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Synthesis of mesomorphic aryl esters bearing a pyridine ring

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Aryl carboxylic esters bearing disubstituted pyridine rings were synthesized starting with various pyridine mono- or dicarboxylic acids by means of reactions, principally, with phenolic compounds. Some of the pyridine monocarboxylates thus synthesized exhibited clear nematic phases at relatively low temperatures, whereas most of the 2,5-pyridine dicarboxylates bearing two benzene rings provided nematic phases, the ranges of which were some times wider and/or lower than those of the corresponding aryl esters bearing benzene rings alone.

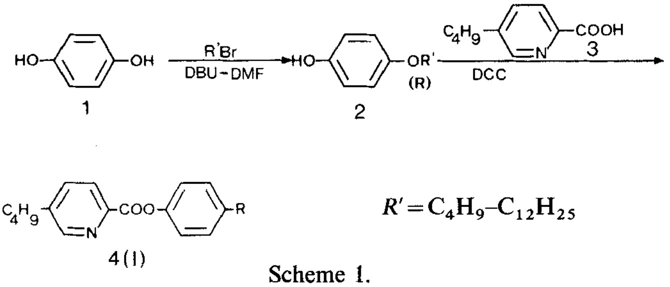
1. Introduction

Liquid-crystalline aryl esters bearing a pyridine ring have rarely been found in the literature [1]. It appears, however, that the use of the pyridine ring as an aromatic component of aryl esters causes mesomorphic behaviour different to that of conventional aryl esters containing the benzene ring alone. Accordingly, various kinds of novel aryl esters bearing disubstituted pyridine rings have been synthesized and their mesomorphic behaviours investigated.

The aryl esters synthesized in this study are shown in figure 1. The mesomorphic behaviour of compounds of general structures **I–V** was investigated.

2. Results and discussion

Compounds of type **I** were synthesized according to the route shown in scheme 1.



$R' = C_4H_9$–$C_{12}H_{25}$

Scheme 1.

Firstly, compound **2** containing the *n*-alkoxy group (*R*) was synthesized by the monoetherification of the hydroquinone **1** with *n*-alkyl bromide using 1,5-diazabicyclo[5,4,0]undecene-5 (DBU) as the H^+ acceptor. A nitrogen atmosphere was required since **1** was susceptible to oxidation by air under alkaline conditions. Yields ranging from 12 to 61 per cent were obtained depending upon the chain lengths of *R'*.

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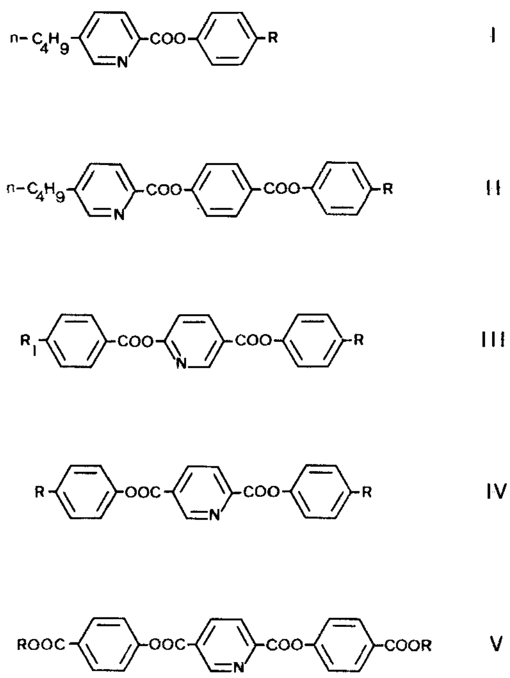
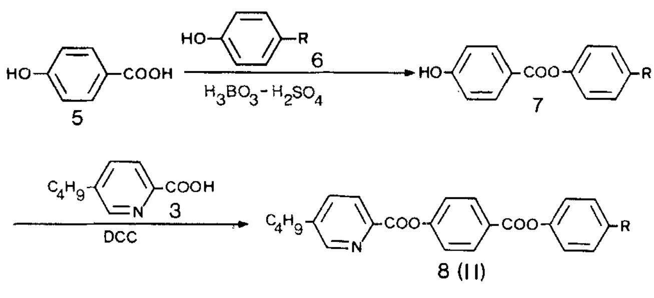


Figure 1.

Compounds of type **I** were then synthesized by the esterification reaction of **2** with 2-(5-*n*-butyl)pyridinecarboxylic acid (fusaric acid; **3**) using *N*,*N*′-dicyclohexylcarbodiimide (DCC) in dicholoromethane giving yields of 7–38 per cent.

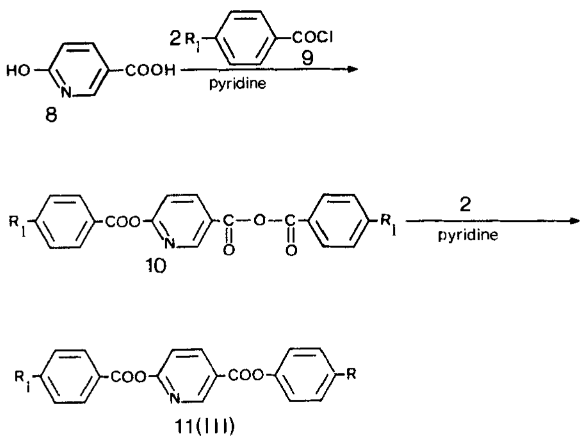
In order to synthesize compounds of general type **II**, *p*-hydroxybenzoic acid (**5**) was esterified with *p*-(*n*-alkyl)phenol (**2**) using a combination of boric acid and sulphuric acid in toluene. A Dean-Stark trap was fitted to afford a crossed ester **7**, which was esterified again with **3** using DCC to provide compounds of type **II** (see scheme 2).



Scheme 2.

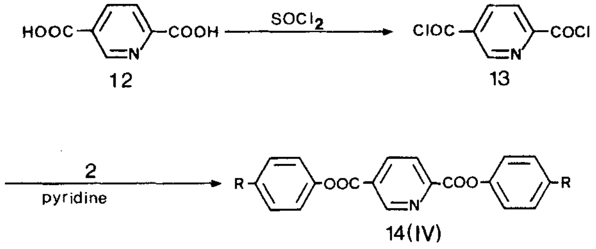
Yields ranging from 3 to 11 per cent were obtained as a result of purification by silica gel column chromatography followed by recrystallization from *n*-hexane.

Compounds of type **III** were prepared starting with 3-(6-hydroxy)pyridinecarboxylic acid(4-hydroxynicotinic acid; **8**) via the reaction product **10** with *p*-(*n*-alkyl)-benzoyl chloride (**9**), followed by esterification with **2** taking advantage of the acid anhydride group of **10** (see scheme 3).



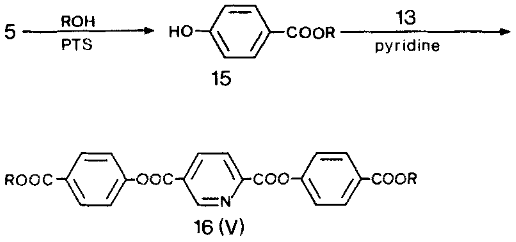
Scheme 3.

Diaryl esters (see compounds of type **VI**) of 2,5-pyridinedicarboxylic acid were prepared by the esterification of diacid chloride (**13**), made from the diacid **12**, with **2** in pyridine (see scheme 4). Yields ranged widely from 9 to 62 per cent based on **12**.



Scheme 4.

Finally, compounds of type **V** were synthesized starting with **5** via their esters (**15**) with *n*-alcohols by refluxing in toluene using *p*-toluenesulphonic acid (PTS) as an acid catalyst and fitted with a Dean-Stark trap (see scheme 5). The same esterification procedure as that in scheme 4 was applied to **15** to obtain the products of type **V** in 12 to 67 per cent yields.



Scheme 5.

The mesomorphic behaviour of the esters, bearing the pyridine ring thus synthesized, is summarized in tables 1–4.

As shown in table 1 compounds of type **I** bearing only one benzene ring in addition to the pyridine ring and having C_{4-5} alkyl or C_{5-6} alkoxy groups as *R* do not exhibit any mesomorphic range above 0°C (see compounds **I-4**, **I-5**, **I-50** and **I-60** in table 1).

Table 1. Mesomorphic behaviour of typical examples of compounds **I**, **II** and **III**.

Compound	*R*	R_1	Phase transition temperature†
I-4	n-C_4H_9	—	C < -40°C‡ I
I-5	n-C_5H_{11}	—	C -8°C–-4°C I
I-50	n-$C_5H_{11}O$	—	C < -40°C‡ I
I-60	n-$C_6H_{13}O$	—	C < -40°C‡ I
I-80	n-$C_8H_{17}O$	—	$C \xrightarrow{37°C} I$ $I \xrightarrow{38°C} N$ $N \xrightarrow{37°C} C$
I-120	n-$C_{12}H_{25}O$	—	$C \xrightarrow{38°C} I$ $I \xrightarrow{38°C} N$ $N \xrightarrow{33°C} C$
II-3	n-C_3H_7	—	C 90°C N 159°C I
II-4	n-C_4H_9	—	C 58°C N 124°C I
II-5	n-C_5H_{11}	—	C 88°C N 156°C I (C 75°C N 179°C I)§
III-4	n-C_4H_9	CH_3	C 120°C N 130°C I

† C, crystal; N, nematic; I, isotropic.

† Lower limit measurable with the instrument.

§ Contains the benzene instead of the pyridine ring.

The mesomorphic behaviour of compounds **I**-80 **I**-120 was also poor, although some monotropic nematic phases were observed.

As for compounds of type **II** bearing three aromatic rings including the terminal pyridine ring, mesomorphic behaviour is discernible even for compounds **II**-3, **II**-4 and **II**-5 with short alkyl groups as *R*.

Comparison of the phase transition temperatures for **II**-5 with those for the corresponding compound bearing the benzene instead of the pyridine ring provided a similar result, with a little narrower nematic range for the former.

The result obtained for **III**-4, with only one compound exhibiting some mesomorphic range among the compounds of type **III** investigated, was not favourable.

It can be seen from table 2 that compounds of type **IV** bearing three aromatic rings, in which the pyridine ring in the middle possesses the same 2,5-disubstituents, generally exhibit the nematic phase, although with rather high ranges.

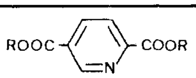
A comparative study with compounds of type **IV′** bearing only one aromatic (pyridine) ring, which indicate no mesomorphic range, might indicate that, in compounds of type **IV**, the presence of two benzene rings as the alkylphenol residue, which may exert the π–π lateral interaction, is necessary for the development of liquid-crystalline behaviour. It is interesting to note, that compounds **IV**-1 and **IV**-3, having an odd number of carbon atoms for *R*, afford significantly wider nematic ranges than **IV**-2 and **IV**-4 having an even number of carbon atoms. It is also interesting that the model compound for **IV**-4 bearing the benzene instead of the pyridine ring indicates a higher and narrower nematic range than that for **IV**-4.

Similar relationships are observed in table 3, where an alkoxy group instead of an alkyl group, as in table 2, was used as *R* in compounds of type **IV**.

Table 2. Mesomorphic behaviours of compounds of type **IV** (1).

Compound	*R*	Phase transition temperature
IV-1	CH_3	$\mathrm{C}\ \underset{130^\circ\mathrm{C}}{\overset{135^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{N}\ \underset{180^\circ\mathrm{C}}{\overset{180^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$
IV-2	C_2H_5	$\mathrm{C}\ \underset{134^\circ\mathrm{C}}{\overset{152^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{N}\ \underset{165^\circ\mathrm{C}}{\overset{165^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$
IV-3	n-C_3H_7	$\mathrm{C}\ \underset{117^\circ\mathrm{C}}{\overset{138^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{N}\ \underset{179^\circ\mathrm{C}}{\overset{179^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$
IV-4	n-C_4H_9	$\mathrm{C}\ \underset{131^\circ\mathrm{C}}{\overset{131^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{N}\ \underset{150^\circ\mathrm{C}}{\overset{150^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$
		(C 161°C N 166°C I)‡
		(C ——126°C—— I)§
IV′-4	n-C_4H_9†	$\mathrm{C}\ \underset{15^\circ\mathrm{C}}{\overset{28^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$
IV′-8	n-C_8H_{17}†	$\mathrm{C}\ \underset{44^\circ\mathrm{C}}{\overset{48^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$
IV′-16	n-$C_{16}H_{33}$†	$\mathrm{C}\ \underset{87^\circ\mathrm{C}}{\overset{88^\circ\mathrm{C}}{\rightleftharpoons}}\ \mathrm{I}$

† For



‡ Contains the benzene instead of the pyridine ring.
§ Contains 2,6-instead of 2,5-disubstituted pyridine.

In this case, however, the model compound for **IV**-60 affords a narrower nematic range than that for **IV**-60, with the same N–I transition temperature (200°C). The fact, that no mesomorphic behaviour is observed in the case of **IV**-120 is considered to be caused by the presence of too long an alkyl chain for *R*, which may bring about crystallization of the *R* portion. As shown from table 3, even short alkoxy groups such as methoxy and ethoxy provide clear nematic ranges, as is also seen in table 2.

Table 4 summarizing the results for compounds of type **V** shows clear mesomorphic behaviour, except for compounds **V**-2 and **V**-12.

Comparison of the phase transition temperatures for **V**-4 with those of the model compound indicates a considerably lower nematic range for **V**-4. No appreciable difference, however, can be found for the range itself, which differs from the results shown in tables 2 and 3.

Summarizing the results obtained for 2,5-pyridinedicarboxylic acid esters in tables 2–4, it can be generally stated that clear nematic ranges are observed and appear to be lower and/or wider, in some cases, than those for the corresponding model compounds bearing the benzene instead of the pyridine ring, presumably indicating the lateral effects of the nitrogen atom within the pyridine ring. This nitrogen atom may

Table 3. Mesomorphic behaviour of compounds of type **IV** (2).

Compound	*R*	Phase transition temperature
IV-10	CH_3O	$C \underset{144^\circ C}{\overset{167^\circ C}{\rightleftharpoons}} N \underset{255^\circ C}{\overset{255^\circ C}{\rightleftharpoons}} I$
		(C ——182°C—— I)†
IV-20	C_2H_5O	$C \underset{157^\circ C}{\overset{164^\circ C}{\rightleftharpoons}} N \underset{252^\circ C}{\overset{252^\circ C}{\rightleftharpoons}} I$
		(C ——160°C—— I)†
IV-30	n-C_3H_7O	$C \underset{178^\circ C}{\overset{182^\circ C}{\rightleftharpoons}} N \underset{225^\circ C}{\overset{225^\circ C}{\rightleftharpoons}} I$
		(C ——171°C—— I)†
IV-40	n-C_4H_9O	$C \underset{165^\circ C}{\overset{165^\circ C}{\rightleftharpoons}} N \underset{208^\circ C}{\overset{208^\circ C}{\rightleftharpoons}} I$
		(C ——172°C—— I)†
		(C —— 68°C—— I)‡
IV-50	n-$C_5H_{11}O$	$C \underset{140^\circ C}{\overset{144^\circ C}{\rightleftharpoons}} N \underset{172^\circ C}{\overset{172^\circ C}{\rightleftharpoons}} I$
IV-60	n-$C_6H_{13}O$	$C \underset{130^\circ C}{\overset{135^\circ C}{\rightleftharpoons}} N \underset{200^\circ C}{\overset{200^\circ C}{\rightleftharpoons}} I$
		(C 164°C N 200°C I)§
IV-70	n-$C_7H_{15}O$	$C \underset{136^\circ C}{\overset{140^\circ C}{\rightleftharpoons}} N \underset{191^\circ C}{\overset{191^\circ C}{\rightleftharpoons}} I$
IV-80	n-$C_8H_{17}O$	$C \underset{170^\circ C}{\overset{172^\circ C}{\rightleftharpoons}} N \underset{180^\circ C}{\overset{180^\circ C}{\rightleftharpoons}} I$
IV-90	n-$C_9H_{19}O$	$C \underset{126^\circ C}{\overset{129^\circ C}{\rightleftharpoons}} N \underset{189^\circ C}{\overset{189^\circ C}{\rightleftharpoons}} I$
IV-100	n-$C_{10}H_{21}O$	$C \underset{112^\circ C}{\overset{115^\circ C}{\rightleftharpoons}} N \underset{175^\circ C}{\overset{175^\circ C}{\rightleftharpoons}} I$
IV-120	n-$C_{12}H_{25}O$	C ——105°—— I

† Contains 2,6- instead of 2,5-disubstituted pyridine.
‡ Contains 2,3-disubstituted pyrazine instead of 2,5-pyridine.
§ Contains the benzene instead of the pyridine ring.

Table 4. Mesomorphic behaviour of compounds of type V.

Compound	*R*	Phase transition temperature
V-2	C_2H_5	$\mathrm{C} \underset{90^\circ\mathrm{C}}{\overset{95^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
V-4	n-C_4H_9	$\mathrm{C} \xrightarrow{110^\circ\mathrm{C}} \mathrm{I}$ $\mathrm{C} \xleftarrow{92^\circ\mathrm{C}} \mathrm{N} \xrightarrow{108^\circ\mathrm{C}} \mathrm{I}$
		$(\mathrm{C} \underset{211^\circ\mathrm{C}}{\overset{215^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{228^\circ\mathrm{C}}{\overset{228^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I})$†
		(C —126°C— I)‡
V-5	n-C_5H_{11}	$\mathrm{C} \underset{105^\circ\mathrm{C}}{\overset{116^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{121^\circ\mathrm{C}}{\overset{121^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
V-6	n-C_6H_{13}	$\mathrm{C} \underset{110^\circ\mathrm{C}}{\overset{127^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{137^\circ\mathrm{C}}{\overset{137^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
		(C —118°C— I)‡
V-7	n-C_7H_{15}	$\mathrm{C} \underset{120^\circ\mathrm{C}}{\overset{125^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{153^\circ\mathrm{C}}{\overset{153^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
V-8	n-C_8H_{17}	$\mathrm{C} \underset{117^\circ\mathrm{C}}{\overset{130^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{155^\circ\mathrm{C}}{\overset{155^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
		(C —117°C— I)‡
V-9	n-C_9H_{19}	$\mathrm{C} \underset{114^\circ\mathrm{C}}{\overset{121^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{155^\circ\mathrm{C}}{\overset{155^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
V-10	n-$C_{10}H_{21}$	$\mathrm{C} \underset{78^\circ\mathrm{C}}{\overset{95^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{N} \underset{111^\circ\mathrm{C}}{\overset{115^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$
		(C —126°C— I)
V-12	n-$C_{12}H_{25}$	$\mathrm{C} \underset{94^\circ\mathrm{C}}{\overset{105^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$

† Contains the benzene instead of the pyridine ring.
‡ Contains 2,6- instead of 2,5-disubstituted pyridine.

exert polar effects such as dipole interactions on the molecular arrangement, which are different from those of the corresponding model compound.

In this case, rod-like molecules derived from 2,5-pyridinedicarboxylic acid appear to be required to achieve mesomorphic behaviour, as expected from the results for conventional aryl esters bearing benzene rings alone. In fact, aryl esters of 2,6-pyridine- and 2,3-pyrazinedicarboxylic acids, which were not considered to assume the rod-like molecular structure, were found to exhibit no mesomorphic behaviour at all (see tables 2–4). The corresponding diesters made from 2,3-pyridinedicarboxylic acid were also found to exhibit no mesomorphic behaviour.

In conclusion, aryl esters bearing a disubstituted pyridine together with two benzene rings show remarkable mesomorphic behaviour due to the presence of the pyridine nitrogen atom and the resulting characteristic laterally polar character. This characteristic behaviour has also been observed for Schiff's bases [3–6] and azoxy compounds [7, 8] bearing a pyridine ring, as previously reported.

3. Experimental

IR, ^{1}H NMR and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX60 spectrometer, and a Hitachi M-808 spectrometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin–Elmer 250 instrument. Mesomorphic ranges were determined by means of either a Yamato MP-21 or a Mitamurariken micro melting point apparatus, each equipped with crossed polarizers.

3.1. *Synthesis of hydroquinone mono(n-alkyl) ether* (*2*)

1,5-Diazabicyclo[5, 4, 0]undecene-5 (DBU; 6·8 g, 45 mmol) was added to a solution of hydroquinone (**1**; 5·0 g, 45 mmol) and an equivalent *n*-alkyl bromide in *N,N'*-dimethylformamide (DMF; 30 ml) under nitrogen, and then stirred at 20°C for 48 h. The reaction mixture was acidified with one molar hydrochloric acid and extracted with ether (150 ml). The organic layer was either subjected to column chromatography with silica gel or extracted with 5 per cent aqueous sodium hydroxide solution (100 ml). In the latter case, the aqueous layer was acidified with 5 per cent hydrochloric acid to isolate the intended product, which was extracted with ether (150 ml). Crystalline colourless needles obtained. Yield: 61 per cent for $R' = C_2$, 41 per cent for C_3, 17 per cent for C_4 (mp 52°C), 14 per cent for C_5 (mp 52°C), 33 per cent for C_6 (mp 57°C), 16 per cent for C_8 (mp 62°C), 12 per cent for C_{10} and 50 per cent for C_{12} (mp 71°C). IR ($CHCl_3$): 3200–3400 (OH), 1100 (ether) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0·5–4·0 (m, alkyl), 5·0–6·0 (s, 1H, OH), 6·7 (s, 4H, aryl).

3.2. *Synthesis of p-(n-alkyl of n-alkoxy)phenyl 2-(5-n-Butyl)pyridinecarboxylate* (*4*; *I*)

A solution of fusaric acid (**3**; 0·54 g, 3·0 mmol), **2** (3·0 mmol), and dicyclohexylcarbodiimide (DCC; 0·68 g,, 3·3 mmol) in dichloromethane (20 ml) was stirred at 20°C for 24 h. Acetic acid (1 ml) was added to the reaction mixture, followed by extraction with cold ether (100 ml) and 0·1 molar aqueous sodium hydroxide (100 ml). The organic layer was subjected to conventional working up and silica gel column chromatography followed by recrystallization from hexane. Yield: 18 per cent for $R = C_4$, 38 per cent for C_5, 13 per cent for OC_5, 9 per cent for OC_6, 9 per cent for OC_8 and 7 per cent for OC_{12}. IR ($CHCl_3$): 1740 (ester) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0·5–4·0 (m, alkyl) and 6·5–8·7 (m, aryl). The results of mass spectroscopy and elemental analyses were satisfactory.

3.3. *Synthesis of p-(n-alkyl)phenyl p-hydroxybenzoate* (*6*) [2]

Yield: 37 per cent for $R = C_3$ (mp 126°C), 32 per cent for C_4 (mp 133°C), 34 per cent for C_5 (mp 134°C).

3.4. *Synthesis of p-[4-(n-alkyl)phenoxycarbonyl]-2-(5-n-butyl)pyridinecarboxylate (7; II)*

The same reaction procedure as that for compounds of type **I** was applied to **6**. Yield: 3 per cent for $R = C_3$, 11 per cent for C_4 and 8 per cent for C_5. IR ($CHCL_3$): 1740 (ester) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 0·5–3·0 (m, alkyl) and 6·5–8·7 (m, aryl). Mass and elemental analyses were also satisfactory.

3.5. *Synthesis of 2-[5-(p-n-alkylphenoxycarbonyl]pyridyl p-(n-alkyl)benzoate (11; III)*

p-(*n*-alkyl)benzoyl chloride (**9**), prepared by refluxing *p*-(*n*-alkyl)-benzoic acid (28 mmol) with a large excess of thionyl chloride for 8 h, was added to a solution of 4-hydroxynicotinic acid (8; 1·9 g, 14 mmol) in anhydrous pyridine (30 ml) and cooled with an ice bath. The mixture was stirred at 20°C for 24 h. To the reaction mixture containing **10** was added **2** (14 mmol), followed by stirring at 20°C for 24 h, then at 70°C for 2 h. The resulting reaction mixture was poured into ice water, extracted with ether (150 ml) and worked up. Silica gel column chromatography gave the purified product.

Yield: 6 per cent for $R_1 = C_1$ and $R = C_4$. Calc. for $C_{24}H_{23}NO_4$: C, 53·43 per cent; H, 4·21 per cent; N, 3·50 per cent. Found: C, 53·04 per cent; H, 4·51 per cent; N, 3·60 per cent. IR (KBr): 1730, 1680 (ester) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 0·5–3·0 (m, alkyl) and 7·0–9·3 (m, aryl). MS: 389 (M^+).

3.6. *Synthesis of di[p-(n-alkyl or n-alkoxy)phenyl]2,5-pyridinedicarboxylate (14; IV)*

A solution of diacid chloride **13**, prepared by refluxing 2,5-pyridinedicarboxylic acid (**12**; 1·7 g, 10 mmol) in excess thionyl chloride for 8 h, and **2** (20 mmol) in anhydrous pyridine (30 ml) was stirred at 20°C for 5 days. The reaction mixture was poured into cold 0·1 molar aqueous sodium carbonate solution (200 ml), extracted with chloroform (200 ml), and worked up as usual. Silica gel column chromatography of the crude product using chloroform as eluent gave a crystalline powder. Yield: 62 per cent for $R = C_1$, 60 per cent for C_2, 35 per cent for C_3, 26 per cent for C_4, 11 per cent for C_1O, 16 per cent for C_2O, 19 per cent for C_3O, 20 per cent for C_4O, 44 per cent for C_5O, 24 per cent for C_6O, 9 per cent for C_7O, 20 per cent for C_8O, 14 per cent for C_9O, 16 per cent for $C_{10}O$ and 13 per cent for $C_{12}O$. IR ($CHCl_3$): 1740 (ester) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 0·5–4·5 (m, alkyl) and 6·5–9·5 (m, aryl). Calc. for $C_{27}H_{29}NO_4$ ($R = C_4$): C, 75·15 per cent; H, 6·77 per cent; N, 3·25 per cent. Found: C, 75·00 per cent; H, 6·78 per cent; N, 3·26 per cent. Ms (C_4): 431 (M^+). Other results of elemental analyses and mass spectrum coincided with calculated values within experimental errors.

3.7. *Synthesis of di[p(n-alkoxycarbonyl)phenyl]2,5-pyridinedicarboxylate (16; V)*

The same procedure as that for compounds of type **IV** was employed using *n*-alkyl *p*-hydroxybenzoate (**15**), prepared following the conventional esterification of **5** and *n*-alcohol with PTS, instead of **2**. Yield: 21 per cent for $R = C_2$, 29 per cent for C_4, 50 per cent for C_5, 26 per cent for C_6, 67 per cent for C_7, 20 per cent for C_8, 60 per cent for C_9, 14 per cent for C_{10} and 12 per cent for C_{12}. IR ($CHCl_3$): 1740, 1720 (ester) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 0·5–4·5 (m, alkyl), 6·5–9·6 (m, aryl). Calc. for $C_{33}H_{37}NO_8$ ($R = C_6$): C, 68·85 per cent; H, 6·48 per cent; N, 2·43 per cent. Found: C, 68·65 per cent; H, 6·46 per cent; N, 2·42 per cent. MS (C_6): 575 (M^+). Other results of elemental analyses and mass spectra were also satisfactory.

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