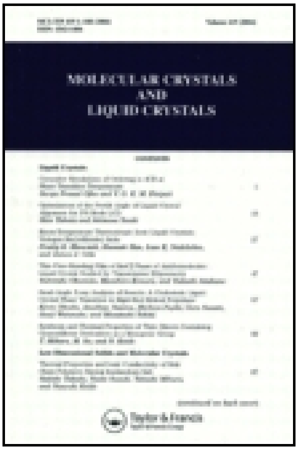

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Properties of the Liquid Crystals Formed by the N-Oxides of Certain 4-(4′-n-Alkoxypheynyl) pyridines: A Comparison with Analogous 4′-n-Alkoxy-4-cyanobiphenyuls

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Properties of the Liquid Crystals Formed by the N-Oxides of Certain 4-(4′-n-Alkoxyphenyl)pyridines: A Comparison with Analogous 4′-n-Alkoxy-4-cyanobiphenyls

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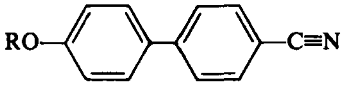
The liquid crystal transition temperatures of the N-oxides of seven 4-(4′-n-alkoxyphenyl)pyridines are reported. The transition temperatures of the mesophases formed by these N-oxides and by the 4′-n-alkoxy-4-cyanobiphenyls are compared and the effects of the N-oxide function and the cyano-group as mesogenic terminal substituents are discussed.

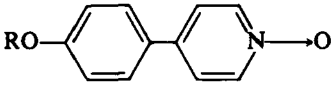
INTRODUCTION

We have recently reported the liquid crystal transition temperatures of the N-oxides of certain 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates.[1] By comparison with similar data for the 4′-cyano-4-biphenylyl 4″-n-alkoxybenzoates[2] and the 4″-n-alkoxyphenyl 4′-cyanobiphenyl-4-carboxylates[3] we concluded that there are resemblances in the effects on liquid crystal thermal stability between the N-oxide function and the cyano-group. When similarly situated in a terminal position both substituents increase liquid crystal thermal stability although the cyano-group has a relatively greater influence on nematic thermal stability than the N-oxide function which substantially enhances smectic properties.

The compounds which furnished the data from which comparisons of the two groups were made give rise to mesophases of relatively high thermal stability, the cyano-compounds having rather higher transition temperatures than the N-oxides. Further comparison of the N-oxide function and the cyano-group has now been achieved by a consideration of the effects of their presence in a terminal position of mesogens that give rise to liquid crystals of much lower thermal stability. Very suitable reference compounds of this type are the 4′-n-alkyl- and 4′-n-alkoxy-4-cyanobiphenyls,[4] which have proved so successful in electro-optical display devices employing the twisted nematic mode. Hence, for comparison with the 4′-n-alkoxy-4-cyanobiphenyls (I), which give rise to mesophases of higher thermal stability than the corresponding 4′-n-alkyl compounds, we have now prepared an analogous series of pyridine-N-oxides, namely, the N-oxides of the 4-(4′-n-alkoxyphenyl)pyridines (II). In both (I) and (II) the powerful dipole moments† due to the cyano-group and the N-oxide function are oriented along the major molecular axis.



(I)



(II)

RESULTS AND DISCUSSION

The N-oxides of seven members (n-hexyloxy through to n-decyloxy and n-dodecyloxy and n-tetradecyloxy) of the homologous series of 4-(4′-n-alkoxyphenyl)pyridines have been prepared. Transition temperatures were measured using a hot stage in conjunction with a polarizing microscope, and the values obtained are listed in Table I and are shown plotted against the number of carbon atoms, n, in the n-alkyl chain in Figure 1 (for comparison, transition temperatures for selected members of the 4′-n-alkoxy-4-cyanobiphenyls[4] are given in Table II). Unlike the N-oxides of the 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates, the N-oxides of the 4-(4′-n-alkoxyphenyl)pyridines are only very slightly sensitive to light and do not decompose when heated to determine their transition temperatures.

In contrast with the 4′-n-alkoxy-4-cyanobiphenyls, the members of the series of N-oxides have no nematic properties and give rise to smectic phases only. In each case these were identified as smectic A by microscopic examination of the focal-conic fan textures shown by the birefringent phases. The N-oxides all have appreciably higher m.p.s (C-I or C-S_A transition temperatures) than the analogous 4′-n-alkoxy-4-cyanobiphenyls and for the first two ($n = 6, 7$) members, monotropic transitions to smectic phases are observed. Thereafter, the S_A-I transitions are enantiotropic and the transition tempera-

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† 4-Cyanobiphenyl and 4-phenylpyridine-N-oxide have dipole moments of 4.33D[5] and 4.61D,[6] respectively.

TABLE I

Transition temperatures and elemental analyses for N-oxides of 4-(4′-n-alkoxyphenyl)pyridines (II)

Substituent R	Transition temperatures[a] (°C) C-I	S_A-I	S_A-C[b]	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
n-C_6H_{13}	95.5	[57.5]	54	75.3	7.7	5.0	$C_{17}H_{21}NO_2$	75.3	7.8	5.2
n-C_7H_{15}	97.5	[72]	55	75.5	8.3	5.0	$C_{18}H_{23}NO_2$	75.8	8.1	4.9
	C-S_A									
n-C_8H_{17}	76.5	85.5	59	76.0	8.2	4.7	$C_{19}H_{25}NO_2$	76.3	8.4	4.7
n-C_9H_{19}	73.5	94.5	59	76.4	8.9	4.4	$C_{20}H_{27}NO_2$	76.7	8.6	4.5
n-$C_{10}H_{21}$	78	102.5	63	76.9	9.0	4.2	$C_{21}H_{29}NO_2$	77.1	8.9	4.3
n-$C_{12}H_{25}$	80	110.5	64	77.3	9.6	4.1	$C_{23}H_{33}NO_2$	77.7	9.3	3.9
n-$C_{14}H_{29}$	84	113	86	78.1	9.6	3.8	$C_{25}H_{37}NO_2$	78.3	9.7	3.7

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

[b] Temperature of recrystallization.

[ ] Monotropic transition.

tures increase rapidly as *n* increases, the curve for the members of the series for which *n* is odd lying only slightly below the curve for the members for which *n* is even. The plots of the transition temperatures against *n* show that for transitions from a mesophase to the isotropic liquid the gradients of the curves (S_A-I transitions) for the N-oxides are substantially greater than those of the corresponding curves (N-I or S_A-I transitions) for the analogous cyano-compounds. Thus, although the first two ($n = 6, 7$) members of the series of N-oxides have a lower liquid crystal thermal stability (S_A-I transitions) than the analogous 4′-n-alkoxy-4-cyanobiphenyls (N-I transitions), the later members ($n \geqslant 8$) of the N-oxide series all have higher transition temperatures than their cyano-analogues.

As the N-oxides of the 4-(4′-n-alkoxyphenyl)pyridines have no nematic properties a comparison with the nematic thermal stability of the 4′-n-alkoxy-4-cyanobiphenyls cannot be made. However, the mean values for the smectic (S_A) thermal stability of corresponding members ($n = 8, 9, 10, 12$) of the two series are 98.3° for the N-oxides and 79.5° for the cyano-compounds, and when individual members of the two series are compared the differences in smectic thermal stability show an increasing trend as *n* increases (eg. $n = 9$, 17.5°; $n = 12$, 21.5°). Hence, it is clear that, when similarly situated in a terminal position, the N-oxide function increases smectic thermal stability substantially more than the cyano-group.

For the N-oxides of the 4-(4′-n-alkoxyphenyl)pyridines structural features responsible for (i) the absence of nematic properties, and (ii) the pronounced smectic behavior, are not readily apparent. However, as was suggested for the

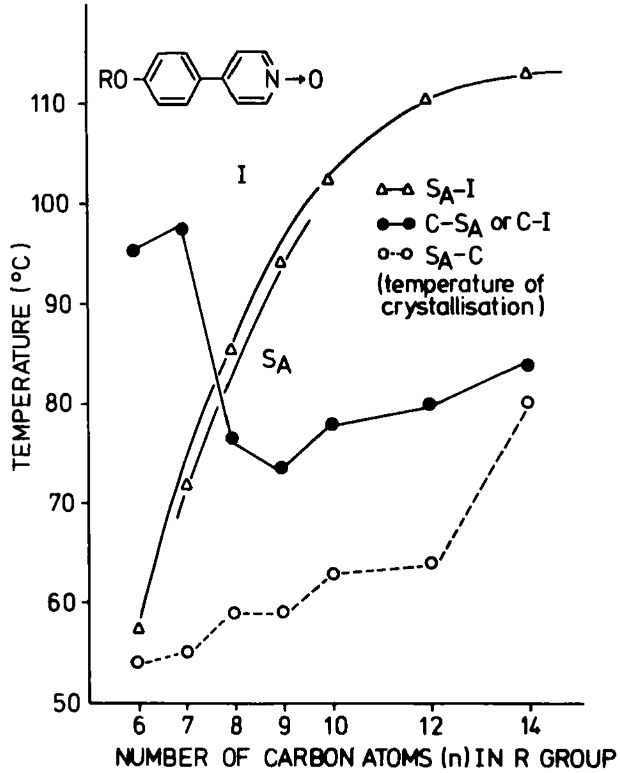

FIGURE 1 Plot of transition temperatures against alkyl chain length (*n*) for N-oxides of 4-(4′-n-alkoxyphenyl)pyridines (II).

TABLE II

Transition temperatures for 4′-n-alkoxy-4-cyanobiphenyls[4] (I)

Substituent R	Transition temperatures (°C) C-N	S_A-N	N-I
n-C_6H_{13}	58		76.5
n-C_7H_{15}	53.5		75
	C-S_A		
n-C_8H_{17}	54.5	67.5	80
n-C_9H_{19}	65	77	79.5
			S_A-I
n-$C_{10}H_{21}$	61		84.5
n-$C_{12}H_{25}$	69		89

smectogenic 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates,[1] it is possible that the presence of the dipolar N-oxide function could give rise to an interdigitated bilayer such as that which has been proposed to account for the S_A layer spacings of 1.5–1.6 molecular lengths observed for the 4′-n-alkoxy- and 4′-n-alkyl-4-cyanobiphenyls.[4,7] For these compounds it has been suggested that the presence of (i) the strongly dipolar terminal cyano-group may be responsible for the bilayer arrangement, and (ii) the interdigitated structure may enhance smectic thermal stability. Thus a bilayer arrangement due to the presence of the terminal dipolar N-oxide function may be the structural factor responsible for the markedly smectic nature of the N-oxides of the 4-(4′-n-alkoxyphenyl)pyridines.

The 4-(4′-n-alkoxyphenyl)pyridines, from which the N-oxides are derived. do not give rise to liquid crystals, although the m.p.s and recrystallization temperatures of individual members are appreciably lower than for the corresponding N-oxides. The lack of mesogenic properties may be due to the significantly smaller dipole moment† (due to the presence of the hetero-nitrogen atom and its lone pair) acting along the long molecular axis, and to the absence of a terminal "substituent" on the pyridine nitrogen atom.

EXPERIMENTAL

Discussion

Synthesis of the 4-(4′-n-alkoxyphenyl)pyridines was not achieved without some difficulty. Two modified Hantzsch-type pyridine syntheses were attempted. In the first of these, the appropriate α-methyl-4-n-alkoxystyrene (obtained from the 4-n-alkoxyacetophenone by Grignard reaction with methyl magnesium iodide followed by dehydration of the resulting tertiary alcohol with toluene-p-sulphonic acid) was treated with 38% formaldehyde in aqueous dioxan. The method was based on that described by Schmidle and Mansfield[9] for the synthesis of 4-phenylpyridine. The resulting tetrahydropyridine was dehydrogenated (Pd/C), but after work-up via the picrate, followed by purification of the free base by column chromatography on alumina, only a very low yield of the required 4-(4′-n-alkoxyphenyl)pyridine was obtained. The second Hantzsch-type synthesis attempted was based on that described by Chennat and Eisner,[10] but using stoichiometric proportions of reactants. Thus, methyl propiolate, an appropriate 4-n-alkoxybenzaldehyde, and ammonium acetate in glacial acetic acid solution gave a dimethyl 1,4-dihydro-4-(4′-n-alkoxyphenyl)pyridine-3,5-dicarboxylate in low yield. Hydrolysis of

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† 4-Phenylpyridine has a dipole moment of 2.55D.[8]

the ester was achieved with some difficulty but attempts to decarboxylate the free acid failed. The copper(I) catalyzed conversion of an aryl halide into an alkyl-aryl ether reported by Bacon and Rennison[11] was attempted on a 4-(4′-halogenophenyl)pyridine (halogen = Br or I). This was heated under reflux in an atmosphere of nitrogen with an appropriate sodium alkoxide in the presence of copper(I) iodide in 2,4,6-trimethylpyridine as solvent. However, the product obtained from reactions of this type was 4-phenylpyridine, showing that reductive substitution rather than nucleophilic substitution had predominated. The required 4-(4′-n-alkoxyphenyl)pyridines were successfully obtained by direct alkylation of 4-(4′-hydroxyphenyl)pyridine. Unchanged starting material was recovered if the alkylation was attempted using a non-polar solvent (eg. with the appropriate alkyl halide in hot cyclohexanone in the presence of potassium carbonate). However, when a polar solvent (N,N-dimethylformamide) was used good yields (67–86%) of the required 4-(4′-n-alkoxyphenyl)pyridines were obtained.

4-(4′-Hydroxyphenyl)pyridine

This was prepared by the method previously reported.[12]

4-(4′-n-Alkoxyphenyl)pyridines

4-(4′-Hydroxyphenyl)pyridine (1.7g, 0.01 mol), anhydrous potassium carbonate (6.0g, 0.04 mol), and the appropriate n-alkyl bromide (0.016 mol) were stirred vigorously in dry N,N-dimethylformamide (40 ml) and the mixture heated, under reflux, for 8 h. After cooling, the salts were filtered off and washed thoroughly with dry N,N-dimethylformamide. The solvent was removed from the combined filtrate and washings and the residue was then distilled under vacuum. The resulting pale yellow solid was recrystallized (and decolorized with charcoal) from light petroleum (b.p. 60–80°) to give the product as a white crystalline solid. The yields, m.p.s and elemental analyses of the *4-(4′-n-alkoxyphenyl)pyridines* prepared by this method are given in Table III.

The 4-(4′-n-alkoxyphenyl)pyridines show broadly similar spectral characteristics, and the following data for the n-octyloxy-compound are representative of the series: ν_{max} (KBr) 2970, 2930, 2855, 1608, 1580, 1520, 1290, 1260, 1225, 1185, 850, 828 cm^{-1}; δ(CDCl$_3$) 0.85 (br, 3H, CH$_3$), 1.48 (br, 12H), 4.00 (t, J6.0 Hz, 2H, OCH$_2$), 7.00 (d, J9.0 Hz, 2H), 7.46 (d, J6.0 Hz, 2H), 7.61 (d, J9.0 Hz, 2H), 8.62 (d, J6.0 Hz, 2H); m/e 299 (M$^+$, 2.7%), 284 (1.9), 283 (7.7), 187 (17.1), 172 (11.8), 171 (100), 154 (3.1), 115 (6.7), 95 (1.9).

N-oxides of 4-(4′-n-alkoxyphenyl)pyridines

These were prepared by the method previously reported,[1] except that after basification of the reaction mixture the N-oxide was extracted with chloro-

TABLE III

4-(4′-n-Alkoxyphenyl)pyridines prepared by alkylation of 4-(4′-hydroxyphenyl)pyridine

Substituent R	Yield (%)	m.p. (°C)	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
n-C_6H_{13}	70	62	80.1	8.4	5.6	$C_{17}H_{21}NO$	80.0	8.2	5.5
n-C_7H_{15}	53	57–58	80.3	8.6	5.2	$C_{18}H_{23}NO$	80.5	8.7	5.1
n-C_8H_{17}	86	67	80.5	8.7	5.0	$C_{19}H_{25}NO$	80.6	8.8	5.0
n-C_9H_{19}	67	65–66	80.5	9.4	4.6	$C_{20}H_{27}NO$	80.8	9.1	4.7
n-$C_{10}H_{21}$	82	72–73	81.4	9.6	4.3	$C_{21}H_{29}NO$	81.0	9.3	4.5
n-$C_{12}H_{25}$	78	73–74	81.6	10.0	4.3	$C_{23}H_{33}NO$	81.4	9.7	4.1
n-$C_{14}H_{29}$	70	75.5–76.5	82.0	9.9	4.0	$C_{25}H_{37}NO$	81.7	10.1	3.8

form before purification by column chromatography. The products were not unduly light sensitive but were recrystallized several times (and decolorized with charcoal) from acetone or aqueous acetone and finally from light petroleum (b.p. 60–80°) before determination of their transition temperatures. Melting points (C-I or C-S_A transitions) and mesophase transition temperatures of the *N-oxides* of the *4-(4′-n-alkoxyphenyl)pyridines* are listed in Table I. Elemental analyses for these compounds are also given in Table I.

The following spectral data for the N-oxide of 4-(4′-n-tetradecyloxyphenyl)pyridine are representative of the series as a whole: ν_{max} (KBr) 2960, 2930, 2850, 1610, 1580, 1500, 1290, 1245, 1180, 838; δ($CDCl_3$) 0.90 (br, 3H, CH_3), 1.52 (br, 24H), 3.97 (t, J6.0 Hz, 2H, OCH_2), 7.00 (d, J9.0 Hz, 2H), 7.50 (d, J6.0 Hz, 2H), 7.61 (d, J9.0 Hz, 2H), 8.20 (d, J9.0 Hz, 2H); m/e 383 (M^+, 10.6%) 368 (12.9), 367 (50), 354 (6.0), 172 (16.8), 171 (100), 154 (3.5), 115 (4.1), 95 (1.8).

(The i.r., n.m.r., and mass spectra were determined, respectively, using a Perkin-Elmer 157G grating spectrophotometer, a Jeol JNM-C-60HL 60 Hz instrument, and an AEI MS 902 mass spectrometer).

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