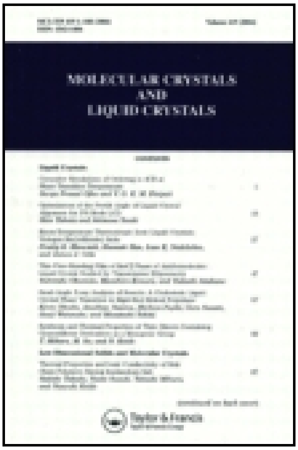

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Synthesis and Properties of Liquid Crystals Containing the 4-Pyridone and Methylene-1,4-Dihydropyridine Structure Unit

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Synthesis and Properties of Liquid Crystals Containing the 4-Pyridone and Methylene-1,4-Dihydropyridine Structure Unit

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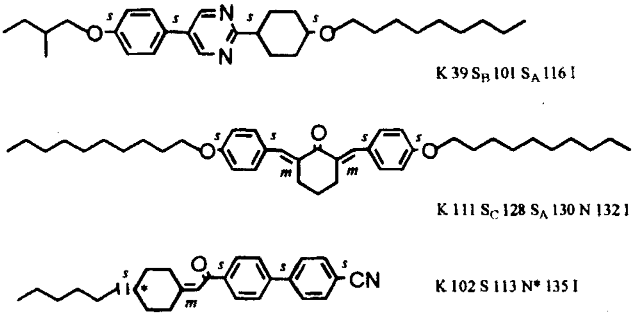
Mesogens that contain a methylene-1,4-dihydropyridine have been prepared from 4-(1H)-pyridone precursors. These heterocyclic substructures are very versatile and permit elaboration into a wide variety of novel liquid crystals. A range of synthetic methodologies for the synthesis of these materials are discussed and, in particular, we compare behavior of homologous series with alkyl, perfluoroalkyl and alkoxy tails.

Keywords: pyridone; dihydropyridine; fluorinated; birefringence

INTRODUCTION

Not too long ago it generally sufficed to classify mesogenic molecules by specifying only two main components: a rigid core (comprised of some ring structures) and one or two flexible tails (comprised of aliphatic groups). Of course, there are now numerous exceptions known to this general rule which, if anything, has become more restrictive and misleading than it is useful. It is now widely appreciated that thermotropic liquid crystals exist which contain an extremely wide variety of chemical structures.[1] As a result, is has become increasingly difficult to define even what the minimum structure requirements for mesomorphic behaviour are.[2]

The ring structures found in thermotropic liquid crystals are most often six-membered and the fully aromatic benzene ring, its condensed derivatives and numerous heterocyclic derivatives are the most widely employed. Likewise, fully saturated cyclohexane rings, annulated cyclohexanes and heterocyclic derviatives are employed too (here again there are many kinds of ring systems utilized that do not fall into either of these categories). Another interesting and overlooked structure feature to consider is the mode of connectivity between these rings and any adjacent parts of the molecule (a tail, another ring or some bridge group between rings). That connecting bond turns out to be, almost without exception, a single bond and only rarely a multiple (double) bond. The number of unsaturations in a ring and their relative locations, especially endocyclic versus exocyclic, has some very interesting and profound ramifications on mesogenic activity.



$K\ 39\ S_B\ 101\ S_A\ 116\ I$ **1**

$K\ 111\ S_C\ 128\ S_A\ 130\ N\ 132\ I$ **2**

$K\ 102\ S\ 113\ N^*\ 135\ I$ **3**

FIGURE 1. Examples of ring connectivity in some liquid crystals (single connectivity "*s*" and multiple connectivity "*m*")

At this point a few examples (Figure 1) are instructive. Consider, for example, the phenyl-pyrimidine-*trans*-cyclohexyl system **1**.[3] This liquid crystal is representative in that it is comprised of an aromatic benzene ring, a heterocyclic pyrimidine ring as well as the saturated cyclohexane ring. Notably, all the bonds linking the rings together and linking the alkoxy tails in this compound are formal single bonds (indicated with an *s*). In contrast, perhaps the best known and documented systems with multiple bond ring connectivity are the bis methylene cyclohexanones of which there are many examples such as **2**.[4] Here the central cyclohexanone ring is bonded to the rest of the molecule via a pair of exocyclic methylene groups (indicated with an *m*). Another particularly interesting example is the axially dissymmetric system containing an exocyclic methylenecyclohexane ring **3**.[5] Here a chiral structure is created by inclusion of the monosubstituted exocyclic olefin and the monosubstituted ring carbon at the 4-position of the cyclohexane ring. If a trisubstituted atom (neutral nitrogen atom) is substituted for this monosubstituted ring carbon then chiral compounds are not obtained. As a general area of study we have begun to examine liquid crystals which possess multiple bond ring connectivity and as a starting point we have begun examining heterocycles with a connecting nitrogen atom in this position, viz., the 4-(1H) pyridones and the 4-(1H) methylenedihydropyridines (Figure 2). The R-groups on the ring nitrogen can be a wide variety of aromatic and aliphatic groups and the A and A' groups a combination of electron withdrawing substituents.

The pyridones are important in that they serve as precursors to the methylenedihydropyridines (A, A' = CN, COOR', COR', etc.; R = 4-X-Ph, etc.) and many of the pyridones themselves have interesting mesogenic behavior.[6] The conversion of the precursor 4-(1H) pyridones to some 4(1H)-methylenedihydropyridine liquid crystals by Knoevenagel condensation has been described.[7] It appears that the 4(1H)-methylenedihydropyridine ring system has some properties which may be of particular value related to mesogenic materials. This is a versatile multifunctional structure that can be incorporated into liquid crystal molecules in a variety of ways via different combinations of A, A' and R. Appropriately substituted (with one or two acceptor groups) methylenedihydropyridines have very interesting optical and electronic properties. A series of cyanoester substituted 2,6-dimethylmethylenedihydropyridines have been utilized as glass forming photorefractive chromophores.[8] The dipole moments and polarizabilities of such molecules has been measured and is often substantial.[9] Analogs with more extended styryl conjugation at the 2 and 6 positions have also been prepared and have been exploited as electrooptic chromophores.[10]

1-R-1H-pyridin-4-one 1-R-4-A,A'-methylenedihydropyridine

FIGURE 2. The heterocycles employed in this study.

EXPERIMENTAL

Phase transitions were determined by polarized light microscopy using a Mettler FP5 controller and FP52 hot stage or Linkam TMS 90 controller and THM600 hot stage. Thermal analysis was run on a Perkin-Elmer DSC 7 at a scan rate of 3 deg/min. NMR spectra were obtained at 300 MHz in a deuterated solvent. Representative synthetic procedures follow:

4'-hexyl-(4-oxo-4H-pyridin-1-yl)-benzene 4(6). A mixture of 4-hexylaniline (3.5g, 20 mmol), chelidonic acid hydrate (4g, 20 mmol) and DMSO (50 ml) was heated and stirred at 160-170°C for 4 hours until gas evolution ceased. The reaction mixture was cooled, filtered and washed with ethyl acetate. The solvent was removed by vacuum. The product was purified via flash chromatography on silica gel with 4:1 ethyl acetate: methanol to give 3.2g (64%) of tan solid: m.p. 50°C; ^1H NMR (300MHz, $CDCl_3$) δ 0.89 (t, J = 6.9Hz, 3H), 1.2-1.4 (m, 6H), 1.55-1.7 (m, 2H), 2.67 (t, J = 7.8Hz, 2H), 6.53 (d, J = 7.5Hz, 2H), 7.26 (d, J = 8.4Hz, 2H), 7.33 (d, J = 8.4Hz, 2H), 7.62 (d, J = 7.8Hz, 2H).

4'-perfluorohexyl-(4-oxo-4H-pyridin-1-yl)-benzene 5(6). A mixture of 16 (2.4g, 8mmol), perfluorohexyliodide (2 ml, 9 mmol), copper powder (2.0g, 30 mmol) and DMSO (20 ml) was stirred at 150°C for 8 hours until TLC showed no starting material. The reaction mixture was cooled, filtered and washed with ethyl acetate. The solvent was removed by vacuum. The product was purified via flash chromatography over silica gel with a gradient of neat ethyl acetate to 4:1 ethyl acetate: methanol. Evaporation of solvent yielded the 1.95g (50%) of the product as a yellow solid: m.p. 152°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 6.62 (d, J = 7.5Hz, 2H), 7.53 (d, J = 8.4Hz, 2H), 7.67 (d, J =7.8Hz, 2H), 7.80 (d, J = 8.4Hz, 2H).

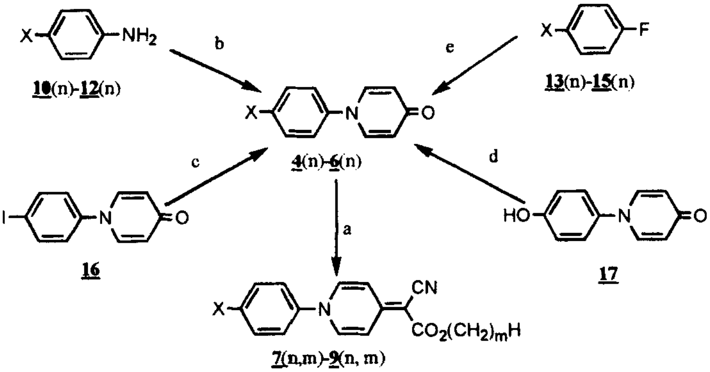
4-hexyloxy-(4-oxo-4H-pyridin-1-yl)-benzene 6(6). A mixture of 17 (1.87g,10 mmol), iodohexane (2.54g, 12 mmol) and K_2CO_3 (1.38g, 10 mmol) in NMP (15 ml) was gradually heated to 100°C and maintained for one hour. The reaction mixture was cooled, water added dropwise and the crude product was filtered and dried under vacuum. The product, obtained in quantitative yield, was of sufficient purity to be used without further purification: m.p. 85°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 0.92 (t, J = 6.9Hz, 3H), 1.20-1.50 (m, 6H), 1.75-1.9 (m, 2H), 4.00 (t, J = 6.6Hz, 2H), 6.55 (d, J = 7.5Hz, 2H), 7.00 (d, J = 9.0Hz, 2H), 7.25 (d, J =8.7Hz, 2H), 7.56 (d, J = 7.8Hz, 2H).

1-(4-hexylphenyl)-4-(octyloxycyanomethylene)-1,4-dihydropyridine 7(6,8). A mixture of 4(6) (0.38g, 1.5 mmol), octyl cyanoacetate (0.8 ml, 3.8 mmol) and acidic anhydride (5 ml) was refluxed for 3 hours. The reaction mixture was cooled to room temperature and the product was filtered and washed with acidic anhydride to yield 0.48g (74%) of the product as a yellow solid: ^{1}H NMR (300MHz, $CDCl_3$) δ 0.9-0.95 (m, 6H), 1.2-1.45 (m, 16H), 1.55-1.75 (m, 4H), 2.68 (t, J = 7.5Hz, 2H), 4.16 (t, J = 6.9Hz, 2H), 7.12 (dd, J = 7.2Hz, 2.4Hz, 1H), 7.26 (d, J = 8.4Hz, 2H), 7.34 (d, J = 8.4Hz, 2H), 7.48-7.56 (m, 2H), 8.46 (dd, J = 7.5Hz, 2.4Hz, 1H). The DSC (peak, J/g) showed two events on heating (144.5°C, 67.0; 180.4°C, 17.9) and two events on cooling (177.8°C, -19.1; 133.5°C, -67.4).

4'-iodo-(4-oxo-4H-pyridin-1-yl)-benzene 16. A mixture of 4-iodoaniline (11.75 g, 54 mmol), chelidonic acid hydrate (11.1g, 55 mmol) and DMSO (50 ml) was slowly heated to 130°C and was then stirred for 4 hours until gas evolution ceased. The reaction mixture was cooled, filtered and washed with ethyl acetate. The solvent was removed by vacuum. The product was purified via flash chromatography on silica gel with a gradient of ethyl acetate to 4:1 ethyl acetate: methanol. Evaporation of solvent yielded 10.18g (66%) of tan solid: m.p. 236°C; ^{1}H NMR (300MHz, DMSO-d_6) δ 6.23 (d, J

= 7.8Hz, 2H), 7.38 (d, J = 8.7Hz, 2H), 7.90 (d, J =8.7Hz, 2H), 7.97 (d, J = 7.8Hz, 2H).

4'-hydroxy-(4-oxo-4H-pyridin-1-yl)-benzene 17. A mixture of 4-aminophenol (2.18g, 20mmol), chelidonic acid hydrate (3.84g, 20mmol) and DMSO (15 ml) was heated and stirred at 150°C for 1 hour until gas evolution ceased and then was kept at 180°C for 30 minutes. The reaction mixture was cooled, water (30ml) was added and the solid was filtered and dried in a vacuum oven. A total of 2.70g of tan solid was obtained: m.p. >300°C; ^{1}H NMR (300MHz, DMSO-d_6) δ 6.19 (d, J = 7.5Hz, 2H), 6.88 (d, J = 8.7Hz, 2H), 7.33 (d, J =8.7Hz, 2H), 7.86 (d, J = 7.5Hz, 2H), 10.0 (s, 1H).



a) $NCCH_2CO_2(CH_2)_mH$, Ac_2O, Δ m=2,4,8 [X= all]

b) chelidonic acid, DMSO, Δ [X= $(CH_2)_nH$, $O(CH_2)_nH$]

c) $F(CF_2)_nI$, Cu, DMSO, Δ [X= $(CF_2)_nF$ only]

d) $H(CH_2)_nBr$, K_2CO_3, NMP, Δ [X= $O(CH_2)_nH$ only]

e) 4-hydroxypyridine, K_2CO_3, NMP, Δ [X= $(CH_2)_nH$, $(CF_2)_nF$]

#	X	n
4, 7, 10, 13	$H(CH_2)_n$-	4, 6, 8
5, 8, 11, 14	$F(CF_2)_n$-	4, 6, 8, 10
6, 9, 12, 15	$H(CH_2)_nO$-	6, 8

FIGURE 3. Synthesis and Structures of Liquid Crystals and Intermediates

RESULTS AND DISCUSSION

We have prepared a subset of a few series of pyridones 4(n)-6(n) and cyanoester methylenedihydropyridines 7(n,m)-9(n,m) in which the heterocyclic ring nitrogen is substituted with a 4-X-substituted benzene ring. The X-substituents utilized here include the simple alkyl group, a perfluoroalkyl group and an alkoxy group. The identity of this X-substituent influences the choice between synthetic methods utilized as is outlined below (Figure 3). The condensation-decarboxylation of a 4-X-aniline and chelidonic acid in DMSO is most efficient when the X-group is electron donating or at least electroneutral (X = alkyl 4, alkoxy 12, etc.).[11] Reactions between chelidonic acid and electron deficient anilines (X = perfluoroalkyl 11, etc.) work poorly or not at all presumably due to the insufficient nucleophilicity or bacisity of the aniline. In contrast, the aromatic nucleophilic substitution reaction between 4-hydroxypyridine on a 4-X-fluorobenzene are most efficient when the X-group is electron withdrawing or at least electroneutral (X = perfluoroalkyl 14, alkyl 13). Reactions of 4-hydroxypyridine with electron rich fluorobenzenes (X = alkoxy 15, etc.) work poorly and only under very aggressive conditions presumably due to the enhanced electron density at the site of nucleophilic attack. We have used only fluoroaromatics as substrates although in some cases where X activation is sufficient other leaving groups (chlorine or pseudohalogen) might also suffice. In all cases the pyridones 4-6 are easily converted to the methylenecyanoesters 7-9 by reaction with the appropriate ester of cyanoacetic acid in acetic anhydride.

Overall, we have two very convenient and complimentary synthetic methods. The chelidonic acid route usually provides modest yields of the pyridone and its main drawback is the expense of the chelidonic acid. The hydroxypyridine route is generally preferable if the appropriate fluoroaromatic starting materials are available. The aromatic nucleophilic substitution reaction with 4-hydroxypyridine is really remarkable in its utility even with what might be expected to be unreactive substrates (X = alkyl 13). The 4-fluoroalkylbenzene 13 can also be obtained by Wolff-Kishner reduction of the appropriate 4-fluorophenylalkanone or hydrogenation of the 4-fluorophenylalkyne (these procedures are not described here in detail). Two additional variants to the general procedure are of mention; reaction of 4-iodoaniline or 4-aminophenol with cheledonic acid under normal conditions in DMSO give the 4-iodophenylpyridone 16 and the 4-hydroxyphenylpyridone 17 respectively. The iodide 16 is readily converted to the perfluoroalkyl derivatives 5 by copper mediated coupling[12] and the phenol 17 is readily alkylated to the ethers 6 providing a convenient means of introducing different lengths of alkoxy and fluoroalkyl tails.

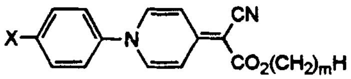


Table 1. Phase Transitions Determined by Optical Microscopy

n	m	**7** X = $(CH_2)_nH$	**8** X = $(CF_2)_nF$	**9** X = $O(CH_2)_nH$
4	2	K 177 I	K 257 S_A 298 I	
	4	K 151 S_A 172 I	K 194 S_A 273 I	
	8	K 140 S_A 170 I	K 181 S_A 214 I	
6	2	K 144 S_A 179 I	K 255 S_A 325 I	K 137 S_A 185 I
	4	K 136 S_A 183 I	K 196 S_A 293 I	K 135 S_A 205 I
	8	K 147 S_A 172 I	K 183 S_A 236 I b	K 141 S_A 198 I
8	2	K 140 S_A 179 I	K 247 S_A 340 I	K 133 S_A 195 I
	4	K 128 S_A 189 I a	K 192 S_A 317 I	K 115 S_A 209 I
	8	K 140 S_A 177 I	K 191 S_A 256 I	K 126 S_A 196 I
10	2	K 127 S_A 177 I	K 240 S_A 340 I	
	4	K 115 S_A 190 I	K 211 S_A 323 I	
	8	K 139 S_A 186 I	K 194 S_A 266 I	

another crystal-crystal transition occurs at a) 113 and b) 176

The cyanoester methylene dihydropyridines examined thus far only possess a smectic A phase. The phase temperatures were studied as a function of both the length of the three different types of benzene X tail (n = 4,6,8,10) and the ester tail (m = 2,4,8). For all the simple aliphatic alkane tail materials we find mesomorphic behaviour except with the very shortest combination of tails (n=4, m=2) and the breadth of the S_A phase is between 20-40°C. Substitution of the perfluorinated tail raises the phase temperatures dramatically and the phase ranges can exceed 100°C which are remarkable for a mesogen with only two rings. The behaviour of the alkoxy tail compounds is reminiscent of the alkyl tail materials except all the phase ranges are a bit broader.

Some of the pyridone intermediates which are used in these preparations also appear to be mesogenic. We will report on them in more detail in the future. Experiments are also underway to measure the birefringence of the methylenedihydropyridines.[13] Calculations substantiate some of the anticipated interesting electronic properties.[14] The calculated ground state

dipole moment is 8.98D and the calculated polarizability anisotropy of these chromophores is quite large. For example, the compound 9(1,1) with the shortest possible tails used for modeling has the zero frequency alpha values along its three major axes XX = 0.4416E-22 (long director axis), YY = 0.1312E-22 (orthogonal to the main axis and approximately coplanar with the rings) and ZZ = 0.3930E-23 (orthogonal to the main axis and approximately orthogonal to the rings). Further studies of the synthesis, mesomorphic behavior and optoelectronic properties of this family of materials are being pursued.

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