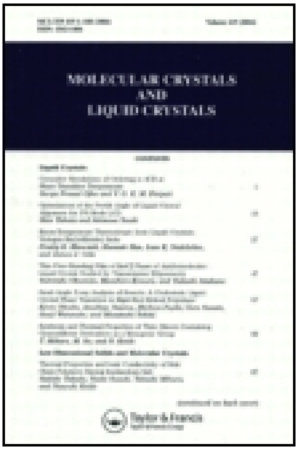

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Comparison of the Properties of Liquid Crystals Derived from Certain Lateral Halogeno-substituted Azomethines

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Comparison of the Properties of Liquid Crystals Derived from Certain Lateral Halogeno-substituted Azomethines

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Twenty eight 4-*n*-alkoxy-*N*-(2- and 2′-halogenobiphenyl-4-ylmethylene)anilines comprising 4, 8, 8, 4, and 4 members derived, respectively, from 2-fluoro-, 2′-fluoro-, 2′-chloro-, 2′-bromo-, and 2′-iodo-biphenyl-4-carbaldehyde, together with six 4-*p*-*n*-alkoxy-2′-fluorobenzylideneaminobiphenyls have been prepared. The liquid crystal behaviour of these compounds has been compared with analogous azomethines with reversed CH═N linkage, previously reported.

INTRODUCTION

Important systematic studies carried out during the 1960's by Gray *et al.* on 4-*p*-*n*-alkoxybenzylideneaminobiphenyls (I) carrying 3-, 2-, 2′-, and 3′-halogeno- and -methyl substituents,[1] and on the analogous 2- and 3-substituted 4,4′-di-(*p*-*n*-alkoxybenzylideneamino)biphenyls (II)[2] established the effect of lateral substitution on the liquid crystal behaviour of biphenyl derivatives.

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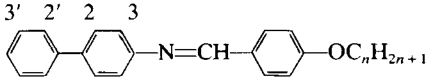
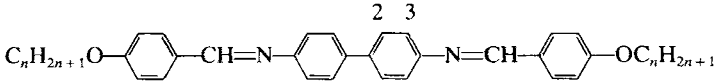
‡Martin E. Cooper, Elizabeth R. Mareya, Kulminder Matharu, Elizabeth A. Norris, Kishor K. Patel, and Mark Schleifer also participated in this work. Their assistance is gratefully acknowledged.



(I)



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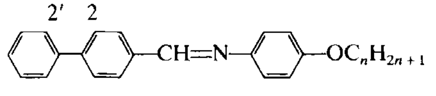


(III)

The original work included only the fluoro-azomethines (I) substituted at the 2-position and four homologues (n = 7–10) of the series were studied. However, there is much current interest in the liquid crystal behaviour of compounds incorporating a fluoro-substituent in various lateral positions. Thus, for comparison with the 2-fluoro-azomethines (I) we have prepared six members (n = 6–10,12) of the 2′-fluoro-analogues (I). In addition, the behaviour of the corresponding fluoro-compounds with reversed CH=N linkage has been investigated by the preparation of eight members (n = 5–10,12,14) of the 2′-fluoro- and four members (n = 7–10) of the 2-fluoro-substituted 4-*n*-alkoxy-*N*-(biphenyl-4-ylmethylene)anilines (III). To compare all 2′-halogeno-derivatives of the reverse azomethines (III), eight homologues (n = 5–10,12,14) of the 2′-chloro-, and four members each (n = 7–10) of the analogous 2′-bromo- and 2′-iodo-azomethines (III) have also been prepared.

RESULTS AND DISCUSSION

The m.p.s and transition temperatures (obtained by thermal optical microscopy) for the azomethines prepared in this work are listed in Table I.

The liquid crystal transition temperatures of the 2′-fluoro-azomethines (I) are plotted against n, the number of C atoms in the alkyl chain in Figure 1(a). The T_{N-I} values give the expected alternation, with the points for the even-n members lying on a rising curve situated below a shallow, falling curve for the odd-n members. For the T_{S_A-N} values, all the points lie on a smoothly rising curve. The 2-fluoro-azomethines (I) (n = 7–10) of the earlier work[1] show virtually identical behaviour for the N–I and S_A–N curves (Figure 1(b)) but do not exhibit the additional (monotropic) S_C (n = 6–10) and S_B (n

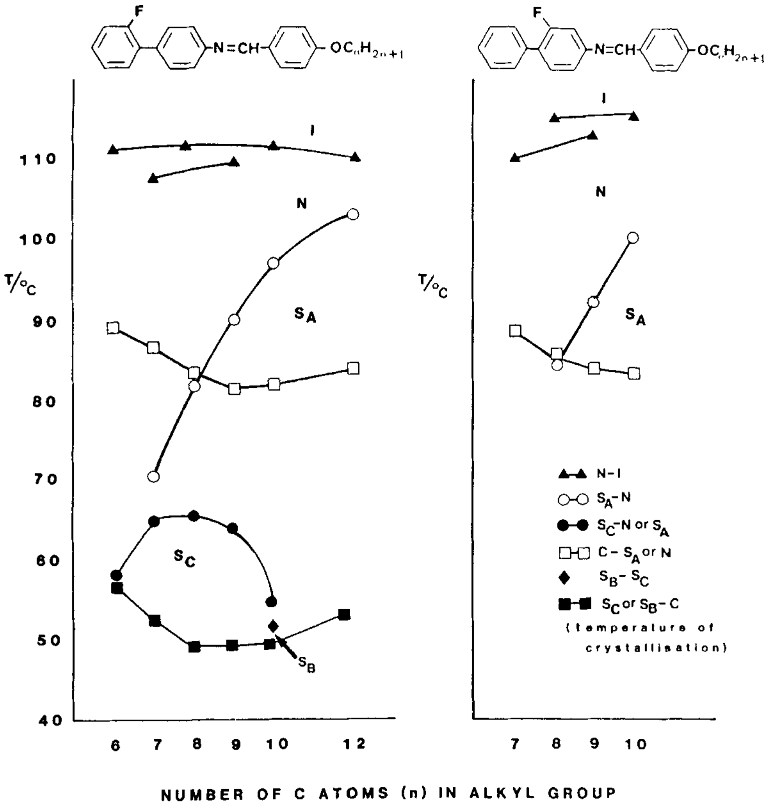


FIG 1(a) FIG 1(b)

FIGURE 1 Plots of transition temperatures against the number of carbon atoms (*n*) in the alkyl chain of 4-*p*-*n*-alkoxybenzylideneaminobiphenyls (I): (a) 2′-fluoro-derivatives; (b) 2-fluoro-derivatives (data taken from reference 1).

= 10) phases shown by the 2′-fluoro-derivatives (I) of the present work. The curve (Figure 1(a)) for the $T_{S_C-S_A}$ values rises to a maximum at *n* = 7,8 then falls steeply.

For the 2′-fluoro-azomethines (III) (*n* = 5–10,12,14) the plot (Figure 2(a)) of the T_{N-I} values against *n* shows similar characteristics except that the curves for both odd-*n* and even-*n* members rise gradually up to *n* = 7,8 and then fall, whereas for the corresponding 2′-chloro-compounds (III) (*n* = 5–10,12,14) the curves continue to rise up to *n* = 12 before the fall commences. Only four members (*n* = 7–10) of the 2′-bromo-azomethines (III) were investigated and for these compounds the T_{N-I} curves for odd-*n* and even-*n* members both rise as *n* increases. The plot (Figure 2(b)) of transition temperatures

TABLE I

Transition temperatures for 4-*n*-alkoxy-*N*-(2- and 2′-halogenobiphenyl-4-ylmethylene)anilines (III) and 4-*p*-*n*-alkoxy-2′-fluorobenzylideneaminobiphenyls (I)

4-*n*-Alkoxy-*N*-(biphenyl-4-ylmethylene)anilines

Substituent	*n*-Alkyl	Transition temperature (°C)[a]			
		C-N	N-I	N-C[b]	
2′-Fluoro-	C_5H_{11}	102.6	105.2	94.2	
	C_6H_{13}	107.4	112	89.1	
		C-I			
	C_7H_{15}	111.5	(109.2)[c]	95.6	
		C-N			
	C_8H_{17}	102	113.2	75.5	
	C_9H_{19}	105.2	110.4	94.2	
	$C_{10}H_{21}$	101.3	112.2	80	
	$C_{12}H_{25}$	100.7	109	85	
	$C_{14}H_{29}$	98.2	101.2	90.3	
		C-I			
2′-Chloro-	C_5H_{11}	78.8	(45.4)	45	
	C_6H_{13}	79.4	(58.1)	36.1	
	C_7H_{15}	75.3	(56)	37.6	
	C_8H_{17}	71.7	(63.5)	41.1	
	C_9H_{19}	68.7	(61.5)	40.5	
	$C_{10}H_{21}$	72.8	(65.5)	49.8	
	$C_{12}H_{25}$	74.6	(66.6)	49.6	
	$C_{14}H_{29}$	76.8	(65)	50.5	
2′-Bromo-	C_7H_{15}	67.2	(38.6)	38.5	
	C_8H_{17}	66.4	(47.5)	47.3	
	C_9H_{19}	64.5	(46.6)	46.5	
	$C_{10}H_{21}$	70.4	(51.5)	48.5	
2′-Iodo-	C_7H_{15}	68.4		56.1	
	C_8H_{17}	70.9		56	
	C_9H_{19}	65.3		49	
	$C_{10}H_{21}$	78.5	(32.5)[d]	51.3	
		C-S_A	S_A-N	N-I	S_A-C[b]
2-Fluoro-	C_7H_{15}	95.3	98	121.1	77.1
	C_8H_{17}	98.7	105	123.3	86.7
	C_9H_{19}	98	108.1	120.4	81.9
	$C_{10}H_{21}$	95.9	111.4	121	80.8

Table I continues on next page

for the 2-fluoro-azomethines (III) (n = 7–10) shows similar characteristics to that (Figure 1(b)) for the 2-fluoro-azomethines (I) except that for both odd- and even-n members the T_{N-I} curves fall as n increases.

TABLE I *Continued*

4-*p*-*n*-Alkoxy-2′-fluorobenzylideneaminobiphenyls

	Transition temperature (°C)[a]					
n-Alkyl	C–N	S_B–S_C	S_C–S_A	S_C–N	N–I	S_C–C^b
C_6H_{13}	89.8			58.1	111.2	57.7
				S_A–N		
C_7H_{15}	86.5		(65.4)	(70.5)	107.5	53.6
C_8H_{17}	83.2		(65.9)	(82.1)	111.3	49
	C–S_A					
C_9H_{19}	81.8		(64.5)	90.1	109.7	48.9
						S_B–C^b
$C_{10}H_{21}$	82.2	(50.6)	(55.1)	97.1	111.7	49.5
						S_A–C^b
$C_{12}H_{25}$	84.1			103.3	110.1	62.7

[a] Symbols have their usual significance, namely: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic A etc. Thus C–S_A represents the temperature (m.p.) at which a transition from the crystalline solid to a smectic A phase occurs.

[b] Temperature of recrystallisation.

[c] Values in parentheses are for monotropic transitions.

[d] The value quoted for 4-*n*-decyloxy-*N*-(2′-iodobiphenyl-4-ylmethylene)aniline is a 'virtual' transition temperature obtained by extrapolation of the monotropic N–I transition temperatures observed for mixtures of the compound with 4-*n*-heptyloxy-*N*-(2′-chlorobiphenyl-4-ylmethylene)aniline. For the following percentages by weight of the *n*-decyloxy-compound in the mixtures, the N–I transition temperatures were: 85% (36.9°); 80% (37.7°); 75% (39.1°); 70% (39.4°).

In contrast with the 2- and 2′-fluoro-azomethines (I) and the 2-fluoro-derivatives (III) of the reverse series, the 2′-fluoro-azomethines (III) do not reveal smectic phases of any type. Only one of these compounds has a melt that can be supercooled below 80°C so that the early onset of crystallisation may obscure the formation of smectic phases. The 2′-chloro- and 2′-bromo-azomethines (III) give rise to monotropic nematic phases and neither series shows smectic properties.

No liquid crystal phases could be detected on cooling the melts of the 2′-iodo-azomethines (III) ($n = 7–10$). However, a T_{N-I} value of 32.5°C has been estimated for the compound $n = 10$, by extrapolation of values obtained for mixtures with the compound $n = 7$ of the 2′-chloro-azomethines (III) in the composition range 70–85% of the iodo-compound.

Recent studies[3] have shown that reversal of the CH=N group does not have a marked effect on the liquid crystal thermal stability of a range of otherwise analogous azomethines derived from various unsubstituted aromatic systems. However, it has yet to be established

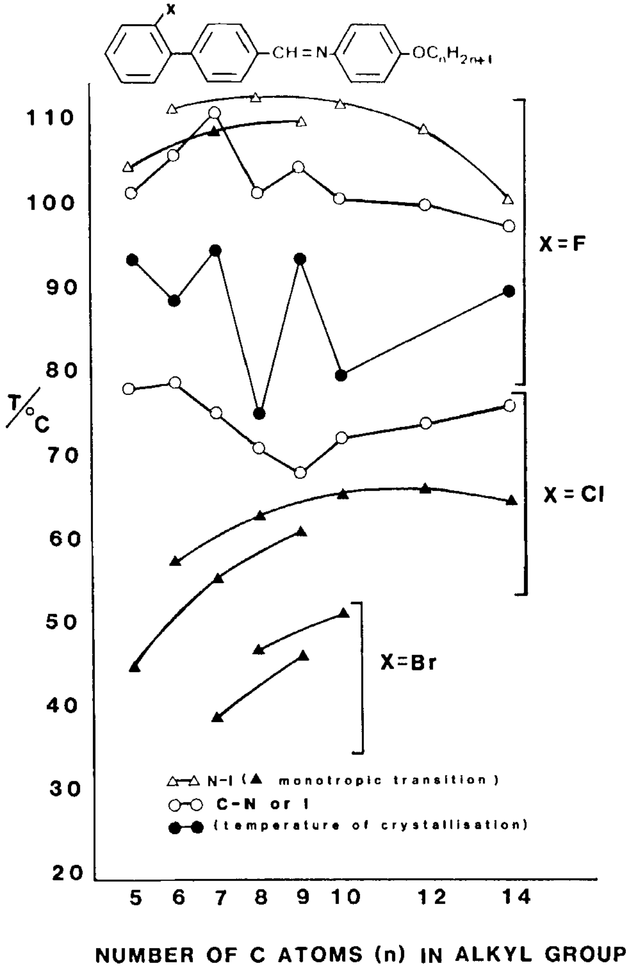


FIG 2(a)

FIGURE 2 Plots of transition temperatures against the number of carbon atoms (*n*) in the alkyl chain of 4-*n*-alkoxy-*N*-(2′-halogenobiphenyl-4-ylmethylene)anilines(III): (a) 2′-halogeno-derivatives; (b) 2-fluoro-derivatives.

Figure 2 continues on next page

that there is similar behaviour when the azomethines contain a *substituted* aromatic system. Thus, these comparative studies are extended in the present work to isomeric azomethines (I) and (III) carrying a range of halogeno-substituents in the 2- or 2′-position. To an extent depending on its size, the halogeno-substituent exerts a steric effect which broadens and also thickens the molecule, as a

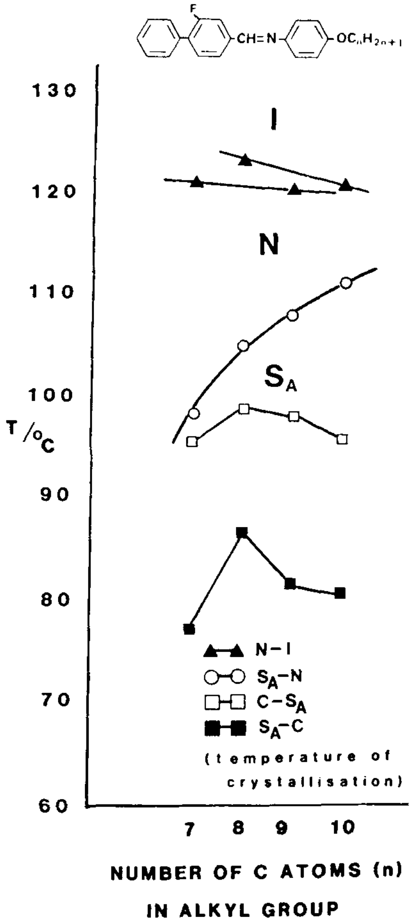


FIG 2(b)

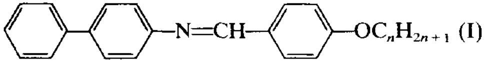
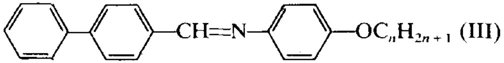
FIGURE 2 *Continued*

result of the increase in the average interplanar angle it imposes on the biphenyl system.

The data given in Table II show that for each 2′-halogeno-substituent (i) the azomethines (III) have only a slightly higher nematic thermal stability than their analogues (I), and (ii) reversal of the CH=N linkage therefore leaves the nematic thermal stability virtually unaffected. This confirms that the overall steric effect[1,2] exerted by the 2′-halogeno-substituent in the two series of azomethines (I) and (III) is similar. The steric effect increases with the size of the 2′-substituent, increasing the separation of the molecular long axes and

TABLE II

Average transition temperatures (T/°C) representing nematic (N) and smectic (S_A) thermal stabilities of 2- and 2′-halogeno-substituted 4-*p*-*n*-alkoxybenzylideneanimobiphenyls (I) and 4-*n*-alkoxy-*N*-(biphenyl-4-ylmethylene)anilines (III)

	 (I)		 (III)	
Substituent	$T_N{}^a$	$T_{S_A}{}^b$	$T_N{}^a$	$T_{S_A}{}^b$
2′-F	110.1	89.8	113.3	—
2′-Cl	59^c	—	61.6	—
2′-Br	44.1^c	—	46.1	—
2′-I	29.5^{c,d}	—	32.5^e	—
2-F	113.3^c	92.2	121.5	108.2

[a] Obtained from average N–I transition temperatures; $n = 7–10$.

[b] Obtained from average S_A–N transition temperatures; $n = 8–10$.

[c] Obtained from data given in reference 1.

[d] Value for $n = 10$ only.

[e] This is a 'virtual' value for $n = 10$ only—see footnote d, Table I.

reducing the thermal stability of the ordered arrangement of molecules in the liquid crystal.

For the 2-halogeno-substituted azomethines, (I) and (III), only the 2-fluoro- compounds have been investigated and the liquid crystal thermal stability of these compounds reveals a rather greater sensitivity to reversal of the CH=N linkage. Thus, whereas for the 2'-fluoro-substituent the nematic thermal stability of the azomethines of type (III) is only 1.2° higher than for those of type (I), in contrast, the corresponding value for the 2-fluoro-substituted azomethines is 8.2°. Further work is planned to establish if this wider difference occurs for other 2-halogeno-azomethines.

A comparison of smectic thermal stability in terms of the position (2- or 2'-) of the substituent is limited to a consideration of the behaviour of the fluoro-derivatives of the azomethines (I) and (III). Empirical statements such as "whenever a lateral fluorine points towards the centre of the molecular core, smectic phases are eliminated or strongly depressed," [4] and "when the lateral fluoro-substituent points towards the longer aliphatic unit it causes a greater depression of smectic properties" [5] have been put forward to describe the effects of lateral fluoro-substituents in other systems. It is clear that the appropriate generalisation applies to the azomethines considered here, but to a differing extent in the two systems.

For the azomethines (III), the 2-fluoro-derivatives have a relatively high smectic thermal stability of 108.2°, whereas change of the orientation of the fluoro-substituent to the 2'-position, which points towards the centre of the molecule, eliminates smectic phases completely. In contrast, for the azomethines (I), a similar change of orientation of the fluoro-substituent from the 2- to the 2'-position reduces smectic thermal stability by only 2.4° showing that the orientation of the C—F bond with respect to the molecular core is relatively unimportant in this series of azomethines.

EXPERIMENTAL

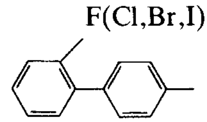
Thermal optical microscopy was carried out with a Vickers M75 polarising microscope in conjunction with a Mettler FP 52 hot-stage and FP 5 control unit. Ir spectra were recorded for KBr discs with a Perkin-Elmer 157 grating spectrophotometer, and ^1H nmr spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as internal standard with a JEOL FX60Q Fourier transform spectrometer. Mass spectra were determined by Dr. G. Haran (Boots plc) with an

AEI MS 902S spectrometer equipped with a Mass Spectrometry Services Analog Series 200 console and an INCOS 2300 data system.

Preparation of Materials

The 2′-halogenobiphenyl-4-carbaldehydes were synthesised by the following route.

Ar =



$$\mathrm{ArH} \xrightarrow{1} \mathrm{ArCOCH_3} \xrightarrow{2} \mathrm{ArCO_2H} \xrightarrow{3} \mathrm{ArCO_2Me} \xrightarrow{4} \mathrm{ArCH_2OH} \xrightarrow{5} \mathrm{ArCHO}$$

Steps 1 and 2 (Friedel-Crafts acylation, followed by hypobromite oxidation) have been described previously.[6] Step 3 was accomplished by heating the carboxylic acid (0.035 mol) with 50% w:v boron trifluoride-methanol complex (15 ml) in dry methanol (120 ml) for 6 h. On cooling, the resulting solution was poured into saturated aqueous sodium bicarbonate (40 ml) and stirred thoroughly. The resulting solid was filtered off, washed with water, dried, and suspended in light petroleum (b.p. 60–80°). Insoluble material was removed by filtration, and evaporation of the solvent afforded the almost pure ester.[6]

Step 4 was accomplished, for the 2′-fluoro- and 2′-chloro-compounds by reduction with lithium aluminium hydride in the usual manner,[3] and for the 2′-bromo- and 2′-iodo-compounds by the dropwise addition, with stirring, during 30 min, of borane-dimethylsulphide[7] (152 mmole) in dry toluene (40 ml) to the ester (0.02 mol) in dry toluene (40 ml) at room temperature. The solution was stirred for a further 30 min, then brought slowly to the boil and heated under reflux for 4 h. A nitrogen atmosphere was employed throughout. After cooling, cold methanol (40 ml) was added, with stirring, and the solution left to stand overnight in a loosely stoppered vessel. The solvents were removed and the resulting pale yellow oil purified by short-path vacuum distillation.

2′-Halogenobiphenyl-4-ylmethanols

2′-F: (73%), b.p. 150°C/0.1 mm; δ_H ($CDCl_3$) 4.60 (*s*, CH_2), 3.05 (*s*, OH); ν_{max} (KBr) 3250, 3050, 2950, 2880 cm^{-1}.

2′-Cl: (48%), b.p. 154°C/0.05 mm; δ_H ($CDCl_3$) 4.57 (*s*, CH_2), 4.01 (*s*, OH); ν_{max} (KBr) 3500–3100, 3025, 2900, 2850 cm^{-1}.

2'-Br: (56%), b.p. 162°C/0.15 mm; δ_H ($CDCl_3$) 4.60 (*s*, CH_2), 3.33 (*s*, OH); ν_{max} (KBr) 3500–3100, 3050, 2900, 2850 cm^{-1}.
2'-I: (60%), b.p. 208–210°C/0.6 mm; δ_H ($CDCl_3$) 4.55 (*s*, CH_2), 4.02 (*s*, OH); ν_{max} (KBr) 3500–3100, 3050, 2900, 2850 cm^{-1}.

Step 5 was carried out by adding a solution of the alcohol (0.01 mol) in dry methylene chloride (15 ml) to a stirred suspension of pyridinium chlorochromate (0.180 mol) in methylene chloride (25 ml) at room temperature.[8] After 2 h, dry ether (125 ml) was added and the solvents decanted off. The black residue was washed with ether (2 × 75 ml), the solvent and washings were combined and evaporated, and the residue was purified by column chromatography on silica gel eluted with 3:1 light petroleum (b.p. 60–80°C): ethyl acetate to give the pure aldehyde.

2-Fluorobiphenyl-4-carbaldehyde was obtained by reaction of the Grignard reagent derived from 4-bromo-2-fluorobiphenyl with triethyl orthoformate.[9] The Grignard reagent was prepared in the usual manner from the bromo-compound (15 g, 0.058 mol), and magnesium (1.46 g, 0.06 g atom) in ether (80 ml). Benzene (40 ml) was added to ensure that the Grignard reagent remained in solution during the slow addition of triethyl orthoformate (8.9 g, 0.06 mol), whereafter the mixture was heated under reflux for 6 h. After cooling in ice, 2M-aqueous hydrochloric acid (30 ml) was added and the mixture stirred overnight. The organic layer was separated, the solvent removed and the crude acetal hydrolysed by heating under reflux with 25% aqueous sulphuric acid (30 ml) for 4 h. The mixture was poured into water (300 ml) and the crude aldehyde extracted into ether and purified *via* the bisulphite addition compound followed by short-path vacuum distillation.

2'- and 2-Halogenobiphenyl-4-carbaldehydes

2'-F: (90%), m.p. 38.5–40.5°C; δ_H ($CDCl_3$) 10.05 (*s*, CHO); ν_{max} (KBr) 1705 cm^{-1} (C=O)
2'-Cl: (95%), m.p. 70–71.5°C; δ_H ($CDCl_3$) 10.08; ν_{max} (KBr) 1690 cm^{-1}
2'-Br: (90%), m.p. 58–60°C; δ_H ($CDCl_3$) 10.07; ν_{max} (KBr) 1690 cm^{-1}
2'-I: (90%), m.p. 80–81°C; δ_H ($CDCl_3$) 10.05; ν_{max} (KBr) 1700 cm^{-1}
2-F: (35%), b.p. 112°/0.35 mm; δ_H ($CDCl_3$) 10.07; ν_{max} (KBr) 1690 cm^{-1}

4-Amino-2'-fluorobiphenyl was obtained as previously described[6] *via* Step 1, then by conversion of the acetyl compound into the oxime which was subjected to a Beckmann rearrangement, followed by hydrolysis of the resulting acetylamine.

The azomethines were prepared by reaction between the 2- and 2′-halogenobiphenyl-4-carbaldehydes and the appropriate 4-*n*-alkoxyanilines and from 2-amino-2′-fluorobiphenyl and the required 4-*n*-alkoxybenzaldehyde by the methods previously described.[10,11]

M.p.s and transition temperatures for the *4-*n*-alkoxy-*N*-(2′-halogenobiphenyl-4-ylmethylene)anilines* and for the *4-*p*-*n*-alkoxybenzylideneamino-2′-fluorobiphenyls* are listed in Table I. Elemental analyses were carried out on one member of each series of halogeno-substituted azomethines and satisfactory results obtained. Confirmation of the structures of the products (and of intermediates, where necessary) was obtained by ^{1}H nmr and ir spectroscopy, and by mass spectrometry. The following data, which are typical of the series, refer to 4-*n*-decyloxy-*N*-(2′-bromobiphenyl-4-ylmethylene)aniline (Found: C, 70.9; H, 6.8; Br, 16.5. $C_{29}H_{34}BrNO$ requires C, 70.7; H, 6.95; Br 16.2%); m/z 494 (30.5%), 493 (M^+, 100), 492 (32.5), 491 (M^+, 93.5), 354 (16), 353 (71), 352 (63.5), 351 (79.5), 350 (46); ν_{max} (KBr) 3050, 2930, 2860, 1625, 1500, 1245 cm^{-1}; δ_H ($CDCl_3$) 1.00 (3H, *t*, CH_3), 1.41 (16H, *br*, *m*), 4.04 (2H, *t*, OCH_2), 6.88–8.08 (8H, *m*, ArH), and 8.57 (1H, *s*, N═CH)

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