatives and/or quaternary derivatives [10].

For the preparation of the azobenzene core materials the diazonium salt of 4-fluoroaniline was reacted with phenol to produce 4-fluoro-4′-hydroxyazobenzene [11] (**13**) in 75 per cent yield (Scheme 1). Intermediate (**13**) could then be further derivatized via two different pathways: First, heating (**13**) with potassium carbonate and 4-hydroxypyridine in NMP provided (**14**) in 89 per cent yield. This reaction is particularly remarkable as the 4-fluoro-4′-hydroxyazobenzene reaction with the 4-hydroxypyridine dominates over its own self-condensation. Phenolic intermediate (**14**) was then treated with a variety of alkylhalides or acid chlorides to yield alkyl ether or ester azobenzene-4-pyridones (**1–3**). Alternatively, intermediate (**13**) was reacted with a variety of alkyl halides and potassium carbonate in NMP to produce the 4-fluoro-4′-alkoxyazobenzene intermediates (**15–21**). Treatment of these arylfluorides with 4-hydroxypyridine and potassium carbonate in NMP yielded azobenzene-4-pyridones (**4–12**). In general, the second two step route was preferred as the final products could often be isolated in a high state of purity without any chromatography.

For the preparation of the stilbene core materials we utilized a modified solid–liquid phase transfer Heck reaction [12] to couple 4-methoxystyrene with 4-iodofluorobenzene giving (**22**) in 69 per cent yield (Scheme 2A). Our modification of this reaction utilizes palladium(II)acetate and the phase transfer catalyst tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1) to couple aryliodides and substituted styrenes in excellent yield. Heating (**22**) with 4-hydroxypyridine and potassium carbonate in NMP gave pyridone (**23**) in 51 per cent yield. The nucleophilic displacement of fluorostilbenes with 4-hydroxypyridine proved somewhat difficult as the olefin appears to be an inferior activating group relative to either the acetylene or the azo group. Therefore, we turned to an alternate route described in Scheme 2B. Reaction of chelidonic acid with 4-iodoaniline in dimethylsulphoxide [13] produced intermediate (**24**) in 41 per cent yield. This versatile intermediate was coupled with 4-acetoxystyrene using the modified Heck reaction to produce mesogen (**25**). Hydrolysis of (**25**) yielded hydroxy derivative (**26**) which was then reacted with 1-iododecane and potassium carbonate in NMP to produce stilbene-4-pyridone (**27**).

The synthesis of tolane-4-pyridones is described in Scheme 3. The THP protected 4-ethynylphenol intermediate (**28**) was synthesized according to established protocols [14]. A modified Stephens–Castro reaction mediated by a copper and palladium co-catalyst [15] was used to couple 4-iodofluorobenzene and phenylacetylene (**28**) to produce intermediate (**29**) in 85 per cent yield. Subsequent removal of the THP protecting group and treatment with 1-iododecane and potassium carbonate yielded fluorostilbene (**31**). Finally, treatment with 4-hydroxypyridine and potassium carbonate in NMP produced tolane-4-pyridone (**32**).

4-[4′-(Acyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl) benzene (1) Acetyl chloride (89 mg, 1·13 mmol) was added to a stirred solution of **14** (66 mg, 0·227 mmol) in 5 ml pyridine. The reaction mixture was stirred for 10 min and then an additional 89 mg of acetyl chloride was added. Stirring was continued for 10 min and then water (~50 ml) was added and the tan solid was filtered and dried in air. A total of 34 mg (45 per cent) of a tan solid was recovered: m.p. 259°C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2·34 (s, 3 H), 6·66 (d, 2 H), 7·27 (d, J=8·9 5 Hz, 2 H), 7·50 (d, J=8·80 Hz, 2 H), 7·71 (d, J=7·68 Hz, 2 H), 7·98 (d, J=8·89 Hz, 2 H), 8·05 (d, J=8·80 Hz, 2 H).

4-[4′-(Benzoyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (2). Benzoyl chloride (150 mg, 1·07 mmol) and **14** (250 mg, 0·86 mmol) were stirred at 120°C in 5 ml NMP. The solution was cooled and then water added, and the yellow precipitate was filtered and washed with water. The crude product was recrystallized from ethanol to yield 160 mg (49 per cent) of a yellow solid: m.p. 250°C; ^{1}H NMR (250 MHz, DMSO-d_6, 120°C) δ 6·67 (d, 2 H), 7·54 (d, 2 H), 7·62 (m, 2 H), 7·78 (m, 3 H), 8·03 (m, 4 H), 8·18 (m, 2 H), 8·25 (d, 2 H).

4-[4′-(Methoxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl) benzene (3). Methyl iodide (1·007 g, 7·1 mmol), **14** (207 mg, 0·71 mmol) and potassium carbonate (196 mg, 1·4 mmol) was stirred at 90°C for 1 h. The reaction mixture was cooled and water added. The solution was filtered and the precipitate washed with methanol : water (50 : 50). The crude product was dissolved in hot methanol (~15 ml), filtered, and then water (~5 ml) added. The solution was concentrated to a slurry and then filtered and washed with water. This yielded 98 mg (45 per cent) of an orange solid: R_F 0·60 (50 : 50 methanol : ethyl acetate); m.p. 213°C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 3·87 (s, 3 H), 6·27 (d, J=7·82 Hz, 2 H), 7·14 (d, J=9·05 Hz, 2 H), 7·75 (d, J=8·86 Hz, 2 H), 7·92 (d, J=8·97 Hz, 2 H), 7·98 (d, J=8·86 Hz, 2 H), 8·09 (d, J=7·77 Hz, 2 H).

4-[4′-(Hexyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl) benzene (4). 4-Hydroxypyridine (960 mg, 10·0 mmol), **15** (1·50 g, 5·0 mmol) and potassium carbonate (1·38 g, 10 mmol) in 10 ml NMP were stirred under nitrogen at 170°C for 2 h. The reaction mixture was cooled and water added. The precipitate was filtered and washed with water. The crude product was recrystallized from a mixture of methanol and water to yield 1·80 g (96 per cent) of the product as a yellow solid: m.p. 142°C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 0·90 (t, 3 H), 1·55–1·20 (m, 4 H), 2·02–1·73 (m, 4 H), 4·04 (t, J=7 Hz, 2 H), 6·58 (d, J=8 Hz, 2 H), 7·01 (d, J=9 Hz, 2 H), 7·45 (d, J= 9 Hz, 2 H), 7·69 (d, J=8 Hz, 2 H), 7·91 (d, J=9 Hz, 2 H), 8·01 (d, J=9 Hz, 2 H).

4-[4′-(Decyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl) benzene (5). 4-Hydroxypyridine (3·20 g, 33·7 mmol), **16** (6·0 g, 16·8 mmol) and potassium carbonate (3·20 g, 28 mmol) in 50 ml NMP were stirred at 140°C for 3 h. The reaction mixture was cooled and water added. The precipitate was filtered and washed with water. The crude product was recrystallized from methanol and again from toluene to yield 6·10 g (84 per cent) of a yellow solid: R_F 0·35 (20:80 ethanol:ethyl acetate); m.p. 132°C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 0·85 (t, J= 6·52 Hz, 3 H), 1·60–1·15 (m, 14 H), 1·77 (m, 2 H), 4·02 (t, J=6·51 Hz, 2 H), 6·49 (d, J=7·74 Hz, 2 H), 6·98 (d, J= 8·97 Hz, 2 H), 7·43 (d, J=8·70 Hz, 2 H), 7·63 (d, J= 7·81 Hz, 2 H), 7·90 (d, J=8·88 Hz, 2 H), 7·98 (d, J= 8·68 Hz, 2 H); ^{13}C (250 MHz, CDCl$_3$) δ 14·12, 22·67, 26·00, 29·16, 29·31, 29·37, 29·55 (2 C), 31·89, 68·48, 114·85 (2 C), 119·21 (2 C), 123·13 (2 C), 124·29 (2 C), 125·14 (2 C), 138·75 (2 C), 143·88, 146·63, 152·03, 162·38, 178·98.

4-[4′-(Dodecyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (6). 4-Hydroxypyridine (1·90 g, 20·0 mmol), **17** (3·84 g, 10·0 mmol) and potassium carbonate (2·76 g, 20·0 mmol) in 20 ml NMP were stirred under nitrogen and gradually heated to 175°C. The reaction mixture was stirred for 30 min at 175°C and was then cooled and water added. The precipitate was filtered and washed with water. The crude product was recrystallized from methanol to yield 4·037 g (88 per cent) of an orange solid: m.p. 99°C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 0·86 (t, 3 H), 2·0–1·15 (m, 20 H), 4·04 (t, J=6·53 Hz, 2 H), 6·67 (d, J=7·54 Hz, 2 H), 6·99 (d, J=9·38 Hz, 2 H), 7·47 (d, J=8·85 Hz, 2 H), 7·71 (d, J=7·73 Hz, 2 H), 7·92 (d, J= 8·96 Hz, 2 H), 8·01 (d, J=8·87 Hz, 2 H).

4-[4′-(Octadecyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (7). 4-Hydroxypyridine (380 mg, 4·0 mmol), **18** (936 mg, 2·0 mmol) and potassium carbonate (560 mg, 4·0 mmol) in 10 ml NMP were stirred under nitrogen at 160°C for 2 h. The reaction mixture was cooled and water was added. The precipitate was filtered, washed with water, and recrystallized from a mixture of methanol and 1-propanol to yield 1·00 g (92 per cent) of a yellow solid: m.p. 100°C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 0·86 (t, J=7 Hz, 3 H), 1·65–1·10 (m, 30 H), 1·75–1·95 (m, 2 H), 4·04 (t, J=7 Hz, 2 H), 6·58 (d, J=8 Hz, 2 H), 6·99 (d, J=9 Hz, 2 H), 7·46 (d, J=9 Hz, 2 H), 7·68 (d, J=8 Hz, 2 H), 7·91 (d, J=9 Hz, 2 H), 7·98 (d, J=9 Hz, 2 H).

4-[4′-(2-Ethyl-hexyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (8). 4-Hydroxypyridine (1·80 g, 20·0 mmol), **19** (3·28 g, 10·0 mmol) and potassium carbonate (2·76 g, 20·0 mmol) in 20 ml NMP were stirred under nitrogen at 170°C for 2 h. The reaction mixture was cooled and water was added. The precipitate was filtered and washed with water. The crude was boiled in methanol, filtered, and then an equal volume of water was added dropwise with stirring. The product was cooled and filtered to yield 3·50 g (87 per cent) of an orange solid: m.p. 90°C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 0·93 (m, 6 H), 1·20–1·90 (m, 9 H), 3·92 (d, J=5·73 Hz, 2 H), 6·61 (d, J=7·72 Hz, 2 H), 7·01 (d, J=8·98 Hz, 2 H), 7·46 (d, J=8·87 Hz, 2 H), 7·68 (d, J=7·76 Hz, 2 H), 7·91 (d, J=9·00 Hz, 2 H), 8·01 (d, J=8·81 Hz, 2 H).

4-[4′-(6-Ol-hexyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (9). 4-Hydroxypyridine (366 mg, 3·85 mmol), **20** (608 mg, 1·92 mmol) and potassium carbonate (532 mg, 3·85 mmol) in 4 ml NMP were stirred at 120°C for 4 h. The reaction mixture was cooled and water added. The precipitate was filtered and washed with water. The crude product was stirred in hot glacial acetic acid (~10 ml), filtered, and then water (~30 ml) added. The solution was heated and stirred until everything dissolved and the solution was then allowed to cool and filtered to yield 503 mg (67 per cent) of an orange solid: R_F 0·60 (50:50 methanol:ethyl acetate); m.p. 230°C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 1·35 (m, 6 H), 1·74 (m, 2 H), 3·35 (m, 2 H), 4·08 (t, 2 H), 4·36 (t, 1 H), 6·26 (d, J=7·66 Hz, 2 H), 7·13 (d, J=8·90 Hz, 2 H), 7·75 (d, J=8·75 Hz, 2 H), 7·90 (d, J=8·80 Hz, 2 H), 7·98 (d, J=8·71 Hz, 2 H), 8·09 (d, J=7·71 Hz, 2 H).

4-[4′-(6-Oxo-hexanoic acid ethyl ester)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (10). 4-Hydroxypyridine (426 mg, 4·48 mmol), **21** (803 mg, 2·24 mmol) and potassium carbonate (619 mg, 4·48 mmol) in 4 ml NMP were stirred at 150°C for 1·5 h. The reaction mixture was cooled and water added. The precipitate was filtered and washed with water to yield 808 mg (83 per cent) of an orange solid: R_F 0·67 (50:50 methanol:ethyl acetate); m.p. 144°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1·24 (t, $J=7·12$ Hz, 3 H), 1·55 (m, 2 H), 1·75 (m, 2 H), 1·84 (m, 2 H), 2·33 (t, $J=7·50$ Hz, 2 H), 4·04 (t, $J=6·22$ Hz, 2 H), 4·12 (q, $J=6·98$ Hz, 2 H), 6·54 (d, $J=7·23$ Hz, 2 H), 6·98 (d, $J=8·69$ Hz, 2 H), 7·45 (d, $J=8·43$ Hz, 2 H), 7·66 (d, $J=7·28$ Hz, 2 H), 7·91 (d, $J=8·58$ Hz, 2 H), 8·00 (d, $J=8·29$ Hz, 2 H).

4-[4'-(6-Oxo-hexanoic acid)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (11). Sodium hydroxide (221 mg, 5·5 mmol), **10** (478 mg, 1·1 mmol), water (3 ml), methanol (10 ml) and tetrahydrofuran (5 ml) were heated at reflux for 1 h. The reaction mixture was acidified with concentrated HCl and water (~20 ml) was added. The solid was filtered and washed with water and then methanol to yield 418 mg (94 per cent) of an orange solid: m.p. 350°C dec; ^{1}H NMR (250 MHz, DMSO-d_6) δ 1·50 (m, 4 H), 1·71 (m, 2 H), 2·20 (t, 2 H), 4·04 (t, $J=5·77$ Hz, 2 H), 6·24 (d, $J=7·83$ Hz, 2 H), 7·10 (d, $J=9·45$ Hz, 2 H), 7·72 (d, $J=8·84$ Hz, 2 H), 7·87 (d, $J=8·92$ Hz, 2 H), 7·94 (d, $J=8·82$ Hz, 2 H), 8·07 (d, $J=7·85$ Hz, 2 H), 11·97 (s, 1 H).

4-[4'-(4''-Decyloxy-benzoyloxy)-phenylazo]-(4-oxo-4H-pyridin-1-yl)benzene (12). Benzoic acid (200 mg, 0·70 mmol) was stirred in thionyl chloride (~3 ml) for 3 h. The excess thionyl chloride was evaporated off and the crude acid chloride added to a stirred solution of **13** (209 mg, 0·70 mmol) in 10 ml pyridine. The reaction mixture was stirred for 24 h and then water added. The orange precipitate was filtered, taken up in dichloromethane, and then adsorbed onto silica gel. The crude product was purified via flash chromatography on silica gel with a gradient of neat ethyl acetate to 60:40 ethyl acetate:methanol. Evaporation of solvent yielded 304 mg (77 per cent) of an orange solid: R_F 0·13 (45:45:10 hexanes:ethyl acetate:methanol); m.p. 140°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·87 (t, $J=6·36$ Hz, 3 H), 1·15–1·60 (m, 14 H), 1·81 (m, 2 H), 4·04 (t, $J=6·51$ Hz, 2 H), 6·57 (d, $J=7·78$ Hz, 2 H), 6·97 (d, $J=8·95$ Hz, 2 H), 7·38 (d, $J=8·85$ Hz, 2 H), 7·49 (d, $J=8·81$ Hz, 2 H), 7·69 (d, $J=7·80$ Hz, 2 H), 8·02 (d, $J=8·83$ Hz, 2 H), 8·07 (d, $J=8·84$ Hz, 2 H), 8·14 (d, $J=8·91$ Hz, 2 H).

4-(4'-Fluorophenylazo)phenol (13). 4-Fluoroaniline (19·1 g, 172·0 mmol) was dissolved in 200 ml of a 2 M HCl solution and cooled with an ice bath. A solution of sodium nitrite (13·0 g, 190 mmol) in water (30 ml) was slowly added keeping the reaction temperature below 8°C. The reaction mixture was stirred for 1 h and then a solution of phenol (17·8 g, 190 mmol) and sodium hydroxide (10·0 g, 250 mmol) in water (150 ml) was slowly added keeping the reaction temperature between 5–10°C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A red precipitate formed and the solution was neutralized with aqueous sodium bicarbonate. The solid was collected by filtration and then dissolved in ether and chloroform and dried over anhydrous sodium sulphate. The product was adsorbed onto silica gel and purified via flash chromatography over silica gel with 80:20 hexanes:ethyl acetate. The product was then recrystallized from a mixture of ether and methylcyclohexane to yield 28·0 g (75 per cent) of an orange solid: R_F 0·48 (80:20 hexanes:ethyl acetate); m.p. 160–161°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5·58 (bd, s, 1 H), 6·91 (d, $J=8·77$ Hz, 2 H), 7·16 (t, $J=8·42$ Hz, 2 H), 7·86 (m, 4 H).

4-[4'-(4-Oxo-4H-pyridin-1-yl)-phenylazo]phenol (14). A mixture of 4-hydroxypyridine (1·92 g, 20·0 mmol), **13** (2·16 g, 10·0 mmol) and potassium carbonate (2·76 g, 20·0 mmol) in 10 ml NMP was stirred at 170°C for 2 h. The reaction mixture was cooled and a mixture of 60 ml water and 4 ml of acetic acid added dropwise with stirring. The precipitate was isolated by suction filtration, washed with water and then air dried to yield 2·60 g (89 per cent) of a yellow solid. The crude product isolated in this fashion was very pure and can be recrystallized from acetic acid: m.p. 300°C (dec); ^{1}H NMR (250 MHz, DMSO-d_6, 110°C) δ 6·27 (d, 2 H), 6·98 (d, 2 H), 7·68 (d, 2 H), 7·80 (d, 2 H), 7·90 (m, 4 H); ^{13}C NMR (250 MHz, DMSO-d_6, 110°C) δ 115·49 (2 C), 117·50 (2 C), 122·57 (2 C), 122·77 (2 C), 124·18 (2 C), 138·56 (2 C), 143·10, 145·22, 150·88, 160·67, 176·75.

4-[4'-(Hexyloxy)-phenylazo]fluorobenzene (15). A mixture of 1-iodohexane (2·12 g, 10·0 mmol), **13** (1·62 g, 7·5 mmol) and potassium carbonate (2·10 g, 15·0 mmol) in 10 ml NMP was stirred at 90°C for 1 h. The reaction mixture was cooled and water added dropwise with stirring. The crude was filtered, washed with water and recrystallized from methanol to yield 2·00 g (89 per cent) of a yellow solid: m.p. 72°C (I 52 N); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·90 (t, 3 H), 1·30–1·50 (m, 6 H), 1·81 (q, $J=6$ Hz, 2 H), 4·02 (t, $J=6$ Hz, 2 H), 6·95–7·02 (m, 2 H), 7·10–7·20 (m, 4 H), 7·83–7·91 (m, 4 H).

4-[4'-(Decyloxy)-phenylazo]fluorobenzene (16). Bromodecane (5·30 g, 24·0 mmol), **13** (4·32 g, 20·0 mmol) and potassium carbonate (5·5 g, 40 mmol) in 40 ml NMP were stirred at 80°C for 3 h. The reaction temperature was raised to 100°C and stirring was continued for an additional 3 h. The reaction mixture was cooled and then poured into water (200 ml) with vigorous stirring. The crude was filtered, washed with water, and recrystallized from methanol:ether (95:5) to yield 6·7 g (93 per cent) of a yellow solid: R_F 0·87 (80:20 hexanes:ethyl acetate); m.p. 83–84°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·87 (t, 3 H), 1·50–1·20 (m, 14 H), 1·79 (m, 2 H), 4·02 (t, 2 H), 7·00 (d, 2 H), 7·18 (t, 2 H), 7·87 (m, 4 H).

4-[4′-(Dodecyloxy)-phenylazo]fluorobenzene (17). A mixture of 1-iodododecane (4·50 g, 15 mmol) **13** (3·24 g, 15·0 mmol) and potassium carbonate (4·14 g, 30·0 mmol) in 20 ml NMP was stirred at 100°C for 1·5 h. More 1-iodododecane (900 mg, 3·0 mmol) was added and stirring continued for an additional 30 min. The reaction mixture was cooled and water added dropwise with stirring. The crude product was recrystallized from a mixture of methanol and 1-propanol to yield 3·85 g (67 per cent) of a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3 H), 1·15–1·65 (m, 18 H), 1·80 (m, 2 H), 4·01 (t, 2 H), 6·99 (d, 2 H), 7·15 (t, 2 H), 7·88 (m, 4 H).

4-[4′-(Octadecyloxy)-phenylazo]fluorobenzene (18). 1-Iodooctadecane (2·09 g, 5·5 mmol), **13** (1·08 g, 5·0 mmol) and potassium carbonate (1·38 g, 10·0 mmol) in 5 ml NMP were stirred at 100°C for 2 h. The reaction mixture was cooled and water added dropwise with stirring. The crude was washed with water and recrystallized from 1-propanol to yield 2·00 g (85 per cent) of a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3 H), 1·15–1·60 (m, 30 H), 4·02 (t, $J = 6$ Hz, 2 H), 6·98 (m, 2 H), 7·15 (m, 2 H), 7·88 (m, 4 H).

4-[4′-(2-Ethyl-hexyloxy)-phenylazo]fluorobenzene (19). 1-Bromo-2-ethylhexane (3·86 g, 20·0 mmol), **13** (3·24 g, 15 mmol) and potassium carbonate (4·14 g, 30·0 mmol) in 25 ml NMP were stirred at 90°C for 2·5 h. The reaction mixture was cooled and water added dropwise with stirring. The crude was filtered, boiled in methanol and filtered again. A small amount of water was added to the filtrate and the resulting solid filtered to yield 4·32 g (88 per cent) of a yellow solid: m.p. 52°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·92 (m, 6 H), 1·15–1·90 (m, 9 H), 3·90 (d, $J = 5·70$ Hz, 2 H), 6·98 (d, $J = 8·99$ Hz, 2 H), 7·15 (t, $J = 8·38$ Hz, 2 H), 7·87 (m, 4 H).

4-[4′-(6-Ol-hexyloxy)-phenylazo]fluorobenzene (20). A mixture of 6-bromo-1-hexanol (1·08 g, 6·0 mmol), **13** (1·08 g, 5·0 mmol) and potassium carbonate (1·38 g, 10·0 mmol) in 5 ml NMP was stirred at 100°C for 2 h. The reaction mixture was cooled and water was added dropwise with stirring. The crude was filtered, boiled in methanol and filtered again. A small amount of water was added to the filtrate and the resulting solid was filtered to yield 1·17 g (81 per cent) of a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1·30–2·00 (m, 8 H), 3·65 (m, 2 H), 4·02 (m, 2 H), 6·97 (d, 2 H), 7·15 (t, 2 H), 7·88 (m, 4 H).

4-[4′-(6-Oxo-hexanoic acid ethyl ester)-phenylazo]-fluorobenzene (21). Ethyl-6-bromohexanoate (1·78 g, 8·0 mmol), **13** (1·62 g, 7·5 mmol) and potassium carbonate (1·38 g, 10·0 mmol) in 10 ml NMP were stirred at 100°C for 2 h. The reaction mixture was cooled and water added dropwise with stirring. The crude was filtered, washed with water, and recrystallized from methanol to yield 2·40 g (90 per cent) of a yellow solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1·24 (t, 3 H), 1·45–1·95 (m, 6 H), 2·33 (t, 2 H), 4·03 (t, 2 H), 4·11 (q, 2 H), 6·97 (d, 2 H), 7·16 (t, 2 H), 7·87 (m, 4 H).

4-(4′-Methoxy)-fluorostilbene (22) [16]. A mixture of 4-methoxystyrene (2·95 g, 22·0 mmol), 4-iodofluorobenzene (4·44 g, 20·0 mmol), potassium carbonate (2·76 g, 20·0 mmol), palladium(II) acetate (45 mg, 0·20 mmol) and tris[2-(2-methoxy ethoxy)ethyl]amine (646 mg, 2·0 mmol) in 10 ml dimethylformamide was stirred under nitrogen at 110°C for 6 h. The reaction mixture was cooled and then 10 per cent HCl was added. The precipitate was filtered and washed with water. The crude product was boiled in 2-propanol and bentonite clay (2 g), and silica gel (2 g) was added. The hot solution was filtered and the filtrate allowed to cool. The resulting solid was recrystallized again from 2-propanol to yield 3·15 g (69 per cent) of white solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 3·81 (s, 3 H), 6·85 (m, 4 H), 7·05 (t, 2 H), 7·43 (m, 4 H).

4-(4′-Methoxy)-(4-oxo-4H-pyridin-1-yl)stilbene (23). 4-Hydroxypyridine (333 mg, 3·5 mmol), **22** (400 mg, 1·75 mmol) and potassium carbonate (484 mg, 3·5 mmol) in 10 ml NMP were stirred for 12 h at 120°C. An additional equivalent of 4-hydroxypyridine and potassium carbonate were added and the reaction mixture was stirred at 150°C for 12 h. The reaction mixture was cooled and then water added. The precipitate was filtered and taken up in dichloromethane and then adsorbed onto silica gel. The crude was purified via flash chromatography over silica gel with gradual elutions from 45:45:10 (hexanes:ethyl acetate:dichloromethane) to 40:40:10:10 (hexanes:ethyl acetate:dichloromethane:methanol). Evaporation of solvent yielded 270 mg (51 per cent) of a tan solid: R_F 0·37 (45:45:10 hexanes:ethyl acetate:methanol); m.p. 230°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3·83 (s, 3 H), 6·52 (d, $J = 7·74$ Hz, 2 H), 6·90 (d, $J = 8·83$ Hz, 2 H), 7·13–6·98 (t, 2 H), 7·30 (d, $J = 8·61$ Hz, 2 H), 7·46 (d, $J = 8·77$ Hz, 2 H), 7·59 (m, 4 H).

4-Iodo-(4-oxo-4H-pyridin-1-yl)benzene (24). 4-Iodoaniline (3·505 g, 16·0 mmol) and chelidonic acid (2·946 g, 16·0 mmol) in 16 ml dimethylsulphoxide was slowly heated to 130°C and was then stirred for 2 h until gas evolution ceased. The reaction mixture was cooled and then water (50 ml) added, and the solution was allowed to stand at room temperature overnight. The precipitate was filtered and washed with water to yield 1·965 g (41 per cent) of a yellow solid: ^{1}H NMR (250 MHz, DMSO-d_6) δ 6·21 (d, 2 H), 7·34 (d, 2 H), 7·89 (d, 2 H), 7·98 (d, 2 H).

4-(4′-Acetoxy)-(4-oxo-4H-pyridin-1-yl)stilbene (25). 4-Acetoxystyrene (304 mg, 1·88 mmol), **24** (507 mg, 1·70 mmol), potassium carbonate (235 mg, 1·70 mmol), palladium(II) acetate (4 mg, 0·017 mmol) and tris-[2-(2-methoxy ethoxy)ethyl]amine (55 mg, 0·17 mmol) in 4 ml dimethylformamide were stirred under nitrogen at 110°C for 2 h. The reaction mixture was cooled and then water added. The precipitate was filtered and washed with water. The crude was taken up in dichloromethane and stirred with magnesium sulphate and bentonite. The solution was filtered and then adsorbed onto silica gel. The product was purified via flash chromatography over silica gel with a gradient of neat ethyl acetate to 50:50 ethyl acetate:methanol. Evaporation of solvent yielded 223 mg (39 per cent) of a tan solid: R_F 0·59 (50:50 ethyl acetate:methanol); m.p. 244°C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 2·30 (s, 3 H), 6·55 (d, $J=7·79$ Hz, 2 H), 7·07 (m, 4 H), 7·32 (d, $J=8·62$ Hz, 2 H), 7·52 (d, $J=8·65$ Hz, 2 H), 7·62 (m, 4 H).

4-(4′-Hydroxy)-(4-oxo-4H-pyridin-1-yl)stilbene (26). Sodium hydroxide (193 mg, 4·8 mmol), **25** (320 mg, 0·97 mmol), water (5 ml), methanol (20 ml) and tetrahydrofuran (10 ml) were refluxed for 45 min. The solution was cooled and then acidified with concentrated HCl. Water was added, and the solid filtered and washed with more water to yield 203 mg (73 per cent) of a tan solid: ^{1}H NMR (250 MHz, DMSO-d_6) δ 6·79 (d, $J=8·62$ Hz, 2 H), 7·11 (d, $J=16·45$ Hz, 1 H), 7·22 (d, $J=7·48$ Hz, 2 H), 7·31 (d, $J=16·39$ Hz, 1 H), 7·46 (d, $J=8·66$ Hz, 2 H), 7·68 (d, $J=8·75$ Hz, 2 H), 7·79 (d, $J=8·78$ Hz, 2 H), 8·74 (d, $J=7·50$ Hz, 2 H).

4-(4′-Decyloxy)-(4-oxo-4H-pyridin-1-yl)stilbene (27). 1-Iodododecane (835 mg, 3·11 mmol), **26** (180 mg, 0·623 mmol) and potassium carbonate (172 mg, 1·25 mmol) in 4 ml NMP were stirred for 3 h at 120°C. The reaction mixture was cooled, water added and the solution filtered. The brown semi-solid was taken up in dichloromethane, dried over magnesium sulphate and adsorbed onto silica gel. The crude was purified via flash chromatography over silica gel with gradual elutions from neat ethyl acetate to 40:40:20 (ethyl acetate:methanol:dichloromethane). Evaporation of solvent yielded 77 mg (29 per cent) of a tan solid: m.p. 154°C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 0·86 (t, $J=6·46$ Hz, 3 H), 1·55–1·15 (m, 12 H), 1·78 (m, 4 H), 3·96 (t, $J=6·59$ Hz, 2 H), 6·50 (d, $J=7·78$ Hz, 2 H), 6·88 (d, $J=8·77$ Hz, 2 H), 7·13–6·97 (t, 2 H), 7·29 (d, $J=8·61$ Hz, 2 H), 7·44 (d, $J=8·77$ Hz, 2 H), 7·58 (m, 4 H).

4-Ethynyl-O-(tetrahydropyran-2-yl)-phenol (28). [12] ^{1}H NMR (250 MHz, CDCl$_3$) δ 1·4–2·1 (m, 6 H), 2·99 (s, 1 H), 3·55 (m, 1 H), 3·83 (m, 1 H), 5·40 (t, 1 H), 6·96 (d, 2 H), 7·42 (d, 2 H); ^{13}C NMR (250 MHz, CDCl$_3$) δ 18·64, 25·13, 30·22, 61·98, 75·95, 83·70, 96·18, 115·00, 116·34 (2 C), 133·48 (2 C), 157·45.

4-[4′-Fluorophenylethynyl]-O-(tetrahydropyran-2-yl) phenol (29). To a solution of 4-fluoroiodobenzene (12·2 g, 55 mmol), **28** (10·1 g, 50 mmol), triphenylphosphine (98 mg, 0·38 mmol) and bis-triphenylphosphine–palladium(II) chloride (175 mg, 0·25 mmol) in 50 ml di-*n*-propylamine was added copper(I) iodide (24 mg, 0·12 mmol) with stirring and under nitrogen at 80°C. The reaction mixture was stirred at 90°C for 2 h and then concentrated via rotary evaporation. The crude solid was taken up in methanol (~200 ml) and then ice water (~200 ml) was added dropwise with stirring. This product was filtered, washed with ice water, and air dried to yield 12·6 g (85 per cent) of a tan solid which was utilized without further purification: ^{1}H NMR (250 MHz, CDCl$_3$) δ 1·40–2·10 (m, 6 H), 3·60 (m, 1 H), 3·87 (m, 1 H), 5·42 (t, 1 H), 6·95 (m, 4 H), 7·40 (m, 4 H).

4-(4′-Fluorophenylethynyl)phenol (30). Tetrahydrofuran (100 ml) and **29** (12·6 g, 42·5 mmol) were stirred at ~40°C until everything dissolved. Methanol (~50 ml) and *p*-toluenesulphonic acid monohydrate (200 mg, 1·05 mmol) were added and the reaction mixture was stirred for 2 h at ~40°C. The reaction mixture was concentrated to a slurry (~45 ml) and then water (400 ml) was added dropwise with stirring. The product was filtered and air dried to yield 7·95 g (88 per cent) of a tan solid. The crude product was taken on without further purification: ^{1}H NMR (250 MHz, CDCl$_3$) δ 4·96 (s, 1 H), 6·69 (d, $J=8·76$ Hz, 2 H), 7·02 (t, $J=8·69$ Hz, 2 H), 7·45 (m, 4 H).

4-(4′-Decyloxyphenylethynyl)-fluorobenzene (31). 1-Iodododecane (6·7 g, 25·0 mmol), **30** (4·24 g, 20·0 mmol) and potassium carbonate (4·2 g, 30·0 mmol) in 25 ml NMP were stirred at 80°C for 6 h and then stirred overnight at room temperature. Water (~250 ml) was added dropwise with stirring and the crude filtered. The product was recrystallized from methanol to yield 6·22 g

(82 per cent) of a white solid: m.p. 70°C (I 45 N); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, 3 H), 1·10–1·60 (m, 14 H), 1·76 (m, 2 H), 3·94 (t, 2 H), 6·83 (d, $J=8{\cdot}77$ Hz, 2 H), 7·00 (t, $J=8{\cdot}71$ Hz, 2 H), 7·39 (m, 4 H).

4-[4′-Decyloxyphenylethynyl]-(4-oxo-4H-pyridin-1-yl)benzene (32). Hydroxypyridine (1·80 g, 20 mmol), 31 (3·80 g, 10·0 mmol) and potassium carbonate (2·76 g, 20·0 mmol) in 15 ml NMP were stirred at 180°C for 4 h. The reaction mixture was cooled and a 1:1 solution of methanol and water (150 ml) added dropwise with stirring. The crude was filtered and washed with water:methanol (1:2). After drying the solid was dissolved in dichloromethane and adsorbed onto silica gel. The product was purified via flash chromatography over silica gel with gradual elutions from neat ethyl acetate to 50:50 (ethyl acetate:methanol). Evaporation of solvent yielded 260 mg (6 per cent) of a white solid: m.p. 124°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0·86 (t, $J=6{\cdot}41$ Hz, 3 H), 1·15–1·55 (m, 12 H), 1·77 (m, 4 H), 3·96 (t, $J=6{\cdot}55$ Hz, 2 H), 6·50 (d, $J=7{\cdot}74$ Hz, 2 H), 6·86 (d, $J=8{\cdot}84$ Hz, 2 H), 7·29 (d, $J=8{\cdot}74$ Hz, 2 H), 7·44 (d, $J=8{\cdot}81$ Hz, 2 H), 7·61 (m, 4 H).

3. Liquid crystalline properties

Liquid crystal phase diagrams were characterized by a combination of differential scanning calorimetry and polarized optical microscopy. LC phases were identified by their characteristic texture on untreated glass slides and should be considered preliminary until a more definitive study is undertaken. The nematic (N) and smectic A (SmA) were the only LC phases observed in these 4-pyridones. The textures were often highly homeotropic, perhaps due to a strong interaction between the polar pyridone group and the glass surface. In some cases samples were melted under vacuum to remove traces of solvent and water prior to preparation of the samples for microscopy and thermal analysis. Melting points ranged from 90° to >300°C and broad enantiotropic phases over >100°C were observed. Table 1 summarizes the different structures and LC phase diagrams.

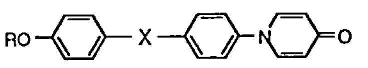
In the original Vorländer paper [1] the phase diagrams of the 4-pyridones were not fully characterized. We synthesized the acetoxy (**1**) and benzoyl (**2**) derivatives originally described by Vorländer using the new synthesis based on aromatic nucleophilic substitutions in order to confirm that they were mesogens. We found that the acetoxy compound (**1**) decomposed upon heating while the benzoyloxy compound (**2**) exhibited an enantiotropic N phase from 259 to 315°C. Vorländer described (**2**) as exhibiting two melting points at 250 and 263°C, respectively. The second melting point corresponds to our data, in addition, we observed several crystal–crystal transitions which may have been the event observed by Vorländer at 250°C. The clearing point for (**2**) was observed by DSC at 315°C. These data confirm that Vorländer was the first to synthesize and describe this unique class of mesogens.

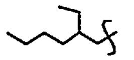
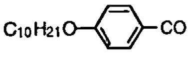
The first series of compounds (**1–12**) possess an azo linkage in the core and exhibit mesogenicity. The simple alkoxy homologues (**3–7**) were synthesized in order to explore the effects of chain length on the LC phase diagram. The very short molecule (**3**) possesses an enantiotropic nematic phase, however, as the chain length increases to six carbons (**4**), a smectic A phase appears. The nematic phase disappears at longer chain lengths as illustrated by (**5–7**) which only possess smectic A phases. In addition, the melting points decrease and the enantiotropic LC phases become broader as the chain length increases. Compounds (**6–7**), with tail lengths of 12 and 18 carbons respectively, exhibit broad enantiotropic A phases over ~100°C. Branching of the alkoxy tail in (**8**) dramatically lowers the melting point and clearing point relative to the unbranched homologue (**4**).

Compounds (**9–12**) in the azobenzene series were synthesized in order to explore the effects of different functional groups in the aliphatic tail on mesogenic behaviour. The terminal hydroxy group in (**9**) had a dramatic effect on the LC phase behaviour when compared to (**4**) which had a similar tail length. Compound (**9**) exhibits a monotropic N phase at 227°C in contrast to the enantiotropic N and A phases present at ~150°C in the alkoxy derivative (**4**). It is possible that (**9**) participates in intermolecular H-bonding which may tend to raise the transition temperatures. Compound (**11**) with a terminal carboxylic acid may also participate in H-bonding, however, it exhibits no LC phases prior to its decomposition ~350°C. Liquid crystal (**12**) incorporates the common phenyl benzoate core system along with the 4-pyridone structure and exhibits a very broad enantiotropic A phase from 140–290°C. Thus, a large variety of functionalities may be combined with the terminal 4-pyridone structural unit in order to produce materials with mesogenic behaviour.

We also examined the effects of changes at the linkage group (X) described in table 1. Therefore, in addition to the azo linker compounds with a *trans* double bond (stilbenes **23**, **25**, **27**) an acetylene (tolane-**32**) was also prepared. Both linkages were readily synthesized and produced mesogens. Interestingly, the acetoxy stilbene (**25**) possessed an enantiotropic N phase at 259°C in contrast to the azo homologue (**1**) which decomposed at the same temperature. In general it appears that the LC behaviour of the stilbenes is very similar to the respective azo homologues. The tolane derivative (**32**) also exhibited very similar LC behaviour to its azo

Table 1. Phase diagrams for the 4-pyridone liquid crystals.



			Temperature/°C						
Compound	X	R	I		N		SmA		Cr
1	N-N	CH_3CO	●		–Decomposed at 259–				●
2	N-N	PhCO	●	315	●		–	259	●
3	N-N	CH_3	●	225	●		–	213	●
4	N-N	C_6H_{13}	●	162	●	146	●	142	●
5	N-N	$C_{10}H_{21}$	●	193	–		●	132	●
6	N-N	$C_{12}H_{25}$	●	197	–		●	98	●
7	N-N	$C_{18}H_{37}$	●	195	–		●	100	●
8	N-N		●	103	–		●	90	●
9	N-N	$HO(CH_2)_6$	●	(227)	●		–	230	●
10	N-N	$CH_3CH_2O_2C(CH_2)_5$	●	(125)	●		–	144	●
11	N-N	$HO_2C(CH_2)_5$	●		–Decomposed at 350–				●
12	N-N		●	291	–		●	140	●
23	HC-CH	CH_3	●	(223)	●		–	230	●
25	HC-CH	CH_3CO	●	259	●		–	251	●
27	HC-CH	$C_{10}H_{21}$	●	223	–		●	129	●
32	C-C	$C_{10}H_{21}$	●	191	●		–	124	●

I = isotropic; N = nematic; SmA = smectic A; Cr = crystal. A (●) means that the phase exists and a (–) means that the phase does not exist. Temperatures in parentheses are monotropic.

homologue (5). Thus, a broad range of core linker groups may be incorporated with the 4-pyridone structural unit in order to produce mesogenic behaviour.

4. Conclusions

An important class of liquid crystalline materials which incorporate the 4-pyridone structural terminus unit have been described. These unique liquid crystals may possess useful properties such as large birefringence or intermolecular H-bonding. The synthesis of 4-pyridones which has been developed is straightforward and will deliver a rich variety of functionalities into the LC core and tail structures. We are currently pursuing further derivatization of the pyridone group in order to establish its utility as a versatile structural component in and an intermediate for the preparation of other liquid crystals. Finally, the original work of Vorländer, who first described liquid crystals containing this 4-pyridone structure, has been substantiated.

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