105. *Mesomorphism and Chemical Constitution. Part X.* The* 2-p-n-*Alkoxybenzylideneaminophenanthrenes and Evidence for the Planarity of the Diphenyl Ring System in the Mesomorphic State.*

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Thirteen anils derived from *p*-*n*-alkoxybenzaldehydes and 2-aminophenanthrene have been prepared and their mesomorphic properties studied. The series is typical of many, but by comparison of the mesomorphic thermal stabilities with those of the 4-*p*-*n*-alkoxybenzylideneaminodiphenyls more evidence is obtained for the planar configuration of diphenyl in the mesophases of its derivatives.

THE homologous series of anils, the melting points and mesomorphic transition temperatures of thirteen members of which are shown in Table 1, exhibits no unusual features, and the plot of the mesomorphic–isotropic transition temperatures against the number of carbon atoms in the alkyl chain shows the usual alternations, *i.e.*, two falling curves can be drawn through the points, the upper one for those anils with an even number of carbon atoms in the alkyl chain, and the lower for those with an odd number. The single curve on which the smectic–nematic transition points lie rises very steeply at first, and the smectic mesophases of the pentyl and hexyl ethers are monotropic. The nematic–smectic transition temperature of the pentyl ether cannot be determined accurately as the nematic mesophase does not supercool sufficiently. The curve gradually levels out as the alkyl chain lengthens, and coincides with the upper transition-point curve between the points for the dodecyl and the hexadecyl ether. The m. p.s along the homologous series are irregularly disposed.

TABLE 1. 2-p-n-*Alkoxybenzylideneaminophenanthrenes.*

Alkyl	Temp. of transition to smectic	nematic	isotropic	Alkyl	Temp. of transition to smectic	nematic	isotropic
Methyl	—	155°	213·5°	Octyl	103°	140°	186·5°
Ethyl	—	152·5	217	Nonyl	120	148·5	181
Propyl	—	152·5	200·5	Decyl............	121	154	179·5
Butyl	—	121·5	204	Dodecyl	109	161	173
Pentyl	(<90°)	132·5	193	Hexadecyl ...	99·5	—	161
Hexyl	(111)	113	194·5	Octadecyl ...	108	—	156
Heptyl	116·5	129·5	187				

The relative mesomorphic thermal stabilities of the *p*-*n*-alkoxybenzylidene derivatives of 4-aminodiphenyl and 2-aminofluorene and of the di-(*p*-*n*-alkoxybenzylidene) derivatives of benzidine and 2 : 7-diaminofluorene have already been discussed.[1] The relative mesomorphic behaviours of these series indicate that the diphenyl ring system is planar and denied freedom of rotation about the 1–1′-bond in the mesomorphic states of its compounds. In the anils derived from 2-aminophenanthrene, the phenanthrene nucleus is planar, so the mesomorphic thermal stabilities of the 2-*p*-*n*-alkoxybenzylideneaminophenanthrenes should provide an interesting comparison with the 4-*p*-*n*-alkoxybenzylideneaminodiphenyls, and may give more evidence for the planarity of diphenyl in its mesophases, work on which is in progress.

Before considering the average mesomorphic transition temperatures used later as a measure of the relative mesomorphic thermal stabilities of the two series of anils, we will discuss the probable effect on the thermal stability of the smectic phase of changing from the assumedly planar diphenyl ring system to the planar phenanthrene one. The thermal

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* Part IX, Gray and Ibbotson, *J.*, 1957, 3228.

[1] Gray, Hartley, Ibbotson, and Jones, *J.*, 1955, 4359; see also Part IX.

stability of the smectic phase depends upon the ability of the molecules to maintain themselves, against the disordering influences of thermal vibration, orientated parallel with their ends in line. A close packing of the molecules, together with permanent reinforcing dipoles acting across the long molecular axes, will therefore favour the formation of a thermally stable smectic phase. If the introduction of a suitable substituent increases the molecular breadth or thickness, then, provided that the atom–substituent dipole is not large enough to counteract this effect, the increased intermolecular separation will reduce the intermolecular forces. The molecules will now be able to move from the smectic layers at a lower temperature, and the compound will be less likely to exhibit a smectic phase. Since the phenanthrene ring system is broader than that of diphenyl and has no permanent dipole moment, anils of the former should be less thermally stable than those of the latter in the smectic phase. The order of this predicted decrease is shown by comparing the average smectic–nematic transition temperatures of the hexyl–decyl ethers of the 2-aminophenanthrene and 4-aminodiphenyl anils; the average in the diphenyl series is 153·5°, and in the phenanthrene 136·6°. The decrease in smectic thermal stability from diphenyl to phenanthrene is therefore 16·9°. Now if there were rotational freedom about the 1–1′-bond in diphenyl, the result would be equivalent to a molecular thickening which should interfere seriously with the closeness of the molecular packing and reduce markedly the lateral intermolecular cohesions in the smectic layers. Since it is difficult to imagine that such non-planar diphenyl anil molecules could produce smectic phases having an average smectic thermal stability 16·9° greater than those of the necessarily planar phenanthrene anil molecules, the smectic phases of the diphenyl anils are probably more thermally stable because the molecules are planar and lath-shaped, whilst the planar phenanthrene molecules give a lower smectic stability as a result of their greater molecular breadth.

To obtain the relative stabilities of the nematic phase, the nematic–isotropic transition temperatures of the methyl–decyl ethers of the phenanthrene and diphenyl anils have been averaged, being 195·6° for the former and 169·2° for the latter, a difference of 26·4°.

The phases of the diphenyl anils are now less stable than those of phenanthrene, reversing the order of stability of the smectic phases. A rotational freedom about the 1–1′-bond in diphenyl might commence in the less highly ordered molecular arrangement of the more mobile nematic phase, and this could account for the lower nematic thermal stability of the diphenyl compounds, but in the light of comparisons already made between mesomorphic mono- and di-anils derived from diphenyl and fluorene,[1] this rotation is unlikely in the nematic phase. For example, it would not be possible to explain the greater nematic thermal stability of di-(*p*-alkoxybenzylidene) derivatives of benzidine than of those of 2 : 7-diaminofluorene. We emphasise that the thermal stability of the nematic phase will not depend solely upon the residual lateral cohesive forces, but also upon the terminal cohesions between molecules. Therefore, increases in breadth, which decrease smectic phase thermal stability, are always less effective in reducing the thermal stability of the nematic phase, so that the breadth of the phenanthrene nucleus is a less important factor when considering the nematic phase. Moreover, the phenanthrene anils will have a higher molecular polarisability than the diphenyl anils in the direction of the major axes of the molecules, as can be inferred from the high double-bond order of the 9 : 10-bond in phenanthrene and the exaltations of molecular refraction,[2] which are 5·53 c.c. and 1·8 c.c. for phenanthrene and diphenyl respectively. Because of the greater conjugation, the terminal intermolecular cohesions should therefore be higher for the phenanthrene anils. It seems more likely that this effect explains the high nematic thermal stability of these compounds, rather than that the diphenyl anils have a low nematic thermal stability because of deviations from planarity.

These results for the phenanthrene anils substantiate previous evidence indicating that diphenyl is planar in the mesomorphic states of its derivatives. From a consideration

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[2] Syrkin and Dyatkina, "Structure of Molecules," Butterworths Scientific Publications, London, 1950, p. 203.

of the potential energies of the phases, this configuration is indeed the most probable. In both phase types, the molecular ordering will minimise the potential energy, the more highly ordered smectic phase having the lower potential energy. Any rotational freedom which increases the molecular dimensions and reduces intermolecular cohesion will therefore increase the potential energy of the mesophase. Thus there will be a potential-energy barrier to such a rotation, particularly in the smectic phase and, whereas the terminal methyl group of the alkyl chain can rotate since this would have little effect on the overall cohesive forces in the mesophase, the rotation of one of the rings in diphenyl should be hindered because of the substantial increase in molecular thickness. The smectic phase would be most affected, but the nematic thermal stability would also be reduced (*a*) by the reduction in residual lateral cohesions and (*b*) by the reduction in conjugation between the two aromatic rings.

EXPERIMENTAL

M. p.s are corrected for exposed stem.

Determination of Transition Temperatures.—The m. p.s and the monotropic and enantiotropic mesomorphic transition temperatures were determined in the usual way, with an electrically heated microscope block[3] in conjunction with a projection system.[4] The smectic phases of the anils did not show well-defined focal-conic groups when mounted in thin sections between a glass slide and cover slip, and the samples always exhibited large homœotropic areas. When the cover slip was slightly displaced, complete homœotropy would often result, and the small regions of focal-conic groups would be destroyed. The nematic phases of the anils were readily distinguished by their typical threaded textures.

Materials.—2-Acetylphenanthrene, together with the 3-isomer, was prepared by Friedel–Crafts reaction on phenanthrene (m. p. 99°) as described by Mosettig and van de Kamp,[5] who record a yield of 63·5% of 3- (m. p. 72°) and 15% of 2-acetylphenanthrene (m. p. 143°). We used their second method to purify the crude 2-acetylphenanthrene, involving two vacuum distillations followed by crystallisation from benzene. The yields were lower than those reported: 10—11% of the 2- (m. p. 142—143°) and 45—46% of the 3-isomer (m. p. 71—72°).

2-*Acetylphenanthrene oxime.* The mixture of *cis* and *trans* oximes (m. p. 190—193°) was obtained in 98% yield by Bachmann and Boatner's method.[6]

2-*Aminophenanthrene.* The mixture of 2-acetamidophenanthrene and *N*-methyl-2-phenanthramide obtained by Beckmann rearrangement of the isomeric oximes was hydrolysed and separated into the acid and the amine as described by Bachmann and Boatner.[6] These authors claim that the 2-aminophenanthrene is almost pure (m. p. 85°) as precipitated from the hydrolysate and that the yield from the ketone is 81—82%, but our yields were lower (65%) and the product (m. p. 80—83°) contained a high-melting impurity. This was removed by hot filtration, and crystallisation from light petroleum (b. p. 100—120°) gave colourless crystals of 2-aminophenanthrene, m. p. 84—85°[6,7] (52—53%).

TABLE 2. 2-p-n-*Alkoxybenzylideneaminophenanthrenes.*

	Found (%)			Required (%)			Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	Alkyl	C	H	Formula	C	H
Me	85·1	5·5	$C_{22}H_{17}ON$	84·9	5·5	C_8H_{17}	84·9	7·4	$C_{29}H_{31}ON$	85·1	7·6
Et	84·8	5·9	$C_{23}H_{19}ON$	84·9	5·8	C_9H_{19}	84·9	7·5	$C_{30}H_{33}ON$	85·1	7·8
Pr^n	84·8	5·9	$C_{24}H_{21}ON$	85·0	6·2	$C_{10}H_{21}$	85·1	8·2	$C_{31}H_{35}ON$	85·1	8·0
Bu^n ...	85·2	6·6	$C_{25}H_{23}ON$	85·0	6·5	$C_{12}H_{25}$	85·4	8·2	$C_{33}H_{39}ON$	85·1	8·4
C_5H_{11}	85·0	6·8	$C_{26}H_{25}ON$	85·0	6·8	$C_{16}H_{33}$	85·2	9·0	$C_{37}H_{47}ON$	85·2	9·0
C_6H_{13} ...	85·0	7·2	$C_{27}H_{27}ON$	85·0	7·1	$C_{18}H_{37}$	85·3	9·4	$C_{39}H_{51}ON$	85·2	9·3
C_7H_{15} ...	85·2	7·5	$C_{28}H_{29}ON$	85·1	7·3						

2-p-n-*Alkoxybenzylideneaminophenanthrenes.*—The anils were prepared by dissolving 2-aminophenanthrene (0·2 g.) in absolute ethyl alcohol (25 ml.), and adding a 10% molar excess of the *p*-alkoxybenzaldehyde, with a few drops of glacial acetic acid as catalyst. The

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[3] Gray, *Nature*, 1953, **172**, 1137.

[4] Gray and Ibbotson, *Nature*, 1955, **176**, 1160.

[5] Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3707.

[6] Bachmann and Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2099.

[7] Kunz and Werner, *Ber.*, 1901, **34**, 2524.

anils were rapidly precipitated, but the mixture was warmed on the water-bath for 15 min. to complete the reaction. Sufficient alcohol was then added to dissolve the anils at the b. p., and the crystalline products were isolated on cooling. The anils were pure after two further crystallisations from an equal volume mixture of benzene and light petroleum (b. p. 40—60°). The m. p.s and transition temperatures are in Table 1 and the combustion analyses in Table 2.

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