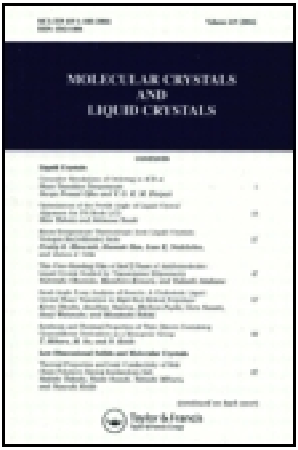

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Steric Effects and Liquid Crystal Behaviour. Properties of the Liquid Crystals Formed by Certain 2'-Fluoro-and 2'-Chloro-4-Biphenylyl 4″-n-Alkoxybenzoates: A Comparison with Analogous 4-(2'-Pyridyl) Phenyl 4″-n-Alkoxybenzoates

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Steric Effects and Liquid Crystal Behaviour. Properties of the Liquid Crystals Formed by Certain 2′-Fluoro- and 2′-Chloro-4-Biphenylyl 4″-*n*-Alkoxybenzoates: A Comparison with Analogous 4-(2′-Pyridyl)Phenyl 4″-*n*-Alkoxybenzoates

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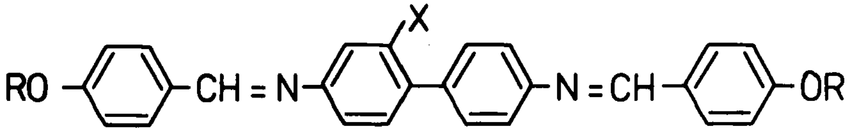
Eight 2′-fluoro- and six 2′-chloro-4-biphenylyl 4″-*n*-alkoxybenzoates have been prepared and their liquid crystal phases have been investigated. The properties of these esters, in which the halogeno-substituent exerts a steric effect which influences liquid crystal behaviour, are compared with those of the analogous 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates in an attempt to evaluate the steric effect of the hetero-nitrogen atom.

INTRODUCTION

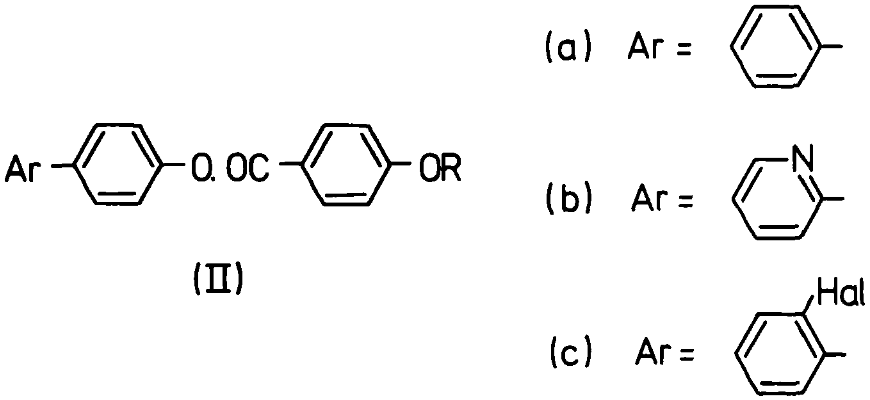
Studies by Gray and his co-workers have established the influence on the thermal stability of smectic and nematic mesophases of substituents in the 2-(and the 2′-) position of biphenyl mesogens. Summaries of this work, including references to the original publications, have been given in reviews by Gray.[1] The Schiff's bases (I), where R = *n*-octyl—*n*-decyl and X = F, Cl, Br,



(I)

I, Me, and NO_2 provided the main results, and these are still valid even though the stereochemistry of the Schiff's bases may be more complicated than was first thought (in certain Schiff's bases it is now known[2] that the molecules are twisted out of coplanarity on either side of the central Schiff's base linkage). The results show that as the size of the 2-substituent, X, increases, the mesophase thermal stability decreases, partly because the molecule is (i) broadened by the presence of the substituent, but mainly because the molecule is (ii) thickened by the increase the substituent causes in the average interplanar angle of the biphenyl system. The overall steric effect [(i) + (ii)] increases the separation of the long molecular axes and reduces the thermal stability of the ordered arrangement of molecules in the liquid crystal, smectic thermal stability being affected more than nematic thermal stability.

We have recently reported the properties of the liquid crystals formed by certain 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates (IIb).[3] Compared with the analogous system in which the hetero-nitrogen atom is absent, namely, the 4-biphenylyl 4″-*n*-alkoxybenzoates (IIa),[4] the 4-(2′-pyridyl)phenyl esters have a lower nematic thermal stability and do not show smectic mesophases. This behaviour is very similar to that resulting from the introduction of the 2-substituent, X, in the Schiff's base derivatives of biphenyl (I). Thus, the hetero-nitrogen atom (associated with its lone pair) may cause twisting about the bond connecting the benzene ring to the 2-pyridyl ring and the result of this steric effect may be to reduce the mesophase thermal stability of the esters (IIb).



(II)

In an attempt to establish whether or not the hetero-nitrogen atom exerts a steric effect, we have now compared the liquid crystal behaviour of certain 2′-fluoro- and 2′-chloro-4-biphenylyl 4″-*n*-alkoxybenzoates (IIc. Hal = F or Cl) with that of the corresponding 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates (IIb). In the former compounds, by analogy with the Schiff's base derivatives (I), the 2′-halogeno-substituent is assumed to exert a steric effect responsible for a decrease in mesophase thermal stability relative to the 4-biphenylyl 4″-*n*-alkoxybenzoates (IIa).

RESULTS AND DISCUSSION

We have prepared eight members (*n*-butyloxy to *n*-decyloxy, and *n*-tetradecyloxy) of the 2′-fluoro-4-biphenylyl 4″-*n*-alkoxybenzoates (IIc. Hal = F) and six members (*n*-hexyloxy to *n*-decyloxy, and *n*-tetradecyloxy) of the corresponding 2′-chloro-substituted esters (IIc. Hal = Cl). Liquid crystal transition temperatures were measured using a hot stage in conjunction with a polarising microscope. Only one compound (the *n*-tetradecyloxy compound of the 2′-fluoro-substituted series of esters) exhibited a smectic mesophase. This (monotropic) phase was assigned as S_A by microscopic examination of the focal conic fan texture of the birefringent phase.

Our results are listed in Table I which also shows, in the columns headed 'ΔT nematic', the differences between the N—I transition temperatures of corresponding 4-(2′-pyridyl)phenyl and 2′-halogeno-4-biphenylyl 4″-*n*-alkoxybenzoates. In Figure 1, plots 3 and 4, respectively, show the N—I transition temperatures of the 2′-fluoro- and 2′-chloro-4-biphenylyl 4″-*n*-alkoxybenzo-

TABLE I

Transition temperatures for 2′-fluoro- and 2′-chloro-4-biphenylyl 4″-*n*-alkoxybenzoates (IIc)

	2′-Fluoro-compounds					2′-Chloro-compounds			
	Transition temperatures (°C)[a]					Transition temperatures (°C)[a]			
Substituent R	C—I	N—S_A	N—I	N—C[b] or S_A—C[b]	ΔT nematic[c]	C—I	N—I	N—C[b] or I—C[b]	ΔT nematic[c]
n-C_4H_9	119.5		[97]	86	22.5				
n-C_5H_{11}	99		[86]	63	22				
n-C_6H_{13}	102		[95.5]	72	20.5	77	[41.5]	38	74.5
n-C_7H_{15}	93.5		[90]	71	22	67	[37]	35	75
	C—N								
n-C_8H_{17}	86		95	67	20	58	[45]	40	70
n-C_9H_{19}	90		92	58	21	60.5	[46]	44	67
n-$C_{10}H_{21}$	88		94	68	20	70		57	
n-$C_{14}H_{29}$	88	[79]	92.5	62	19	76.5		66	

[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] ΔT nematic is the difference between the N—I transition temperatures of corresponding 4-(2′-pyridyl)phenyl and 2′-halogeno-4-biphenylyl 4″-*n*-alkoxybenzoates.

[ ] monotropic transition.

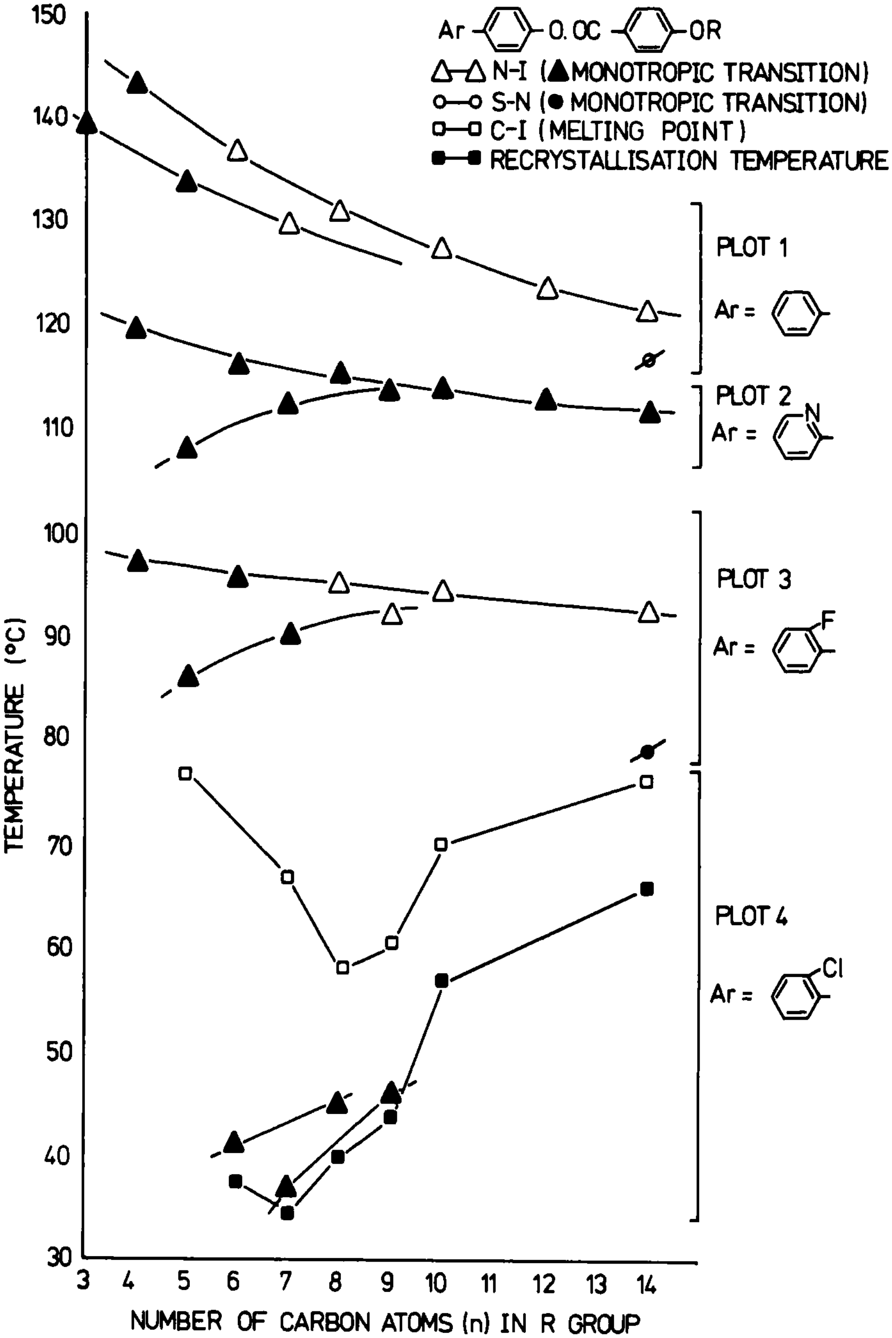


FIGURE 1 Plots of transition temperatures against alkyl chain length (*n*) for various 4-substituted phenyl 4″-*n*-alkoxybenzoates (II).

ates plotted against the number of carbon atoms, *n*, in the *n*-alkyl chain. For the latter series, the m.p. and recrystallisation temperatures are also plotted. The Figure also includes, for comparison, a representative part of the analogous plot† for the 4-biphenylyl 4″-*n*-alkoxybenzoates (plot 1) and that for the 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates (plot 2). Substitution of the 4-biphenylyl 4″-*n*-alkoxybenzoates by 2′-chloro- and 2′-fluoro-substituents, as expected, markedly lowers nematic thermal stability and almost completely eliminates smectic behaviour. The extent of the substituent effect, which is clearly in proportion to the size of the substituent (i.e., a steric effect), is apparent by inspection of Figure 1.

Plot 3 for the 2′-fluoro-derivatives lies in the lower part of the 'cross-over' region, and the curve for the N—I transition temperatures for the members of the series for which *n* is odd rises to meet the falling curve for the members for which *n* is even. The *n*-butyloxy through to the *n*-heptyloxy compounds have monotropic nematic phases, and even though the members of the series as a whole supercool by 30° or more, only the *n*-tetradecyloxy compound exhibits a smectic mesophase. Comparison of mean values for analogous members of the 4-biphenylyl 4″-*n*-alkoxybenzoates and their 2′-fluoro-derivatives (Table II) reveals that the 2′-fluoro-substituent decreases the thermal stability of both the smectic and nematic mesophases by 37.5°. Corresponding values for the effect of a 2-fluoro-substituent on the thermal stability of the mesophases of the 4,4′-di-(*p*-*n*- alkoxybenzylideneamino)biphenyls (I) are 58.5° (smectic) and 29.4° (nematic).[1]

Plot 4 for the 2′-chloro-compounds shows N—I transition temperature curves (for both odd and even values of *n*) that rise as *n* increases. Only monotropic nematic transitions were detected, and the plot shows both the m.p. (C—I transition) and recrystallisation temperature of members of the 2′-chloro-substituted series. No mesophase transitions could be obtained by supercooling the melts of the *n*-decyloxy and *n*-tetradecyloxy compounds. Comparison of the mean values for analogous members of the 4-biphenylyl 4″-*n*-alkoxybenzoates and their 2′-chloro-derivatives (Table II) shows that the 2′-chloro-substituent reduces the thermal stability of the nematic phase by 88.5°, which is comparable with the value of 84.1° by which the 2-chloro-substituent decreases the nematic thermal stability of the 4,4′-di-(*p*-*n*-alkoxybenzylideneamino)biphenyls (I).[1]

Plot 2 for the 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates (which we have discussed in a recent paper)[3] lies in the upper part of the 'cross-over' region, approximately midway between the analogous plots for the 4-biphenylyl 4″-*n*-alkoxybenzoates and their 2′-fluoro-derivatives. Comparison of mean

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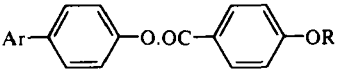
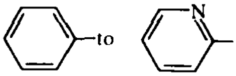
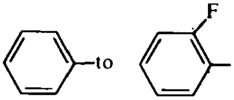
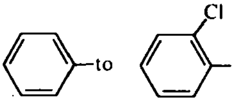
† Only the S_A—IN transition temperature for the *n*-tetradecyloxy compound of this series is plotted for comparison with the S_A—N transition temperature for 2′-fluoro-4-biphenylyl 4″-*n*-tetradecyloxybenzoate.

TABLE II

Decreases in smectic and nematic thermal stability caused by changes of the aryl group of the series



Change of Ar group	Decrease in liquid crystal thermal stability (°C)	
	Smectic[a]	Nematic[b]
	41.5	16.6
	37.5(58.5)[c]	37.5(29.4)
	– (157.5)	88.2(84.1)

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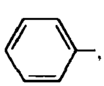
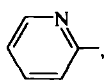
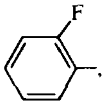
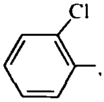
[a] Decreases are for the *n*-tetradecyl ethers. For 4-(2′-pyridyl)phenyl 4″-*n*-tetradecyloxybenzoate, the S_A—N transition temperature is estimated as 75°. This approximate value was obtained by extrapolation of the monotropic S_A—N values observed for mixtures of the compound with 4-biphenylyl 4″-*n*-tetradecyloxybenzoate. For the following percentages by weight of the 4-(2′-pyridyl)phenyl 4′-*n*-tetradecyloxybenzoate in the mixtures, the S_A—N values were: 40%, [99°]; 60%, [91°]; 70%, [88°]; 75%, [84°]; 80%, [83°]. On cooling the mixtures between a slide and cover slip, homeotropic textures were adopted and the transitions were very difficult to detect. When more than 80% of the *n*-tetradecyloxy compound was present the mixtures crystallised before the appearance of the S_A phase.

[b] Decreases are derived from the following mean values (°C) for the *n*-hexyl—*n*-nonyl ethers:

Ar = , 130.60; 

, 114; 

, 93.1; 

, 42.4.

[c] Values in parentheses are corresponding values (*n*-heptyl—*n*-decyl ethers) for 2-substituted 4,4′-di-(*p*-*n*-alkoxybenzylideneamino)biphenyls.

values for analogous members of the 4-biphenylyl 4″-*n*-alkoxybenzoates and the 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates (Table II) indicates that the presence of the hetero-nitrogen atom reduces the thermal stability of the nematic phase by 16.6°. Although the 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates do not exhibit smectic phases, the S_A—N transition temperature for the *n*-tetradecyloxy compound has been estimated as 75° (see footnote to Table II). This approximate value was obtained by extrapolation of the monotropic S_A—N transition temperatures obtained for mixtures of the compound with 4-biphenylyl 4″-*n*-decyloxybenzoate. By comparison with the S_A—N transition temperature for 4-biphenylyl 4″-*n*-tetradecyloxybenzoate alone, the extrapolated value infers that the decrease in the thermal stability of the smectic phase due to the presence of the hetero-nitrogen atom is 41.5°.

These results suggest (i) that the presence of the hetero-nitrogen atom at the 2-position of the terminal ring of the 4-(2′-pyridyl)phenyl 4″-*n*-alkoxybenzoates causes an increase in separation of the long molecular axes which reduces the thermal stability of the ordered arrangement of the molecules in the liquid crystal, and (ii) that this is due to a steric effect similar to that which reduces mesophase thermal stability when a fluoro- or chloro-substituent is present in the 2-position of biphenyl mesogens. A hetero-nitrogen atom associated with its lone pair has a smaller size and hence a smaller steric effect than a benzenoid carbon atom bound to a halogeno-substituent. It is not unexpected, therefore, that the decrease in nematic thermal stability caused by the hetero-nitrogen atom (at the 2-position of the terminal ring) is smaller than that caused by a 2-fluoro-substituent in the analogous biphenyl derivatives. Conversely, however, the reverse trend is observed for the effect on smectic thermal stability. It is possible that this may be due to repulsive interactions between the nitrogen lone pairs of adjacent molecules giving rise to an added adverse effect on smectic thermal stability.

EXPERIMENTAL

2′-Fluoro-4-hydroxybiphenyl Preparations of 2-fluorobiphenyl, 4-acetyl-2′-fluorobiphenyl and its oxime, and the Beckmann rearrangement of this oxime to give (after hydrolysis of the resulting acetylamin-compound) 4-amino-2′-fluorobiphenyl were carried out by methods previously reported.[5] The m.p.s. of these compounds were in good agreement with the values quoted in the literature.[5]

4-Amino-2′-fluorobiphenyl (0.088 mol) was diazotised in 1:3 glacial acetic acid:40% (v/v) aqueous sulphuric acid (200 ml) in the usual manner. The cold solution of the diazonium salt was then added slowly to a boiling solution of 40% (v/v) aqueous sulphuric acid (200 ml), heated under reflux for 30 min. and then diluted with water (1500 ml). The precipitate was digested with 4M-aqueous sodium hydroxide (300 ml), insoluble material was removed, and the phenol liberated by acidification. The crude phenol was purified by vacuum sublimation (120°/0.2 mm) and the resulting solid was recrystallised several times from chloroform to give *2′-fluoro-4-hydroxybiphenyl,* 10.7 g (64%), m.p. 135–137° (Found: C, 76.5; H, 4.8. $C_{12}H_9OF$ requires C, 76.6; H, 4.8%), ν_{max} (KBr): 3450 cm^{-1}.

2′-Chloro-4-hydroxybiphenyl 2-Chlorobiphenyl and 4-acetyl-2′-chlorobiphenyl were obtained by methods previously reported[5] for the preparation of

TABLE III

Elemental analyses for 2'-chloro- and 2'-fluoro-4-biphenylyl 4"-*n*-alkoxybenzoates

Substituent	Molecular	2'-Fluoro-compounds (X = F)				2'-Chloro-compounds (X = Cl)					
R	Formula	Found (%)		Required (%)		Found (%)			Required (%)		
		C	H	C	H	C	H	Cl	C	H	Cl
n-C_4H_9	$C_{23}H_{21}XO_3$	75.6	5.7	75.8	5.8						
n-C_5H_{11}	$C_{24}H_{23}XO_3$	75.8	6.3	76.2	6.1						
n-C_6H_{13}	$C_{25}H_{25}XO_3$	76.5	6.6	76.5	6.4	73.1	6.2	8.6	73.4	6.1	8.7
n-C_7H_{15}	$C_{26}H_{27}XO_3$	76.6	6.9	76.9	6.7	74.2	6.6	8.6	73.9	6.4	8.4
n-C_8H_{17}	$C_{27}H_{29}XO_3$	77.1	7.1	77.1	6.9	74.6	6.9	7.9	74.2	6.6	8.1
n-C_9H_{19}	$C_{28}H_{31}XO_3$	77.3	7.4	77.4	7.1	74.8	7.1	8.0	74.6	6.9	7.9
n-$C_{10}H_{21}$	$C_{29}H_{33}XO_3$	77.9	7.5	77.7	7.4	75.0	7.2	7.4	74.9	7.1	7.6
n-$C_{14}H_{29}$	$C_{33}H_{41}XO_3$	78.6	8.3	78.6	8.1	75.9	7.9	7.0	76.1	7.9	6.8

these compounds. Beckmann rearrangement of the *oxime* of 4-acetyl-2'-chlorobiphenyl, m.p. 136–137° (Found: C, 68.4; H, 5.2; N, 5.9. $C_{14}H_{12}NOCl$ requires C, 68.4; H, 4.9; N, 5.7%) by the procedure used for the 2'-fluoro-compound, gave (after hydrolysis of the acetylamino-compound) 4-amino-2'-chlorobiphenyl, 55%, m.p. 39–41° (lit.[5] m.p. 42–43°). 2'-Chloro-4-hydroxybiphenyl was prepared by a similar method to that described above for the 2'-fluoro-compound. The crude phenol was extracted from the reaction mixture with ether before digestion with 4M-aqueous sodium hydroxide. The crude phenol, liberated by acidification with hydrochloric acid, was extracted with chloroform and purified by column chromatography on silica gel eluting with chloroform, and finally by recrystallisation from chloroform. The 2'-chloro-4-hydroxybiphenyl was obtained as colourless needles, 57%, m.p. 91° (lit.[6] m.p. 90.5-91°).

2'-Chloro- and 2'-fluoro-4-biphenylyl 4"-n-alkoxybenzoates These esters were prepared[4] by interaction of the appropriate 4-*n*-alkoxybenzoic acid[4] with 2'-chloro- or 2'-fluoro-4-hydroxybiphenyl in dry pyridine, and purified by methods previously reported.[4]

The transition temperatures of the *2'-chloro-* and *2'-fluoro-4-biphenylyl 4"-n-alkoxybenzoates* are given in Table I and their elemental analyses are listed in Table III.

The 4-biphenylyl 4"-*n*-alkoxybenzoates and their 2'-halogeno-derivatives give broadly similar i.r. spectra and the data previously reported[4] are also representative of the homologous series of 2'-halogeno-substituted esters, as are the following n.m.r. data for 2'-fluoro-4-biphenylyl 4"-*n*-hexyloxybenzoate. δ($CDCl_3$) 0.83 (br, 3H, CH_3), 1.50 (br, 9H), 4.04 (t, J6.0 Hz, 2H, OCH_2), 6.96 (d, J9.0 Hz, 2H), 7.25 (m, 8H), 8.18 (d, J9.0 Hz, 2H). (A Perkin-Elmer 157G grating spectrophotometer and a Jeol JNM-C-60HL 60 Hz instrument with TMS as internal standard were used, respectively, to determine i.r. and n.m.r. spectra).

Acknowledgements

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