Properties of the Liquid Crystals formed by Certain 4-Alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)anilines

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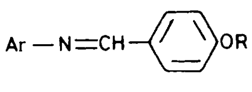
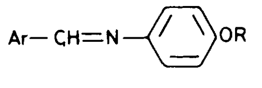
The liquid crystal transition temperatures of twelve 4-alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)-anilines are reported and discussed. The liquid crystal behaviour of the homologous series is very similar to that of the analogous compounds in which the –CH=N– linkage is reversed. The form of the transition temperature plots indicates the existence of very low lateral relative to terminal cohesive forces in the mesophases of the azomethine derivatives of 9,10-dihydrophenanthrene.

We recently reported properties of the liquid crystals formed by certain members of the homologous series of 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes[1] (1a). These compounds, also investigated by Behnam and Hall,[2] show unusual mesomorphic behaviour. Graphical presentation of the N–I transition temperatures of the early homologues reveals a fall to a minimum followed by a rise to a maximum, and for the higher homologues the curves for the falling N–I and the rising S_A–I transition temperatures do not converge, so that nematic phases are observed to a late stage in the homologous series. In agreement with another similar reported instance,† we attributed this behaviour to very low lateral cohesive forces operating throughout the homologous series. In order to establish whether or not this unusual effect persists when the –CH=N– linkage is reversed, we have now prepared and measured the liquid crystal transition temperatures of twelve members (methoxy through to decyloxy, tetradecyloxy, and hexadecyloxy) of the homologous series of 4-alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)anilines (2a). The transition temperatures are listed in Table 1 and are shown plotted against the number of carbon atoms, *n*, in the alkyl chain in the Figure. Smectic mesophases were identified as S_A by microscopic observation of the focal conic and fan textures adopted by a thin sample of the compound mounted between a slide and cover slip and allowed to cool slowly from the isotropic liquid.

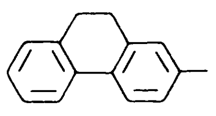


(1)

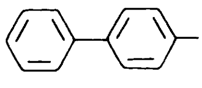


(2)

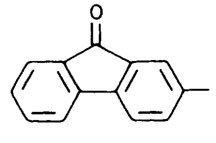
a; Ar =



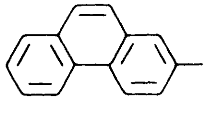
c; Ar =



b; Ar =



d; Ar =



R = C_nH_{2n+1}

Previous studies[7] of compounds which can be regarded as consisting of a core to which two alkyl chains (R and R′) are attached have shown that when R and R′ are interchanged the resultant effect on liquid crystal behaviour is markedly dependent on the overall core shape and on the length of the terminal alkyl chains. In the present study, the imine linkage represents merely one small part of the core and it has been reversed in a system with only one terminal alkyl chain. We have previously investigated[8] the effect of this structural change for the biphenyl analogues [the 4-*p*-alkoxybenzylideneaminobiphenyls (1c) and the 4-alkoxy-*N*-(4-phenylbenzylidene)anilines (2c)] corresponding to the 9,10-dihydrophenanthrene azomethines (1a) and (2a). The results for the biphenyl compounds indicated that, for individual members of the series, reversal of the imine linkage has little effect on the incidence of different phases nor on their thermal stability, although the S_B phases shown by compounds of series (1c) have significantly higher thermal stability than the S_B phases of corresponding members of series (2c). As a result of this previous work, it was expected that the two series, (1a) and (2a), of analogous azomethine derivatives of 9,10-dihydrophenanthrene would not show pronounced differences in mesomorphic behaviour.

The plot (Figure) of transition temperatures against *n* for the series (2a) reveals the same general trends as previously discussed[1] for the series (1a), although the N–I transition for the methoxy compound is monotropic. The usual alternation of the N–I transition temperatures occurs and is shown by separate curves for odd and even carbon chain homologues. For the odd carbon chain homologues the points for the first three members show an initial fall to a minimum, followed by a rise to a maximum, before giving the expected gradual fall for the remaining members. For the even carbon chain homologues a smooth curve, without the appearance of a maximum, may be drawn through the points for the falling N–I transition temperatures.‡ The N–I curves for odd and even carbon chain homologues converge in the region $n \approx 9$ and smectic phases also appear at this stage. This is rather later in the series than for (1a) (S_A at $n = 7$) which may be cooled to lower temperatures in order to detect the monotropic S_A phases. Nevertheless, as is the case for the latter

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† The analogous 2-*p*-alkoxybenzylideneaminofluorenones.[3] Certain esters of 4,4′-azoxyphenol,[4] the 4-(*p*-alkoxybenzylideneamino)acetophenones,[5] and the 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls[6] also give transition temperature plots showing maxima and/or minima.

‡ The even-*n* curve *could* be drawn with a slight inflection in the region $n = 3$ so as to follow the trend of the odd-*n* curve, as was necessary for the corresponding members of series (1a)[1] in order to avoid crossing the lower odd-*n* curve. The reason for the absence of this necessity for series (2a) may be seen by comparison of the odd-*n* curves for (1a) and (2a). Series (2a) shows a steep fall (7.0 °C) in N–I transition temperature in passing from the methoxy to the propyloxy compound, followed by a shallow rise (2.5 °C) to the pentyloxy compound, whereas the reverse trend (a 4.5 °C fall, then a 5.5 °C rise) is apparent for series (1a).

Table 1. Transition temperatures for 4-alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)anilines (2a)

R	Transition temperature (°C)			
	C–S_A/N/I	S_A–N	N–I	S_A/N–C[a]
CH_3	157		[136]	60
CH_3CH_2	139.5		149.5	70
$CH_3[CH_2]_2$	121		129	77
$CH_3[CH_2]_3$	109.5		141	59
$CH_3[CH_2]_4$	93.5		131.5	56.5
$CH_3[CH_2]_5$	89.5		135.5	58
$CH_3[CH_2]_6$	84		129	59
$CH_3[CH_2]_7$	81.5		129.5	55
$CH_3[CH_2]_8$	81.5	[70.5][b]	126	68
$CH_3[CH_2]_9$	84.5	[80.5][b]	125	66
$CH_3[CH_2]_{13}$	92	102.5	118	76.5
$CH_3[CH_2]_{15}$	96	107	115.5	69

[a] Temperature of crystallisation. [b] Monotropic transition.

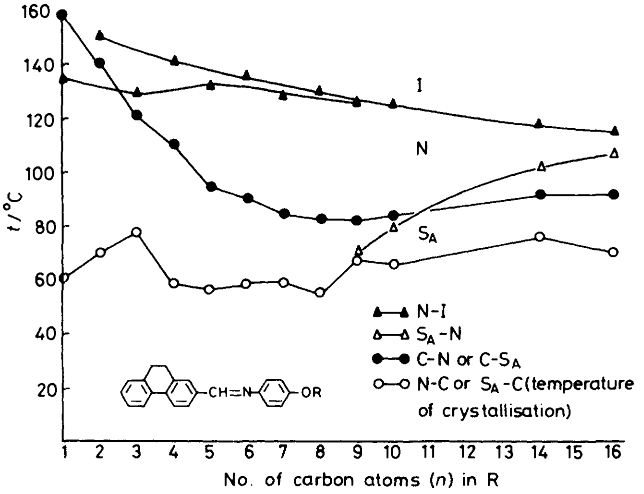

Figure. Plot of transition temperature against the number of carbon atoms (*n*) in the alkyl chain (R) of the 4-alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)anilines (2a)

compounds, nematic properties remain throughout the series, as the rising S_A–N transition temperature curve does not meet the falling N–I curve even at *n* = 16; for the hexadecyloxy compound the S_A–N value is 8.5 °C lower than the N–I transition temperature.

The unusual form of the N–I transition temperature curves for the early members of the homologous series, together with a delay to very long chain lengths of the stage at which the smectic phase passes directly to the isotropic liquid, is attributable to very low lateral relative to terminal cohesive forces operating in the liquid crystal phases. A comparison of the thermal stabilities of the smectic and nematic mesophases for analogous homologues gives an indication of the relative strengths of both lateral and terminal cohesive forces, and average values of appropriate transition temperatures for analogous members in a part of the series where normal behaviour is observed may be used for this purpose. The average values of S_A–N (for *n* 9 and 10) and N–I (for *n* 7—10) for certain related series (Table 2) indicate that the series (2a) is more closely related to series (1a)[1] and (1b),[3] which also give an unusual plot of transition temperature against *n*, than those for the corresponding biphenyl [(1c) and (2c)][8] and phenanthrene (1d)[9] series which have a much higher thermal stability for both smectic and nematic mesophases. In the three series that are characterised by an unusual transition temperature plot, the low values for the smectic thermal stability indicate that low lateral cohesive forces are operative. The principal cause of the low lateral cohesive forces in the mesophases of the azomethine derivatives of 9,10-dihydrophenanthrene is, presumably, the presence of the ethylene bridge. This may (i) allow flexing of the 9,10-dihydrophenanthrene system to occur,* so interfering with the packing and space-filling properties of the molecules in the mesophases, and (ii) result in an adverse effect on $\Delta\alpha$, the anisotropy of molecular polarisability, relative to the analogous phenanthrene derivatives.

In contrast with the azomethine derivatives of biphenyl [(1c) and (2c)], for which the average S_A–N and N–I values are closely similar, the two series of azomethine derivatives of 9,10-dihydrophenanthrene [(1a) and (2a)] reveal significant differences in mesophase thermal stability. In each case, the value for (2a) is lower (by 10 °C for the nematic phase and by 21.5 °C for the smectic phase, this value indicating very low lateral cohesive forces in this series). There is no obvious reason for this behaviour.

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 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 Limited 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-(9,10-*dihydro*-2-*phenanthrylmethylene*)*anilines*.—9,10-Dihydrophenanthrene[10] was acetylated,[11] and the resulting 2-acetyl derivative, m.p. 48—49 °C (lit.,[12] 48 °C), was oxidised with sodium hypobromite in aqueous dioxane.[11] The crude acid (95%) was purified by recrystallisation from glacial acetic acid, affording the 9,10-*dihydrophenanthrene-2-carboxylic acid* as colourless plates, m.p. 214—215 °C (Found: C, 80.2; H, 5.3%; *m/z* 224. $C_{15}H_{12}O_2$ requires C, 80.35; H, 5.35%; *M*, 224); $\nu_{max.}$ (KBr) 3 140 (OH) and 1 680 cm^{-1} (C=O); δ_H ($CDCl_3$) 2.93 (4 H, s, $ArCH_2CH_2Ar$), 7.23 (3 H, m, ArH), 8.91 (4 H, m, ArH), and 0.70 (1 H, br s, CO_2H). The carboxylic acid was treated with thionyl chloride, and, as described by Johnstone *et al.*,[13] the resulting acid chloride was dissolved in acetonitrile and dry ether, and added at 35 °C to a suspension of cadmium chloride in acetonitrile to which a

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* The ^1H n.m.r. spectra ($CDCl_3$) of the azomethine derivatives of 9,10-dihydrophenanthrene show a single signal corresponding to the four protons of the methylene groups at C-9 and C-10: a chemical shift difference between the protons cannot be detected even at 220 MHz.[2] The equivalence of these protons is presumably due to the non-rigid nature of the 9,10-dihydrophenanthrene system, which has a certain degree of flexibility about the inter-ring bond. Consonant with the permitted limits of rotation about this bond, the methylene groups at C-9 and C-10 become disposed, in turn, on opposite sides of the molecule. It is reasonable to assume that the 9,10-dihydrophenanthrene system is non-rigid in the mesophases as well as in $CDCl_3$ solution.

Table 2. Average transition temperatures (°C) for azomethines of type (1) and (2)

	(1)		(2)	
Ar	S_A–N (n = 9, 10)	N–I (n = 7—10)	S_A–N (n = 9, 10)	N–I (n = 7—10)
(a) 9,10-Dihydro-2-phenanthryl	97	137	75.5	127.5
(b) 9-Oxofluoren-2-yl	84.5	139.9 [a]		
(c) Biphenyl-4-yl	157.25	161.9	157.75	165
(d) 2-Phenanthryl	151.25	183.5		

[a] The value of 131.9 °C quoted previously [1] is a typographical error.

Table 3. Elemental analyses for 4-alkoxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)anilines (2a)

	Found (%)				Required (%)		
R	C	H	N	Molecular formula	C	H	N
CH_3	84.2	5.9	4.5	$C_{22}H_{19}NO$	84.3	6.1	4.5
CH_3CH_2	84.3	6.3	4.2	$C_{23}H_{21}NO$	84.4	6.5	4.3
$CH_3[CH_2]_2$	84.2	6.7	4.0	$C_{24}H_{23}NO$	84.4	6.8	4.1
$CH_3[CH_2]_3$	84.3	6.9	3.8	$C_{25}H_{25}NO$	84.5	7.1	3.9
$CH_3[CH_2]_4$	84.3	7.4	3.7	$C_{26}H_{27}NO$	84.5	7.4	3.8
$CH_3[CH_2]_5$	84.5	7.6	3.3	$C_{27}H_{29}NO$	84.6	7.6	3.7
$CH_3[CH_2]_6$	84.4	7.7	3.5	$C_{28}H_{31}NO$	84.6	7.8	3.5
$CH_3[CH_2]_7$	84.6	8.0	3.3	$C_{29}H_{33}NO$	84.6	8.1	3.4
$CH_3[CH_2]_8$	84.5	8.1	3.3	$C_{30}H_{35}NO$	84.7	8.3	3.3
$CH_3[CH_2]_9$	84.5	8.4	3.1	$C_{31}H_{37}NO$	84.7	8.5	3.2
$CH_3[CH_2]_{13}$	84.6	9.1	2.9	$C_{35}H_{45}NO$	84.8	9.2	2.8
$CH_3[CH_2]_{15}$	84.8	9.4	2.9	$C_{37}H_{49}NO$	84.9	9.4	2.7

solution of sodium borohydride in dimethylformamide and acetonitrile had been added at 0—5 °C. After 30 min stirring, the solid was removed by filtration, the solvents were removed from the filtrate, and the residual oil was distilled under reduced pressure affording 9,10-dihydrophenanthrene-2-carbaldehyde (60%), b.p. 148 °C at 0.2 mmHg (lit.[14] 185 °C at 2 mmHg), as the main fraction. The azomethine derivatives were prepared [from the 9,10-dihydrophenanthrene-2-carbaldehyde (0.5 g portions) and a slight molar excess of the appropriate *p*-alkoxyaniline [8]] and purified as described in a previous publication.[1] The compounds were more readily purified than those of series (1a). The transition temperatures for the derivatives are listed in Table 1 and their elemental analyses in Table 3.

The following data for 4-tetradecyloxy-*N*-(9,10-dihydro-2-phenanthrylmethylene)aniline are typical of the series as a whole: m/z 495 (M^+, 96%), 299 (100), 178, 120, 108, 69, 57, and 55; $\nu_{max.}$ (KBr) 3 020, 2 925, 2 855, 1 600, 1 578, 1 510, 1 310, 1 250, 1 020, 895, 830, 768, 732, 642, and 630 cm^{-1}; δ_H ($CDCl_3$) 0.88 (3 H, s, CH_3), 1.27 br (26 H), 2.94 (4 H, s, $ArCH_2CH_2Ar$), 4.01 (2 H, t, J 7.4 Hz, OCH_2), 6.90—7.90 (11 H, m, ArH), and 8.42 (1 H, s, N=CH).

Acknowledgements

We thank Professor G. W. Gray F.R.S. for his interest and Dr. G. Haran of the Boots Co. Ltd., for mass spectral determinations.

References

1 D. J. Byron, D. J. Harwood, and R. C. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 197.
2 B. A. Behnam and D. M. Hall, *J. Chem. Soc., Perkin Trans. 2*, 1982, 465.
3 G. W. Gray, J. B. Hartley, A. Ibbotson, and B. Jones, *J. Chem. Soc.*, 1955, 4359.
4 H. Kelker and B. Scheurle, *J. Phys. (Paris)*, 1969, **30**, C4, No. 11—12, 104.
5 J. A. Castellano, J. E. Goldmacher, and J. A. Nash, *Electron. Lett.*, 1973, **9**, 130.
6 G. W. Gray and A. Mosley, *J. Chem. Soc., Perkin Trans. 2*, 1976, 97.
7 J. W. Goodby and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 157; 1978, **48**, 127.
8 D. J. Byron, J. W. Goodby, G. W. Gray, D. A. Keating, M. T. O'Neill, and R. C. Wilson, *Mol. Cryst. Liq. Cryst.*, 1980, **58**, 179.
9 G. W. Gray, *J. Chem. Soc.*, 1958, 552.
10 D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 1950, 711; D. P. Phillips, *Org. Synth.*, 1963, Coll. Vol. IV, p. 313; P. W. Rabideau and R. G. Harvey, *J. Org. Chem.*, 1970, **35**, 25.
11 D. J. Byron, G. W. Gray, and R. C. Wilson, *J. Chem. Soc. C*, 1966, 840.
12 E. Mosettig and J. Van der Kamp, *J. Am. Chem. Soc.*, 1930, **52**, 3704.
13 I. D. Entwistle, P. Boehm, R. A. W. Johnstone, and R. P. Telford, *J. Chem. Soc., Perkin Trans. 1*, 1980, 27.
14 A. Burger and E. Mosettig, *J. Am. Chem. Soc.*, 1937, **59**, 1302.

Received 9th *June* 1983; *Paper* 3/962