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A MESOGENIC HOMOLOGOUS SERIES CONTAINING A PHENOLIC END GROUP

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ABSTRACT: The first extensive homologous series of phenolic derivatives exhibiting mesomorphic properties, 4(4'-n-alkoxybenzoyloxy)benzylidene-4"-aminophenols(I), has been synthesized and their mesomorphic behaviour studied.

Very few compounds with free hydroxy and amino groups are reported to be mesomorphic.[1-5] Gray[6] had explained this rarity of mesomorphism in such compounds by suggesting that intermolecular hydrogen bonding raises the melting point above the mesophase-isotropic liquid transition temperature and perhaps also encourages a non-linear molecular arrangement that is incompatible with mesophase formation. Recently Schroeder and Schroeder[7,8] have reported some mesogenic compounds with terminal hydroxy and amino groups. Here we are reporting the first extensive homologous series having a terminal hydroxy group attached to a benzene moiety.

Thirteen compounds were synthesized by condensing 4-n-alkoxybenzoyloxy-4'-benzaldehydes with p-aminophenol in ethanol. The Schiff bases, 4(4'-n-alkoxybenzoyloxy)benzylidene-4"-aminophenols(I), separated out. These were filtered and recrystallized from ethanol until constant transition temperatures were obtained.

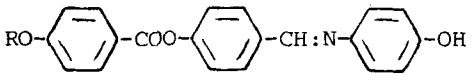
p-n-Alkoxybenzoic acids were prepared by the modified method of Dave and Vora.[9] The p-n-alkoxybenzoyl chlorides obtained by the reaction of p-n-alkoxybenzoic acids and thionyl chloride were condensed with p-hydroxybenzaldehyde in the presence of pyridine to obtain 4-n-alkoxybenzoyloxy-4'-benzaldehydes. The melting points and transition temperatures of all the aldehydes agree well with the reported values.[10]

The melting points and transition temperatures of the Schiff bases are reported in Table 1.

The behaviour of the present phenolic homologous series is similar to the normal nematogenic homologous series. The first members of the series exhibit purely nematic mesophases, middle members exhibit both smectic and nematic mesophases, whereas, the last two members are purely smectic. This behaviour is quite interesting as Schroeder and Schroeder[7,8] have proposed a hypothesis that a phenolic end group is compatible with both nematic and smectic mesomorphism via end-to-end and sidewise hydrogen bonding, respectively.

The structure of the Schiff bases(I), has close similarity with the structures of Steinstrasser's mesomorphic phenol[2] and the p-phenylene dibenzoates reported by Schroeder and Schroeder.[7,8] In the present series of Schiff bases(I), the middle groups are ester and azomethine, whereas, in the above mentioned mesomorphic phenols both the middle groups are esters. This indicates, the Schiff bases do indeed conform to the picture that is emerging of the requisite structural characteristics for mesomorphic phenols.

Table 1



I

R= n-Alkyl group	Transition temperatures °C Smectic	Nematic	Isotropic
Methyl	-	205	275 (d)
Ethyl	-	197	275 (d)
Propyl	-	193	245 (d)
Butyl	-	194	250 (d)
Pentyl	-	190	235
Hexyl	-	178	235
Heptyl	-	175	215
Octyl	-	131	216
Decyl	(142)*	150	205
Dodecyl	152	160	191
Tetradecyl	145	175	188
Hexadecyl	135	-	194
Octadecyl	145	-	188

*Value in the parentheses indicates monotropy.

The transition temperatures of some of these compounds exhibit variations depending on the thermal history. This shows the presence of more than one solid modification. In some of the nematic mesophases the typical textures are observed which are not focal-conic in nature. The smectic mesophases exhibit focal-conic texture. All these compounds

are being investigated further for their thermal history and detailed characteristics of different textures.

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