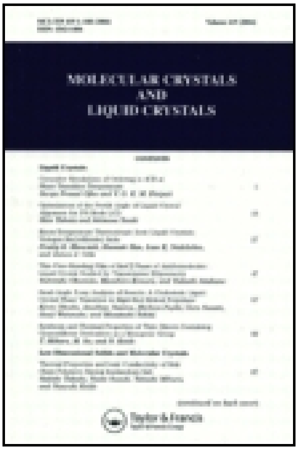

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The Liquid Crystal Properties of Some Cyano-Substituted Aryl Esters

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The Liquid Crystal Properties of Some Cyano-Substituted Aryl Esters†

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Forty-five aryl esters (R—Ar—CO·O—Ar′—CN) containing terminal cyano and R = alkyl or alkoxy substituents were prepared. The aryl moieties of the esters were either 1,4-phenylene, 2,6-naphthylene or 4,4′-biphenylene. All combinations of these aryl groups were examined and the liquid crystal properties are compared with one another and with those for analogous phenyl benzoate esters. All the compounds were nematogenic, and it was found possible to predict the effect of a naphthylene or biphenylene group, relative to a phenylene group, on the nematic-isotropic liquid (N–I) value. This information was used to predict the properties of other esters. Some side-substituted esters of the same kind were also examined, and depressions in melting point and in N–I values compared with the unsubstituted compounds were found. The effects of each aromatic moiety on the dielectric permittivities were determined and the results are compared for the various esters.

INTRODUCTION

Suitably substituted aryl esters of aromatic acids provide a convenient source of fairly readily prepared nematogenic compounds. The aromatic systems employed in such esters have usually been simple 1,4-phenylene rings and the molecules have incorporated either one or two ester linkages, e.g., *p*-substituted benzoic acids esterified with *p*-substituted phenols[1,2] or substituted benzoyloxybenzoate esters[3] or derivatives of terephthalic acid.[2,5] Recently we reported[6] on some esters derived from 4-substituted biphenyl-4-carboxylic acids and *p*-substituted phenols. In the present work we have extended that study to cover various combinations of 1,4-disubstituted phenylene, 4,4′-disubstituted biphenylene and 2,6-disubstituted naphthylene ring systems. The effects of changing the aromatic entity on the liquid crystal properties have therefore been established.

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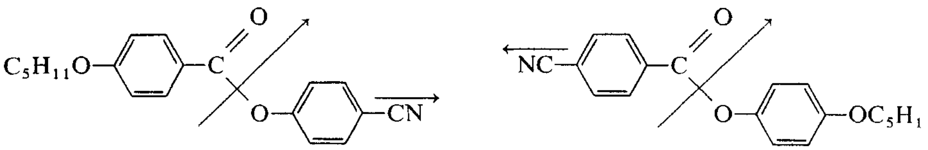
Certain modes of electro-optical display device require compounds having as large a positive dielectric anisotropy as possible, along with the usual desirable features such as low melting point, stability, and lack of colour. To obtain esters having a high positive dielectric anisotropy, a highly polar group, such as a cyano group, is usually incorporated terminally, with its dipole acting along the long axis of the molecule. However, in esters which are already polar by virtue of the —CO·O— group, the position of the cyano group relative to the ester linkage is also important. Klingbiel *et al.*[7] have shown this for phenyl benzoate esters of structures I(a) and I(b).



$\varepsilon_{\parallel} = 27.80$; $\varepsilon_{\perp} = 11.66$

$\Delta\varepsilon = 16.14$

(a)

I

$\varepsilon_{\parallel} = 10.60$; $\varepsilon_{\perp} = 6.04$

$\Delta\varepsilon = 4.56$

(b)

These results are explained in terms of the dipole moments of the cyano group and the ester linkage either opposing (I(b)) or reinforcing (I(a)) each other.

However, the liquid crystal transition temperatures are also affected by the relative positions of the cyano and ester groups. Table I gives some results which show that the presence of the cyano group in the phenolic moiety, which will lead to much higher positive dielectric anisotropies, gives slightly lower N–I transition temperatures.

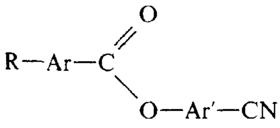
Since our main interest was in compounds of high positive dielectric anisotropy, we therefore examined esters of general structure II in which the cyano group is attached to the phenolic residue.

TABLE I

Temperatures of transition, in °C for various esters incorporating phenylene and biphenylene systems

	C–N	N–I	Ref.
$C_6H_{13}O{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CN$	121°	233°	6
$NC{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}OC_6H_{13}$	119.8°	253°	6
$C_5H_{11}{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CN$	110.8°	229.1°	–
$NC{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}C_5H_{11}$	122.7°	241.6°	6
$C_5H_{11}O{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CN$	87°	[77°]	7
$NC{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}C_5H_{11}$	93°	[90°]	7

[ ] = monotropic transition.



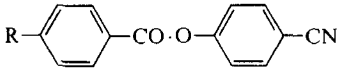
II

where R = *n*-alkyl or *n*-alkoxy and Ar and Ar′ = 1,4-phenylene, 2,6-naphthylene or 4,4′-biphenylene.

Useful standard materials with which the aryl esters (II) can be compared are the 4-cyanophenyl 4′-alkyl- (and 4′-alkoxy-) benzoates.[7–9] Data for such standard esters are given for comparison in Table II.

TABLE II

Temperatures of transition, in °C, for 4-cyanophenyl 4′-*n*-alkyl- and 4′-*n*-alkoxy-benzoate esters.



R	C–N	N–I	Ref.
n-C_4H_9	67.1°	42.6°	9
n-C_5H_{11}	64.6°	[57.8°]	8
n-C_6H_{13}	44.5°	47°	9
n-C_7H_{15}	44°	57°	7
n-$C_5H_{11}O$	87°	[77°]	7
n-$C_7H_{15}O$	70.4°	77.8°	8

[ ] = monotropic transition.

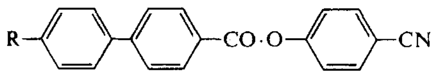
DISCUSSION AND RESULTS

The results in Table III, compared with the data in Table II, show the effects of replacing a 1,4-phenylene group by a 4,4′-biphenylene group. The N–I value has been increased by 160–170° for esters of type (A) and by 170–180° for esters of type (B). The very large increases in N–I value compared with the corresponding phenyl benzoates (Table II) can be explained in terms of the increased molecular lengths and polarisabilities of the biphenylene esters. However, it is interesting to find that the greater increases in N–I values occur when the phenolic residue is replaced (type (B) esters). Due to their unpredictable nature, melting points cannot be compared in the same way as N–I values. However, a range over which the melting points typically occur can often be quoted for the C_4–C_8 members of an homologous series. In these examples, type (A) esters have melting points some 35–50° higher and type (B) esters have melting points some 20–45° higher than the corresponding phenyl benzoate esters.

TABLE III

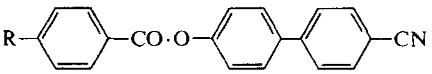
Transition temperatures, in °C, for (A) 4-cyanophenyl 4″-substituted-biphenyl-4′-carboxylates and (B) 4-cyano-4′-biphenylyl 4″-substituted benzoates

(A)



R	C-N	N-I
n-$C_6H_{13}O$	121°	233°
n-$C_8H_{17}O$	114°	221°
n-C_5H_{11}	110.8°	229.1°

(B)



R	C-N, S_A or S_B	S_B-S_A	S_A-N	N-I
n-$C_6H_{13}O$	103°	—	—	246°
n-$C_8H_{17}O$	97.3°	138.3°	198.7°	235.3°
n-C_4H_9	110°	—	—	242°
n-C_5H_{11}	109°	—	—	237.5°
n-C_6H_{13}	91°	—	—	229.6°
n-C_7H_{15}	92.1°	—	—	224.4°
n-C_8H_{17}	88°	—	183°	215.3°
n-C_9H_{19}	91.5°	—	196.1°	210.2°

The 2,6-disubstituted naphthylene system was clearly shown[10] to be conducive to forming liquid crystals in the case of the series of 6-*n*-alkoxy-2-naphthoic acids. However, rather few other liquid crystal systems have been prepared which incorporate this aryl group. Table IV now shows the results of using this group in esters.

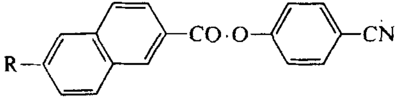
Relative to the corresponding phenyl benzoate esters, the esters listed in Table IV have much higher N-I values—some 65–75° for type (A) esters and 85–95° for type (B) esters; the greater increases in N-I values relative to phenyl benzoate esters are found when the phenolic residue is replaced (type (B) esters). The effects on the melting points cannot be realistically compared for type (A) esters, but for type (B) esters, an increase of 25–35° is typical compared with the phenyl benzoate esters.

Relative to the biphenylene/phenylene esters (Table III), the naphthylene/phenylene esters have lower melting points (typically 10–20°) and lower N-I values (80–90°). The difference in N-I value can be explained in terms of the naphthylene system being shorter and broader than the biphenylene system.

TABLE IV

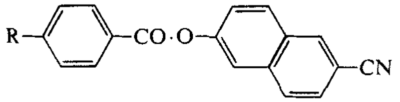
Transition temperatures, in °C, for (A) 4′-cyanophenyl 6-substituted-2-naphthoates and (B) 6-cyano-2-naphthyl 4′-substituted-benzoates

(A)



R	C–N	N–I
n-C_5H_{11}	84.5°	139.5°
n-$C_5H_{11}O$	145°	153.5°
n-$C_6H_{13}O$	102°	148.8°
n-$C_7H_{15}O$	90–107°	143.1°

(B)



R	C–N or S_A	S_A–N	N–I
n-$C_6H_{13}O$	95°	—	160°
n-$C_8H_{17}O$	92.8°	—	156.1°
n-C_3H_7	99.5°	—	159.9°
n-C_4H_9	80.8°	—	142.3°
n-C_5H_{11}	96.5°	—	154.3°
n-C_6H_{13}	72.8°	—	138.4°
n-C_7H_{15}	69.5°	—	135.3°
n-C_8H_{17}	68.6°	—	131.2°
n-C_9H_{19}	74°	105.9°	131.1°

Melting point differences for these esters cannot really be discussed in very precise terms. For instance, in Table IV, there is a great difference in melting point between the C_5 and C_6 compounds which are nonetheless adjacent members of an homologous series (type (A) esters). Also, in Table IV, the *n*-heptyloxy compound melts over a very wide temperature range, even though it was rigorously purified. Differential thermal analysis (DTA) shows that a very broad hump-shaped peak occurs at the "melting point," after a sharp crystal–crystal change. Presumably several different solid forms must be melting at similar temperatures. Indeed, many of the esters can exist in several crystal forms, and throughout this article, the melting point of the most stable solid form is quoted. This was determined on a first heating cycle either using DTA or a Mettler FP52 hot stage. Even after a week, the original melting point of many of the esters could not be re-obtained after they had once been melted and allowed to recrystallise from the melt.

When combinations of naphthylene and biphenylene ring systems are used, mesogens with very high N–I values result (Table V).

If the general effects of naphthylene and biphenylene ring systems, relative to the phenylene ring system, on the N–I values found earlier in this work are used to predict the N–I values of the *n*-heptyloxy members of these series (Table V), N–I values of about 310° are to be expected; this is in reasonable agreement with the experimental results. Decomposition of the esters at such high temperatures inevitably means lower recorded N–I values than the real values. The melting point prediction is however a little high at 140–160°.

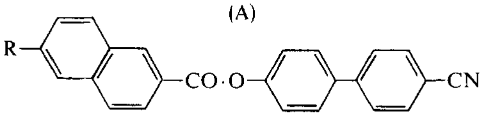
Table VI shows the results obtained when two biphenylene ring systems are used. The N–I values were too high to measure before extensive decomposition occurred. The N–I values predicted for these compounds are very high—about 380° for the *n*-pentyl compound.

When two naphthylene systems are used, the N–I value is still quite high; some results are given in Table VII.

TABLE V

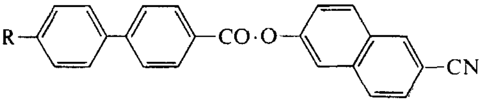
Temperatures of transition, in °C, for (A) 4-cyano-4′-biphenylyl 6″-substituted-2″-naphthoates and (B) 6-cyano-2-naphthyl 4″-substituted-biphenyl-4′-carboxylates

(A)



R	C–N	C–I
n-$C_7H_{15}O$	136°	304°(d)

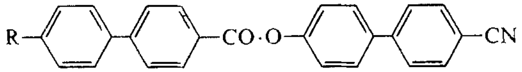
(B)



R	C–N	N–I
n-C_4H_9O	158°	>300°(d)
n-$C_7H_{15}O$	132°	292°(d)
n-$C_8H_{17}O$	109°	269°
n-C_5H_{11}	136°	307°

TABLE VI

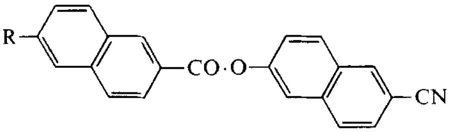
Temperatures of transition, in °C, for 4-cyano-4'-biphenylyl 4'''-substituted-biphenyl-4''-carboxylates



R	C–S_A	S_A–N	N–I
n-C_5H_{11}	140°	166.0°	$\gg$280°(d)
n-$C_7H_{15}O$	128°	173.4°	$\gg$300°(d)

TABLE VII

Temperatures of transition, in °C, for 6-cyano-2-naphthyl 6'-substituted-2'-naphthoates



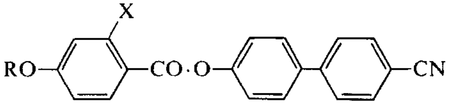
R	C–N	N–I
n-C_5H_{11}	145°	224°
n-$C_5H_{11}O$	105°	231.1°
n-$C_6H_{13}O$	118°	230.8°
n-$C_7H_{15}O$	110°	216°

The n-pentyl member of this series is predicted, from the earlier results, to have an N–I value of about 210–230° and the n-pentyloxy member to have an N–I value of about 230–250°. Both these predictions are in close agreement with the experimental values. However, the predicted melting points are either too high (the n-pentyloxy member is predicted to melt at about 135–145°) or too low (the n-pentyl member is predicted to melt at about 115–125°).

It is often found[3,11] that suitably side-substituting a molecule lowers the melting point of the compound, although the mesophase thermal stability is usually also lowered. Table VIII shows the effect of a methyl substituent in the position ortho to the carboxyl group of one ester system; this position has been found to be the best for obtaining depressions of melting point. Compared with the unmethylated compounds (Table III), the melting points of the substituted esters are 16–27° lower. However, the N–I value has been lowered by about 65°, and as a result the nematic range is much shorter. When the side-substituent is chloro, a group of very similar size to methyl but one

TABLE VIII

Temperatures of transition, in °C, for 4-cyano-4'-biphenylyl 2''-substituted-4''-alkoxy-benzoates



R	X	C-N	N-I
n-C_4H_9	CH_3	113.3°	201.5°
n-C_5H_{11}	CH_3	85°	188.8°
n-C_6H_{13}	CH_3	80°	184.0°
n-C_7H_{15}	CH_3	79.1°	170.7°
n-C_8H_{17}	CH_3	81.5°	169°
n-C_6H_{13}	Cl	89°	178.5°

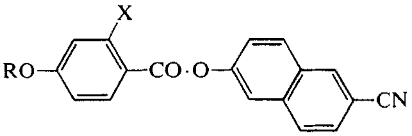
which is much more polar, the N-I value is 3.5° lower and the melting point is 13° higher than for the methyl-substituted analogue.

The results in Table IX show that when a shorter molecule is side-substituted, the lowering of the N-I value is even greater; the decrease is 77° for the methyl substituent. In the cases quoted, the effect on the melting point is a lowering by 10° for the methyl substituted compound and an increase of 18° for the chloro substituted compound.

In conclusion therefore, by extending the length and polarisability of the molecule by the use of different aromatic systems, compounds with higher N-I values than the simple phenyl benzoates can be obtained. The increase in N-I value can often be predicted with reasonable accuracy, considering that the *overall* shape of the molecule is not being taken into account. The prediction of melting points is naturally less secure, but often a range can be quoted which lies somewhere near the experimental value.

TABLE IX

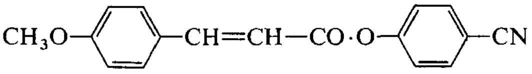
Temperatures of transition, in °C, for 6-cyano-2-naphthyl 2'-substituted-4'-alkoxy benzoates



R	X	C-I	N-I
n-C_6H_{13}	Cl	103°	—
n-C_6H_{13}	CH_3	85°	[83°]

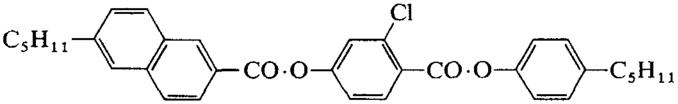
[ ] = monotropic transition

It should also be noted that olefinic linkages can be used to lengthen a molecule and increase its polarisability. However, compounds containing such double bonds are fraught with the dangers of instability, cf., stilbenes,[12] and certain vinyl compounds.[13] We did however examine a cinnamate ester, namely 4-cyanophenyl 4′-methoxycinnamate (III). This compound has the constants, C–N, 155°; N–I, 160.7°. However, after a few days' exposure to ordinary light, at room temperature and in a closed sample tube, the N–I value fell to 149–151° and the C–N value to 151°. After a week's exposure under the same conditions, it was found by n.m.r. spectroscopy that about 25% of the *cis*-cinnamate ester had formed. Originally, the entire sample consisted of the *trans*-cinnamate ester which is the isomer that is conducive to formation of liquid crystal phases. This marked instability to light did not of course occur with the other esters under study or indeed with phenyl benzoate esters.

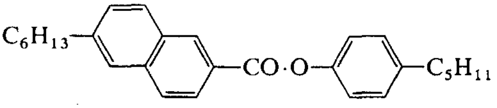


III

The results of this work can be used to help in the design of other interesting mesogenic materials with different degrees of dielectric anisotropy. For instance, certain other esters have been prepared of which structures IV(a) and (b) are examples (further, detailed results relating to such esters will be published later).



(a)



(b)

IV

The compound IV(a)—4-*n*-pentylphenyl 4′-(6″-*n*-pentyl-2″-naphthoyloxy)-2′-chlorobenzoate—has the constants C–N, 60°; N–I, 191.5°. The corresponding ester containing only 1,4-phenylene rings has the constants[4] C–N, 40°; N–I, 122°. Therefore, an increase in N–I value of 69.5° is found, which is within the range predicted earlier (65–75°). The melting point increase of 20° is slightly less than the predicted increase of 25–30°.

The compound IV(b)—*n*-pentylphenyl 6-*n*-hexyl-2-naphthoate—has the constants C–N, 47.0°; N–I, 84.5°; the corresponding, purely phenylene compound has the constants[2] C–I, 28°; N–I, [19°]. Therefore, an increase in N–I value of 65.5° and an increase in melting point of 19° are obtained. These increases are again close to the predicted increases quoted above for ester IV(a).

The dielectric permittivities, measured perpendicular ($\varepsilon_\perp$) and parallel ($\varepsilon_\parallel$) to the long molecular axes, were obtained for several of the esters using a frequency of 10 kHz and a temperature of 120°C. Table X shows the results obtained. It is estimated that the error in these measurements could be ±10-15%. Therefore, the values are used for qualitative comparisons only.

When the esters contain either a naphthylene or a biphenylene system, it is clear that the dielectric anisotropy ($\Delta\varepsilon$) is lower for the ester containing that ring system in the phenolic residue, than when it is in the carboxylate residue.

From a comparison of the $\Delta\varepsilon$ value for examples C and D in Table X, with the $\Delta\varepsilon$ value for the phenyl benzoate ester of structure I(a), it is seen that the dielectric anisotropy is higher for the phenyl benzoate ester than it is for the corresponding ester containing the naphthylene ring system. It should be noted that the values quoted for structure I(a) were measured at $0.98 \times T_{N-I}$ °K, that is at about 7°C below the N–I value, whereas those given in Table X, for examples C and D, were measured 36° and 28°C below the N–I value, respectively. It is known that $\Delta\varepsilon$ values decrease with increasing temperature up to the N–I value, and therefore, it is to be expected that the actual difference in $\Delta\varepsilon$ (measured at the same reduced temperature) between say a phenylene and a naphthylene ester will be even larger than indicated. Also, the values for the biphenylene—containing esters (examples A and B) indicate that $\Delta\varepsilon$ will be much smaller than that for the phenyl benzoate esters (structure I(a)) if these are measured at the same reduced temperature.

TABLE X

(a) Temperatures of transition, in °C, (b) dielectric permittivities measured at 120°C both perpendicular ($\varepsilon_\perp$) and parallel ($\varepsilon_\parallel$) to the long molecular axes, and (c) the dielectric anisotropies ($\Delta\varepsilon$) for a range of cyano-substituted aryl esters

		C–N	N–I	$\varepsilon_\perp$	$\varepsilon_\parallel$	$\Delta\varepsilon$
A	$n\text{-}C_7H_{15}\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot C_6H_4\cdot CN$	92.1°	224°	6.8	17.6	10.8
B	$n\text{-}C_5H_{11}\cdot C_6H_4\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CN$	110.8°	229.1°	8.2	21.4	13.2
C	$n\text{-}C_8H_{17}O\cdot C_6H_4\cdot CO\cdot O\cdot C_{10}H_6\cdot CN$	92.8°	156°	7.3	18	10.7
D	$n\text{-}C_6H_{13}O\cdot C_{10}H_6\cdot CO\cdot O\cdot C_6H_4\cdot CN$	102°	148.8°	9.9	21.3	11.4
E	$n\text{-}C_8H_{17}O\cdot C_6H_4\cdot C_6H_4\cdot CO\cdot O\cdot C_{10}H_6\cdot CN$	109°	269°	5.9	13.2	7.3
F	$n\text{-}C_5H_{11}O\cdot C_{10}H_6\cdot CO\cdot O\cdot C_{10}H_6\cdot CN$	105°	231.1°	7.8	19.2	11.4
G	$n\text{-}C_6H_{13}O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot C_6H_4\cdot CN$	93°	246°	4.8	16.2	11.4
H	$n\text{-}C_6H_{13}O\cdot OC_6H_3Cl\cdot CO\cdot O\cdot C_6H_4\cdot C_6H_4\cdot CN$	89°	178.5°	8.1	21.7	13.6
J	$n\text{-}C_6H_{13}O\cdot C_6H_3CH_3\cdot CO\cdot O\cdot C_6H_4\cdot C_6H_4\cdot CN$	80°	184°	7.0	22.1	15.1

The most realistic comparison of analogous naphthylene—and biphenylene—containing esters is given by examples E and F in Table X. These indicate that a much lower $\Delta\varepsilon$ value occurs for the biphenylene-containing esters than for the naphthylene-containing esters.

Examples G, H and J in Table X show the effects of side-substituents on $\Delta\varepsilon$. Not surprisingly, the $\varepsilon_\perp$ value is increased greatly on passing from compound (G) to the chloro-substituted compound (H). However, the $\Delta\varepsilon$ value is greater for (H) than for unsubstituted compound (G) due to the latter's much increased $\varepsilon_\parallel$ value. The methyl-substituted compound (J) has however the largest $\Delta\varepsilon$ value due to its lower $\varepsilon_\perp$ value than that for (H), and its very large $\varepsilon_\parallel$ value.

Further development work on esters of the kind described in this paper and on the formulation of mixtures is in progress.

EXPERIMENTAL

Preparation of 4-alkylbenzoic acids

These known materials were prepared by Friedel–Crafts acylation[15] of alkylbenzenes, followed by hypobromite oxidation[16] of the 4-alkylacetophenones to the corresponding acids.

Preparation of 4-alkoxybenzoic acids

These known materials were prepared by alkylating[16] 4-hydroxybenzoic acid.

Preparation of 2-methyl-4-alkoxybenzoic acids

These acids were prepared from *m*-cresol which was first acetylated,[17] and the resultant 3-methylphenyl acetate was reacted with aluminium chloride, thereby undergoing a Fries Rearrangement.[19] The product, 4-hydroxy-2-methylacetophenone, was alkylated[18] by stirring and heating under reflux with a mixture of alkyl bromide, anhydrous potassium carbonate and cyclohexanone. Attempts to purify the acids[16] were first made by repeated recrystallisation of the products from ethanol/water. However, mass spectrometry showed that a small percentage of impurity containing bromine was always present. This could not be removed from the acids, but when these were esterified, the esters (see Tables VIII and IX) were easily separated from the impurity by column chromatography using silica gel and chloroform/hexane as eluent. The bromine-containing impurity arose due to bromination of the very active aromatic ring during the hypobromite oxidation.

Preparation of 4′-*n*-pentylbiphenyl-4-carboxylic acid

This acid was prepared by interaction[20] of pentanoyl chloride with biphenyl, followed by reduction[21] of the ketone to 4-*n*-pentylbiphenyl. This was then acetylated[20] and the ketone oxidised[16] to 4′-*n*-pentylbiphenyl-4-carboxylic acid, C–S, 174°; S–N, 201°; N–I, 258°.

Preparation of 4′-*n*-alkoxybiphenyl-4-carboxylic acids

These acids were prepared as described in the literature.[6]

Preparation of 6-alkyl-2-naphthoic acids

These acids were prepared by Friedel–Crafts acylation of naphthalene by adding the appropriate alkanoyl chloride (0.33 mol) to a cooled (0°C) mixture of naphthalene (0.3 mol), and nitrobenzene (155 ml). Aluminium chloride (0.35 mol) was gradually added to the cold, stirred reaction mixture over 2 h. The mixture was allowed to stand at 0°C overnight; the reaction mixture was protected from atmospheric moisture by calcium chloride tubes. The dark mixture was then poured onto ice, concentrated hydrochloric acid and water and stirred for 30 min. The nitrobenzene layer was separated, dried and the solvent distilled. The required ketones boil at about 170–180°C at 4 mm Hg, and solidify on cooling.

The corresponding 2-alkylnaphthalenes were prepared by reducing[8] the ketones.

The corresponding 6-acetyl-2-alkylnaphthalenes were prepared by Friedel-Crafts acylation, using a procedure similar to that described earlier, except that acetyl chloride was added last to a cold mixture of aluminium trichloride, nitrobenzene and the 2-alkylnaphthalene. The reaction mixture was allowed to stand at room temperature for 40 h. The products were isolated by distillation (b.p. about 160° at 0.2 mm Hg). The isomers formed and isolated from the reaction mixture were separated by column chromatography on silica gel using chloroform/hexane as eluent. This gave the 6-acetyl-2-alkylnaphthalene whose purity was checked by nuclear magnetic resonance spectroscopy. The yields from this step were usually about 30%.

The corresponding acids were then obtained by hypobromite oxidation[16] of the ketones. Transition temperatures for three of the 6-alkyl-2-naphthoic acids were: *n*-butyl, C–N, 156°; N–I, 183°: *n*-pentyl, C–N, 143°; N–I, 185°: *n*-hexyl, C–N, 141°; N–I, 178°.

Preparation of 6-alkoxy-2-naphthoic acids

These were prepared by the methods used by Gray and Brynmor Jones.[16]

Preparation of 4-cyano-4′-hydroxybiphenyl

This was prepared from 4-bromo-4′-benzenesulphonyloxybiphenyl by first hydrolysing it to 4-bromo-4′-hydroxybiphenyl using sodium hydroxide dissolved in a mixture of water and dioxan. The colourless crystals obtained by recrystallisation from ethanol had m.p. 166°. Cyanation of the 4-bromo-4′-hydroxybiphenyl by a method described earlier,[18] and purification of the product by recrystallisation from water/ethanol gave a m.p. of 198°.

Preparation of 6-cyano-2-hydroxynaphthalene

This was prepared by cyanation[18] of 6-bromo-2-hydroxynaphthalene and purified (m.p. 160°) by recrystallisation from water/ethanol.

Preparation of esters

These were prepared by reacting the acid chloride (Ar·COCl) (0.01 mol) prepared by the reaction of the acid and thionyl chloride, with the corresponding phenol (4-cyano-4′-hydroxybiphenyl, 6-cyano-2-hydroxynaphthalene or 4-cyanophenol) (0.012 mol) in dry pyridine (80 ml) at 0°C. The reaction mixture was stirred overnight, during which time the temperature was allowed to rise to room temperature. It was then heated to 70° for 30 min, evaporated to dryness, under reduced pressure, and the residual ester purified by column chromatography on silica gel using either chloroform or chloroform/hexane as eluent. Some of the esters were chromatographed twice, particularly those derived from 2-methyl-4-alkoxybenzoic acids and naphthoic acids, in order to ensure that they were absolutely pure, single component materials. Each ester was then recrystallised until constant liquid crystal transition temperatures (see Tables III to IX) were obtained. The identity of each ester was checked by mass spectrometry and nuclear magnetic resonance spectroscopy, and in all cases satisfactory elemental analysis results were obtained.

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