Low-temperature Mesomorphism in Ring-substituted Benzylideneanilines

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Summary Several new mesomorphic ring-substituted Schiff bases, *i.e.*, *N*-(4-n-alkoxybenzylidene)-4-n-alkyl-2-methylanilines, with low crystalline to nematic transition temperatures are reported.

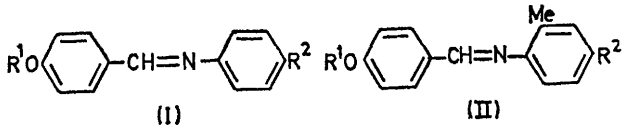
THERE has been intense interest in the preparation of liquid crystals that exhibit a nematic mesophase at room temperature. The Schiff base *N*-(4-methoxybenzylidene)-4-n-butylaniline has a crystalline to nematic (K→N) transition temperature of 22 °C.[1] It has been shown by Young, Aviram, and Cox[2] with substituted stilbenes and by van der Veen and Grobben[3] with ring-substituted azomethines that the introduction of nonplanarity and/or bulkiness in the molecule will lower the crystalline–nematic transition temperature. None of these compounds have particularly low m.p.s., however.

TABLE

Transition temperature (in °C) of N-(4-n-alkoxybenzylidene)-4-N-n-alkylanilines and N-4(-n-alkoxybenzylidene)-4-n-alkyl-2-methylanilines

	K→N	N→I		K→N	N→I
(Ia)	39·6	80·2	(IIa)	24·2	24·8
(Ib)	77·0[a]	80·7	(11b)	17·5	24·1
(Ic)	63·7[a]	79·0	(IIc)	17·8	24·2
(Id)	81·7[a]	82·5	(IId)	28·1	28·8
(Ie)	—[a]	—	(IIe)	27·2	27·6
(If)	61·4[a]	73·0	(IIf)	32·0[b]	—
(Ig)	40·7	62·8	(IIg)	14·2[b]	2·3[c]

[a] Smectic to nematic transition temperature. [b] Crystalline to isotropic transition temperature. [c] Monotropic nematic phase, *i.e.*, obtained only on cooling from melt.



(I) (II)

	R^1	R^2
a;	Et	C_6H_{13}
b;	C_6H_{13}	C_6H_{13}
c;	Bu	C_8H_{17}
d;	C_6H_{13}	C_8H_{17}
e;	C_7H_{15}	C_8H_{17}
f;	C_5H_{11}	C_6H_{13}
g;	Pr	C_6H_{13}

Several *N*-(4-alkoxybenzylidene)-4-alkyl-2-methylanilines have now been synthesized. 4-Alkyl-2-methylanilines were prepared by rearrangement of the appropriate *N*-alkyltoluidines. The Schiff bases were synthesized by refluxing equimolar amounts of the *p*-alkyltoluidines and *p*-alkoxybenzaldehyde in alcohol, and purified by repeated recrystallizations. Purity was checked by g.l.c., and structures were assigned by n.m.r. spectroscopy and elemental analysis. Transition temperatures and mesophases were determined by differential scanning calorimetry and thermal microscopy.

The increase in molecular breadth by a methyl group has dramatic effects on the mesomorphic behaviour of these Schiff bases as shown in the Table. Data for the corresponding unsubstituted benzylideneanilines[4] have been included for comparison.

Five of the unsubstituted compounds used in comparison here have one or more smectic phases. Since the aniline ring and benzaldehyde ring are approximately perpendicular to one another, the substitution of a methyl group for an *ortho*-hydrogen atom increases the thickness of the molecule by *ca.* 0·9 Å. This increase in bulkiness of the molecule, *i.e.*, decrease in the length to breadth ratio, has several effects. The crystal lattice packing is less favourable than that of the unsubstituted compound and a low m.p. results Lateral intramolecular interactions are reduced sufficiently to destroy the attractions necessary for smectic phase formation. The thermal stability of the nematic mesophase is reduced.

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