Properties of the Liquid Crystals formed by Certain 4-Alkoxy-*N*-(2-phenanthrylmethylene)anilines

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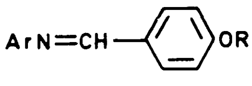
The liquid crystal transition temperatures of twelve 4-alkoxy-*N*-(2-phenanthrylmethylene)anilines are reported and compared with those of corresponding members of similar homologous series of azomethines. Differences in liquid crystal thermal stability between comparable azomethines in which the -CH=N- linkage is reversed are discussed.

Twelve members (methoxy through to decyloxy, dodecyloxy, and tetradecyloxy) of the homologous series of 4-alkoxy-*N*-(2-phenanthrylmethylene)anilines (**2d**) have been prepared and their liquid crystal transition temperatures measured. This work completes our comparative study of the liquid crystal behaviour of homologous series of isomeric azomethines (**1**) and (**2**) derived from a number of related aromatic systems (**a**—**e**).[1–7]

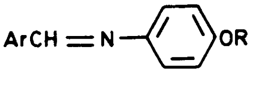
The transition temperatures for the 4-alkoxy-*N*-(2-phenanthrylmethylene)anilines (**2d**) are listed in Table 1. When these temperatures are plotted (Figure) against the number of carbon atoms, *n*, in the alkyl chain, the points for the N–I transition temperatures lie on two falling curves (even-*n* above odd-*n* members) which converge as *n* increases, with a rising curve for the S_A–N† transition temperatures. The graph resembles the corresponding plot for the analogous 2-*p*-alkoxybenzylideneaminophenanthrenes (**1d**),[7] in which the -CH=N- linkage is reversed, and, for the odd-*n* members, the N–I transition temperature curve has a similar shape, showing a slight inflection, to the corresponding curve for the azomethines (**2c**) where Ar = biphenyl-4-yl.

Table 2 gives the average values (in °C) for the N–I (n = 7—10) and S_A–N (n = 9 and 10) transition temperatures of the azomethines (**1a**—**e**) and (**2a**—**e**). For ease of comparison, Table 2 also shows differences [$\Delta T = T_{(1)} - T_{(2)}$] in smectic and nematic thermal stabilities. The results of the present work indicate that when Ar = 2-phenanthryl both smectic and nematic thermal stability are higher, by 11.5 and 8.6 °C, for the azomethines of type (**1**) as compared with type (**2**).

As the difference between the azomethines (**1**) and (**2**) is merely the mode of linkage of the -CH=N- group, only quite a small and relatively constant effect on liquid crystal thermal stability would be expected. In fact, the values of ΔT, *i.e.* the amounts by which both smectic and nematic thermal stability are greater for the azomethines (**1**) than for (**2**), vary, and lie in the order Ar = 9,10-dihydro-2-phenanthryl (**a**) > 2-phenanthryl (**d**) > fluoren-2-yl (**e**) > biphenyl-4-yl (**c**) > 9-oxofluoren-2-yl (**b**). In the latter two instances, the mesophases are more stable for the azomethines (**2**) than for (**1**). The larger values of ΔT are given by the more bulky (*i.e.* broader, thicker) Ar groups, and, with the exception of Ar = 9-oxofluoren-2-yl, the lowest ΔT value is shown by Ar = biphenyl-4-yl, for which it is known that there is a very small inter-ring angle,[8] and hence minimal molecular broadening, in the liquid crystal phases.

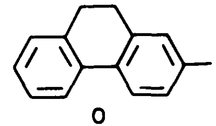


(**1**)



(**2**)

a; Ar =



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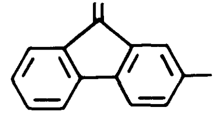
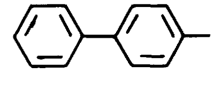
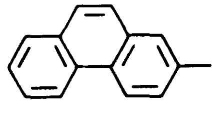


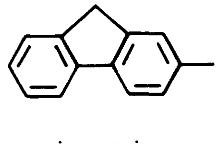
c; Ar =



d; Ar =



e; Ar =



R = C_nH_{2n+1}

It is possible that the relationship between the ΔT value and the size of the Ar group is fortuitous and without physical significance. However, in certain azomethines it is known that the molecules are twisted out of coplanarity on either side of the central -CH=N- group, the plane of the N–Ar group making an angle of 40—60° with the rest of the molecule,[9] and this is also likely to be true of the azomethines discussed in this paper. Thus, a more favourable molecular arrangement in the mesophases may result for a particular type of azomethine, depending on the size of the Ar group, so that for the more bulky Ar groups the molecules may pack more closely in the liquid crystal phases of the azomethines of type (**1**) than of type (**2**). This could be responsible for the differences, ΔT, in thermal stability of the liquid crystal phases. The anomalous position of Ar = 9-oxofluoren-2-yl may be associated with different

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† 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 a cover slip and allowed to cool from the isotropic liquid.

molecular interactions due to the presence of the laterally disposed dipole of the carbonyl function.

The significance of these observations will be explored in future work.

The synthesis of phenanthrene-2-carbaldehyde, from which the azomethines (**2d**) were derived, was attempted by the route previously successfully employed for the 9,10-dihydro-analogues[4] in which the final step ($-COCl \longrightarrow -CHO$) was accomplished by using the metal-assisted reducing medium of Johnstone *et al.*,[10] which utilises the addition of Cd^{2+} with dimethylformamide to sodium borohydride in acetonitrile. However, this method gave unsatisfactory results for the reduction of 2-phenanthroyl chloride. At the recommended temperature (− 36 °C) the reduction was extremely slow, owing to the insolubility of the acid chloride in the acetonitrile–ether solvent, even when the quantity of solvent was doubled. At more elevated temperatures considerable over-reduction accompanied the formation of the aldehyde, so that at − 5 °C the product was almost entirely 2-phenanthrylmethanol. In these cases it was possible to oxidise the alcohol back to the aldehyde. Nevertheless, a less troublesome, more efficient route involved conversion of phenanthrene-2-carboxylic acid into its methyl ester with BF_3–MeOH complex, then reduction ($LiAlH_4$) to the alcohol followed by oxidation to the aldehyde with pyridinium chlorochromate.[11]

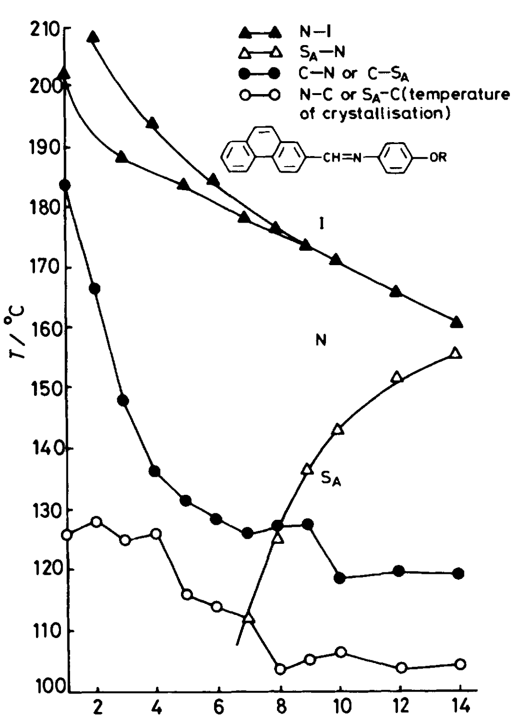

Figure. Plot of transition temperatures against the number of carbon atoms (n) in the alkyl chain (R) of the 4-alkoxy-*N*-(2-phenanthrylmethylene)anilines (**2d**)

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. 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 (Boots 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*-(2-phenanthrylmethylene)anilines.*—2-Acetylphenanthrene was prepared by Friedel–Crafts acylation, by addition of phenanthrene (0.45 mol) and acetyl chloride (0.6 mol) to finely powdered aluminium chloride (1.0 mol) in ice-cold nitrobenzene (700 cm^3). The resulting solution was stirred at 0 °C for 30 min and then at room temperature for 8 h, then poured into ice-cold water (2 000 cm^3) and concentrated hydrochloric acid (80 cm^3), after which the nitrobenzene was removed by steam distillation. Separation of the 2- from the 3-acetyl

Table 1. Transition temperatures for 4-alkoxy-*N*-(2-phenanthrylmethylene)anilines (**2d**)

R	Transition temperature (°C)			
	C–N/S_A	S_A–N	N–I	S_A/N–C[a]
CH_3	184		203	126
CH_3CH_2	166.5		208.5	128
$CH_3[CH_2]_2$	148		188.5	125
$CH_3[CH_2]_3$	136.5		194	126
$CH_3[CH_2]_4$	131.5		184	116
$CH_3[CH_2]_5$	128.5		184.5	114
$CH_3[CH_2]_6$	126	[112][b]	178.5	112
$CH_3[CH_2]_7$	127	[125][b]	176.5	103.5
$CH_3[CH_2]_8$	127.5	136.5	173.5	105
$CH_3[CH_2]_9$	118.5	143	171	106
$CH_3[CH_2]_{11}$	119.5	151.5	165.5	103.5
$CH_3[CH_2]_{13}$	119	155	160	104

[a] Temperature of crystallisation. [b] Monotropic transition.
Other symbols have their usual significance, namely: C, crystal; N, nematic phase; S_A, smectic phase; I, isotropic liquid. Thus C–N/S_A represents the m.p. of the compound at which a transition from the crystalline solid to a liquid crystal phase (either a nematic or a smectic A phase) occurs.

Table 2. Average transition temperatures (T/°C) and differences (ΔT/°C) in smectic and nematic thermal stability for azomethines of types (**1**) and (**2**)

Ar	(**1**)		(**2**)			
	T_{S_A}[a]	T_N[b]	T_{S_A}[a]	T_N[b]	ΔT_{S_A}[a,d]	ΔT_N[b,d]
(**a**) 9,10-Dihydro-2-phenanthryl	97	137	75.5	127.5	+21.5	+9.5
(**b**) 9-Oxofluoren-2-yl	84.5 (122.0)[c]	139.9	(125.5)[c]	148.1	−3.5[c]	−8.2
(**c**) Biphenyl-4-yl	157.25	161.9	157.75	165	−0.5	−3.1
(**d**) 2-Phenanthryl	151.25	183.5	139.75	174.9	+11.5	+8.6
(**e**) Fluoren-2-yl	169.75	186.4	168	180.6	+1.75	+5.8

[a] T obtained from average S_A–N values; n = 9 and 10. [b] T obtained from average N–I values; n = 7—10. [c] T refers to values for n = 16. [d] $\Delta T = T_{(1)} - T_{(2)}$.

Table 3. Elemental analyses for 4-alkoxy-*N*-(2-phenanthrylmethylene)-anilines (**2d**)

R	Found (%) C	Found (%) H	Molecular formula	Required (%) C	Required (%) H
CH_3	85.1	5.6	$C_{22}H_{17}NO$	84.9	5.5
CH_3CH_2	85.0	5.6	$C_{23}H_{19}NO$	84.9	5.8
$CH_3[CH_2]_2$	84.8	5.9	$C_{24}H_{21}NO$	85.0	6.2
$CH_3[CH_2]_3$	85.2	6.6	$C_{25}H_{23}NO$	85.0	6.5
$CH_3[CH_2]_4$	85.2	6.9	$C_{26}H_{25}NO$	85.0	6.8
$CH_3[CH_2]_5$	85.0	7.2	$C_{27}H_{27}NO$	85.0	7.1
$CH_3[CH_2]_6$	85.2	7.1	$C_{28}H_{29}NO$	85.1	7.3
$CH_3[CH_2]_7$	84.9	7.3	$C_{29}H_{31}NO$	85.1	7.6
$CH_3[CH_2]_8$	84.9	7.5	$C_{30}H_{33}NO$	85.1	7.8
$CH_3[CH_2]_9$	85.0	8.2	$C_{31}H_{35}NO$	85.1	8.0
$CH_3[CH_2]_{11}$	85.1	8.1	$C_{33}H_{39}NO$	85.1	8.4
$CH_3[CH_2]_{13}$	85.0	8.4	$C_{35}H_{43}NO$	85.2	8.7

compound in the residue was achieved by utilising the differing solubilities of the isomers in ether. After digestion with ether, the insoluble 2-isomer was distilled under reduced pressure; the distillate immediately solidified and was crystallised from methanol affording 2-acetylphenanthrene (14%) as colourless needles, m.p. 142—143 °C (lit.,[12] 143 °C). The ketone (0.1 mol) was oxidised by heating with aqueous 2% sodium hypochlorite (600 cm^3) under reflux for 24 h, whereafter water (400 cm^3) was added to dissolve the sodium salt of the resulting carboxylic acid, then aqueous hydrochloric acid to precipitate the crude acid, which was purified by crystallisation from glacial acetic acid. The phenanthrene-2-carboxylic acid (50—55% in several preparations), m.p. 259—260 °C (lit.,[12] 258—260 °C), was esterified by heating the acid (0.035 mol) with 12% boron trifluoride–methanol complex (60 cm^3) in dry methanol (120 cm^3) under reflux for 6 h. After treatment with saturated aqueous sodium hydrogen carbonate (40 cm^3) the ester was recrystallised from methanol, affording methyl phenanthrene-2-carboxylate (87%) as white needles, m.p. 96—97 °C (lit.,[12] 96—96.5 °C). By the usual procedure, the ester (0.03 mol) in dry ether (100 cm^3) was reduced under nitrogen by rapid addition to a stirred solution of powdered lithium aluminium hydride (0.05 mol) in the same solvent (100 cm^3). After being heated under reflux for 30 min, the solution was cooled, and water (150 cm^3) was added carefully to remove the excess of reducing agent, followed by aqueous 4M-hydrochloric acid (100 cm^3) to break down the complex. The aqueous layer was separated and extracted with ether (2 × 100 cm^3), and the extract combined with the ether layer. The ether was removed and the residue was crystallised from chloroform–light petroleum (b.p. 60—80 °C) giving 2-phenanthrylmethanol (93%) as a white powder, m.p. 126° (lit.,[13] 125—125.5 °C). The alcohol (0.02 mol) in dry methylene dichloride (50 cm^3) was added to a stirred suspension of pyridinium chlorochromate (0.03 mol) in the same solvent (30 cm^3) and the mixture stirred at room temperature for 2 h.[11] Dry ether (200 cm^3) was added, the solvent was decanted, and the residue was washed with ether. The combined solvent and washings were evaporated and the residue was applied to a silica gel column, which was eluted with light petroleum (b.p. 60—80 °C)–ethyl acetate (3:1). The resulting white solid was crystallised from aqueous methanol yielding the phenanthrene-2-carbaldehyde (85%) as colourless needles, m.p. 58 °C (lit.,[13] 59—59.5 °C), $\nu_{max.}$(KBr) 1 690 cm^{-1} (C=O); δ_H($CDCl_3$) 10.1. The *4-alkoxy-*N*-(2-phenanthrylmethylene)anilines* were prepared from phenanthrene-2-carbaldehyde (0.25 g) and a slight molar excess of the appropriate *p*-alkoxyaniline as previously described,[4] and were purified by recrystallisation several times from ethanol and from chloroform–light petroleum (b.p. 40—60 °C). Transition temperatures and elemental analyses for the azomethine derivatives are listed in Tables 1 and 3, respectively. The following data for 4-heptyloxy-*N*-(2-phenanthrylmethylene)aniline are typical of other members of the homologous series: *m/z* 396 (31.5%), 395 (M^+, 100), 325 (14), 298 (15.5), 297 (76), and 296 (89); $\nu_{max.}$(KBr) 3 060, 2 930, 2 860, 1 620, 1 500, and 1 245 cm^{-1}; δ_H($CDCl_3$) 0.91 (3 H, t, CH_3), 1.37 (10 H, br, m), 3.99 (2 H, t, OCH_2), 6.89—8.30 (9 H, m, ArH), and 8.66 (1 H, s, N=CH).

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