Properties of the Liquid Crystals formed by Certain 4-Alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines

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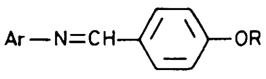
The liquid crystal transition temperatures of 13 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines are reported and discussed. The series gives a transition temperature plot of a similar type to that of the 2-*p*-alkoxybenzylideneaminofluorenones (in which the –CH=N– linkage is reversed), the N–I transition temperatures showing minima then maxima for the early homologues, but smectic properties do not occur until a late stage in the homologous series. Differences in liquid crystal thermal stability between the two series of azomethines of 9-oxofluorene are compared with the corresponding values for the 9,10-dihydrophenanthrene and biphenyl derivatives.

The properties of the liquid crystals formed by certain members of the homologous series of 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes[1,2] (**1a**) and the analogous 4-alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)anilines[3] (**2a**) have recently been reported. The two series of azomethines derived from 9,10-dihydrophenanthrene show similar anomalous mesomorphic behaviour to that first reported by Gray *et al.*[4] for the 2-*p*-alkoxybenzylideneaminofluorenones (**1b**). The usual odd–even alternation of the N–I transition temperatures occurs, but as the alkyl chain is lengthened the N–I transition temperatures initially decrease to a minimum then increase to a maximum before showing the expected gradual decrease for the longer chain homologues. In addition, although the smectic phases that appear in the middle of the series show an increase in thermal stability with increase in the alkyl chain length, even at the longest chain lengths studied nematic phases are still observed (*i.e.* the increase in smectic thermal stability is insufficiently large for S–I transitions to replace the N–I transitions).

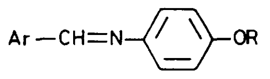
For many years the behaviour shown by the 2-*p*-alkoxybenzylideneaminofluorenones (**1b**) remained unique, but, more recently, other series have been reported showing similar maxima and/or minima.† However, the two series of azomethines derived from 9,10-dihydrophenanthrene, (**1a**) and (**2a**), are the most closely related compounds to the 2-*p*-alkoxybenzylideneaminofluorenones to show similar anomalous properties.

Average values of S–N (or I) and N–I transition temperatures for analogous members of related series may be used to compare mesophase thermal stability. The azomethines of type (**1**) differ from those of type (**2**) because of the reversed mode of linkage of the –CH=N– group, and this relatively minor structural modification to the central core of the molecules is not expected to have a major effect on liquid crystal thermal stability. The results for azomethines of biphenyl[8] confirm this expectation; both smectic and nematic thermal stability show a slight *increase* (by 0.5 and 3.1 °C respectively) on passing from (**1c**) to (**2c**). However, the corresponding azomethines of 9,10-dihydrophenanthrene do not conform to this pattern and the change from (**1a**) to (**2a**) causes a significant *decrease* in smectic (by 21.5 °C) and in nematic (by 9.5 °C) thermal stability.

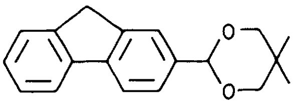
It is possible that the differences in liquid crystal thermal stability of the azomethines of 9,10-dihydrophenanthrene, (**1a**) and (**2a**), caused by reversal of the –CH=N– group may be associated with the structural factors which are responsible for their unusual behaviour (T_{N-I} minima and maxima, *etc.*) described above. In order to investigate this possibility by extension to other 'anomalous' series, we expected that the 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines (**2b**) would also show unusual transition temperature plots and hence enable a comparison to be made with their counterparts with the –CH=N– linkage reversed, the 2-*p*-alkoxybenzylideneaminofluorenones (**1b**). Accordingly, 13 members (methoxy through to decyloxy, dodecyloxy, tetradecyloxy, and hexadecyloxy) of the homologous series of 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines (**2b**) have been prepared and their liquid crystal transition temperatures measured. The transition temperatures for this series are listed in Table 1 and are shown plotted against the number of carbon atoms, *n*, in the alkyl chain in the Figure. As expected, the plot (Figure) of transition temperatures against *n* for the 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines (**2b**) shows the same general trends for the N–I transition temperatures as discussed above for their counterparts with the –CH=N– linkage reversed, the 2-*p*-alkoxybenzylideneaminofluorenones (**1b**), and for the azo-



(1)

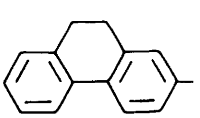


(2)



(3)

a; Ar =



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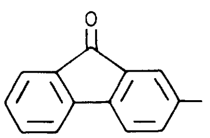
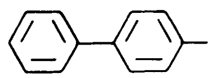


c ; Ar =



$R = C_nH_{2n} + 1$

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† *E.g.*, certain esters of 4,4′-azoxyphenol,[5] the 4-*p*-alkoxybenzylideneaminoacetophenones,[6] and the 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls.[7]

Table 1. Transition temperatures for 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines (**2b**)

R		Transition temperatures/°C		
	$C-S_A/N$	S_A-N	N-I	$S_A/N-C$[a]
Me	145		152.5	37.5
$MeCH_2$	161.5		166.5	125
$Me[CH_2]_2$	135		146	78
$Me[CH_2]_3$	126		158	75
$Me[CH_2]_4$	103.5		149.5	72
$Me[CH_2]_5$	119.5		153.5	65
$Me[CH_2]_6$	112.5		148.5	71.5
$Me[CH_2]_7$	101.5		150	82
$Me[CH_2]_8$	101.5		147	77
$Me[CH_2]_9$	104.5		147	82
$Me[CH_2]_{11}$	107		144	87
$Me[CH_2]_{13}$	109.5		141	90
$Me[CH_2]_{15}$	111.5	125.5[b]	137.5	95

[a] Temperature of crystallisation. [b] A monotropic S_C-S_A transition also occurs at 108.5 °C

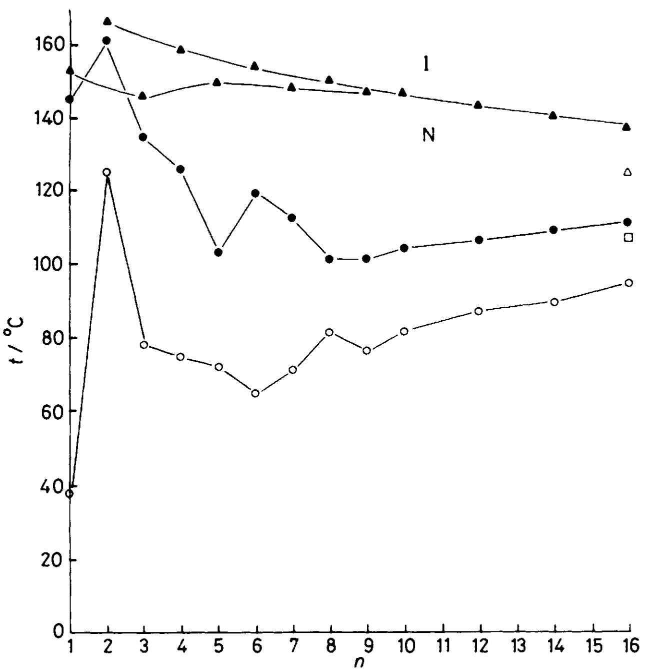

Figure. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkyl chain (R) of the 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines (**2b**): ▲, N-I; △, S_A-N; □, S_C-S_A; ●, C-N or C-S_A; ○, N-C or S_A-C (temperature of crystallisation)

methines of 9,10-dihydrophenanthrene, (**1a**) and (**2a**). However, smectic properties are absent until a sudden incursion occurs at the hexadecyloxy compound which has both S_A and S_C phases.* This is much later in the homologous series than is found for the other three series of azomethines showing anomalous transition temperature plots; for example, smectic properties occur at *n* = 7 for the analogous 2-*p*-alkoxybenzylideneaminofluorenones (**1b**). The absence of smectic properties before *n* = 16 does not seem to be due to a high recrystallisation temperature for earlier homologues. These supercool to an extent that monotropic smectic phases could have been detected if a similar rising S_A-N curve to that found in series (**1b**) occurred.

Table 2. Differences (ΔT °C) in smectic and nematic thermal stability between azomethines (**1**) and (**2**)

Ar	ΔT_{S_A}[a,b]	ΔT_N[a,c]
(**a**) 9,10-Dihydro-2-phenanthryl	+21.5	+9.5
(**b**) 9-Oxofluoren-2-yl	−3.5[d]	−8.2
(**c**) Biphenyl-4-yl	−0.5	−3.1

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

An assessment of smectic thermal stability of the azomethines of 9-oxofluorene, (**1b**) and (**2b**), is necessarily restricted to a comparison of a single member (*n* = 16) of each series, and the values used may not be strictly comparable as they are taken from different parts of the respective S_A-N curves: at the commencement in one case (**2b**) and, in the other (**1b**), where the steeply rising curve has begun to flatten out. However, even if the difference in smectic thermal stability is discounted in this instance, the differences in nematic thermal stability between azomethines (**1**) and (**2**), clearly show (Table 2) more correspondence between the azomethines with Ar = 9-oxofluoren-2-yl (**b**) and Ar = biphenyl-4-yl (**c**) rather than with Ar = 9,10-dihydro-2-phenanthryl (**a**). Thus, for the two pairs of related series of azomethines of 9-oxofluorene, (**1b**) and (**2b**), and 9,10-dihydrophenanthrene, (**1a**) and (**2a**), that give rise to unusual N-I transition temperature plots there does *not* seem to be a relationship between the structural factors responsible for this behaviour and differences in liquid crystal thermal stability caused by reversal of the –CH=N– linkage.

The 9-oxofluorene-2-carbaldehyde required to prepare the azomethine derivatives was obtained from fluorene-2-carbaldehyde. After protection of the aldehyde group of this compound by formation of the cyclic acetal (3) with 2,2-dimethylpropane-1,3-diol, oxidation of the 9-methylene group was accomplished with oxygen from the air in the presence of Triton B in pyridine solution.[9] This very mild method gave an excellent yield. The 9-methylene group was also oxidised by fusion with nickel peroxide[10] but the yield was not as good. Hydrolysis of the cyclic acetal was successfully achieved with hydrochloric acid. Substantial oxidation of the aldehyde group occurred when the hydrolysis was carried out with perchloric acid.

Experimental

Measurements of transition temperatures and microscopic observations of textures of mesophases were made using a Vickers M75 polarising microscope in conjunction with a Metler FP 52 heating 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 P.L.C. 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-(9-*oxofluoren*-2-*ylmethylene*)*anilines*.—Fluorene-2-carbaldehyde and 2,2-dimethylpropane-1,3-diol

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* Microscopic examination of a thin sample mounted between a slide and cover-slip and cooled slowly from the isotropic liquid revealed focal conic fan and homeotropic textures for the S_A phase[2] and broken focal conic fan and schlieren textures for the S_C phase.

Table 3. Elemental analyses for 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines (**2b**)

R	Found (%) C	Found (%) H	Found (%) N	Molecular formula	Required (%) C	Required (%) H	Required (%) N
Me	80.5	4.9	4.6	$C_{21}H_{15}NO_2$	80.5	4.8	4.5
$MeCH_2$	80.6	5.3	4.1	$C_{22}H_{17}NO_2$	80.7	5.2	4.3
$Me[CH_2]_2$	80.8	5.7	4.2	$C_{23}H_{19}NO_2$	80.9	5.6	4.1
$Me[CH_2]_3$	81.1	5.9	3.9	$C_{24}H_{21}NO_2$	81.1	6.0	3.9
$Me[CH_2]_4$	81.4	6.4	3.9	$C_{25}H_{23}NO_2$	81.3	6.3	3.8
$Me[CH_2]_5$	81.5	6.7	3.6	$C_{26}H_{25}NO_2$	81.4	6.6	3.6
$Me[CH_2]_6$	81.6	6.9	3.7	$C_{27}H_{27}NO_2$	81.6	6.8	3.5
$Me[CH_2]_7$	81.9	7.3	3.1	$C_{28}H_{29}NO_2$	81.7	7.1	3.4
$Me[CH_2]_8$	82.0	7.4	3.4	$C_{29}H_{31}NO_2$	81.8	7.3	3.3
$Me[CH_2]_9$	82.2	7.3	3.4	$C_{30}H_{33}NO_2$	81.9	7.5	3.2
$Me[CH_2]_{11}$	82.4	7.8	2.9	$C_{32}H_{37}NO_2$	82.2	8.0	3.0
$Me[CH_2]_{13}$	82.4	8.4	3.0	$C_{34}H_{41}NO_2$	82.4	8.3	2.8
$Me[CH_2]_{15}$	82.6	8.7	2.5	$C_{36}H_{45}NO_2$	82.5	8.7	2.7

were heated under reflux in toluene in the presence of a small quantity of toluene-4-sulphonic acid. Water was removed by the Dean and Stark method and, after work-up, the residue was recrystallised from methanol to give 2-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)*fluorene* as pale cream plates (87%), m.p. 148.5—150 °C (Found: C, 81.5; H, 7.3. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.2%); $\nu_{max.}$(KBr) 3 060, 2 950, and 2 860 cm^{-1}; $\delta_H(CDCl_3)$ 0.80 (3 H, s, CH_3), 1.33 (3 H, s, CH_3), 3.74 (4 H, s, CH_2), 3.89 (2 H, s, ArCH_2Ar), 5.45 (1 H, s, ArC*H*), and 7.23—7.84 (7 H, m, ArH). Pyridine (50 cm^3) was added to commercial 40% Triton B in methanol (50 cm^3) and the solution concentrated to 50 cm^3. The cyclic acetal (0.02 mol) in pyridine (40 ml) was added dropwise to the Triton B solution over a period of 20 min. Air was bubbled through the stirred mixture during the addition and for the subsequent 20 min.[9] The colour of the mixture progressively changed from the initial pale yellow of the reagent to golden brown, to green-brown, to dark green. After acidification with glacial acetic acid (resulting in a change in colour from dark green to golden brown) the solution was poured into water and the resulting solid recrystallised from aqueous ethanol to give 2-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-9-*oxofluorene* (85%) as bright yellow needles, m.p. 118—119 °C (Found: C, 77.6; H, 6.2. $C_{19}H_{18}O_3$ requires C, 77.6; H, 6.1%): $\nu_{max.}$(KBr) 3 060, 2 950, 2 840, and 1 705 (C=O) cm^{-1}: $\delta_H(CDCl_3)$ 0.79 (3 H, s, CH_3), 1.29 (3 H, s, CH_3), 3.70 (4 H, s, CH_2), 5.36 (1 H, s, ArC*H*), and 7.25—7.80 (7 H, m, ArH). The oxidation step was also effected by fusion of the cyclic acetal with nickel peroxide[10] at 150 °C but the yield was not as high.

The cyclic acetal (0.015 mol) was hydrolysed by heating under reflux with concentrated hydrochloric acid (3 cm^3) in 75% aqueous dioxane (40 cm^3) for 90 min. On cooling, the solid was collected and recrystallised from glacial acetic acid and from ethanol affording 9-*oxofluoren*-2-*carbaldehyde* as yellow platelets (50%), m.p. 203—204 °C (Found: C, 80.7; H, 3.9. $C_{14}H_8O_2$ requires C, 80.8; H, 3.8%); $\nu_{max.}$(KBr) 2 840 (C–H), 1 715 (C=O), and 1 680 (CH=O) cm^{-1}; $\delta_H(CDCl_3)$ 7.24—8.13 (7 H, m, ArH) and 10.01 (1 H, s, CHO). The azomethine derivatives were prepared from the 9-oxofluoren-2-carbaldehyde (0.5 g) and a slight molar excess of the appropriate *p*-alkoxyaniline[1] and purified by recrystallisation several times from hexane, aqueous ethanol, and methanol–light petroleum (b.p. 40—60 °C). The transition temperatures for the 4-alkoxy-*N*-(9-oxofluoren-2-ylmethylene)anilines are given in Table 1 and their elemental analyses are listed in Table 3.

The following data are for the butoxy compound and are representative of the whole series: *m*/*z* 356 (16%), 355 (M^+, 61%), 300 (20%), 299 (100%), and 298 (87.5%); $\nu_{max.}$(KBr) 3 060, 2 945, 2 875, 1 712, 1 611, 1 502, 1 245, 846, 835, 795, 772, and 742 cm^{-1}; $\delta_H(CDCl_3)$ 0.96 (3 H, t, CH_3), 1.23—1.89 (4 H, br m, CH_2CH_2), 3.94 (2 H, t, OCH_2), 6.82—8.10 (11 H, m, ArH), and 8.52 (1 H, s, CH=N).

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