Properties of the Liquid Crystals formed by Certain 2-*p*-Alkoxybenzylideneamino-9,10-dihydrophenanthrenes

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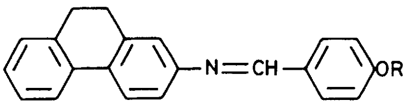
The liquid crystal transition temperatures of 11 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes are reported and discussed. Graphical presentation shows a fall to a minimum followed by a rise to a maximum for the N–I transition temperatures of the early homologues and lack of convergence of the rising S_A–N and the falling N–I transition temperature curves for the higher homologues, *i.e.* there is persistence of nematic phases to a late stage in the homologous series. This behaviour is consistent with very low lateral cohesive forces operating throughout the homologous series.

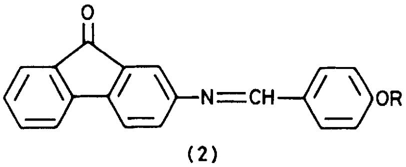
Behnam and Hall[1] have recently reported the mesogenic behaviour and spectroscopic properties of azomethines derived from 2-amino-9,10-dihydrophenanthrene and certain aromatic aldehydes. Of particular interest are the results quoted for the liquid crystal transition temperatures of the five members (methoxy, ethoxy, butoxy, hexyloxy, and octyloxy) of the homologous series of 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes (1). We have prepared and measured the liquid crystal transition temperatures of 11 members (methoxy through to decyloxy, and tetradecyloxy) of this homologous series. Our results are listed in Table 1 (together with values quoted by Behnam and Hall, in italics) and are shown plotted against the number of carbon atoms, *n*, in the alkyl chain in Figure 1. Smectic mesophases were identified as S_A by microscopic observation of the focal conic and fan textures adopted by thin samples when mounted between a slide and a cover slip and allowed to cool slowly from the isotropic liquid.

Comparison of the two sets of results shows excellent correspondence for the m.p.s (C–N) and N–I transition temperatures of the methoxy, ethoxy, and butoxy compounds. However, this is not the case for the hexyloxy and octyloxy compounds. Behnam and Hall quote lower N–I transition temperatures for both compounds and a substantially higher m.p. for the hexyloxy compound than we have recorded, and did not observe a smectic mesophase for the octyloxy compound.

We found that certain members of the series of 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes were difficult to purify and required as many as 12 recrystallisations (in turn, from hydroxylic and from hydrocarbon solvents) before the liquid crystal transition temperatures remained constant after successive crystallisations. This fact may be associated with the discrepancies in the two sets of transition temperatures reported in this work and by Behnam and Hall.



(1)



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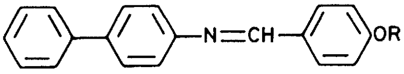

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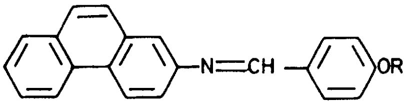

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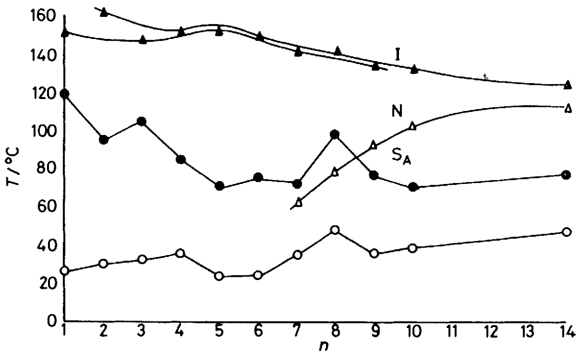

Figure 1. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkyl chain (R) of the 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes (1): ▲, N–I; △, S_A–N; ●, C–N or C–S_A; ○, N–C or S_A–C (temperature of crystallisation)

When our results for the extended series are presented graphically (Figure 1) the outstanding feature of the plot is a fall to a minimum followed by a rise to a maximum for the N–I transition temperatures of the early members of the homologous series. In Figure 1 the usual alternation of the N–I transition temperatures has been shown by drawing separate curves through the points for odd and even carbon-chain homologues. It has been assumed that the curve for the members of the series for which *n* is even lies, throughout, closely above the curve for the members for which *n* is odd and hence that both curves pass through a maximum in the region of $n = 5$. Thereafter, the normal gradual fall is observed but the nematic phases persist to a very late stage in the homologous series without the rising S_A–N curve becoming coincident with the upper N–I curve; even at the tetradecyloxy compound the two curves are still 11.5° apart. A plot of this general form has been observed previously for one other comparable series of azomethines, the 2-*p*-alkoxybenzylideneaminofluorenones.[2] For this series the unusual

Table 1. Transition temperatures for 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes (1)

R	Transition temperatures (°C) C–N	S_A–N	N–I	N–C[a]
CH_3	119, *118*[b]		151.5, *151*[b]	26
CH_3CH_2	95, *93.5*[b]		162, *162*[b]	30
$CH_3(CH_2)_2$	104.5		147	33
$CH_3(CH_2)_3$	84, *83*[b]		152, *151.5*[b]	34
$CH_3(CH_2)_4$	70		152.5	25
$CH_3(CH_2)_5$	75, *83.5*[b]		148.5, *141.5*[b]	26
$CH_3(CH_2)_6$	72.5	[63]	141.5	32
$CH_3(CH_2)_7$	98, *96*[b]	[78]	142, *137.5*[b]	41.5
$CH_3(CH_2)_8$	76.5	92	134	35.5
$CH_3(CH_2)_9$	75	102	132.5	43
$CH_3(CH_2)_{13}$	78	113	124.5	46

[a] Temperature of crystallisation. [b] Value reported by Behnam and Hall.[1] [ ] = Monotropic transition.

Table 2. Elemental analyses for 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes (1)

R	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
CH_3	84.2	6.0	4.3	$C_{22}H_{19}NO$	84.3	6.1	4.5
CH_3CH_2	84.3	6.6	4.3	$C_{23}H_{21}NO$	84.4	6.5	4.3
$CH_3(CH_2)_2$	84.3	6.6	4.0	$C_{24}H_{23}NO$	84.4	6.8	4.1
$CH_3(CH_2)_3$	84.5	7.1	3.8	$C_{25}H_{25}NO$	84.5	7.1	3.9
$CH_3(CH_2)_4$	84.3	7.4	3.8	$C_{26}H_{27}NO$	84.5	7.4	3.8
$CH_3(CH_2)_5$	84.3	7.5	3.6	$C_{27}H_{29}NO$	84.6	7.6	3.7
$CH_3(CH_2)_6$	84.4	7.8	3.4	$C_{28}H_{31}NO$	84.6	7.8	3.5
$CH_3(CH_2)_7$	84.4	8.0	3.4	$C_{29}H_{33}NO$	84.6	8.1	3.4
$CH_3(CH_2)_8$	84.6	8.4	3.3	$C_{30}H_{35}NO$	84.7	8.3	3.3
$CH_3(CH_2)_9$	84.8	8.6	3.1	$C_{31}H_{37}NO$	84.7	8.5	3.2
$CH_3(CH_2)_{13}$	84.5	9.1	2.8	$C_{35}H_{45}NO$	84.8	9.2	2.8

behaviour is attributed to the very low lateral cohesive forces operating in the homologous series, and it seems likely that this is the cause of the similar behaviour in the azomethines derived from 9,10-dihydrophenanthrene.

An estimate of the strength of both lateral and terminal cohesive forces may be made by assessing the thermal stability of smectic and nematic mesophases. The points for the S–N and N–I transition temperatures for the four compounds, heptyloxy–decyloxy, lie in a region of the plot of transition temperatures against *n* where a normal fall of the N–I values is generally observed. Average values for these four compounds thus may be used to give an indication of the relative thermal stabilities of the smectic and nematic phases and enable the mesomorphic behaviour of related series of compounds to be compared.

Azomethines of	Average transition temperature (°C) (heptyloxy–decyloxy compounds) S–N	N–I
9,10-Dihydrophenanthrene (1)	83.9	137.4
Fluorenone (2)	73.3	131.9
Biphenyl (3)	155.4	161.9
Phenanthrene (4)	143	183.5

For the azomethines, the values for the 9,10-dihydrophenanthrene series (1) more closely resemble those for the corresponding fluorenone compounds (2),[2] which also give an unusual plot of transition temperature against *n*, than those for the analogous biphenyl (3)[2,*] and phenanthrene (4)[5] series, which have a much higher smectic and nematic thermal stability and which give rise to a normal transition temperature plot. In particular, it may be noted that the thermal stability of the smectic phase of the 9,10-dihydrophenanthrene series is only *ca.* 10.5° higher than that of the fluorenone series confirming that very low lateral cohesive forces also operate in this series. Relative to the corresponding biphenyl and phenanthrene compounds, the lower lateral cohesive forces in the 9,10-dihydrophenanthrene series result from the molecular breadth increase and the decrease in molecular polarisability caused by the presence of the bismethylene bridge. The corresponding substantial molecular breadth increase caused by the laterally disposed carbonyl group of the fluorenone series more than offsets the effectiveness of the dipole in enhancing lateral cohesions.

Further investigations of related series are in progress. We have found that certain series also show maxima and minima for the early homologues and the results of this work will be reported in future publications.

Experimental

Measurements of transition temperatures and microscopic observation of textures of mesophases were made using a Vickers M75 polarising microscope in conjunction with a Mettler FP52 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 in $CDCl_3$ solution with tetramethylsilane as internal standard on a JEOL FX60Q Fourier transform spectrometer. Mass spectra were determined by Dr. G. Haran of the Boots Company Limited on an AEI MS 902S mass spectrometer equipped with a Mass Spectrometry Services Analog Series 200 console and an INCOS 2300 data system.

2-p-*Alkoxybenzylideneamino*-9,10-*dihydrophenanthrenes*.—9,10-Dihydrophenanthrene[6] was nitrated[7] and the resulting 2-nitro-derivative was reduced catalytically (H_2, PtO_2, dry EtOH) or with methanolic sodium hydrogen sulphide.[8] The 2-amino-9,10-dihydrophenanthrene (0.5 g portions) and a slight molar excess of the appropriate *p*-alkoxybenzaldehyde[9]

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[*] Values for the 4-*p*-alkoxybenzylideneaminobiphenyls are taken from the 1955 paper by Gray *et al.* More recently these compounds have been reinvestigated[3,4] and the occurrence of both S_A and S_B modifications for the hexyloxy–hexadecyloxy compounds has been established.

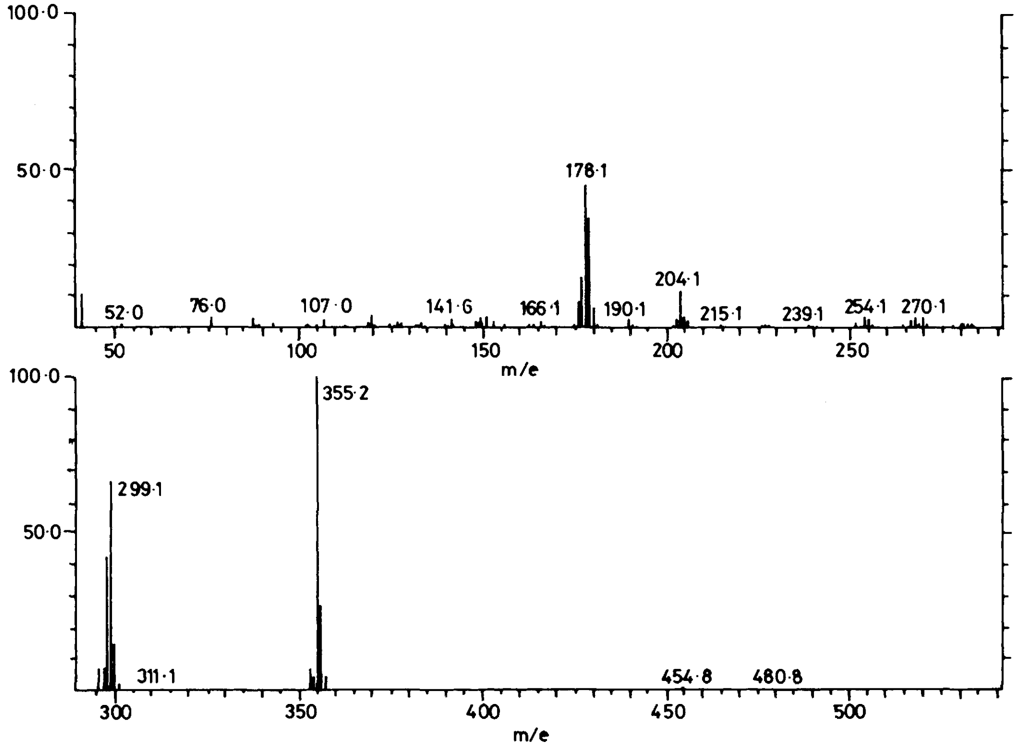

Figure 2. Relative intensities of ions in the mass spectrum of 2-*p*-butoxybenzylideneamino-9,10-dihydrophenanthrene

were each dissolved in ethanol (20 cm^3). The solutions were combined, heated to boiling, and five drops of glacial acetic acid added. After a few minutes the solutions were set aside to cool. The crystalline azomethines were purified by recrystallisation several times from chloroform–light petroleum (b.p. 60—80°) or from benzene–light petroleum (b.p. 60—80°) and from methanol. The transition temperatures for the 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes are listed in Table 1 and their elemental analyses are given in Table 2.

The members of the homologous series of azomethines show broadly similar spectral characteristics. The following data for 2-*p*-decyloxybenzylideamino-9,10-dihydrophenanthrene are representative of the series: $\nu_{max.}$ (KBr) 3 050, 2 940, 2 920, 2 852, 1 640, 1 618, 1 595, 1 542, and 1 510 cm^{-1}; δ_H ($CDCl_3$) 0.88 (3 H, s, CH_3), 1.29br (16 H), 2.89 (4 H, s, $ArCH_2CH_2Ar$), 4.01 (2 H, t, *J* 7.4 Hz, OCH_2), 6.89—7.91 (11 H, m, ArH), and 8.43 (1 H, s, N=CH).

With regard to the mass spectra of the 2-*p*-alkoxybenzylideneamino-9,10-dihydrophenanthrenes, we can confirm the fragmentation pattern reported by Behnam and Hall,[1] but with rather different intensities for the major ions observed (see Figure 2 which refers to the butoxy-compound). The variations are probably due to the different instruments and techniques used for the mass spectral determinations.

Acknowledgements

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