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Properties of the Liquid Crystals Formed by Some 4′,4″-Disubstituted Phenyl Biphenyl-4-carboxylates

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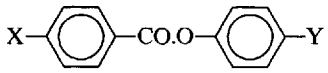
Thirteen 4′,4″-disubstituted phenyl biphenyl-4-carboxylates have been prepared and their liquid crystal transition temperatures measured. In each case, one of the substituents is a cyano-group and the nematic phases are of positive dielectric anisotropy. The potential of these esters to produce low melting eutectic compositions with a wide nematic range on admixture with simpler 4,4′-disubstituted phenyl benzoates is assessed in relation to requirements for electro-optical displays such as the twisted nematic type.

INTRODUCTION

The 4,4′-disubstituted phenyl benzoates (I) are well known mesogens, and when one of the substituents, X or Y is a cyano-group, the nematic phases

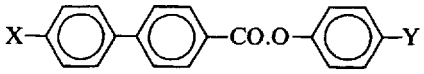


(I)

formed are of interest because of their high positive dielectric anisotropies.[1–4] However, the melting points (C–N temperatures) of such cyano-esters are not particularly low, e.g., with $X = n\text{-}C_7H_{15}O$ and $Y = CN$, C–N is 71.6° and the nematic-isotropic transition (N–I) is at 82°, and with $X = n\text{-}C_7H_{15}$ and $Y = CN$, C–N is 44° and N–I is 56.6°. Therefore, to obtain materials with C–N < 0° suitable for use in electro-optical displays of the twisted nematic type,[5] it is necessary to formulate eutectic mixtures of such cyano esters either alone[1] or in admixture with lower melting esters,

often of lower positive dielectric anisotropy, e.g., $X = n$-alkoxy, $Y = n$-alkyl,[3] and/or with esters with much higher N–I values such as the 4′,4″-disubstituted derivatives of phenyl 4-benzoyloxybenzoate.[2] For such a three ring ester to be useful, it should also have a low C–N value ($< 100°$) and a low enthalpy of fusion (< 6 kcal mol^{-1}). The methods for obtaining such mixtures are either experimental[3] or based on ideal solution theory.[3,6]

We have investigated the mesomorphic properties of the esters (II) derived from 4′-substituted biphenyl-4-carboxylic acids, i.e., the 4′,4″-disubstituted phenyl biphenyl-4-carboxylates, where either X or Y is CN and either Y or X is n-alkyl or n-alkoxy, respectively.



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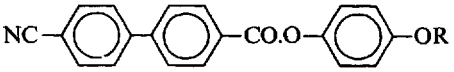
RESULTS AND DISCUSSION

The 4″-n-alkoxyphenyl 4′-cyanobiphenyl-4-carboxylates ((III), where $R = n$-alkyl) from methoxy to n-heptyloxy were prepared and exhibit very high



(III)

N–I transition temperatures (Table I). The plot (Figure 1) of the N–I transition temperatures against the number of carbons (n) in the n-alkyl chain shows the usual odd-even alternation, i.e., two falling curves can be drawn through the points, the lower curve for esters with an odd value of n. The melting points are rather irregular in their distribution along the series, the lowest being 110–110.5°C for the n-pentyloxy compound. Smectic properties are not pronounced in this series; in fact, smectic phases are observed readily only for the n-pentyloxy and n-heptyloxy members. In each case, the smectic phase is monotropic with respect to the solid. The n-hexyloxy compound crystallises very easily on cooling the nematic phase, and it was not possible to determine the monotropic smectic-nematic (S–N) transition temperature with any accuracy because rapid cooling is required if the phase is to be seen at all. Therefore, it could not be established whether an alternation of the S–N transition temperatures occurs along the series. The smectic phases of the C_5 and C_7 members were identified microscopically as smectic A.

TABLE I

Thermodynamic data for *4′4″-disubstituted phenyl biphenyl-4-carboxylates* (II)

Substituents		Transition temperatures[a]			Enthalpy of fusion[b]
X	*Y*	C–N	S_A–N	N–I	ΔH (kcal mol^{-1})
CN	OCH_3	158°	—	315°	6.4
CN	OC_2H_5	161	—	308	7.4
CN	OC_3H_7-*n*	146	—	281	6.7
CN	OC_4H_9-*n*	114.5	—	272	10.2
CN	OC_5H_{11}-*n*	110.5	[98.2°]	258.2	7.0**
CN	OC_6H_{13}-*n*	119.8	—	253	7.7***
CN	OC_7H_{15}-*n*	121.5	[108.5]	241	8.0***
n-$C_6H_{13}O$	CN	121	—	233	9.3*
n-$C_8H_{17}O$	CN	114	—	221	11.4*
CN	CH_3	189	—	272	6.2
CN	C_2H_5	147	—	257	6.8
CN	C_3H_7-*n*	125.8	—	245	7.1
CN	C_4H_9-*n*	108.5	—	225	6.9

[a] Transition temperatures were measured using a Mettler FP52 or a Kofler hot stage.

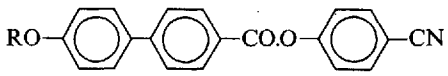
[b] Enthalpies of fusion were measured using a Stanton–Redcroft differential thermal analyser, model 671. The ΔH values for the S_A–N transitions were in the range 0.8–1.0 kcal mol^{-1} and for the N–I transitions in the range 0.3–0.5 kcal mol^{-1}.

* Each asterisk indicates the occurrence of a crystal-crystal change detected on heating the sample from room temperature.

[ ] Monotropic transition.

The enthalpies of fusion are rather high and, bearing in mind the rather high melting points, could limit the usefulness of these compounds in forming eutectic mixtures of low melting point.

With the possibility of obtaining lower melting points and enthalpies of fusion in these types of ester, the end groups were reversed. Two members of the series of 4″-cyanophenyl 4′-*n*-alkoxybiphenyl-4-carboxylates ((IV), where R = *n*-alkyl) were prepared.



(IV)

However, their enthalpies of fusion are even higher than those of the 4″-alkoxyphenyl esters (III), and the melting points are similar. These properties, combined with the considerably lower N–I transition temperatures (Table I) may limit the value of these compounds as additives in eutectic compositions. This series was not explored further.

However, a point in favour of the esters (IV) is the lowering of the smectic phase thermal stability compared with the 4″-alkoxyphenyl esters. No

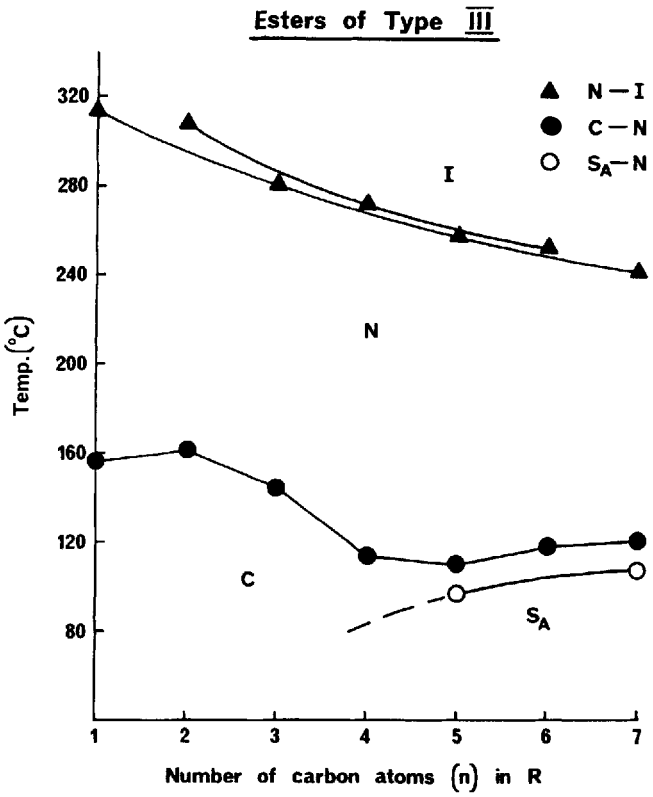
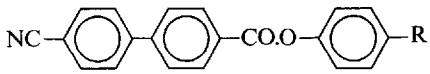


FIGURE 1 Plot of transition temperatures against alkyl chain length (n) for the 4″-n-alkoxyphenyl 4′-cyanobiphenyl-4-carboxylates (III).

smectic phase could be detected even on rapid cooling of the nematic phase of the n-hexyloxy ester, and it is estimated that the "S–N" transition temperatures must have been lowered by more than 20°C. Therefore a nematic mixture containing esters (IV) will be less likely to contain pre-transitional, smectic cybotactic groups than a nematic mixture involving the more smectogenic esters (III). Such cybotactic groups can lead to adverse viscosity increases in the lower regions of a nematic temperature range.

It is often found that the aryl-alkyl analogues of aryl-alkoxy compounds have appreciably lower melting points and somewhat lower N–I transition temperatures; the effect of this structural change on C–N enthalpies is not well documented. In an attempt to obtain considerably lower melting points and C–N enthalpies without diminishing the N–I transition temperatures too much, four 4″-alkylphenyl 4′-cyanobiphenyl-4-carboxylates ((V),



(V)

where R = n-alkyl) were prepared. As can be seen from the results in Table I, the N–I transition temperatures are in fact lowered considerably (about 40–50°) compared with those for the esters (III); except for R = methyl, the melting points are also lower, as are the enthalpies of the C–N transitions. No smectic phases were detected. Taking into account the much lower N–I transition temperatures and the slightly lower melting points and C–N enthalpies, it would seem that the potential usefulness of the compounds (V) might be similar to that of the esters (III) for the formulation of eutectic mixtures of low melting point. From work[13] on dielectric anisotropies of benzoate esters, esters of type (IV) would be expected to have a larger positive dielectric anisotropy than esters (III) and (V). However, in the small concentrations in which it is subsequently shown that these esters can be used in mixtures, it seems unlikely that any significant difference in device performance would be observed as a consequence.

Because of the enhanced anisotropies of molecular polarisability, the esters (III), (IV) and (V) have much higher N–I transition temperatures than the ester (I), but on the debit side, their melting points are higher than those of the simpler esters (I). Therefore, it is unlikely that mixtures of the esters (III), (IV) and (V) alone will produce low melting mixtures. However, these esters might, when added to other low melting nematogens having similar structures, e.g., esters of type (I), or quite different structures, produce eutectic mixtures with wider nematic ranges, i.e., they could perform a similar function to that of the disubstituted derivatives of phenyl 4-benzoyloxybenzoate.[2]

Calculations based on ideal solution theory and involving the Le Chatelier, Schröder, and van Laar equation,[6] were performed using a Digico Micro 16V computer for binary, ternary, and quaternary mixtures of the esters ((III), (IV) and (V)). These indicated that very wide nematic range mixtures could be obtained. For instance, the mixture containing ester (III), where X = CN and Y = OC_5H_{11}-n, and ester (V), where X = CN and Y = C_4H_9-n, in the molar ratio 46.4:53.6%, respectively, has the calculated constants, C–N, 78°; N–I, 240°C. However, experimentally this mixture has the constants, C–N, 98–100°; N–I, 240°C. This deviation from the calculated C–N value is not uncommon when compounds of very similar molecular structure are mixed together, and it has been noted before with other three-ring mesogens. For instance, the 4-alkyl-4″-cyano-p-terphenyls show very little depression in melting point when mixed together, but when mixed with 4-alkyl-4′-cyanobiphenyls, they show large melting point depressions[6,7] and

obey the equation mentioned above. Likewise, when esters (III), (IV) and (V) are mixed with 4-alkyl-4′-cyanobiphenyls or with various benzoate esters of type (I), large depressions in melting point are observed.

Therefore, to explore the possibility that the high N–I temperatures of the esters (III), (IV) and (V) could be used to advantage in formulating mixtures involving lower melting esters of type (I), with the object of obtaining higher N–I values and lower C–N values, the data presented in Table II were calculated using thermodynamic results for the simpler esters (I) contained in Reference 3.

As can be seen from the results in Table II, a ternary mixture of esters of type (I) alone gives a calculated nematic range from 8.7–48.8°. The last four mixtures listed in Table II demonstrate how the addition of esters (III) and/or (V) can be used to increase the N–I temperature. The effect on the C–N temperature is variable, but in the case of the third and fourth mixtures in the Table, the C–N values are slightly lowered, and the nematic range is increased to 48.5° and 47.5°, respectively, from 40.1° for the mixture of esters of type (I) alone. The fact that the C–N values resulting from the use of esters of type (III) and (V) are not particularly low is of course a consequence of the high C–N values for the biphenyl esters and their fairly high enthalpies of fusion. As a result, the eutectic mixtures contain quite small amounts of these esters. When considering the admixture of any higher molecular weight compound, it must also be remembered that the solubility

TABLE II

Calculated transition temperatures for some mixtures of esters I, III and V

Type	Ester X	Ester Y	Composition mol %	Transition temperatures C–N	Transition temperatures N–I
I	CH_3O	C_5H_{11}-*n*	55.0	8.7°	48.8°
I	*n*-$C_5H_{11}O$	C_5H_{11}-*n*	25.0		
I	*n*-$C_7H_{15}O$	CN	20.0		
I	CH_3O	C_5H_{11}-*n*	63.7	13.5	56.9
I	*n*-$C_5H_{11}O$	C_5H_{11}-*n*	31.7		
III	CN	OC_5H_{11}-*n*	4.6		
I	CH_3O	C_5H_{11}-*n*	53.4	8.0	56.5
I	*n*-$C_5H_{11}O$	C_5H_{11}-*n*	23.7		
I	*n*-$C_7H_{15}O$	CN	19.4		
III	CN	OC_5H_{11}-*n*	3.5		
I	CH_3O	C_5H_{11}-*n*	53.4	7.8	55.3
I	*n*-$C_5H_{11}O$	C_5H_{11}-*n*	23.8		
I	*n*-$C_7H_{15}O$	CN	19.0		
V	CN	C_4H_9-*n*	3.8		
I	CH_3O	C_5H_{11}-*n*	61.5	12.3	64.4
I	*n*-$C_5H_{11}O$	C_5H_{11}-*n*	29.5		
III	CN	OC_5H_{11}-*n*	4.3		
V	CN	C_4H_9-*n*	4.7		

of the compound may be less than that concentration calculated to produce the eutectic mixture. As a result, a smaller concentration has to be used in practice, and somewhat lower experimental N–I values (and higher C–N values) than those calculated could ensue.

Experimental data for mixtures of esters of type (I) alone are not numerous, but the best result seems to be that quoted[3] for a quinary mixture of positive dielectric anisotropy, having a C–N value of $-7°$ and an N–I value of 58°. Even with the above mentioned limitations on the amounts of biphenyl esters of type (III) and (V) that can be used, it would seem that the incorporation of even a low concentration of one or more of these esters in a similar mixture could well take one nearer to or beyond the desirable range from a C–N value of $-10°$ to an N–I value of 60° required for commercial applications in displays.

EXPERIMENTAL

4-Acetyl-4′-bromobiphenyl This was prepared by Friedel–Crafts acylation of 4-bromobiphenyl with acetyl chloride in the presence of aluminium trichloride; dichloromethane was the solvent. A 92% yield was obtained, m.p. 129° (lit.[8] 129–130°).

4-Acetyl-4′-cyanobiphenyl 4-Acetyl-4′-bromobiphenyl (82 g) was stirred and heated under reflux for 1.5 h with cuprous cyanide (41 g) and N-methyl-2-pyrrolidone (160 ml). After cooling, the mixture was poured into a warm solution of ferric chloride (120 g), concentrated hydrochloric acid (36 ml), and water (1.5 l) and stirred for 0.5 h. The cooled mixture was shaken with ether, and the combined ether extracts were evaporated to dryness. The residue was crystallised from ethanol to give *4-acetyl-4′-cyanobiphenyl*, 51 g (78%), m.p. 118° (Found: C, 81.0; H, 5.1; N, 6.3. $C_{15}H_{11}NO$ requires C, 81.4; H, 5.0; N, 6.3%).

4′-Cyanobiphenyl-4-carboxylic acid Hypohalite oxidation[9] of 4-acetyl-4′-cyanobiphenyl and crystallisation from acetic acid gave a yield of 82% of the *mesomorphic acid*, C–N, 263°; N–I, 315° (Found: C, 75.5; H, 4.2; N, 6.3. $C_{14}H_9NO_2$ requires C, 75.4; H, 4.0; N, 6.3%).

4-Alkoxybiphenyls Alkylation of 4-hydroxybiphenyl using the appropriate alkyl bromide gave *4-n-hexyloxybiphenyl*, m.p. 68° in 84% yield and *4-n-octyloxybiphenyl*, m.p. 72° in 85% yield. Mass spectrometry and infra-red spectroscopy confirmed the structure of each compound.

4-Acetyl-4-alkoxybiphenyls These were prepared by Friedel–Crafts acylation of the 4-*n*-alkoxybiphenyls at $-7°$ using aluminium trichloride and

dichloromethane as solvent. The yield of *4-acetyl-4'-n-hexyloxybiphenyl*, m.p. 132°, was 30% and of *4-acetyl-4'-n-octyloxybiphenyl*, m.p. 132°, 28%. Mass spectrometry and infra-red spectroscopy confirmed the structure of each compound.

4-Alkoxybiphenyl-4'-carboxylic acids Hypohalite oxidation[9] of the acetyl compounds gave an average yield of 82% of 4'-*n*-hexyloxy biphenyl-4'-carboxylic acid, C–S_c, 211°; N–I, 270° (lit.[10] C–S_c, 213°; N–I, 272.5°) and of 4'-*n*-octyloxybiphenyl-4-carboxylic acid, C–S_c, 181°; N–I, 263° (lit.,[10] C–S_c, 183°; N–I, 264.5°).

Preparation of esters A solution of *4'-cyano-* or *4'-n-alkoxybiphenyl-4-carboxylic acid chloride* (0.067 mol—prepared from the corresponding acid using thionyl chloride) and the appropriate 4-*n*-alkoxy-,[11] 4-*n*-alkyl-,[12] or 4-cyano-phenol (0.089 mol, either commercially available or prepared by standard methods) in the minimum volume of dry pyridine, initially at 0°, was stirred overnight; finally the mixture was warmed for 1 h at 90–100°. The reaction mixture was rotary evaporated to dryness; the solid was dissolved in chloroform and the solution washed successively with cold dilute sulphuric acid, sodium carbonate solution, and water. Rotary evaporation to dryness gave a solid which was crystallised (ethanol), and when necessary decolourised with charcoal, until the mesophase transition temperatures (Table I) remained constant on successive crystallisations. The average final yield over many esterifications was 45%; analytical data for the esters are given in Table III.

TABLE III

Elemental analyses for esters of type II

		Found (%)				Required (%)		
X	*Y*	C	H	N	Formula	C	H	N
CN	OCH_3	76.3	4.6	4.1	$C_{21}H_{15}NO_3$	76.6	4.6	4.3
CN	OC_2H_5	76.7	4.9	4.2	$C_{22}H_{17}NO_3$	77.0	4.9	4.1
CN	OC_3H_7-*n*	77.5	5.4	4.0	$C_{23}H_{19}NO_3$	77.3	5.3	3.9
CN	OC_4H_9-*n*	77.4	5.5	3.9	$C_{24}H_{21}NO_3$	77.6	5.7	3.8
CN	OC_5H_{11}-*n*	78.0	5.9	3.5	$C_{25}H_{23}NO_3$	77.9	6.0	3.6
CN	OC_6H_{13}-*n*	77.8	6.3	3.6	$C_{26}H_{25}NO_3$	78.2	6.3	3.5
CN	OC_7H_{15}-*n*	78.2	6.7	3.4	$C_{27}H_{27}NO_3$	78.4	6.6	3.4
n-$C_6H_{13}O$	CN	78.0	6.2	3.5	$C_{26}H_{25}NO_3$	78.2	6.3	3.5
n-$C_8H_{17}O$	CN	78.5	6.8	3.4	$C_{28}H_{29}NO_3$	78.6	6.8	3.3
CN	CH_3	80.3	4.5	4.6	$C_{21}H_{15}NO_2$	80.5	4.8	4.5
CN	C_2H_5	80.6	5.0	4.2	$C_{22}H_{17}NO_2$	80.7	5.2	4.3
CN	C_3H_7-*n*	80.7	6.0	3.9	$C_{23}H_{19}NO_2$	80.9	5.6	4.1
CN	C_4H_9-*n*	81.0	5.8	3.9	$C_{24}H_{21}NO_2$	81.1	5.9	3.9

Acknowledgement

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