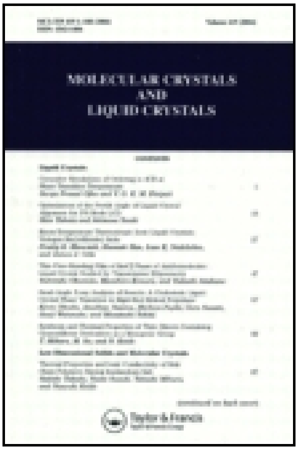

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Properties of the Liquid Crystals Formed by Certain 4-(2′-Pyridyl)phenyl and 4-(4′-Pyridyl)phenyl 4″ -n-Alkoxybenzoates

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Properties of the Liquid Crystals Formed by Certain 4-(2′-Pyridyl)phenyl and 4-(4′-Pyridyl)phenyl 4″-*n*-Alkoxybenzoates

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Nine members of each of two homologous series of esters, the 4-(2′-pyridyl)phenyl and the 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates, have been prepared and their liquid crystal transition temperatures measured. Both homologous series were investigated by differential thermal analysis and the enthalpy changes at the various transitions were measured. Differences in behaviour between the two series are discussed. By comparison of the transition temperatures of certain members of each series with those of corresponding 4-biphenylyl 4″-*n*-alkoxybenzoates, the order of the effect of the terminal phenyl, and 2- and 4-pyridyl rings in promoting the thermal stability of smectic A and nematic phases has been assessed. The nematic order differs from that reported previously for certain Schiff's bases.

INTRODUCTION

As Gray[1] has pointed out, relatively little systematic work on mesogens containing heterocyclic rings has been carried out. However, the success of the 4-*n*-alkyl-4′-cyanobiphenyls[2] in electro-optical "field effect" displays of the twisted nematic type has led to increased interest in liquid crystals with a positive dielectric anisotropy. The search for lower melting liquid crystals of this type has stimulated work[3] on various heterocyclic analogues of the alkylcyanobiphenyls which has furnished information on the effect of heterocyclic rings in promoting mesophase thermal stability. For example,

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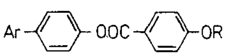
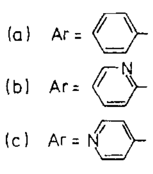
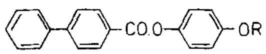
the four isomeric 2,5-disubstituted cyano-alkylphenyl- and alkyl-cyanophenyl-pyrimidines have recently been reported.[4] Certain of these compounds have a high positive dielectric anisotropy and give rise to enantiotropic liquid crystals at relatively low temperatures. Nevertheless, it is significant that the alkylcyanobiphenyls give rise to nematic mesophases of lower thermal stability than the correspondingly substituted phenylpyrimidines[†] i.e., a 2- or 5-pyrimidyl ring promotes nematic thermal stability to a greater extent than a phenyl ring. The results of previous studies[5] (concerning replacement of the central ring of a three-ring mesogen) have left undecided the effect of phenyl relative to pyrimidyl in promoting nematic thermal stability.

Rather more work has been carried out to determine the effect of 2-, 3-, and 4-pyridyl rings relative to phenyl in promoting mesophase thermal stability. However, the results are conflicting and vary according to the system under investigation.[6,7] As we have recently reported the properties of the liquid crystals formed by certain 4-biphenylyl 4″-*n*-alkoxybenzoates[8][‡] (Ia) and the isomeric 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates[9] (II), we felt that the effect of replacing the terminal phenyl ring of the biphenyl system by a 2- or 4-pyridyl ring was sufficiently important to warrant investigation.



(I)





(II)

RESULTS AND DISCUSSION

This paper describes certain properties of the liquid crystals formed by the 4-(2′-pyridyl)phenyl and the 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates, (Ib) and (Ic). These compounds were chosen for study in preference to the corresponding homologous series with the ester linkage reversed (as in (II)),

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[†] For example, the transition temperatures for 4′-*n*-pentyl-4-cyanobiphenyl[2] are C-N, 22.5°; N-I, 35°, whereas the corresponding values for 5-cyano-2-(4-*n*-pentylphenyl) pyrimidine[4] are C-N, 96°; N-I, 109°, and those for 5-*n*-pentyl-2-(4-cyanophenyl)pyrimidine[4] are C-N, 70.5–71°; N-I, [52°].

[‡] Similar data for this series of esters, differently named, have recently been reported again in this journal by Sadashiva.[10]

for two reasons: (i) for comparison with the analogous biphenyl esters which give rise to the most common type of plot† of liquid crystal transition temperature against the number of carbon atoms (*n*) in the *n*-alkyl chain and (ii) because the synthetic work involved in the preparation of these esters was more straightforward than for the compounds with the ester linkage reversed.

Nine members (*n*-butyloxy to *n*-decyloxy and *n*-dodecyloxy and *n*-tetradecyloxy) of each homologous series were prepared. The liquid crystal transition temperatures were measured using a hot stage in conjunction with a polarising microscope and the existence of all the transitions was confirmed by differential thermal analysis (DTA).‡ DTA was also used to determine the enthalpies of fusion and the enthalpies of the mesophase transitions. Smectic phases were assigned to the S_A type by (i) microscopic examination of the focal-conic fan texture of the birefringent phase, and (ii) the complete miscibility of the smectic phases over the entire composition range when mixed with compounds with known S_A phases. Our results are listed in Tables I and II and the transition temperatures are shown plotted against the number of carbon atoms, *n*, in the *n*-alkyl chain in Figures 1 and 2.

The two series of compounds, (Ib) and (Ic), differ quite markedly in the shapes of the transition temperature plots. Transitions to the isotropic liquid show the usual odd-even alternation, the uppermost curve corresponding with members for which *n* is even. However, for the 4-(4′-pyridyl) phenyl 4″-*n*-alkoxybenzoates these transitions are enantiotropic S_A-I transitions which lie on rising curves, and only the first three ($n = 4, 5, 6$) members of the series show (monotropic) nematic phases. Only the *n*-pentyloxy and *n*-hexyloxy compounds give rise to S_A-N transitions, the points for which lie on a curve which rises to meet the S_A-I transition temperature curve for the members of the series for which *n* is odd.

The 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates give rise to monotropic nematic mesophases and the N-I transition temperature lie on two curves that oppose each other in gradient as the homologous series is ascended.

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† For this type of plot the N-I transition temperatures alternate; the points lie on two falling curves, which tend towards coincidence as *n* increases, the upper for even and the lower for odd numbers of C atoms in the alkyl chain of the *n*-alkoxy group. In general,no smectic properties are observed for the early members of the series. Smectic properties may appear at $n = 4$ or 5 and the S-N transition temperatures, which do not alternate, lie on a single curve which rises steeply as *n* increases, then levels out and merges with the falling N-I curves. Subsequently, no nematic properties are observed in the homologous series and the S-I transition temperatures for the higher members fit extensions of the falling N-I curves. The melting points (i.e., C-S, C-N, or C-I transition temperatures) do not usually show any regular trends.

‡ The N-I transition temperatures for 4-(4′-pyridyl)phenyl 4″-*n*-butyloxybenzoate and for 4-(2′-pyridyl)phenyl 4″-*n*-pentyloxybenzoate were *determined* by DTA because the samples crystallized before the appearance of the monotropic nematic phases when measurements were attempted by the optical method.

TABLE I

Transition temperatures and enthalpies of fusion for 4-(2′-pyridyl)-phenyl 4″-*n*-alkoxybenzoates (Ib)

Substituent R	Transition temperatures[a] (°C) C-I	N-I	N-C[b]	Enthalpy of fusion[c] ΔH (kcal mol^{-1})
n-C_4H_9	159	[119.5]	111	11.0
n-C_5H_{11}	145.5	[108][d]	115	10.8
n-C_6H_{13}	126	[116]	105.5	10.2
n-C_7H_{15}	126.5	[112]	102	13.7
n-C_8H_{17}	122	[115]	90	9.2
n-C_9H_{19}	129	[113]	96	15.5
n-$C_{10}H_{21}$	121	[114]	89	14.2
n-$C_{12}H_{25}$	119.5	[112.5]	98.5	14.7
n-$C_{14}H_{29}$	121.5	[111.5]	91	16.1

TABLE II

Transition temperatures and enthalpies of fusion for 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates (Ic)

Substituent R	Transition temperatures[a] (°C) C-I	S_A-N	N-I	S_A-C[b]	Enthalpy of fusion[c] ΔH (kcal mol^{-1})
n-C_4H_9	144		[111][d]	114[e]	10.1
n-C_5H_{11}	116	[101.5]	[110]	95	8.4
	C-N				
n-C_6H_{13}	113	[110.5]	116	83	8.3
	C-S_A		S_A-I		
n-C_7H_{15}	111		115	99	6.7
n-C_8H_{17}	105.5		121.5	95	8.5
n-C_9H_{19}	107		121	92	6.7
n-$C_{10}H_{21}$	115		124.5	108	12.9
n-$C_{12}H_{25}$	109		126	89	12.8
n-$C_{14}H_{29}$	110		126.5	86	13.8

[a] Transition temperatures were measured using a Reichert-Kofler hot stage in conjunction with a polarising microscope. The hot stage was calibrated using Analar standards and the precision of measurements thereon is estimated as better than ±0.5°.

[b] Temperature of recrystallisation.

[c] Enthalpies of fusion were measured using Stanton-Redcroft differential thermal analysers, models 670 and 671, with pure indium as the standard. The estimated accuracy of the quoted values is 5%. The ΔH values for the S_A-N, S_A-I and N-I transitions were in the ranges 0.3–0.8, 0.8–1.0, and 0.2–0.5 kcal mol^{-1}, respectively.

[d] Values not obtained by optical microscopy because the samples crystallised before the appearance of the nematic phase. The temperatures quoted correspond with those at which small peaks appear on the DTA thermograms immediately preceeding crystallisation on the cooling cycle.

[e] N-C transition.

[ ] Monotropic transition.

The upper curve for which *n* is even falls, whereas the lower curve for which *n* is odd is a rising one.† It was possible to cool the monotropic nematic phases of these esters to temperatures substantially lower than the m.p. before crystallisation occurred (see Figure 1), but no smectic properties were apparent even for the tetradecyloxy compound.

Both the 4-(2′-pyridyl)phenyl and 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates, (Ib) and (Ic), have lower mesophase thermal stabilities than the corresponding 4-biphenylyl 4″-*n*-alkoxybenzoates (Ia), and the 4-(2′-pyridyl)-phenyl esters have a slightly higher average m.p. (C-I transition) than that of the other two series of esters, reflecting slightly greater cyrstal forces in this series of compounds. The three series differ only by replacement of the terminal phenyl ring by a 2- or 4-pyridyl ring. This alteration causes no marked change in molecular size or shape, but has a pronounced effect on liquid crystal behaviour. Thus, the compounds for which Ar = phenyl exhibit a "normal" plot of transition temperature against *n*, but nematic properties are confined to the early members of the series when Ar = 4-pyridyl, the later members showing only smectic behaviour, and when Ar = 2-pyridyl the series is entirely nematogenic having no smectic properties at all.

Despite these differences, the three series may be compared by evaluation of the effect of the terminal substituent on the thermal stability of the smectic and nematic phases. The mean values of the transition temperatures of certain comparable members of each series (shown in Table III) indicate that the order of smectic (S_A) thermal stability is Ar = 4-pyridyl > phenyl > 2-pyridyl, whereas the order of nematic phase thermal stability is Ar = phenyl > 2-pyridyl > 4-pyridyl.

According to its position in the terminal ring, the hetero-nitrogen atom influences the thermal stability of the S_A and the nematic phases differently. The smectic thermal stability is increased by approximately 16.5° when Ar = phenyl is replaced by Ar = 4-pyridyl. Apparently the anisotropy of the molecular polarisability is slightly increased by the presence of the terminal 4-pyridyl nitrogen atom. However, when the lone pair of the nitrogen atom is laterally positioned, as when Ar = 2-pyridyl, the adverse dipole that this creates, possibly associated with a small angle of twist between the 2-pyridyl ring and the benzene ring to which it is attached, disrupts the lateral cohesive forces to such an extent that when Ar = 2-pyridyl the compounds do not

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† Sadashiva[10] has recently reported a very similar plot (but with the expected reversal of the odd-even effect) for the 4-biphenylyl 4″-*n*-alkylbenzoates. This suggests that replacement of an *n*-alkoxy group by an *n*-alkyl group influences the intermolecular cohesive forces in a similar manner as the change from a terminal phenyl ring to a 2-pyridyl ring.

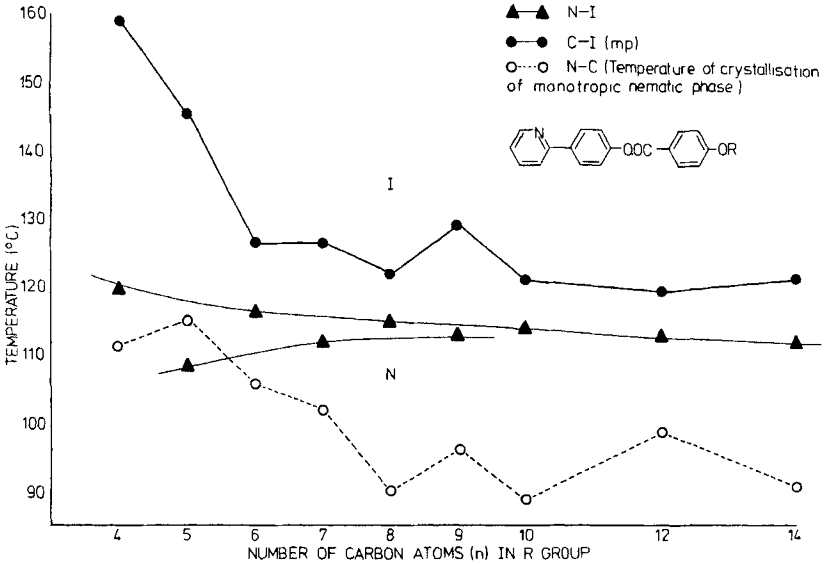


FIGURE 1 Plot of transition temperatures against alkyl chain length (*n*) for 4-(2′-pyridyl)-phenyl 4″-*n*-alkoxybenzoates (Ib).

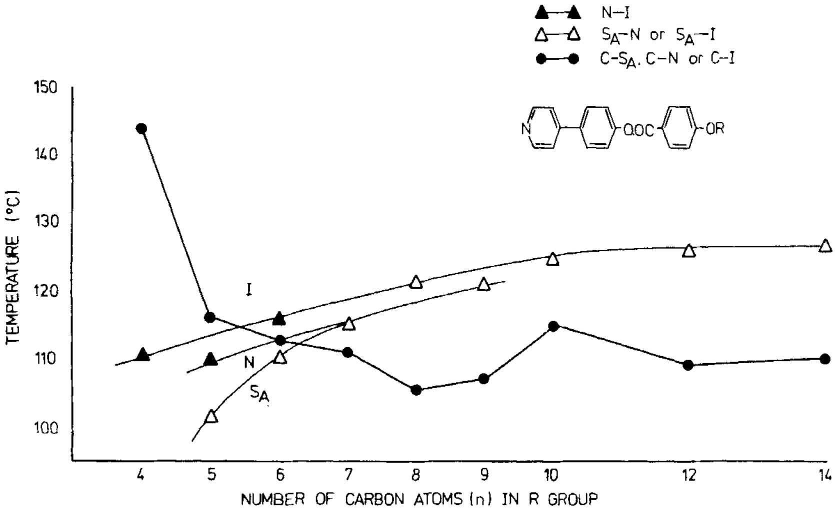
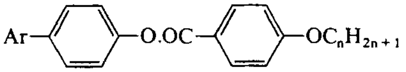
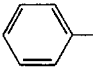
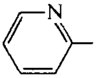
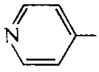


FIGURE 2 Plot of transition temperatures against alkyl chain length (*n*) for 4-(4′-pyridyl)-phenyl 4″-*n*-alkoxybenzoates (Ic).

TABLE III

Mean m.p. and mesophase thermal stabilities (°C) for



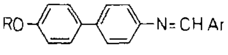
Ar	m.p.[a] (n = 4–10, 12, 14)	Smectic A (n = 8, 10, 12, 14)	Nematic (n = 4, 5, 6)
	127[b]	10.8.1[b]	137.7[b]
	130	—	114.5
	114.5	124.6	112.3

[a] C-S, C-N, or C-I transition.

[b] Values obtained from D. J. Byron, D. Lacey, and R. C. Wilson, *Mol. Cryst. Liq. Cryst.*, **45**, 267 (1978).

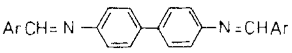
show smectic phases. The nematic thermal stability is substantially decreased by the introduction of the hetero-nitrogen atom in either the 2- or the 4-position of the terminal ring. Relative to Ar = phenyl, the decreases are approximately 25.5° for Ar = 4-pyridyl and 23° for Ar = 2-pyridyl.

These results are partly in agreement with the conclusions reported by Young *et al.*[6] and by Nash and Gray[7] on Schiff's bases of the type (III), where



(III)

Ar = various heterocyclic rings. For the thermal stability of the S_A (R = n-octyl) and nematic (R = CH_3) phases, identical orders, namely: Ar = 4-pyridyl > phenyl > 2-pyridyl were obtained. This order is the same as that observed for the S_A thermal stability in the present work, but contrasts with that obtained for the nematic order. However, for compounds of the type (IV), Nash and Gray obtained the order Ar = phenyl > 4-pyridyl and



(IV)

2-pyridyl (neither of the last two compounds being mesomorphic) for the influence of the terminal substituents on nematic phase thermal stability and this order is similar to that obtained in the present work. Nash and Gray suggest that the inversion in the positions of phenyl and 4-pyridyl in the nematic thermal stability order in passing from the Schiff's bases (III) to the corresponding di-anils (IV) may be due to the large repulsive interactions between two 4-pyridyl rings placed end to end. This will adversely affect the thermal stability of the nematic phase, and it is possible that the arrangement of the molecules in the nematic phases of the 4-(2′-pyridyl)phenyl and 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates is such that repulsions between the nitrogen lone pairs of the heterocyclic rings and/or the oxygen of the alkoxy group is responsible for the relatively low thermal stability of these heterocyclic mesogens. In addition, it may be significant that the molecules of the series that exhibits no smectic properties at all, the 4-(2′-pyridyl) phenyl 4″-*n*-alkoxybenzoates, contain a hetero-nitrogen atom which may exert a steric effect that can cause twisting about the bond connecting the benzene ring to the 2-pyridyl ring. It is known[11] that steric effects of this type cause an increase in separation of the long molecular axes and reduce the thermal stability of the ordered arrangement of molecules in the liquid crystal, and that smectic thermal stability is affected more than nematic thermal stability in such instances. Work is in progress to evaluate the extent to which the hetero-nitrogen atom exerts such a steric effect and the results of these studies will be reported in a subsequent paper.

The enthalpies of fusion of the three series of 4″-*n*-alkoxybenzoates (I) are all of the same order of magnitude, although the average value of the enthalpy of fusion for members of the series when Ar = 2-pyridyl (Ib) is 3.0 units greater than when Ar = 4-pyridyl (Ic), and approximately 3.5 units greater than when Ar = phenyl (Ia). As *n* increases, the values of ΔH for members of the series for which Ar = 4-pyridyl show an odd-even alternation in the opposite sense to that of the N-I and S_A-I transition temperatures, although after the first two members the reverse trend is shown when Ar = 2-pyridyl. With some exceptions, the ΔH values for the N-I and S_A-I transitions of the two series (Ar = 2-pyridyl and Ar = 4-pyridyl) show a gradual increasing trend as *n* increases, and all ΔH values involving transitions between mesophases or from a mesophase to the isotropic liquid are of the expected magnitude.

EXPERIMENTAL

4-Phenylpyridine

4-Phenylpyridine was prepared from α-methylstyrene (2 mol) by the method of Schmidle and Mansfield.[12] After work-up of the reaction mixture, the crude product was distilled and the large fraction, b.p. 100–104°/1.3 mm was collected. The amine solidified on cooling, and was recrystallised from light petroleum (b.p. 60–80°) when the 4-phenylpyridine was obtained as colourless flakes, m.p. 74–75° (lit.[12] m.p. 74°). The average yield of several preparations was 23 %.

4-(4′-Nitrophenyl)pyridine

Nitration[13] of 4-phenylpyridine (0.5 ml) gave a mixture from which the 3′- and 4′-nitro-isomers were separated by fractional recrystallisation.[14] Each isomer was then purified by recrystallisation from ethanol. 4-(4′-Nitrophenyl)pyridine, m.p. 123–124°, and 4-(3′-nitrophenyl)pyridine, m.p. 109–110°, were obtained as pale yellow needles in yields of 33 % and 20 % respectively. Katritzky and Simmons[13] report m.p.s. of 124–125° and 109–110° for the 4′- and 3′-nitro-isomers, respectively.

4-(4′-Aminophenyl)pyridine

Reduction of 4-(4′-nitrophenyl)pyridine (20g, 0.1 mol) was carried out with 95 % hydrazine hydrate (20 ml) and 5 % palladium on charcoal (5 g–added in small portions) in boiling ethanol (900 ml). After 90 min., the catalyst was filtered off and the volume of the filtrate reduced to about 150 ml, when the crude product crystallised out on cooling. Recrystallisation from ethanol gave the 4-(4′-aminophenyl)pyridine as a colourless solid, 15.1 g (89 %), m.p. 234–235° (lit.[14] m.p. 232–234°).

4-(4′-Hydroxyphenyl)pyridine

4-(4′-Aminophenyl)pyridine (0.14 mol) was diazotised in 1:1 concentrated hydrochloric acid: water (150 ml) in the usual manner. The solution of the diazonium chloride was diluted with water (4000 ml), stirred vigorously, and heated. The temperature was maintained at 60°, then at 75°, and finally at 90°, for periods of 1 h. The solution was then cooled, made slightly alkaline with 20 % aqueous ammonia, and the resulting crude phenol was collected.

The phenol was purified *via* its picrate, as follows. The crude, dry phenol (13 g, 0.076 mol) was stirred vigorously with boiling ethanol, insoluble material was filtered off, and the filtrate was added to a warm solution of picric acid (17.4 g, 0.076 mol) in ethanol (100 ml). On cooling, the picrate crystallised out and was washed with small portions of ethanol, then with ether. The picrate was then stirred with a warm saturated aqueous solution of lithium hydroxide (700 ml) to precipitate the lithium salt. This was filtered off, dissolved in 2M-aqueous hydrochloric acid and the 4-(4′-hydroxyphenyl)pyridine was liberated by the addition of 20 % aqueous ammonia. Recrystallisation from ethanol (with treatment with decolorising charcoal) gave the 4-(4'-hydroxyphenyl)pyridine as a colourless crystalline slid, 10.5 g (45 %), m.p. 254–255° (lit.[15] m.p. 253–254°).

A small portion of the *picrate* of *4-(4'-hydroxyphenyl)pyridine*, after several recrystallisations from ethanol, had m.p. 260–262° (Found: C, 50.6; H, 2.9; N, 13.9. $C_{17}H_{12}N_4O_8$ requires C, 51.0; H, 3.0; N, 14.0 %).

2-(4'-Nitrophenyl)pyridine

4-Nitroaniline (140 g, 0.99 mol) was diazotised in 1:1 concentrated hydrochloric acid: water (500 ml) in the usual fashion. The cold solution of the diazonium chloride was added, with stirring, during a period of 3 h, to pyridine (1000 m) at 40°.[16] After work-up, the crude mixture was dissolved in the minimum quantity of benzene and purified by passage through a short column of alumina (100 g), eluting with benzene. The resulting mixture of 2-, 3-, and 4-(4'-nitrophenyl)pyridines was obtained as an orange-brown solid. 135 g (78 %), m.p. 105–115°. When the mixture (100 g) was subjected to column chromatography on alumina (1800 g) the 2-(4'-nitrophenyl)pyridine, which was more rapidly eluted with benzene, was still slightly contaminated with 3-(4'-nitrophenyl)pyridine. Purification of the 2-(4'-nitrophenyl)pyridine was achieved by recrystallisation of the hydrochloride from 4M-aqueous hydrochloric acid followed by recrystallisation of the free base (released from the hydrochloride by treatment with dilute aqueous ammonia) from methylated spirit. The resulting 2-(4'-nitrophenyl)pyridine was obtained as colourless flakes, 34 g (22 %), m.p. 130–131°. Forsyth and Pyman[14] quote m.p. 130.5–131.5° for this compound.

2-(4'-Aminophenyl)pyridine

2-(4'-Nitrophenyl)pyridine (20 g, 0.1 mol) was reduced in an analogous manner to that described above for the 4-isomer. The crude product was recrystallised from ether giving the 2-(4'-aminophenyl)pyridine as colourless flakes, 12.5 g (67 %), m.p. 97° (lit.[14] m.p. 98°).

2-(4'-Hydroxyphenyl)pyridine

2-(4'-Hydroxyphenyl)pyridine was prepared by a similar method to that described above for 4-(4'-hydroxyphenyl)pyridine, except that in this case purification *via* the picrate was unnecessary. The crude product was recrystallised from chloroform and the 2-(4'-hydroxyphenyl)pyridine was obtained as pale buff micro-crystals, 22.0 g (61 %), m.p. 161°. Butterworth, Heilbron, and Hey[15] quote m.p. 160° for this compound.

4-(2′-pyridyl)phenyl and 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates

The esters were prepared[8] from 4-(4′-hydroxyphenyl)pyridine and from 2-(4′-hydroxyphenyl)pyridine by interaction with the appropriate 4-*n*-alkoxybenzoyl chloride in dry pyridine, and were purified[8] by column chromatography on alumina, eluting with chloroform. Following recrystallisation from ethanol and/or from acetone the yields of the 4-(2′-pyridyl)phenyl and the 4-(4′-pyridyl)phenyl 4″-*n*-alkoxybenzoates were in the ranges 51–80% and 43–75%, respectively.

The transition temperatures for the two homologous series of esters are recorded in Tables I and II and their elemental analyses are listed in Table IV.

The members of each homologous series show broadly similar spectral characteristics, and the data for the following compounds are representative of the series to which the compounds belong.

TABLE IV

Elemental analyses for 4-(2′-pyridyl)phenyl and 4-(4′pyridyl)phenyl 4″-*n*-alkoxybenzoates, (Ib) and (Ic)

Substituent	4-(2′-pyridyl)phenyl esters. Found %			4-(4′-pyridil)phenyl esters. Found %			Molecular	Required %		
R	C	H	N	C	H	N	Formula	C	H	N
n-C_4H_9	76.4	6.2	4.0	75.9	6.1	3.9	$C_{22}H_{21}NO_3$	76.1	6.1	4.0
n-C_5H_{11}	76.3	6.4	4.1	76.3	6.5	3.9	$C_{23}H_{23}NO_3$	76.5	6.4	3.9
n-C_6H_{13}	77.0	6.8	3.8	76.8	6.7	3.6	$C_{24}H_{25}NO_3$	76.8	6.6	3.7
n-C_7H_{15}	77.1	6.9	3.9	76.9	7.1	3.8	$C_{25}H_{27}NO_3$	77.1	6.9	3.6
n-C_8H_{17}	77.4	7.4	3.7	77.1	7.4	3.2	$C_{26}H_{29}NO_3$	77.4	7.2	3.5
n-C_9H_{19}	77.6	7.2	3.4	77.7	7.6	3.4	$C_{27}H_{31}NO_3$	77.7	7.4	3.4
n-$C_{10}H_{21}$	78.2	7.7	3.2	77.8	7.9	3.0	$C_{28}H_{33}NO_3$	78.0	7.7	3.2
n-$C_{12}H_{25}$	78.5	8.0	3.3	78.3	8.1	3.0	$C_{30}H_{37}NO_3$	78.4	8.1	3.1
n-$C_{14}H_{29}$	79.1	8.5	3.0	78.9	8.7	2.9	$C_{32}H_{41}NO_3$	78.9	8.4	2.9

4-(2′-pyridyl)phenyl 4″-*n*-hexyloxybenzoate: ν_{max} (KBr) 2950, 2910, 2855, 1730, 1605, 1580, 1510 cm^{-1}; δ($CDCl_3$) 0.87 (br, 3H, CH_3), 1.58 (br, 9H), 3.96 (t, J 6.0 Hz, 2H, OCH_2), 6.95 (d, J 9.0 Hz, 2H), 7.34 (m, 5H), 8.01 (dd, J 9.0 Hz, 4H), 8.64 (d, J 5.0 Hz, 1H).

4-(4′-pyridyl)phenyl 4″-*n*-hexyloxybenzoate: ν_{max} (KBr) 2960, 2930, 2855, 1740, 1610, 1580, 1515 cm^{-1}; δ($CDCl_3$) 0.92(br, 3H, CH_3), 1.54 (br, 9H), 4.04 (t, J 6.0 Hz, 2H, OCH_2), 7.01 (d, J 9.0 Hz, 2H), 7.53 (m, 6H), 8.22 (d, J 9.0 Hz, 2H), 8.72 (d, J 6.0 Hz, 2H).

(The i.r. and n.m.r. spectra were determined, respectively, on a Perkin–Elmer 157G grating spectrophotometer and on a Jeol JNM–C–6OHL 60 Hz instrument with TMS as internal standard).

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