S U M M A R Y   O F   C O N C L U S I O N S

SUMMARY OF CONCLUSIONS

The following five series comprising three different types of molecular structures and dimensions have been prepared and their various transitions have been determined:

I p-n-Alkoxybenzylidene-p-aminobenzoic acids

II Methyl p-n-alkoxybenzylidene-p-aminobenzoates

IIIa. p-n-Alkoxybenzylidene-p-n-propoxyanilines

IIIb p-n-Alkoxybenzylidene-p-n-butoxyanilines

IIIc p-n-Alkoxybenzylidene-p-n-amyloxyanilines

The first series viz. p-n-alkoxybenzylidene-p.-aminobenzoic acids is a typical mesomorphic series in which all the members exhibit mesomorphism of very high thermal stability. The high thermal stability of the mesophases may be attributed to the length of the dimerized acid molecules giving rise to increased intermolecular attractions. 4'-n-Alkoxydiphenyl-4-carboxylic acids series exhibit greater thermal stability of the mesophases than this series though p-n-alkoxybenzylidene-p-aminobenzoic acid molecule is longer by a -CH=N- group in the monomer than the analogous 4'-n-alkoxydiphenyl-4-carboxylic acid molecule; this may be attributed to the stereochemistry of the -CH=N- link which causes the molecule to be broader than the analogous molecule of 4'-n-alkoxydiphenyl-4-carboxylic acids series.

Methyl p-n-alkoxybenzylidene-p-aminobenzoates series comprises methyl esters of the above acid series. Here, the molecular length is reduced considerably (almost half) compared to the acid series; eventhen the mesomorphic compounds exhibit smectic mesophase only. The purely smectic mesomorphism in this series may be attributed to the strong dipole moment of the carbmethoxy ($-COOCH_3$) group acting at an angle to the major molecular axis. This dipole moment together with the dipole moment due to the alkoxy group on the other end also acting at an angle to the long axis of the molecule essentially supplements the intermolecular lateral cohesions which determine smectic mesomorphism. This ester series also provides an evidence that a smectic-isotropic transition temperature curve can rise to a maximum and then fall. The purely smectic mesomorphism of this series accounts for the relatively high thermal stabilities of the mesophases of the parent acid series. The appearance of the smectic mesomorphism at butyl ether of this ester series and the absence of mesomorphism in methyl 4'-n-butoxydiphenyl-4-carboxylate may be attributed to the extra dipole moment of -CH=N- group acting at an angle to the main molecular axis.

In the remaining three series viz. IIIa, IIIb and IIIc, all the mesomorphic-isotropic transition points relating to the even number of carbon atoms in the alkoxy chain, lie on one falling curve while the similar points relating to the odd number of carbon atoms in the alkoxy chain lie on a curve which rises from C_1-ether to C_7-ether and then falls or shows a falling tendency from C_7-ether to C_9-ether. The rising nature of the nematic-isotropic curve for the odd homologues may probably be due to the relative difference between the terminal and lateral cohesions or may be due to the differences in the packing and cohesion between the terminal methyl groups of alkyl chains containing odd and even number of carbon atoms.

A striking feature of these three series is the polymesomorphism of the smectic phase in atleast some higher homologues. p-n-Alkoxybenzylidene-p-n-amyloxyanilines provide a good example of polymesomorphism of the smectic mesophases; $smectic_1$-$smectic_2$ transition curve rises from octyl to decyl ether and then falls through dodecyl ether to hexadecyl ether. This behaviour suggests that polymesomorphic transitions among the smectic mesophases occur at some definite temperature with certain regularity as the homologous series is ascended.

No doubt, molecular shape is an important criterion to indicate whether mesomorphism would occur or not, but it is rather difficult to postulate where the smectic properties should first originate in the homologous series. However, in the series IIIa, IIIb and IIIc the smectic phase first originates in nonyl, octyl and heptyl ethers respectively. Here it is worth-noting that all these three compounds have same molecular weights and lengths. Therefore, it can be suggested that, closely similar molecules would exhibit changes in the molecular packing at the same total alkyl chain length.

From the present investigation it can be concluded that longer the molecule, the more mesomorphic is the system likely to become, provided, the increase in the lateral intermolecular cohesion is in proportion with the length. A simple increase in the length by a definite increase in the alkyl chain would simply lower the cohesions as found in aliphatic open chain carboxylic acids which are deprived of mesomorphic properties.

It is rather difficult to draw quantitative conclusions from the study of the smectic mixed mesomorphism regarding the influence of molecular structure on mixed mesomorphic properties and phase transitions as the transition lines are not straight. The study indicates that the anisotropic smectic mixed liquids are in all cases homogeneous one-phase mixed liquid crystals. It is found that the binary mixtures, in which nitro-compound is the non-mesomorphic component, exhibit maximum in the smectic-isotropic transition line in the phase diagram. It may be suggested that very high dipole moment due to terminal $C-NO_2$ link acting in the direction of long axis of the molecule, not only favours the smectic mixed liquid crystal formation but also raises the smectic thermal stability to a considerable extent compared to the smectic thermal stability of the pure smectic component.