Liquid Crystal Monomers: *N*-(*p*-Alkoxybenzylidene)-*p*-aminostyrenes

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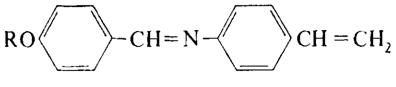
WE report the preparation and properties of three *N*-(*p*-alkoxybenzylidene)-*p*-aminostyrenes (I) which have well-defined mesomorphic character, as shown by both the optical approach to mesophase identification and by differential thermal analysis.[1]

Zinc-dust reduction[2] of *p*-nitrostyrene, obtained *via* a nitration of 2-bromoethylbenzene,[3,4] gave the corresponding amine. Coupling of the appropriate aldehyde with *p*-aminostyrene in a controlled-atmosphere box at room temperature with ethanol as solvent in the presence of a trace of hydroquinone as an inhibitor gave the anils; their properties are summarized in the Table. Analyses and i.r. and u.v. spectral data are consistent with the general structure. The methoxy-compound was purified by vacuum sublimation at 90°; the butoxy- and octadecyloxy-derivatives have been obtained only as precipitates from the coupling reaction.



(I)

The melting behaviour of the octadecyloxy-compound in a capillary tube shows the characteristic sticking to the capillary walls, typical of the smectic phase,[5] whereas the methoxy- and butoxy-compounds appear to be nematic. Microscopic observation on a Mettler FP2 hot-stage with crossed polarizers showed optical birefringence and interference crosses. The observed transition temperatures are in agreement with the determinations made with a Perkin-Elmer DSC-1B Differential Scanning Calorimeter. In all cases, the enthalpies

TABLE

Properties of N-(p-*alkoxybenzylidene*)-p-*aminostyrenes*

p-Alkoxy-group	Found: *M*	Transition temperatures Solid–mesophase	 Mesophase–liquid	Probable mesophase
MeO	244	97·3°	110·6°	Nematic
BuO	242	88·3	120·6	Nematic
$C_{18}H_{37}O$	427	98	104	Smectic

of the solid–mesomorphic transitions are much greater than the mesomorphic–liquid transitions.

After several cyclings of the compounds through their mesophase range, evidence for reaction is observed as a lowering of the mesophase–liquid transition; the solid–mesophase transition temperature shows little change. Polymerization of all three compounds occurs either spontaneously or upon irradiation with a 100 w mercury lamp; the rate of polymerization was MeO > BuO > $C_{18}H_{37}O$. Below the solid–mesophase transition temperatures, polymerization is very slow. We believe that a study of the polymerization of compounds of this type will allow us to ascertain the role of ordering in the liquid crystalline phase on product orientation.

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