Liquid Crystal Properties of Certain 4-Alkoxy-*N*-(fluoren-2-ylmethylene)-and -(2-naphthylmethylene)-anilines†

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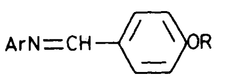
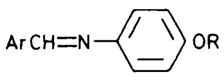
The liquid crystal transition temperatures of 12 4-alkoxy-*N*-(fluoren-2-ylmethylene)anilines are reported. Differences in liquid crystal thermal stability between pairs of related series of azomethines of fluorene, 9-oxofluorene, 9,10-dihydrophenanthrene, and biphenyl are compared. Only one member of the 4-alkoxy-*N*-(2-naphthylmethylene)anilines shows liquid crystal behaviour.

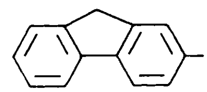
Twelve members of the homologous series of 4-alkoxy-*N*-(fluoren-2-ylmethylene)anilines (**2a**) have been prepared and their liquid crystal transition temperatures measured in order to compare their mesomorphic behaviour with the analogous 2-*p*-alkoxybenzylideneaminofluorenes (**1a**).[1]

Azomethines of type (**1**) differ from those of type (**2**) because of the reversed mode of linkage of the –CH=N– group. We have previously investigated the effect of this small change in the molecular core for three other related pairs of homologous series of azomethines, namely the corresponding compounds where Ar = biphenyl-4-yl, (**1b**)[2] and (**2b**),[2] Ar = 9,10-dihydro-2-phenanthryl, (**1c**)[3] and (**2c**),[4] and Ar = 9-oxofluoren-2-yl, (**1d**)[1] and (**2d**).[5] For the last two pairs of series, (**1c**) and (**2c**), and (**1d**) and (**2d**), plots of N–I transition temperatures against the number of carbon atoms, *n*, in the alkyl chain show minima then maxima for the early homologues and the absence of S–I transitions for the long-chain homologues, *i.e.* the persistence of nematic phases to a late stage in the homologous series. The present work extends the comparison to Ar = fluoren-2-yl, (**1a**) and (**2a**). The 2-*p*-alkoxybenzylideneaminofluorenes (**1a**), first reported[1] in 1955, give a transition temperature plot, typical of the majority of series investigated at that time, showing normal regularities (*i.e.* smoothly falling N–I transition temperature curves for odd-*n* and even-*n* members, without the appearance of minima or maxima, and a rising S_A–N transition temperature curve that becomes coincident with the falling N–I curve at long alkyl chain lengths). The same trends are also found for the 4-alkoxy-*N*-(fluoren-2-ylmethylene)anilines (**1b**) for which the transition temperatures are summarised in Table 1 and shown plotted against *n* in the Figure.‡

For comparison with other related compounds the relative thermal stability of the liquid crystal phases of the two series, (**1a**) and (**1b**), of azomethines of fluorene is of particular interest. This may be evaluated, as previously for other series, using average values for the S_A–N ($n = 9,10$) and N–I ($n =$ 7—10) transition temperatures. The values (°C) so obtained are: S_A–N, 169.75 (**1a**) and 168 (**2a**); N–I, 186.4 (**1a**) and 180.6 (**2a**). Thus, for Ar = fluoren-2-yl, both smectic and nematic thermal stability are slightly higher for the azomethines of type (**1**) than for type (**2**), the differences being ΔT_{S_A} 1.75° and ΔT_N 5.8°. These ΔT values are intermediate between those shown for Ar = 9,10-dihydro-2-phenanthryl, (**1c**) and (**2c**), on the one hand and Ar = biphenyl-4-yl, (**1b**) and (**2b**), and Ar = 9-oxofluoren-2-yl, (**1d**) and (**2d**), on the other.[4]


(1)


(2)

a; Ar =


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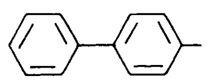

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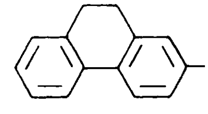

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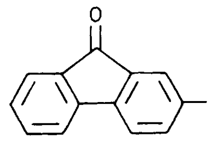
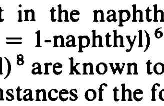


e; Ar =


$R = C_nH_{2n+1}$

Liquid crystal properties have not been reported for corresponding simple azomethines, (**1**) and (**2**), where Ar = 1- or 2-naphthyl, although several such derivatives carrying a substituent in the naphthalene ring either at the 4-position (when Ar = 1-naphthyl)[6,7] or the 6-position (when Ar = 2-naphthyl)[8] are known to form liquid crystals. The absence of reported instances of the formation of liquid crystals by simple benzylidenenaphthylamines or naphthylideneanilines is surprising as the presence of the naphthalene ring is known to confer considerable mesogenic character on other systems.[9,10] Accordingly, we have prepared 12 members of the 4-alkoxy-*N*-(2-naphthylmethylene)anilines (**2e**) in order fully to investigate the homologous series for liquid crystal behaviour.

Only the decyloxy compound was found to form a (monotropic nematic) mesophase, and the following transition temperatures were obtained for this compound: C–I, 99.0; I–N, 78.8; N–C, 76 °C.

Studies of other members of the series of azomethines in the region of the decyloxy compound in binary mixtures with K6§ revealed monotropic N–I transition temperatures for the heptyloxy and octyloxy compound and by extrapolation to 0% of the additive, 'virtual' transition temperatures for the pure compounds could be estimated. However, it is clear that when Ar = 2-naphthyl (**2e**) the liquid crystal thermal stability is substantially lower than for other Ar groups investigated.[1–5]

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† As with other similar papers this work was carried out mainly by final year undergraduates as part of their research projects.

‡ The S_A phases were identified by microscopic examination of the focal conic fan textures adopted by thin samples of the compounds mounted between a slide and cover slip and allowed to cool from the isotopic liquid.

§ Obtained from B.D.H. Chemicals Ltd., Broom Road, Poole, Dorset BH12 4NN.

Table 1. Transition temperatures for 4-alkoxy-*N*-(fluoren-2-ylmethylene)anilines (**2a**)

R	Transition temperatures (°C)			
	C–S_A/N	S_A–N/I	N–I	S_A/N–C
CH_3	173		203.5	122
CH_3CH_2	179		213.5	140
$CH_3(CH_2)_2$	163		197	136
$CH_3(CH_2)_3$	154		202	135
$CH_3(CH_2)_4$	151	145	191	129
$CH_3(CH_2)_5$	144	153	191	118.5
$CH_3(CH_2)_6$	139	160	185	114.5
$CH_3(CH_2)_7$	135	164.5	183.5	110
$CH_3(CH_2)_8$	133	167.5	178.5	108.5
$CH_3(CH_2)_9$	130	168.5	175.5	114.5
$CH_3(CH_2)_{11}$	126.5	168.5	169.5	112
$CH_3(CH_2)_{13}$	125.5	165.5		108

Table 2. Elemental analyses for 4-alkoxy-*N*-(fluoren-2-ylmethylene)-anilines (**2a**)

R	Found (%)			Molecular formulae	Required (%)		
	C	H	N		C	H	N
CH_3	84.1	5.6	4.8	$C_{21}H_{17}NO$	84.2	5.7	4.7
CH_3CH_2	84.3	5.9	4.6	$C_{22}H_{19}NO$	84.3	6.1	4.5
$CH_3(CH_2)_2$	84.2	6.4	4.8	$C_{23}H_{21}NO$	84.4	6.4	4.3
$CH_3(CH_2)_3$	84.1	6.8	4.0	$C_{24}H_{23}NO$	84.4	6.7	4.1
$CH_3(CH_2)_4$	83.6	7.1	3.9	$C_{25}H_{25}NO$	84.5	7.0	3.9
$CH_3(CH_2)_5$	84.5	7.2	3.6	$C_{26}H_{27}NO$	84.5	7.3	3.8
$CH_3(CH_2)_6$	84.6	7.4	3.9	$C_{27}H_{29}NO$	84.6	7.6	3.7
$CH_3(CH_3)_7$	84.7	7.8	3.6	$C_{28}H_{31}NO$	84.6	7.8	3.5
$CH_3(CH_2)_8$	84.4	8.1	3.2	$C_{29}H_{33}NO$	84.7	8.0	3.4
$CH_3(CH_2)_9$	84.7	8.0	3.5	$C_{30}H_{35}NO$	84.7	8.2	3.3
$CH_3(CH_2)_{11}$	84.8	8.4	3.3	$C_{32}H_{39}NO$	84.8	8.6	3.1
$CH_3(CH_2)_{13}$	84.6	9.0	2.9	$C_{34}H_{43}NO$	84.8	9.0	2.9

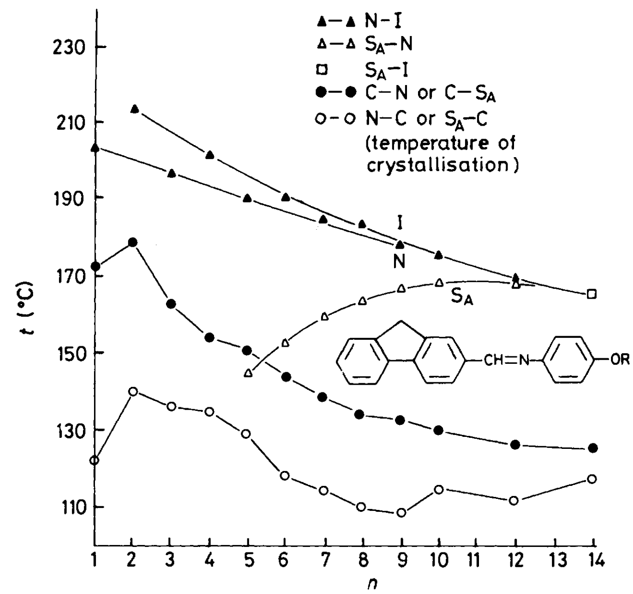

Figure. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkyl chain (R) of the 4-alkoxy-*N*-(fluoren-2-ylmethylene)anilines (**2a**)

Experimental

Measurements of transition temperatures and microscopic observations of textures of mesophases were made using a Vickers M75 polarising microscope in conjunction with a Mettler FP 52 hot-stage and FP 5 control unit. I.r. spectra were recorded for KBr discs with a Perkin-Elmer 157 grating spectrophotometer, and ^1H n.m.r. 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 of the Boots Company plc with an A.E.I. MS 902S spectrometer equipped with a Mass Spectrometry Services Analog Series 200 console and an INCOS 2300 data system.

*4-Alkoxy-*N*-(fluoren-2-ylmethylene)anilines and 4-Alkoxy-*N*-(2-naphthylmethylene)anilines.*—The azomethines were prepared[2] from fluorene-2-carbaldehyde or naphthalene-2-carbaldehyde and a slight molar excess of the appropriate *p*-alkoxyaniline[4] and purified by recrystallisation several times from light petroleum (b.p. 100—120 °C) and from cyclohexane or ethanol.

The transition temperatures for the *4-alkoxy-*N*-(fluoren-2-ylmethylene)anilines* are listed in Table 1 and their elemental analyses are given in Table 2. The following data for the butoxy compound are typical of the homologous series as a whole: m/z 342 (20.5%), 341 (M^+, 78.5), 286 (16), 285 (77), 284 (100), 165 (18), and 120 (18); $\nu_{max.}$ (KBr) 3 040, 2 968, 2 878, 1 624, 1 612, 1 503, 1 477, 1 398, 1 250, 837, 830, 800, 773, and 739 cm^{-1}; δ_H ($CDCl_3$) 0.98 (3 H, t, CH_3), 1.25—1.93 (4 H, br m, CH_2CH_2), 3.96 (4 H, m ArCH_2Ar and OCH_2), 6.83—8.12 (11 H, m, ArH), and 8.53 (1 H, s, CH=N).

For *4-decyloxy-*N*-(2-naphthylmethylene)aniline* (C, 83.9; H, 8.5; N, 3.5. $C_{27}H_{33}NO$ requires C, 83.7; H, 8.6; N, 3.6%) the following spectroscopic data were obtained, $\nu_{max.}$ (KBr) 2 950, 2 850, 1 620, 1 590, 1 500, 1 460, 1 390, 1 280, 1 240, 1 160, 1 100, 1 050, 980, 860, 830, 810, and 740 cm^{-1}; δ_H ($CDCl_3$) 0.90 (3 H, t, J 6.0 Hz, CH_3), 1.2—2.0 (16 H, br, m), 3.95 (2 H, t, J 6.0 Hz, OCH_2), 7.0—8.22 (11 H, m, ArH), and 8.62 (1 H, s, CH=N).

Acknowledgements

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