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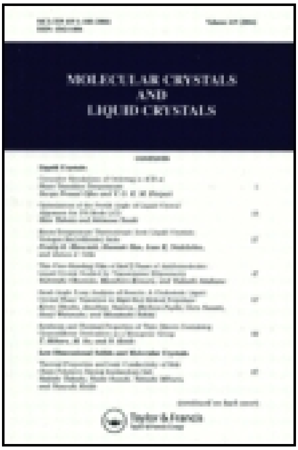

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# Properties of the Liquid Crystals Formed by the N-Oxides of Certain 4-(4′-pyridyl)phenyl 4″-n-Alkoxybenzoates: Comparison of the N-Oxide and Cyano-groups as Mesogenic Terminal Substituents

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# Properties of the Liquid Crystals Formed by the N-Oxides of Certain 4-(4′-pyridyl)phenyl 4″-n-Alkoxybenzoates: Comparison of the N-Oxide and Cyano-groups as Mesogenic Terminal Substituents

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The liquid crystal transition temperatures of the N-oxides of certain 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates are reported. The effects on smectic and nematic thermal stability of the N-oxide function and the cyano-group in terminal positions in mesogens are compared and discussed.

## INTRODUCTION

No systematic structural investigations of mesogens containing the pyridine N-oxide group have been reported. The N-oxide function has certain similarities to the cyano-group. For example, 4-phenylpyridine-N-oxide (I) and 4-cyanobiphenyl (II) have dipole moments of 4.61 D[1] and 4.33 D[2] respectively, and in each case the dipole is similarly oriented along the major axis of the molecule. We have recently published the properties of the liquid crystals formed by certain substituted 4-phenylpyridines, namely, the 4-(4′-pyridyl)-phenyl 4″-n-alkoxybenzoates,[3] and we have now prepared the N-oxides (III) of certain of these esters in order to explore whether or not the N-oxide func-

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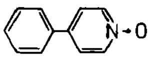
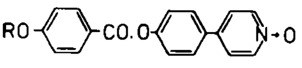
tion and the cyano-group, as terminal substituents, influence liquid crystal behavior in a similar manner. Coates and Gray have reported the properties of the liquid crystals formed by certain cyano-compounds comparable with the N-oxides (III), namely the 4′-cyano-4-biphenylyl 4″-n-alkoxtbenzoates (IVa)[4] and the 4″-n-alkoxyphenyl 4′-cyanobiphenyl-4-carboxylates (IVb).[5]† Thus, it is possible to make a direct comparison of the cyano-group and the N-oxide function as mesogenic terminal substituents.


(I)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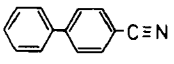
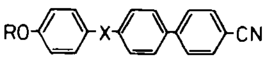

(II)


(IV) (a) X = CO.O
(b) X = O.OC

## RESULTS AND DISCUSSION

We have prepared the N-oxides of six members (n-hexyloxy through to n-nonyloxy and n-dodecyloxy and n-tetradecyloxy) of the homologous series of 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates. The transition temperatures, which were measured using a hot stage in conjunction with a polarizing microscope, are listed in Table I and are shown plotted against the number of carbon atoms, *n*, in the n-alkyl chain in Figure 1. Certain values, especially those for the relatively high N—I transitions must be regarded as slightly inaccurate because the N-oxides were: (i) difficult to maintain in a pure state as they were adversely affected by light, rapidly becoming yellow in color; and (ii) subject to substantial decomposition during slow heating to determine the transition temperatures. In order to minimize thermal decomposition due to prolonged heating, the transition temperatures were determined by insertion of the sample into the hot stage only a few degrees below the transition temperature (determined approximately on a previous sample). However, even using this technique, transitions were not precisely reversible and a repeat determination on a given sample gave a slightly lower value as a result of the progressively increasing decomposition.

Some members of the series of N-oxides exhibited two smectic mesophases, but only the most thermally stable smectic modification was identified, as smectic A, by microscopic observation of the focal conic and fan textures adopted by the birefringent phase. No assignment of type to other smectic phases was achieved because: (a) the optical textures shown were not of a type

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† Properties of the liquid crystals formed by members of the unsubstituted homologous series corresponding with (IVa)[6] and (IVb)[7] have also been published.

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TABLE I

Transition temperatures and elemental analyses for N-oxides of 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates(III)

| Substituent | | Transition Temperatures[a] (°C) | | | Found % | | | Molecular | Required % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| R | C—N | $S_A$—N | N—I | $S_A$—C[b] | C | H | N | Formula | C | H | N |
| n-$C_6H_{13}$ | 144 | [141] | 187 | 97 | 76.6 | 6.5 | 3.5 | $C_{24}H_{25}NO_4$ | 76.8 | 6.4 | 3.6 |
| | C—S | | | | | | | | | | |
| n-$C_7H_{15}$ | 129.5 | 174.5 | 185.5 | 91 | 73.9 | 6.8 | 3.3 | $C_{25}H_{27}NO_4$ | 74.1 | 6.7 | 3.5 |
| | | S—$S_A$ | $S_A$—I | S—C[b] | | | | | | | |
| n-$C_8H_{17}$ | 135 | [128.5] | 191.5 | 87 | 74.7 | 6.7 | 3.3 | $C_{26}H_{29}NO_4$ | 74.5 | 6.9 | 3.3 |
| n-$C_9H_{19}$ | 141 | 181 | 192 | 95 | 74.6 | 7.3 | 3.1 | $C_{27}H_{31}NO_4$ | 74.8 | 7.2 | 3.2 |
| n-$C_{12}H_{25}$ | 132 | [97.5] | 200 | 90 | 75.6 | 7.8 | 2.8 | $C_{30}H_{37}NO_4$ | 75.8 | 7.8 | 2.9 |
| n-$C_{14}H_{29}$ | 132 | [104.5] | 203.5 | 91 | 76.0 | 8.3 | 2.8 | $C_{32}H_{41}NO_4$ | 76.3 | 8.2 | 2.8 |

[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.

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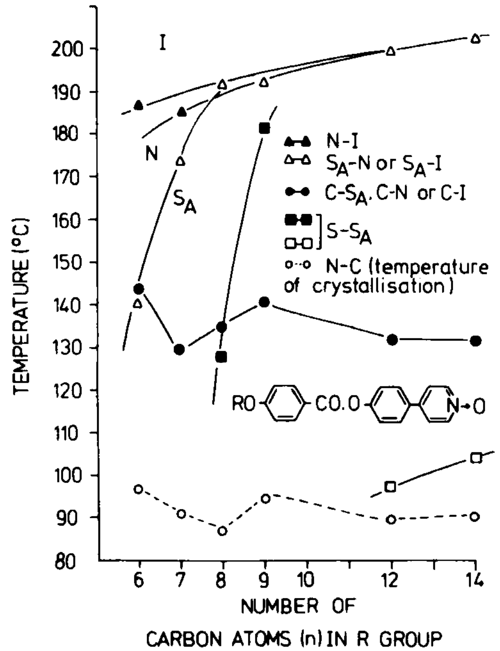

FIGURE 1 Plot of transition temperatures against alkyl chain length (*n*) for N-oxides of 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates (III).

that we were able to identify; and (b) miscibility studies with compounds having smectic mesophases of known type were not undertaken due to the problems associated with the thermal decomposition of the N-oxides.

The general shape of the plot (Figure 1) of transition temperatures against the number of carbon atoms, *n*, in the n-alkyl chain for the N-oxides of the 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates is very similar to that shown by the esters from which they are derived, namely, the 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates,[3] the points for which lie on rising curves as n increases.† As expected for a terminal substituent which is conjugated with the phenylpyridyl system and which therefore markedly increases the polarizability along the long molecular axis, the N—I transition temperatures are raised by the presence of the N-oxide group. However, this is also true of the $S_A$—I transition temperatures, and, in fact, smectic behavior dominates the series of N-oxides. Transitions to the isotropic liquid show the usual odd-even alternation, the uppermost curve corresponding with members for which n is even. Only for

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† For the N-oxides, the N—I and $S_A$—I transition temperatures lie in the region 185–205°, i.e. at the upper end of the "crossover" region where the N—I and/or S—I transition temperatures normally lie on falling curves as *n* increases.

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the first two ($n = 6, 7$) members are N—I transitions observed, the remaining ($n = 8, 9, 12, 14$) members giving $S_A$—I transitions. The n-hexyloxy and n-heptyloxy compounds also give $S_A$—N transitions, the points for which lie on a curve which rises steeply to meet the $S_A$—I transition curve for the members of the series for which $n$ is even. The n-octyloxy and n-nonyloxy and the n-dodecyloxy and n-tetradecyloxy compounds each show an S—$S_A$ transition but the phase type of this second smectic mesophase was not identified.

The effect of the dipolar N-oxide function on liquid crystal thermal stability may be evaluated in the following two ways. (i) By comparison of the series of N-oxides with the esters from which they are derived, namely the 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates.[3] This seems an appropriate comparison since the general shapes and trends of the plots of transition temperature against $n$ are very broadly similar. This comparison shows that the presence of the N-oxide function substantially increases both smectic and nematic thermal stability: $S_A$ (mean value; $n = 8, 9, 12, 14$) by 73°† and N($n = 6$) by 71°.† (ii) By comparison of the series of N-oxides with analogous members of the series of 4-biphenylyl 4″-n-alkoxybenzoates[6] (i.e. the series in which the terminal heterocyclic ring of (III) is replaced by a phenyl ring). The plot of transition temperature against $n$ for this series is of a different type,‡ and the comparison in this case indicates that the N-oxide function increases smectic thermal stability appreciably more than nematic thermal stability: $S_A$ (mean value; $n = 8, 9, 12, 14$) by 90°† and N($n = 6$) by 51°.†

Results already published enable the effect on liquid crystal thermal stability of the introduction of the cyano-group in the terminal position of the esters of biphenyl, (IVa)[4] and (IVb)[5] (relative to the corresponding unsubstituted esters[6,7]) to be assessed. The available data suggest that the terminal cyano-group, which can conjugate with the aromatic system so increasing the overall axial molecular polarizability, enhances both nematic *and* smectic thermal stability. Compared with analogous members of the unsubstituted series of esters[6,7] nematic thermal stability is substantially increased: for series (IVa) (mean value; $n = 6, 8$) by 107°,† and for series (IVb) (mean value; $n = 4, 5, 6, 7$) by 122°.† The available data limit the comparison of smectic behavior to only one member ($n = 8$ of the former series (IVa)) for which the introduction of the terminal cyano-group increases smectic ($S_A$) thermal stability by 101°.†

Although the available results are not extensive they show that the presence of the terminal cyano-group does not greatly alter the general pattern of the plots of transition temperature against $n$ observed for the unsubstituted esters, except that both nematic and smectic properties are enhanced and certain

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† The values quoted are rounded to the nearest whole number.

‡ In fact, the most commonly observed type—see footnote on p. 105 of reference 3.

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members† of both cyano-substituted series (IVa and IVb) exhibit an $S_B$ phase in addition to the $S_A$ modification. This behavior (i.e. similar plots of transition temperature against *n* together with an enhancement of smectic and nematic thermal stability and the occurrence of smectic polymorphism) is very similar to that which results when the terminally situated hetero-nitrogen atom of the 4-(4′-pyridyl)phenyl 4″-n-alkoxybenzoates is converted into the corresponding N-oxide. It is possible that the relationship between the N-oxide function and the parent hetero-nitrogen atom is chemically more fundamentally accurate as a basis for comparison than the relationship between the N-oxide function and a benzenoid >C—H group.

The comparisons indicate that there are major resemblances in the effects on liquid crystal thermal stability between the N-oxide function and the cyano-group (both of which are strongly dipolar). In a terminal position in a mesogen both substituents enhance liquid crystal thermal stability but the cyano-group has a relatively greater influence on nematic thermal stability than the N-oxide function which substantially enhances smectic properties.

An interdigitated bilayer has been proposed[8] to account for the $S_A$ layer spacings of 1.5–1.6 molecular lengths observed for the 4′-n-alkoxy- and alkyl-4-cyanobiphenyls. It has been suggested that this structure may be due to the presence of the terminal cyano-group (which is strongly dipolar). Other smectic phases of mesogens substituted by a terminal cyano-group may also possess this bilayer arrangement, and it has been suggested that a secondary consequence of the interdigitated structure may be an enhancement of smectic thermal stability. In this context it is significant that the dipolar N-oxide function also markedly enhances smectic thermal stability and it would be of interest to learn (by X-ray studies) whether or not such a bilayer arrangement exists in the $S_A$ phases of mesogens with the N-oxide function in a terminal position.

Further work on mesogenic N-oxides is in progress. However, it may be noted that the N-oxides of the 4-(2′-pyridyl)phenyl 4″-n-alkoxybenzoates are not mesogenic. Due to steric interactions these compounds are likely to be twisted about the pyridyl-phenyl bond and a steric effect of this type is known to lower mesophase thermal stability.[9,10] Nevertheless, despite this effect the compounds are high melting (e.g. the N-oxide of 4-(2′-pyridyl)phenyl 4″-n-hexyloxybenzoate melts at 163°) and no mesophases were detected presumably because the lateral cohesive forces in the crystal are markedly increased due to the presence of the laterally situated dipolar N-oxide group.

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† Coates and Gray[5] quote the following values for the transition temperatures of 4″-n-heptyloxyphenyl 4′-cyanobiphenyl-4-carboxylate: C—$S_A$, 121.5°; $S_A$—N, 108.5°; N—I, 241°. However, during the course of the present work we also synthesized this compound and found it to have both an $S_B$ and an $S_A$ phase. Professor Gray confirms that the correct data for this compound are C—$S_A$, 121.5°; $S_B$—$S_A$ [108.5°]; $S_A$—N, 153.1°; N—I, 241°. The error arose due to an editoral omission from the Table in which the results are listed in the paper by Coates and Gray.

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## EXPERIMENTAL

### 4-(4'-Pyridyl)phenyl 4"-n-alkoxybenzoates

These compounds were prepared by the method previously reported.[3]

### N-Oxides of 4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoates

The appropriate 4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoate (2.0 g) was added to a solution of glacial acetic acid (5 ml) in 100 vol hydrogen peroxide (2 ml). The reaction mixture was heated to 80° and maintained at this temperature for 24 h (half-way through this period an additional quantity of 100 vol hydrogen peroxide (2 ml) was added). The solution was then cooled and basified with 5 M-aqueous sodium hydroxide. The N-oxide was filtered off and dried, dissolved in chloroform and purified by column chromatography on alumina (100 g), eluting† with chloroform. The products were obtained in yields of 60–84% but became yellow in color on storage, especially on exposure to light. Hence, before determination of their transition temperatures the N-oxides were recrystallized several times from acetone or aqueous acetone, decolorized by treatment with charcoal, and finally recrystallized from light petroleum (b.p. 60–80°). Melting points (C—I, C—S, and C—N transitions), and mesophase transition temperatures of the *N-oxides* of the *4-(4'-pyridyl)phenyl 4"-n-alkoxybenzoates* 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'-pyridyl)phenyl 4"-n-tetradecyloxybenzoate are broadly representative of the homologous series as a whole.

$\upsilon_{max}$ (KBr) 2950, 2930, 2850, 1735, 1605, 1580, 1500, 1290, 1230, 1180 $cm^{-1}$; $\delta$ 0.85 (br, 3H, $CH_3$), 1.50 (24H), 4.04 (t, J6.0 Hz, 2H, $OCH_2$), 6.96 (d, J9.0 Hz, 2H), 7.48 (m, 6H), 8.17 (d, J9.0 Hz, 2H), 8.27 (d, J6.0 Hz, 2H); m/e 503 ($M^+$), 487, 317 (acylium ion), 205, 191, 187, 186, 172, 171, 170.

(The i.r. and n.m.r. spectra were determined, respectively, on a Perkin-Elmer 157 G grating spectrophotometer and on a Jeol JNM-C-60HL 60 Hz instrument with TMS as internal standard. Mass spectra were obtained using an A.E.I. MS 902 instrument.)

### Acknowledgments

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† The fractions collected were monitored by tlc (alumina/$CHCl_3$). The N-oxides had $R_f$ values of approximately 0.10.

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