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## Liquid Crystals

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# Mesomorphic 2,2'-bipyridine diesters

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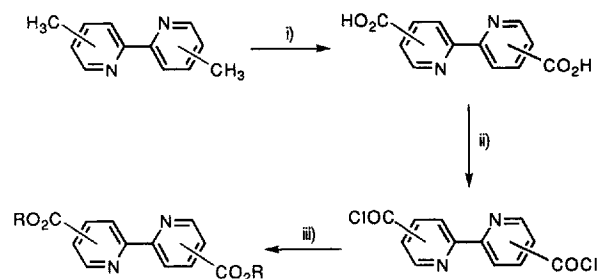
Esterification of 2,2'-bipyridine-5,5'- and 4,4'-dicarboxylic acids with 4-alkoxyphenols leads to new mesomorphic bipyridine esters. The synthesis and properties of the compounds are discussed and compared with some carbocyclic analogues.

A major part of the realization of new metal-containing liquid crystal systems is the identification of potential ligands and their subsequent modification into a suitable mesogenic form [1]. This approach works well, but with a few exceptions, the number of possible metal/ligand combinations tends to be rather limited for a given ligand type. However 2,2'-bipyridine (see figure 1) enjoys an extensive coordination chemistry [2], forming complexes with a very wide variety of metals from low to high oxidation states. It is also rather readily modified. Thus, the synthesis of suitable mesogenic bipyridine derivatives might be expected to form the basis for a wide range of mesomorphic metal complexes. Indeed, we have already demonstrated *lyotropic* mesomorphism in a series of monosubstituted *tris*(2,2'-bipyridine) complexes of ruthenium(II) [3], while Hanabusa [4] has synthesized thermotropic polymers of 5,5'-disubstituted 2,2'-bipyridines. Some metal complexes of alkanoyl derivatives of 6,6'-diamino-2,2'-bipyridine have also recently been described [5].

In this and the preceding communication by Douce *et al.* [6], the synthesis of some mesomorphic 2,2'-bipyridines is described and we will shortly assess the potential of our materials for the production of mesomorphic metal complexes.

The starting point for the present work was either 4,4'-dimethyl-2,2'-bipyridine (Aldrich) or 5,5'-dimethyl-2,2'-bipyridine, the latter obtained in high yield via a Raney nickel coupling of 3-picoline [7]. Using aqueous

permanganate [8], these dimethyl compounds were readily oxidized to the corresponding (and very insoluble) diacids which were then converted into the acid chlorides using thionyl chloride. Esterification was then achieved using an alcohol (or phenol) in pyridine (5,5'-diesters) or toluene (4,4'-diesters) (see Scheme). All of the new compounds were analysed by elemental analysis and NMR by means of which satisfactory results were obtained. Alkyl ester (I) were made only from the 5,5'-dicarboxylic acids, but none was mesomorphic, all melting simply to isotropic liquids. For example, melting points for  $R = C_8H_{17}$  and  $C_{12}H_{25}$  were 117 and 120°C, respectively. Better results were however obtained for alkoxyphenyl esters.



R = alkyl; I  
R = 4-alkoxyphenyl (5,5'-isomer); II  
R = 4-alkoxyphenyl (4,4'-isomer); III

Synthesis of the bipyridine esters. (i)  $KMnO_4$ ; (ii)  $SOCl_2$ ; (iii) ROH/py (for 5,5'-isomer); toluene/ROH (for 4,4'-isomer).

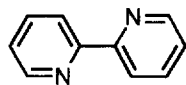


Figure 1. 2,2'-Bipyridine.

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The 4-alkoxyphenol precursors were obtained via alkylation of hydroquinone in 1,4-dioxan/water for the butoxy- and octyloxy-phenols and in poly(ethylene glycol)/1,4-dioxan for dodecyloxyphenol, which gave moderate yields ( $\approx 50$ – $60$  per cent) of the monoalkylated product [9]. The method used for esterification gave only low conversions ( $\approx 20$  per cent), although work is now in hand to enhance the yields.

Table 1. Thermal data for bis(4-alkoxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylates.

Alkyl	Transition†	Temperature/ °C	$\Delta H/kJ mol^{-1}$
CH <sub>3</sub>	C → S <sub>A</sub>	220	40.4
	S <sub>A</sub> → N	241	—§
	N → I	428‡	—
C <sub>4</sub> H <sub>9</sub>	C → S <sub>C</sub>	194	31.5
	S <sub>C</sub> → S <sub>A</sub>	256	—§
	S <sub>A</sub> → N	299	—
	N → I	370‡	—
C <sub>8</sub> H <sub>17</sub>	C → Cryst J	135	18.9
	Cryst J → S <sub>C</sub>	155	30.5
	S <sub>C</sub> → S <sub>A</sub>	275	—§
	S <sub>A</sub> → N	280	—§
	N → I	290	1.23
C <sub>12</sub> H <sub>25</sub>	C → S <sub>C</sub>	140	33.5
	(S <sub>C</sub> → Cryst J)	(138)	—
	S <sub>C</sub> → N	260	1.67
	N → I	265	2.03

† Assignment as a Cryst J phase is preliminary.

‡ These temperatures are influenced by decomposition of the materials (see text).

§ Not seen by DSC.

|| Enthalpy is that C–C'–Cryst J which is identified by DSC, but not readily seen by microscopy.

( ) Monotropic transition.

Four ester derivatives (II) were synthesized with *R* = methoxy-, butyloxy-, octyloxy- and dodecyloxyphenyl (table 1). The mesomorphism is dominated by the formation of wide range nematic and/or smectic C phases, with much shorter smectic A phases appearing in three derivatives. In the shorter chain examples, the nematic phases exist over 190° (methoxyphenyl diester) and 70° (butyloxyphenyl diester), persisting right up to dodecyloxyphenyl diester, albeit with a 5° range. Similarly, smectic C ranges of 120° are found for the octyloxyphenyl and dodecyloxyphenyl diesters. It should be noted however that the upper transition temperatures for the methoxyphenyl and butyloxyphenyl diesters are slightly unreliable as decomposition begins around 360°C, accelerating markedly above 390°C. In two derivatives, a crystal smectic phase was found below the S<sub>C</sub> phase and on the basis of optical texture alone, a preliminary assignment as a crystal smectic J phase has been made. It is then of interest to compare these new compounds with their biphenyl analogues (see figure 2) [10].

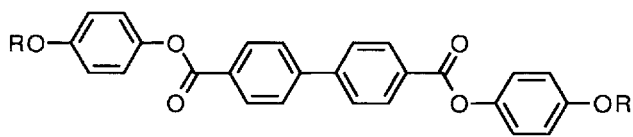


Figure 2. Bis(4-alkoxyphenyl) biphenyl-4,4'-dicarboxylates.

Only the methoxy- and butyloxy-phenyl derivatives may be compared directly as follows:

(Methoxy ester-bipyridine)	C 220 S <sub>A</sub> 241 N > 428 I
(Methoxy ester-biphenyl)	C 193 S <sub>A</sub> 231 N > 400 I
(Butyloxy ester-bipyridine)	C 194 S <sub>C</sub> 256 S <sub>A</sub> 299 N 370 I
(Butyloxy ester-biphenyl)	C 171 S <sub>A</sub> 339 N 367 I

The mesomorphism of the two methoxyphenyl diesters is rather similar, but comparison of the data for the two butyloxyphenyl diesters shows for the bipyridyl derivative a destabilization of the smectic A phase in favour of the nematic phase, and the preferential introduction of a smectic C phase. Although not directly comparable, it is interesting that in the heptyloxyphenyl diester with a biphenyl core, the smectic C range is 80° with a 100° range for the smectic A phase and a 1° nematic range. This compares with the octyloxyphenyl diester with the bipyridine core which has a 120° smectic C range, a 5° smectic A range and a 10° nematic range.

Thus, it would appear that the 2,2'-bipyridine core is able strongly to promote the smectic C phase and to some extent the nematic phase compared to the biphenyl core.

In order to examine the relationship between structure and mesomorphism in these systems, we also undertook the synthesis of the related diesters of the 4,4'-dicarboxylic acid. Here, only three derivatives were synthesized and the thermal data are collected in table 2. As can

Table 2. Thermal data for bis(4-alkoxyphenyl) 2,2'-bipyridine-4,4'-dicarboxylates.

Alkyl	Transition	Temperature/°C
CH <sub>3</sub>	C → N	208
	N → I	210
C <sub>4</sub> H <sub>9</sub>	C → I	199
	(I → N)	(195)
C <sub>8</sub> H <sub>17</sub>	C → I	169

( ) Monotropic transition.

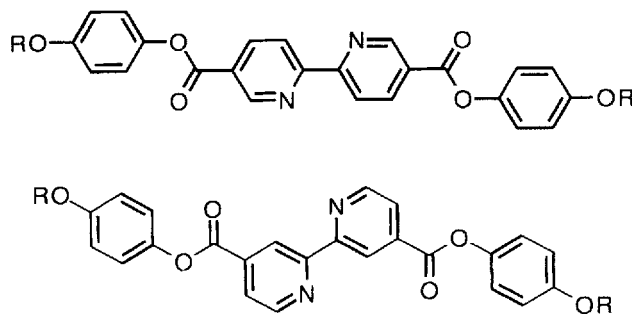


Figure 3. Comparison between structures of the 5,5'-diesters (upper) and the 4,4'-diesters (lower).

be readily seen from figure 3, the 4,4'-diesters are much less anisometric than the 5,5'-diesters and this is reflected in the much lower clearing points the nematic phases in the methoxy- and butyloxy-phenyl diesters. However, melting points are little affected by the change in substitution and so the nematic phases are now just enantiotropic for the methoxyphenyl diester and monotropic for the butyloxyphenyl diester. Thus, the chains have a greater destabilizing effect on the nematic phase as opposed to the crystal phase. While the molecular shape of the 4,4'-diesters is (obviously) able to support nematic phase formation, it is clear from the thermal behaviour of the octyloxyphenyl diester that smectic phases are not similarly supported and mesomorphism is lost at these chain lengths.

Having established the mesomorphism of these new compounds, studies are underway to assess their potential as ligands for the synthesis of mesomorphic metal complexes.

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