D I S C U S S I O N

A : MESOMORPHISM IN HOMOLOGOUS SERIES

A large number of mesomorphic compounds and homologous series of various molecular structures have been prepared in attempts, for the systematic study of the structural features which contribute to mesomorphism in the organic compounds. However, it is not possible to lay down the specific conditions which impart mesomorphic properties to an organic molecule.

The important systematic contributions in this field regarding the effect of various groups in homologous series are due to Bennett and Jones (78), Weygand et al. (79,133), Wiegand (181), Brown and Shaw (97) and Gray et al. (80, 84-86, 134-141). Gray and Jones repeated p-n-alkoxybenzoic acids and trans p-n-alkoxycinnamic acids series of Bennett and Jones and also prepared 6-n-alkoxy-2-naphthoic acid and 4'-n-alkoxydiphenyl-4-carboxylic acid series. In all these series, the lower homologues are either non-mesomorphic or purely nematic while the middle members are both smectic and nematic and the higher ones are purely smectic. These results clearly exhibit the effect of regular increase in the molecular length on the mesomorphism, but considerations of the smectic phase and particularly the stage at which the smectic properties first appear in a series suggest that the molecular shape is critical because of its effect in the packing of the molecules in the crystal lattices.

Weygand and Gabler (133) have examined the homologous series of p-n-alkoxybenzylidene-p-phenetidines, azo- and azoxy- compounds. Although monotropic mesomorphism is found in several of these compounds, the effect of increase in the

length of the molecules by each $-CH_2$ group agrees with the observations of Bennett, Jones and Gray. Brown and Shaw have formulated a homologous series of 4,4'-di(n)alkoxy-benzalazines wherein they have found alternation in the mesomorphic-isotropic points with respect to odd and even number of carbon atoms in the alkyl chain as found in many other series. The same general effect of length-increase on mesomorphism has been observed in the present investigation in the analogous series.

It would be rather difficult to correlate the behaviour of Weygand's p-n-alkoxybenzylidene-p-phenetidines with the findings of Gray and Jones for the alkoxyarenecarboxylic acids, in view of the fundamental difference in their molecule types. It was, therefore, decided to synthesize p-n-alkoxybenzylidene-p-aminobenzoic acids and their methyl esters to investigate the behaviour of these series and also to prepare three series of anils - p-n-alkoxybenzylidene-p-n-propoxyanilines, p-n-alkoxybenzylidene-p-n-butoxyanilines and p-n-alkoxybenzylidene-p-n-amyloxyanilines and to study the contribution of molecular length and different groups ($-OR$, $-COOH$, $-COOCH_3$) on mesomorphism. The study of p-n-alkoxybenzylidene-p-aminobenzoic acids and their methyl esters can be utilized for comparision with 4'-n-alkoxydiphenyl-4-carboxylic acids and their methyl esters respectively and the study of p-n-alkoxybenzylidene-p-n-alkoxyanilines would facilitate the comparision with analogous p-n-alkoxybenzylidene-p-phenetidines.

In the five series studied here, p-n-alkoxybenzylidene-

p-aminobenzoic acids give rise to the curves which are the most common in many series; methyl p-n-alkoxybenzylidene-p-aminobenzoates give another type of curves and p-n-alkoxybenzylidene-p-n-alkoxyanilines give the third type of curves. The factors causing these types of curves are discussed below:

Series I : p-n-Alkoxybenzylidene-p-aminobenzoic acids :

The series, p-n-alkoxybenzylidene-p-aminobenzoic acids, comprises the alkyl groups methyl to decyl, dodecyl, hexadecyl and octadecyl (Table 11, Fig. 4). In this potentially mesomorphic series, all the members are mesomorphic as in trans p-n-alkoxycinnamic acids, 6-n-alkoxy-2-naphthoic acids and 4'-n-alkoxydiphenyl-4-carboxylic acids. When the transition points are plotted against the number of carbon atoms in the alkyl chain, the transition points relating to the change mesomorphic to isotropic fall on two curves, one relating to the ethers with odd number of carbon atoms in the alkoxy group and the other to those with an even number. The five smectic-nematic transition points lie on one smooth rising curve which meets the falling nematic-isotropic curve for even members. At the points marked with + sign in the figure 4, very highly threaded nematic structure sets in which vanishes soon and a cloudy melt remains. This phenomenon is observed both during heating and cooling but no clear change like smectic-nematic transition is observed; this may probably be due to the setting of the nematic threads depending upon the temperature. Wayne (182) gives the melting point of

p-methoxybenzylidene-p-aminobenzoic acid as 194° - 195°C. It seems that he has misobserved the solid-nematic point as the clearing point.

When a compound is heated, at the solid-smectic transition, the primary terminal cohesions between the ends of the molecules are overcome. As the temperature of the smectic mesophase is raised further, the thermal vibrations become great enough to overcome the strong lateral intermolecular attractions, and the molecules are no longer maintained in their arrangement. Consequently smectic-nematic change takes place and molecules arrange in parallel orientation but not in strata. Thus a nematic mesophase is formed. The parallel arrangement of the molecules in the nematic swarm is maintained by the residual lateral and terminal cohesions, the weaker of these two determining the nematic-isotropic transition temperature. The change can be represented tentatively as shown in figure 30.

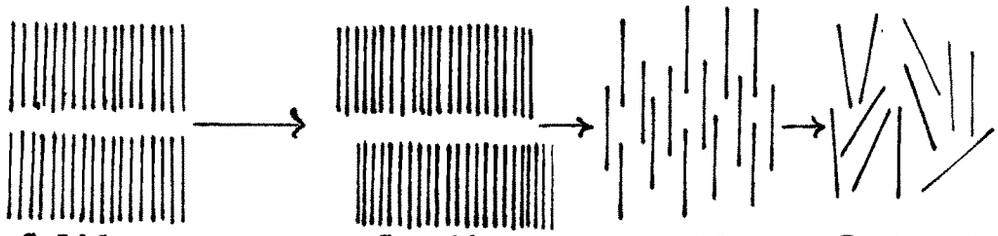
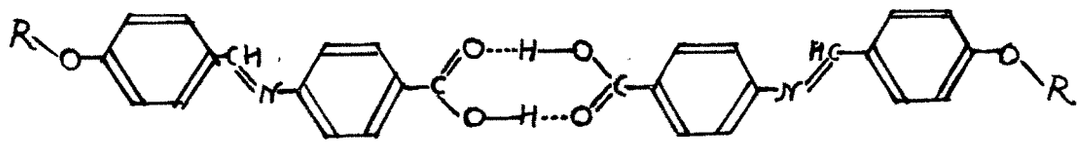


Fig. 30

The acid molecules of this series can be written as follows :



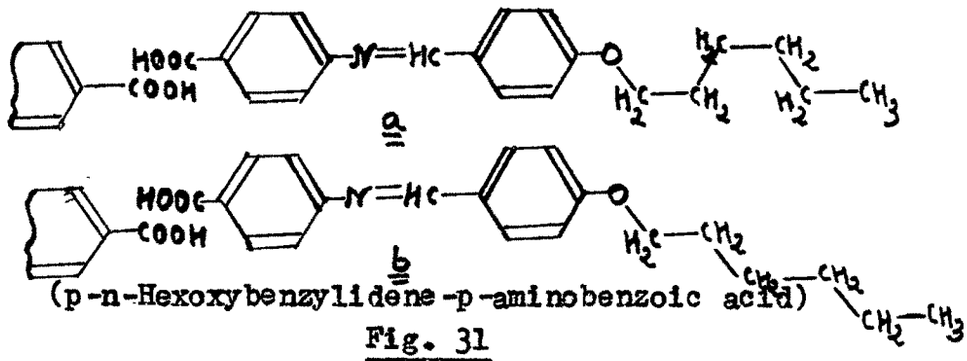
(one dimerised molecule)

As the methylene chain is lengthened, the separation of the aromatic centres which are highly polarizable and which carry permanently dipolar substituents, is increased; consequently there should be a decrease in the strength of the terminal intermolecular cohesions. However, Maier and Saupe (183) have suggested that the addition of methylene group simultaneously increases the overall polarizability of the molecule and so the lateral intermolecular attractions may also increase with the growing chain length. In the p-n-alkoxybenzylidene-p-aminobenzoic acid series investigated here, it is observed that, only the lower homologues (C_1-C_5) are purely nematic as, for the shorter chain compounds, the separation of the aromatic nuclei is at a minimum and the terminal cohesive forces are the strongest determining nematic-isotropic transition. In the middle members of the series (C_6-C_{10}) the smectic properties are found alongwith the nematic properties as the alkyl chain increases the lateral cohesive forces, and the molecules maintain themselves in the layer arrangement. From this observation, it becomes evident that the tendency of a compound to remain nematic decreases as the alkyl chain is lengthened and at the same time its tendency to exhibit smectic properties increases. Therefore, it can be rationally expected that a stage might be reached in the homologous series at which nematic properties would cease to exist and the system should become purely smectic as is observed in dodecyl, hexadecyl and octadecyl ethers of this series. So, p-n-dodecyloxybenzylidene-p-aminobenzoic acid is a stage in this homologous series

when the smectic mesophase passes directly over to the isotropic liquid; probably at this stage, the terminal intermolecular attractive forces are not capable enough to maintain parallel molecular orientation required for the nematic mesophase.

The smectic mesophase is a system of lower kinetic and potential energy than the nematic mesophase and hence one cannot expect a nematic mesophase giving rise to a smectic mesophase at higher temperatures. Usually, the solid compound melts to a smectic mesophase which gives rise to a nematic mesophase at a higher temperature and ultimately at the clearing temperature, the nematic mesophase passes into an isotropic liquid; no case seems to have been reported in which solid melts to a nematic phase giving rise to a smectic phase at a higher temperature and finally at the clearing point passing into an isotropic liquid.

However, this discussion does not explain the regular changes in the mesomorphic transition temperatures as the series is ascended. To explain these changes, Gray (142a) assumes that the alkyl chain in the alkoxy group adopts the cog-wheel arrangement (Fig.31a) rather than the zig-zag mode (Fig.31b).



(p-n-Hexoxybenzylidene-p-aminobenzoic acid)

Fig. 31

As it is pointed out earlier that the nematic-isotropic transition temperatures are determined by the terminal intermolecular attractions, it would be expected that these cohesive forces will change with some constant change being brought to the length of the alkyl chain as the series is ascended. So the separation of the aromatic centres which are polarizable will be successively increased by the constant amount for the odd members of the series by the group $-CH_2$ and for the even members of the series by the group CH_2-CH_3. Therefore, the nematic-isotropic transition temperatures for the even members of the series as well as the odd members of the series should change in a regular manner along the homologous series in question and as a result, probably the mesomorphic-isotropic transition temperature curves of this type (drawn for this series) are obtained.

The above discussion contributes to an explanation of the fact that two curves exist for the mesomorphic-isotropic transition temperatures for a homologous series, but it does not explain why the curve relating to the even members lies above the other relating to the odd members.

Cog-wheel arrangement of the alkyl chain explains the regular change in the mesomorphic-isotropic transitions. Reference to figure 31a will show that the separation is increased more on passing from odd to even and least from even to odd carbon chain homologues. Hence, it may be concluded that the terminal cohesive forces and the nematic-isotropic transition temperatures would decrease more on passing from odd to even than on passing from even to odd members of the

series. This suggests that the curve passing through the nematic-isotropic transition temperatures for the odd members would lie above the one which represents the nematic-isotropic transitions for the even members of the series. However, in practice this type of reversal has not been observed; so, to explain the uppermost nature of the curve for the even members, polarizability of the alkyl chain should be given proper consideration.

As the alkyl chain is lengthened by the replacement of one of the hydrogen atoms of the end methyl group by another methyl group, the polarizability of the system increases largely by the polarizabilities of the C-H bonds of the new terminal methyl group. The three new C-H bonds will seek symmetrical arrangement about the new C-C bond. The spatial distribution of the new C-C bond is determined by the number of carbon atoms in the chain. Using the cog-wheel arrangement of the chain, when the number of carbon atoms falls in the category of an even number by the addition of a $-CH_3$ group, the terminal C-C bond lies in the direction of the major axis of the chain. When the number of carbon atoms in the chain falls in the category of an odd number by the addition of a $-CH_3$ group, the terminal C-C bond makes an angle of about 70^0 with the major axis of the chain as shown in figure 32.

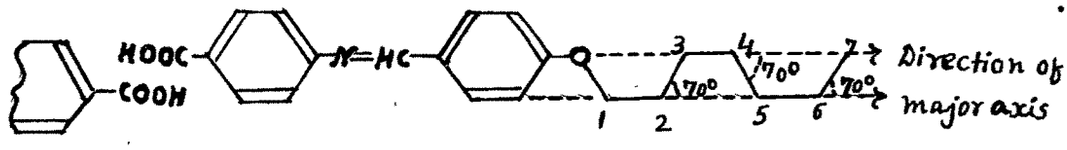


Fig. 32

Thus, for an even number of carbon atoms in the new chain, the terminal C-CH_3 unit makes a given contribution to the polarizability of the chain in the direction of its major axis. However, when the chain contains an odd number of carbon atoms, the contribution to the polarizability is reduced by a factor of cos 70°. Hence, the polarizability of the alkyl chain in the direction of the major axis of the molecules increases most on passing from odd to even members of the series and, therefore, possibly the nematic-isotropic transition temperatures for the homologues containing an even number of carbon atoms in the chain should lie on a curve which is above the nematic-isotropic transition curve for the odd members of the series.

But the increase in the polarizability of the alkyl chain due to the chain length increase should not necessarily increase the nematic-isotropic transition temperatures as there will not be an increase in the terminal attractions between the molecules. The cohesive forces between the ends of the shorter chain homologues mainly depend on the induced polarization effects operating between the ends of the molecules. These attractive forces decrease with increase in the chain length, as the separation of the dipolar aromatic centres of the neighbouring molecules is increased and they are further forced away from the alkyl chains of neighbouring terminally situated molecules. Of course, the dispersion forces between the ends of the chain may increase as the chain lengthens. A net decrease in the terminal attractive forces is therefore likely, the interaction energy at definite

chain length approaching that for pure dispersion forces between the molecules of two long open chain paraffins.

As it is observed in this series and in many other series, the extent of the alternation of the nematic-isotropic transition temperatures always decreases as the alkyl chains grow longer. As the alkyl chain length increases, the effects of the polarizing field set up by neighbouring terminally situated molecules on the alkyl chain of one particular molecule grow less and less and the attraction between the ends of the two molecules approaches that for the limiting case of the molecules of two open chain paraffins between which only dispersion forces operate. The sensitivity of the terminal attractions to the spatial distribution of the terminal methyl group which is added on passing from homologue to homologue, would, therefore, be expected to grow less and the extent of the alternation to diminish.

So far, the effects of changes in terminal attractions between the molecules on nematic-isotropic transition temperatures have been discussed; but the effect of residual lateral interactions between the molecules, which also play some part in determining the thermal stability of the nematic mesophase, has not been taken into account. In the p-n-alkoxybenzylidene-p-aminobenzoic acid series, p-n-alkoxybenzylidene-p-n-alkoxyaniline series and other series studied by other workers, the middle members exhibit smectic as well as nematic mesophases at different temperatures and hence it may be assumed that the lateral intermolecular attractions for such homologues must be considerably strong.

As the alkyl chain lengthens, the residual lateral attractions are increasing, causing the disruption of the weaker residual terminal attractions which are responsible for the nematic-isotropic transition temperature. This increase in the residual lateral attraction reduces the rate of decrease in the nematic-isotropic transition temperatures causing ultimate levelling off in the nematic-isotropic curve for the longer chain homologues for which the residual lateral attractions may be the strongest.

To explain the alternation in nematic-isotropic transition temperatures of the lower homologues of the series 4,4'-di-n-alkoxyazoxybenzenes, Maier and Baumgartner (183 and 184) carried out the experiments for measuring dipole moments and dielectric anisotropies. They concluded that the dielectric constant and, therefore, the polarization is greater at right angles to the major axis of the molecule and advocated that, it is the difference in the polarization effects between the sides of the molecules containing even and odd number of carbon atoms in the alkyl chains that explains the alternation effect. However, Gray argues that the polarizability of the alkyl chain will be the greatest in the direction of its long axis and that, the alternation of the transition temperatures is explained by the alternation of the polarization effects in this direction on passing from odd to even to odd carbon chain homologues, i.e. the terminal attractions will be weaker than the lateral interactions. The nematic-isotropic transition temperature will be predetermined by the weaker interactions and the alternation of the strength of the

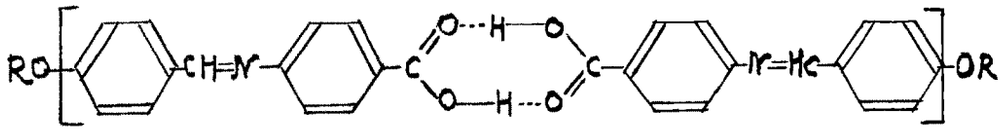
weaker interactions as the series is ascended, will impose an alternation of the nematic-isotropic transition temperatures.

This series is not a purely nematic one as smectic properties begin to appear from the hexyl-ether; therefore, this transition should also be discussed. The appearance of the smectic properties in the series is influenced by the melting point of the compound and/or by the supercooling tendency of the melt. Both these factors are related to the crystal structures of the compounds; and even within the homologous series, as X-ray studies by Bryan (98) has shown, the crystal lattice types may vary considerably and irregularly as the series is ascended.

The smectic-nematic curve for this series is a rising one and merges with the falling nematic-isotropic transition curve for the even members of the series. The increase in the smectic-nematic transition temperatures as the series is ascended can be explained by the overall increase in the polarizability of the molecules. This effect will increase the cohesive forces operating between the sides and planes of the molecules which are lying parallel to one another, with their ends in line, forming the smectic layers. Moreover, increasing molecular weight tends to make it more difficult for the thermal vibrations to cause the sliding of the molecules out of the layers to give an imbricated orientation pattern of the nematic melt. Of course, it is difficult to comprehend the rising smectic-nematic curve merging with the falling nematic-isotropic curve for the even members of the series and then showing falling smectic-isotropic transition

temperatures. Various possibilities can be accounted for such transitions.

The intermolecular forces which operate between the ends of the molecules across the smectic strata are relatively weak since the layers slide over one another. When sliding is not taking place, residual attraction can tend to locate the ends of the molecules near to one another across the strata. Hence, the forces which tend to resist the sliding of a molecule in the direction of its long axis from one stratum to another must be the lateral cohesive forces between the molecules and the residual terminal cohesive forces operating across the strata. Bennett and Jones (78) have suggested that alkoxyarene carboxylic acids form dimers and thus help for the formation of long narrow molecules favouring the conditions needed for mesomorphism. The acid molecule of this series may be written as follows:



If the portion of the molecule within the bracket is represented by a rectangle and the two end alkoxy groups are represented by small lines, then the molecular arrangement in the smectic melt may be as shown in figure 33.

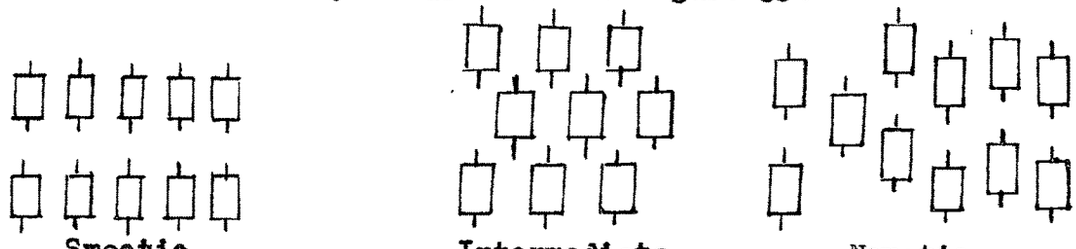


Fig. 33

As the chain lengthens, the residual terminal attractions become weaker and offer less resistance to interpenetration, the distortion of individual bond in the alkyl groups necessary to achieve interpenetration becoming less. Therefore, an intermediate state of the type as shown in figure 33b is formed where ends of the molecules are still in line. As the temperature rises, the tendency for the interpenetration of the chains grows, thus forcing apart the aromatic centres giving an imbricated nematic orientation to the melt as shown in figure 33c. The dislocation of the residual terminal intermolecular cohesions at the smectic-nematic transition is probably temporary. As the interpenetration of the layers becomes great and the normal imbricated arrangement of the molecules of the nematic melt is reached, the ends of the molecules may once again become associated; consequently the terminal interactions can again start to influence the thermal stability of the nematic melt as they do in purely nematic liquid crystals. As the alkyl chain lengthens, the increasing molecular mass and polarizability tend to increase the resistance to the gliding of the molecules from one stratum to another and also increase the tendency for interpenetration of the layers, thus causing the terminal attractions between them to become weaker. The role of these effects explains the smectic-nematic transition temperature curve and the levelling off of this curve at C_{12}-ether in this series where the alkyl chain is reasonably long, the residual terminal cohesions being quite weak and sufficiently unable to maintain nematic order at all; hence,

smectic mesophase passes directly into the isotropic liquid. Naturally, in the higher homologues like C_{16}-ether and C_{18}-ether where the smectic phase passes directly into the isotropic liquid, the smectic-isotropic transition will be dependent on the weakening terminal intermolecular attractions responsible for the nematic-isotropic transition. As a result of this, a complete falling curve for mesomorphic-isotropic transition temperatures is obtained in the case of even members of the series.

A point worth taking into consideration in this series is that, all the smectic-nematic transition points lie on one smooth curve irrespective of odd or even members of the series. It is not easy to predict how the change from an odd to an even carbon-chain homologue in the smectic phase is likely to affect the overall flexibility of the alkyl chain and the relative ease of interpenetration of the smectic strata. However, it has already been shown earlier that the decrease in intermolecular terminal cohesions gets less as one passes from an odd to an even carbon-chain homologue. Hence the alternation effect which is likely to arise from the effect of the residual terminal attractions on the smectic-nematic transition temperatures can oppose that effect arising from the polarizability increase of the added $-CH_2-$ groups on the lateral intermolecular attractions. Therefore, the situation regarding the possible alternation of smectic-nematic transition temperatures gets a little complicated. If the chain adopts a zig-zag conformation rather than a cog-wheel one in the smectic mesophase, no

alternation of the smectic-nematic transition temperatures arising from the relative polarizability effects of odd or even alkyl chains on either lateral or terminal cohesions would be expected. Therefore, it is quite possible that the flexible alkyl chain may have a zig-zag conformation in the smectic phase which after the smectic-nematic transition, changes to a cog-wheel arrangement in the nematic melt. This argument does not seem to persuade thoroughly the smooth curve for smectic-nematic transition and the views to explain this transition still remain purely speculative.

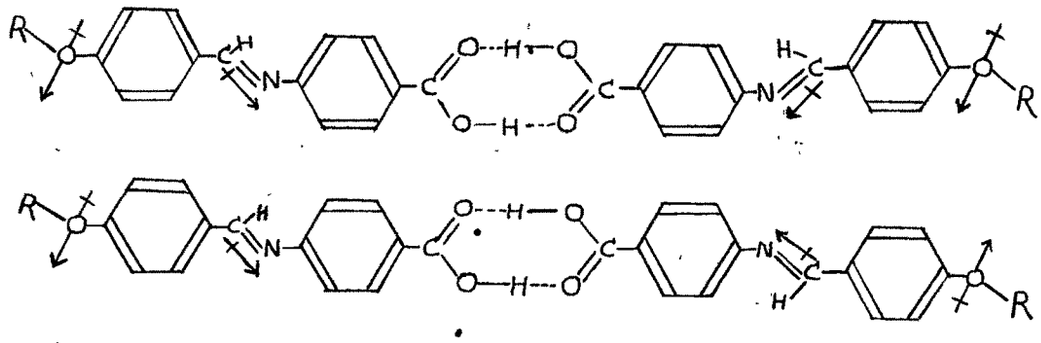
The usual common characteristics and the curve relationships for the acid series have already been discussed and now are compared the average mesomorphic thermal stabilities. Table 37 summarizes the average thermal stabilities of smectic and nematic mesophases of the series, viz. p-n-alkoxybenzoic acids (A), trans p-n-alkoxycinnamic acids (B), 6-n-alkoxy-2-naphthoic acids (C), 4'-n-alkoxydiphenyl-4-carboxylic acids (D) and p-n-alkoxybenzylidene-p-aminobenzoic acids (E). This data shows that the average thermal stability of smectic and nematic phases of these series increases with the increase of double bonds; however, in the case of series (E, the average thermal stability value is less than in the case of series D. The high thermal stabilities of naphthoic acids and diphenylcarboxylic acids may be attributed to the presence of the second aromatic ring contributing more to the intermolecular cohesion than a single benzene ring. The molecules of 6-n-alkoxy-2-naphthoic acids are shorter than the molecules of 4'-n-alkoxydiphenyl-4-carboxylic acids because in the previous one two benzene rings

TABLE - 14

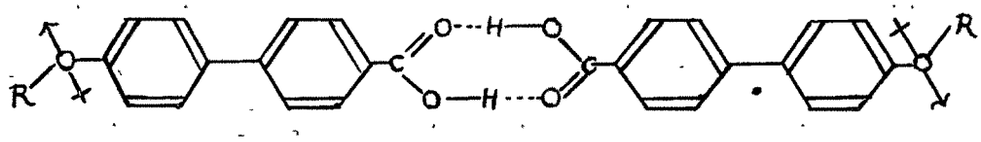
Comparison of average thermal stabilities of mesophases of various acid series

Series	A	B	C	D	E
Average mesomorphic-isotropic transition temperatures (C_3-C_{10},C_{12},C_{16},C_{18})	145.1°	$\xrightarrow{28.2^{\circ}}$ 173.3°	$\xrightarrow{13.5^{\circ}}$ 186.8°	$\xrightarrow{76.5^{\circ}}$ 263.3°	$\xrightarrow{-15.5^{\circ}}$ 247.8°
Average nematic-isotropic transition temperatures (C_3-C_{10})	149.5°	$\xrightarrow{28.6^{\circ}}$ 178.1°	$\xrightarrow{17.0^{\circ}}$ 195.1°	$\xrightarrow{75.5^{\circ}}$ 270.6°	$\xrightarrow{-14.0^{\circ}}$ 256.6°
Average smectic-nematic and/or smectic-isotropic transition temperatures (C_9,C_{10},C_{12},C_{16},C_{18})	126.3°	$\xrightarrow{27.3^{\circ}}$ 153.6°	$\xrightarrow{-0.6^{\circ}}$ 153.0°	$\xrightarrow{96.0^{\circ}}$ 249.0°	$\xrightarrow{-22.8^{\circ}}$ 226.2°

are fused together whereas in the latter case they are united by ring carbon atoms in 1,1'-positions. Therefore, the latter acids are more mesomorphic than the previous ones. Now the question arises about less mesomorphic thermal stability of p-n-alkoxybenzylidene-p-aminobenzoic acids than 4'-n-alkoxydiphenyl-4-carboxylic acids eventhough the former acids are longer by polarizable -CH:N- links than the latter ones. The average mesomorphic thermal stabilities, smectic thermal stabilities and nematic thermal stabilities of p-n-alkoxybenzylidene-p-aminobenzoic acids are less by 15.5^{0}, 22.8^{0} and 14.0^{0} respectively than those of 4'-n-alkoxydiphenyl-4-carboxylic acids. This behaviour suggests that -CH:N- groups play some part either in the packing of the molecules in the crystal lattices or on the linearity of the molecules. In fact, the dimer molecule of the series under study has two extra dipole moments due to -CH:N- groups acting at an angle to the main molecular axis and quite naturally, at least smectic thermal stability of this series should be expected to be higher than that of 4'-n-alkoxydiphenyl-4-carboxylic acids but actually reverse is the case. Taking into consideration the space arrangement of the -CH:N- link, the dimer may be written as follows:



Anyway, this molecule is not as strictly linear as the corresponding 4'-n-alkoxydiphenyl-4-carboxylic acid shown below:



Probably the breadth of the molecules should be responsible for the decreased thermal stabilities of various phases in this series; hence, the role of a strictly linear and an almost linear molecule on mesomorphic thermal stability seems to be significant.

Series II : Methyl p-n-alkoxybenzylidene-p-aminobenzoates :

Methyl esters of this acid series form another homologous series; the alkyl groups used are methyl to decyl, dodecyl and octadecyl. Methyl esters of p-n-alkoxybenzoic acids and trans p-n-alkoxycinnamic acids are non-mesomorphic; probably the molecules in these series are not sufficiently elongated for mesomorphism because the tendency to form a dimer through -COOH is eliminated by esterification. However, methyl esters of 4'-n-alkoxydiphenyl-4-carboxylic acids in the higher homologues exhibit smectic mesomorphism, hence, it can be logically expected that at least higher homologues of methyl p-n-alkoxybenzylidene-p-aminobenzoates should display mesomorphism; and in fact, many higher homologues exhibit smectic mesophase. The melting points and smectic-isotropic transition points of this series are summarised in table 12 and are plotted against the number of carbon atoms in the alkoxy groups in figure 5.

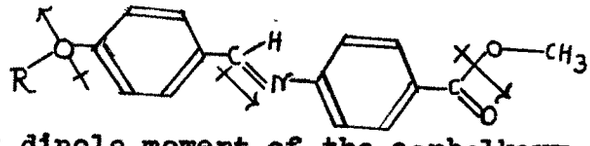
The mesomorphic homologues of methyl p-n-alkoxybenzylidene-p-aminobenzoate series possess only smectic mesophases - methyl, ethyl and propyl ethers being non-mesomorphic. The smectic-isotropic transition temperatures constitute two curves - the curve passing through the smectic-isotropic points for the even members shows a maximum at C_{10}-ether and lies above the other which passes through the similar points for the odd members and reaches a maximum at C_9-ether. These curves are similar to smectic-nematic and smectic-isotropic curves found in the other homologous series and naturally one

may expect the similar attractive forces to be responsible for this transition. Therefore, in the lower homologues exhibiting a rising smectic-isotropic curve, the smectic-isotropic transition should be guided by weaker lateral cohesive forces which are increasing as the chain lengthens; consequently, smectic-isotropic transitions increase up to a point say C_{10}-ether for the even members and C_9-ether for the odd members in this particular series. Thus these esters provide an evidence that a smectic-isotropic transition temperature curve can rise to a maximum and then fall as found in propyl 4'-n-alkoxydiphenyl-4-carboxylates (135). A reference to figure 5 shows that the smectic-isotropic curve rises very steeply from C_5- to C_7-ethers and less steeply from C_7- to C_9-ethers; however, it rises gradually from C_4- to C_8-ethers and falls gradually through C_{10}-, C_{12}- and C_{18}-ethers. The smectic-isotropic transition temperatures for octyl and decyl ethers are the same (122.0^{0}C); thus these two points are the optimum portion of this curve.

An increase in the alkyl chain causes the terminal cohesions to be weaker and therefore, probably interpenetration of the smectic strata may occur at a lower temperature; thus the smectic-isotropic change may occur at a lower temperature. This explains the subsequent fall in the smectic-isotropic transition curve for the even members as the series is ascended. In the case of ethers having odd number of carbon atoms in the chain, only C_9-ether, as stated before, shows the maximum smectic-isotropic transition temperature and as the higher homologues like C_{11}-ether and C_{13}-ether have not been

studied, it is difficult to postulate the shape of that curve in the higher homologues; but one can expect it to be a falling one because nematic-isotropic curve for the odd members does not cross the same curve for the even members in the higher homologues and does not lie above the one for even members in homologous series examined so far by many workers in this field.

The striking feature of this series is that the mesomorphic homologues exhibit smectic phase only while in the other series, purely smectic property is found only in the higher homologues like hexadecyl and octadecyl ethers. The molecules of this series are shorter than the corresponding dimerised acid molecules; eventhen purely smectic properties are found in short alkyl chain ethers like methyl p-n-butoxybenzylidene-p-aminobenzoate. This behaviour definitely suggests that carbalkoxy group plays some decisive role for the occurrence of smectic mesomorphism. Here, the molecule is narrow and elongated with a terminally situated carbalkoxy group on one end and an alkoxy group on the other end as shown below:



The strong dipole moment of the carbalkoxy group operates at an angle to the long axis of the molecule. This may help the molecule to adopt a layer lattice when crystallization occurs and when melting takes place it may preserve the molecules in the layer arrangement which is the basic characteristic of the smectic mesophase. Of course, the dipole

moment of carbalkoxy group alone may not be able to cause this phenomenon because methyl benzylidene-p-aminobenzoate does not exhibit mesomorphism. Therefore, it can be inferred that at the other end of the molecule, the dipole moment of the alkoxy group which also acts at an angle to the long axis of the molecule is essential to supplement the intermolecular lateral cohesion.

The purely smectic mesomorphism found in this series accounts for the relatively high thermal stabilities of the mesophases of p-n-alkoxybenzylidene-p-aminobenzoic acid series. The first member to exhibit mesomorphism in the methyl 4'-n-alkoxydiphenyl-4-carboxylate series is the hexyl ether and in the case of methyl p-n-alkoxybenzylidene-p-aminobenzoate series, butyl ether is the first to show smectic properties. This may be attributed to the extra dipole moment caused by a -CH:N- link acting at an angle to main molecular axis, thus supporting lateral cohesive forces. However, the average smectic thermal stability of this series (A) is less than that of methyl 4'-n-alkoxydiphenyl-4-carboxylates (B) as shown below:

Series	A	B
Average smectic-isotropic transition temperatures (C_6-C_{12})	119.0°	131.8°

In fact, it should be expected that the smectic thermal stability of this series should be greater than methyl

4'-n-alkoxydiphenyl-4-carboxylates, because the compounds of this series contain one more dipole of -CH:N- group acting at an angle to the major molecular axis, thus reinforcing the lateral cohesive forces. This again indicates the roles, a strictly linear molecule and an almost linear molecule can play on mesomorphism.

Series IIIa : p-n-Alkoxybenzylidene-p-n-propoxyanilines

The third series investigated in the present study is the p-n-alkoxybenzylidene-p-n-propoxyanilines, the transition temperatures of which are given in table 13 and are plotted in figure 6. The alkyl groups used in this series and other succeeding series are methyl to decyl, dodecyl, hexadecyl and octadecyl. Methyl, propyl and octadecyl ethers of this series are not mesomorphic; ethyl and butyl ethers are monotropic nematic while amyl, hexyl, heptyl and octyl ethers are purely enantiotropic nematic. Nonyl ether exhibits one enantiotropic nematic and one monotropic smectic phases; decyl ether exhibits one enantiotropic nematic and two monotropic smectic phases while dodecyl ether shows one monotropic nematic and two monotropic smectic phases; however, hexadecyl ether is purely monotropic smectic. When mesomorphic-isotropic transition temperatures are plotted against the number of carbon atoms in the alkoxy group, an alternation in these points for lower homologues is observed for odd and even carbon chain ethers. When these points are joined, two curves are formed - the curve representing this transition for even carbon chain ethers is a falling one and lies above the other which represents odd carbon chain ethers. When the latter curve is extrapolated legitimately towards short carbon chain ethers, the overall curve becomes a rising one. The value of isotropic-nematic transition temperatures obtained by extrapolation of the curve are 102.0 ^{o}C and 104.0 ^{o}C for methyl and propyl ethers respectively; though Weygand and Gabler (185)

give melting point 133.0°C and isotropic-nematic transition value as 107.0°C (calculated) for propyl ether. As a matter of fact, methyl and propyl ethers do not supercool thoroughly and crystallization starts at 108.0°C and 129.0°C for these ethers respectively before giving isotropic-nematic transition. When isotropic liquid of octadecyl ether is chilled, it starts crystallizing at 103.5°C without giving any mesophase; however, when the mesomorphic-isotropic curve for even homologues is extrapolated, the temperature 100.0°C is obtained as the possible isotropic-smectic transition.

The non-mesomorphic character of methyl, propyl and octadecyl ethers is rather peculiar because their melting points are not so unusually high as to cause high thermal agitation for spontaneous disorder in the molten state; liquid crystallinity is not uncommon in the temperature range of 80.0° - 300.0°C. The highest melting point in this series is 134.5°C of p-n-propoxybenzylidene-p-n-propoxyaniline. Thereafter melting points decrease with the increase in the length of the alkoxy chain, the lowest melting point 98.0°C being obtained for hexyl ether and then the melting points rise with increase in chain length upto 108.5°C for octadecyl ether.

Series IIIb : <u>p-n-Alkoxybenzylidene-p-n-butoxyanilines</u>

The fourth series synthesized in the present study is p-n-alkoxybenzylidene-p-n-butoxyanilines. The mesomorphic transitions of this series are given in table 14 and are plotted in figure 7. All the members of this series exhibit

mesomorphism - methyl, propyl, butyl and amyl derivatives being purely monotropic nematic while octadecyl is a purely monotropic smectic. Ethyl, hexyl and heptyl ethers are enantiotropic nematic while octyl ether shows one enantiotropic nematic phase and one monotropic smectic phase. Nonyl ether shows one enantiotropic smectic phase and one enantiotropic nematic phase while decyl and dodecyl ethers exhibit one monotropic smectic, one enantiotropic smectic and enantiotropic nematic phases. Hexadecyl ether is a purely enantiotropic smectic exhibiting one smectic phase. The smectic property starts from octyl ether unlike nonyl ether of the series IIIa. The transition temperatures of p-n-butoxybenzylidene-p-n-butoxyaniline agree with the constants given by Weygand and Gabler (185).

When various transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, two distinct curves for the change mesomorphic to isotropic are obtained, one passing through the points related to the even members and the other passing through the points related to the odd members of the series; the former curve is a falling one and lies above the latter which first rises and then falls from heptyl ether to nonyl ether. The transition points for the change smectic to nematic lie on one smooth rising curve which coincides with the falling nematic-isotropic curve drawn for the ethers having even number of carbon atoms in the chain.

Series IIIc : p-n-Alkoxybenzylidene-p-n-amyloxyanilines

p-n-Alkoxybenzylidene-p-n-amyloxyaniline series, the transition temperatures of which are recorded in table 15 and are plotted in figure 8, is a higher homologue of the previous series IIIa and IIIb. Methyl and amyl ethers of this series are non-mesomorphic; propyl and butyl ethers are monotropic nematic while ethyl and hexyl ethers are purely enantiotropic nematic. Heptyl ether exhibits one smectic and one nematic enantiotropic phases. Octyl and decyl ethers show one monotropic smectic, two enantiotropic smectic and one enantiotropic nematic phases, while nonyl ether shows one monotropic smectic, one enantiotropic smectic and one enantiotropic nematic phases. Dodecyl ether is purely smectic having one monotropic and two enantiotropic smectic phases. Hexadecyl and octadecyl ethers are purely smectic, the former having one monotropic and one enantiotropic smectic phases while the latter has only one monotropic smectic phase. In this series, smectic properties start from heptyl ether unlike octyl ether of the series IIIb and nonyl ether of the series IIIa.

When various transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, two curves are obtained for mesomorphic to isotropic transition, one passing through the points related to the even number of carbon atoms in the chain and the other passing through the points related to the odd number of carbon atoms in the chain. The former curve is a falling one and lies above the latter which first

rises and then falls from C_7- ether to C_9- ether. When the curve for odd mambers is extrapolated towards the short carbon chain ethers, it gives 101.0°C for isotropic-nematic change for methyl ether and 108.5°C for the similar transition for amyl ether. When the isotropic liquid of methyl and amyl ethers is cooled, crystallization takes place at about 102.5°C and 110.0°C respectively before giving isotropic-nematic transition. Weygand and Gabler (185), however, give 113.0°C as the melting point and 103.0°C as the isotropic-nematic transition point for p-n-alkoxybenzylidene-p-n-amyloxyaniline. The transition points for the smectic-nematic change lie on one smooth rising curve which coincides with the falling nematic-isotropic curve for the even homologues at C_{12}- ether. $Smectic_1$-$smectic_2$ and $smectic_2$-$smectic_3$ transition points also form one curve each.

General characteristic of series IIIa, IIIb, and IIIc :

As discussed individually, all the three series exhibit more or less similar characteristics. Smectic-nematic transition points, irrespective of odd or even number of carbon atoms in the chain, lie on one smooth rising curve which merges with the falling nematic-isotropic curve for the even homologues. $Smectic_1$-$smectic_2$ and $smectic_2$-$smectic_3$ transition points also lie on smooth curves.

In the propyl ether series (IIIa), smectic phase appears first in the nonyl ether while in the butyl ether series (IIIb) it appears first in the octyl ether and in the amyl ether series (IIIc) it appears first in the heptyl ether.

This behaviour indicates a definite effect of increase in the alkoxy chain by $-CH_2-$ unit, on the appearance of the smectic phase in the homologous series.

The mesomorphic-isotropic transition curve for the even homologues in these series resembles the similar transition curve for even homologues of the series p-n-alkoxybenzylidene-p-aminobenzoic acids. Therefore, similar factors discussed earlier should be operating for the falling nature of the curve for even homologues of these series. However, the curve for the odd members is a rising one. This type of unusual curves for similar transitions for the odd members are found in the series p-n-alkylbenzoic acids (79) and p-n-alkoxybenzylidene-p-phenetidines (166).

While discussing the shape of the smectic-nematic transition curve of p-n-alkoxybenzylidene-p-aminobenzoic acids, it was pointed out that the relatively weaker lateral cohesive forces determine this change and smectic-isotropic change is determined now by the weaker terminal attractive forces. So, when the molecules get oriented under the strengths of these cohesions, the weaker of these two types of cohesive forces would determine the temperature at which the molecular order breaks down. However, when the lateral intermolecular attractions are weak, the terminal attractions must be strong and it is likely that the strong terminal cohesions may preserve the order even after the lateral attractions have been disruptured. The three series p-n-alkoxybenzylidene-p-n-alkoxyanilines seem to contribute weak lateral attractions because the average smectic thermal stability in these series

is quite low compared to the smectic thermal stability of p-n-alkoxybenzylidene-p-aminobenzoic acid series. As the chain length increases, the lateral cohesion increases and it may support the terminal forces. On this bases, a rising nematic-isotropic transition curve should be expected in these series. If these effects are taken into consideration, the nematic-isotropic transition curves for both odd and even homologues would be of rising nature but in these series only the odd homologues form a rising curve which falls or shows a falling tendency from C_7-ether to C_9-ether. Therefore, it may be suggested that differences in packing and cohesion between the terminally situated methyl groups of alkyl chains containing odd and even number of carbon atoms should play some decisive role in determining the transition temperatures. In the Schiff's base compounds investigated here, the two alkoxy groups of different size present in the molecule are situated at each end and the study of the mode of their end-to-end arrangement in the crystal lattice may probably explain this type of behaviour. In the case of odd homologues of these series, the nematic-isotropic transition should have been guided by the weakening terminal attractions because from C_7-ether to C_9-ether, the transition curve either levels off or falls.

The middle members (e.g. nonyl to dodecyl ethers of series IIIa, octyl to dodecyl ethers of series IIIb and heptyl to decyl ethers of series IIIc) in all the three series exhibit smectic-nematic transition, which is similar to the one obtained in p-n-alkoxybenzylidene-p-aminobenzoic acids.

If the melting points show a rising tendency, the system may become monotropic as found in dodecyl and hexadecyl ethers of series IIIa and octadecyl ether of series IIIb and IIIc, or the system may become non-mesomorphic as in the case of octadecyl ether of series IIIa. Quite analogous phenomenon is shown by the series p-n-alkoxybenzylidene-p-phenetidines (166).

One more striking behaviour in these series is the polymesomorphism of smectic phase found in at least some higher homologues. In series IIIa and IIIb, only decyl and dodecyl ethers exhibit smectic$_1$-smectic$_2$ transitions, therefore, it is not possible to understand the nature of the curve passing through these points. However, in series IIIc i.e. p-n-alkoxybenzylidene-p-n-amyloxyanilines, five members - octyl, nonyl, decyl, dodecyl and hexadecyl ethers exhibit smectic$_1$-smectic$_2$ and smectic$_2$-smectic$_3$ transitions; this facilitates to understand the nature of smectic$_1$-smectic$_2$ and smectic$_2$-smectic$_3$ transition curves. Smectic$_1$-smectic$_2$ transition curve rises from octyl to decyl ether and then falls through dodecyl ether to hexadecyl ether while smectic$_2$-smectic$_3$ transition points lie on a rising curve. 4'-n-Alkoxy-3'-nitrodiphenyl-4-carboxylic acids (138) and 6-n-alkoxy-5-nitro-2-naphthoic acids (84) exhibit such a behaviour. In general, this behaviour suggests that polymesomorphic transitions amongst smectic mesophases take place at some definite temperatures with certain regularity as the homologous series is ascended. In the series p-n-alkoxybenzylidene-p-n-amyloxyanilines, smectic$_1$-smectic$_2$

transition curve rises smoothly to C_{10}-ether and then falls to C_{16}-ether while smectic$_2$-smectic$_3$ transition curve rises from C_8-ether to C_{12}-ether and does not fall but when extrapolated towards higher homologues, it passes through the smectic$_1$-smectic$_2$ transition point of C_{16}-ether; thus indicating that smectic$_2$-smectic$_3$ transition in hexadecyl and octadecyl ethers will be absent. Whatever factors may be governing these polymesomorphic transitions, it is suggestive that these transitions are quite sensitive to the intermolecular cohesion changes arising from the successive growth of the alkyl chain. The smooth curve relationship found in smectic$_1$-smectic$_2$ and smectic$_2$-smectic$_3$ transitions shows that the polymesomorphic changes are real and bring some changes in the molecular ordering in the smectic mesophases.

Comparison of the average nematic thermal stability for butyl to nonyl ethers of the series p-n-alkoxybenzylidene-p-n-alkoxyanilines gives the following order:

Series ----------	$-OC_2H_5$ >	$-OC_4H_9$ >	$-OC_5H_{11}$ >	$-OC_3H_7$
	(166)	(IIIb)	(IIIc)	(IIIa)
Average temperatures for nematic-isotropic transition (C_4-C_9)	120.5°C	116.6°C	111.1°C	108.7°C

This order emphasises the falling nature of the curve passing through nematic-isotropic transition temperatures for the even members of the series and the rising nature of the curve for the similar transitions for the odd members of the series.

From this limited data, one cannot postulate that the series p-n-alkoxybenzylidene-p-n-nonoxyaniline would possess higher nematic thermal stability than that of p-n-alkoxybenzylidene-p-n-heptyloxyaniline series because it is observed in all the three series studied here that the nematic-isotropic curve for the odd members shows a falling tendency or falls from C_7-ether to C_9-ether.

The order obtained for the smectic thermal stability of the three series studied here is as follows:

Series --------	$-OC_3H_7$ (IIIa)	<	$-OC_5H_{11}$ (IIIc)	<	$-OC_4H_9$ (IIIb)
Average temperatures for smectic-nematic or smectic-isotropic transition (C_9-C_{12})	101.6°C		106.6°C		108.0°C

Here again, series IIIb shows the highest smectic thermal stability like the nematic thermal stability among the three series. This is suggestive of the nature of the smectic-nematic and smectic-isotropic curve which rises in the initial stages and then falls.

B : MIXED MESOMORPHISM IN THE SMECTIC PHASE

Numerous miscibility experiments on liquid crystals (18, 154-156, 158-161, 186-194) show that the liquid crystalline substances form homogeneous mesomorphic solutions with organic substances which may or may not be liquid crystalline. The binary systems studied so far mainly comprise of components, one or both of which may be nematic liquid crystal or non-mesomorphic. Recently Arnold and Sackmann (195) have done considerable work to test the miscibility of liquid crystal phases: nematic phases of two different compounds are completely miscible and form a homogeneous nematic liquid crystalline region; smectic phases of two different compounds are likewise miscible forming a homogeneous smectic mesomorphic region. However, the smectic phase of one compound and the nematic phase of the other compound are not miscible. It appears no investigation on the line of Dewar, Dave and Lohar on the nematic mixed mesomorphism has been made to study the mixed smectic mesomorphism in the binary mixtures where one of the components is a smectic liquid crystal and the other a non-mesomorphic one. Some twentyone binary systems of this type where ethyl p-axocybenzoate, a prototype smectic liquid crystal is mixed with non-mesomorphic Schiff's base compounds are studied here and listed in table 38.

TABLE - 38

Component A : Ethyl p-azoxybenzoate (a smectic liquid crystal)

Mixed with

Component B (a non-liquid crystal) :

1. Methyl p-chlorobenzylidene-p-aminobenzoate
2. Methyl p-nitrobenzylidene-p-aminobenzoate
3. Ethyl p-nitrobenzylidene-p-aminobenzoate
4. p-Nitrobenzylidene-p-toluidine
5. p-Nitrobenzylidene-p-bromoaniline
6. p-Nitrobenzylidene-p-phenetidine
7. Methyl p-anisylidene-p-aminobenzoate
8. Methyl p-dimethylaminobenzylidene-p-aminobenzoate
9. p-Anisylidene-p-toluidine
10. p-Acetoxybenzylidene-p-bromoaniline
11. p-Chlorobenzylidene-p-phenetidine
12. p-Methylbenzylidene-p-toluidine
13. p-Dimethylaminobenzylidene-p-chloroaniline
14. p-Chlorobenzylidene-p-dimethylaminoaniline
15. p-Chlorobenzylidene-p-toluidine
16. Ethyl p-chlorobenzylidene-p-aminobenzoate
17. Ethyl p-anisylidene-p-aminobenzoate
18. p-Anisylidene-p-bromoaniline
19. p-Anisylidene-p-anisidine
20. p-Anisylidene-p-chloroaniline
21. p-Anisylidene-p-phenetidine

Compounds 1 to 20 are non-mesomorphic i.e. they do not exhibit enantiotropic or monotropic mesophases, while compound 21 (p-anisylidene-p-phenetidine) is a monotropic nematic liquid crystal. The solid-mesomorphic and mesomorphic-isotropic transition temperatures of various molar compositions of these binary mixtures are given respectively in tables 16 to 36 and

are plotted against the mole per cent composition of the smectic component in figures 9 to 29 correspondingly.

In the nematic binary mixtures where one component is a nematic liquid crystal and the other a non-liquid crystal, one general type of curves for the nematic-isotropic transition is obtained where the nematic-isotropic transition lines are regularly depressed. In the binary mixtures studied in the present investigation comprising one smectic component and the other non-liquid crystalline component, when the transition temperatures are plotted against the mole per cent of the smectic component, two general types of curves for the smectic-isotropic transitions are obtained: (1) a usual curve where the transition lines are depressed regularly (figures 15 to 29) as found for the compounds 7 to 21 and (2) a rising curve showing a maximum (figures 9 to 14) as exhibited by the compounds 1 to 6 in their mixtures with ethyl p-azoxybenzoate. The maximum smectic-isotropic transition temperatures observed for the compounds 1 to 6 in their binary mixtures with ethyl p-azoxybenzoate are 127.0°, 149.0°, 139.5°, 133.5°, 138.0° and 147.5°C respectively which correspond to 84.5, 77.5, 81.0, 83.0, 85.5 and 77.5 mole per cent of ethyl p-azoxybenzoate in the respective binary mixtures.

A smectic mesophase is a system of stratified molecular structure where rod-shaped molecules lie parallel in each stratum; hence, unlike the nematic phase in which the molecules have translational freedom but restricted rotational freedom, the molecules in the smectic phase should have restricted translational and rotational freedom. Another substance

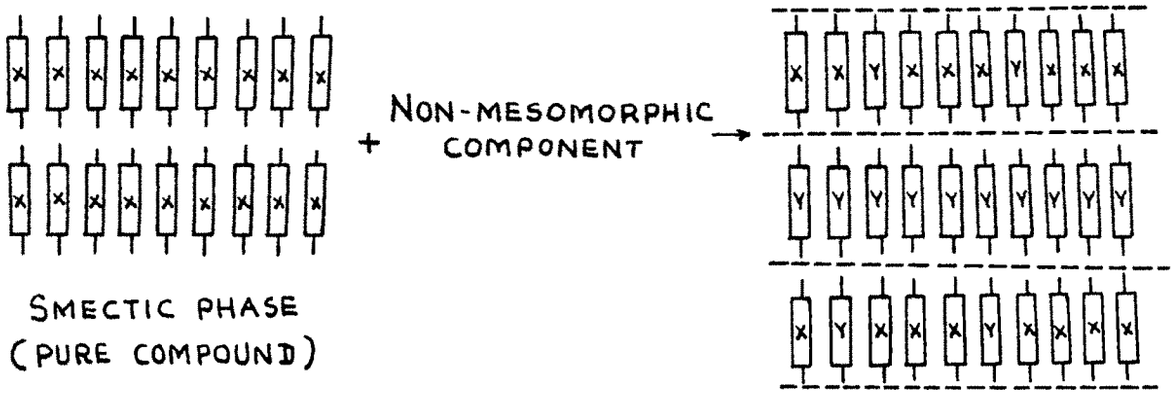

NON-MESOMORPHIC
COMPONENT
SMECTIC PHASE
(PURE COMPOUND)
SMECTIC PHASE
(MIXTURE)

FIG. 34

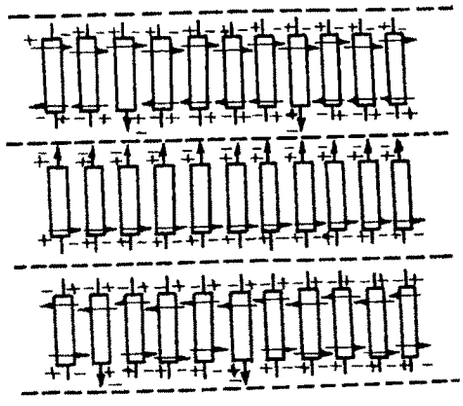


FIG. 35

dissolved in such a smectic liquid would be in an anisotropic environment and it would affect the properties of the mesomorphic substance in an unexpected manner; the orientation of the molecules of the mesomorphic substance will be affected to a more or less extent depending on the similarity or dissimilarity of the structure of the solute molecule and the effective dipole moments of its functional groups. Unlike the nematic mesophase, the smectic phase consists of strata of the molecules; therefore, some of the molecules of the compound dissolved in such a phase can occupy the place between the smectic molecules in each stratum and the rest of the molecules may form molecular strata in which the non-mesomorphic molecules in each stratum lie parallel to each other. Such a stratum of non-mesomorphic molecules should pack itself between the two strata of the smectic component and should thus form a homogeneous smectic melt. The tentative possible picture of the molecular arrangement of such a smectic phase is shown in figure 34 where X represents the molecules of ethyl p-azoxybenzoate - the smectic component, and Y represents the molecules of the non-mesomorphic component. The degree of packing in this mode will depend upon the molecular shape, size and the functional groups of the solute molecules. When the parallel molecules of the solute component are arranged in layers where each molecule is perpendicular to the layer interfaces (figure 35), carrying terminal groups which have effective dipole moment parallel to the major molecular axis i.e. in the direction of the major molecular axis as in p-nitro- or p-chloro- compounds, it becomes logical

to assume that the terminal dipole moment due to such groups may disturb the efficiency of the dipole moment arising from the terminal groups of the smectic molecules. This effect may result in causing the reduction in the lateral intermolecular cohesions and quite naturally one may expect reduced thermal stability of the mesophase compared to the pure smectic component, in various compositions of the mixtures as the mole per cent of the smectic component decreases. Hence, a curve for the smectic-isotropic transition temperatures where the transition line is depressed regularly is obtained. There is nothing particularly surprising about this behaviour. However, in the course of this study, some compositions of binary mixtures comprising a nitro-compound and even in one case, a chloro-compound as the non-mesomorphic component with ethyl p-azoxybenzoate, exhibit higher thermal stability than the pure smectic component. Such systems exhibit a maximum when smectic-isotropic points are plotted against the mole per cent of the smectic component. Such a behaviour demands an explanation. Gray and Byron (142b) have explained the enhanced smectic thermal stability of 4-p-n-nonoxybenzylideneamino-4'-chlorobiphenyl in which terminal C-Cl dipole moment acts parallel to the major molecular axis, by assuming that the molecules are tilted at an angle to the layer interfaces. By thus tilting of the molecules away from the perpendicular arrangement, the separation of the positive and negative charges of C-Cl dipoles does not necessarily increase but the positive charge of one dipole can be brought nearer to the negative centre of the neighbouring dipole. At some suitable angle, the attractive

forces will outweigh the repulsive forces and the net energy of attraction will enhance the lateral attraction and the smectic properties. Now, in the mixtures studied here, the smectic component has two dipole moments arising from two terminal carbethoxy ($-COOC_2H_5$) groups. These dipole mements act at an angle to the main molecular axis, However, one dipole moment due to one of the two terminal groups of the non-mesomorphic component acts parallel and the other at an angle to the major molecular axis. In some cases, both the dipole moments of the two terminal groups act parallel to the major molecular axis. Now, if the molecular arrangement of the mixture in the smectic mesophase is considered as shown in the figures 34 and 35, to account for the enhanced smectic properties of the binary mixtures comprising non-mesomorphic components which possess terminal groups of high dipole moment (e.g. $-NO_2$ etc), the molecular strata formed in the smectic melt should be tilted at an angle to the planes of the smectic strata where the net energy of attraction should become effective to enhance the lateral attractions and the smectic properties. The extent to which the smectic-isotropic transition temperature is raised, should, therefore, depend upon the molecular constitution of the non-mesomorphic component and the direction and the magnitude of the dipole moments of the terminal groups. All the nitro- compounds studied here in their mixtures with the smectic component exhibit a maximum. Such a phenomenon is not observed in the nematic binary systems studied by Dewar, Dave and Lohar.It is also note-worthy that the compounds like p-chlorobenzylidene-p-toluidine where the end groups have their

dipole moment in the direction of the major axis of the molecule do not give a maximum in the smectic-isotropic curve in the phase diagram. Probably high dipole moment of C-NO_2 group favours most for the smectic mixed mesomorphism just like the formation of polymesomorphism of smectic phases in 4'-n-alkoxy-3'-nitrodiphenyl-4-carboxylic acids (138) and the absence of the same phenomenon in 4'-n-alkoxydiphenyl-4-carboxylic acids (135).

Gray et al. (142b) have observed that 4-p-chlorobenzylidene-amino-4'-n-octoxybiphenyl possesses greater smectic thermal stability (smectic-isotropic transition at 261.5°C) than that for 4-p-nitrobenzylideneamino-4'-n-octoxybiphenyl (smectic-nematic transition at 169.0°C). They suggest from their observations that the terminal dipoles contribute to the terminal intermolecular attractions, either by polarization or dipole dipole interactions, as well as to the lateral attractions. If such terminal attractions occur, the contribution of the dipole to the lateral attractions will be decreased and the balance of the lateral and terminal cohesions will be affected. In the present investigation, to study the effect of the nitro group and the chloro group on mixed smectic thermal stability in the binary mixtures with ethyl p-azoxybenzoate four compounds viz. methyl p-chlorobenzylidene-p-aminobenzoate, methyl p-nitrobenzylidene-p-aminobenzoate, ethyl p-chloro-benzylidene-p-aminobenzoate and ethyl p-nitrobenzylidene-p-aminobenzoate are selected for comparison. Surprisingly, it is observed that the binary mixtures containing methyl p-nitrobenzylidene-p-aminobenzoate shows a higher maximum in the

smectic-isotropic transition curve than the maximum found for the binary mixture containing methyl p-chlorobenzylidene-p-aminobenzoate while ethyl p-nitrobenzylidene-p-aminobenzoate shows a maximum in the smectic-isotropic transition curve and ethyl p-chlorobenzylidene-p-aminobenzoate does not give rise to a maximum. These observations of the present investigation and those of Gray and co-workers lead to suggest that the effect of the terminal groups on the smectic thermal stability in the pure smectic compound and in the binary smectic mixtures may not be the same. However, it is interesting to note that in all the four binary mixtures mentioned above, the mixtures containing chloro-compounds show enantiotropic smectic mesomorphism over a wider range of mole per cent composition of the smectic component than the nitro-compounds, e.g. methyl p-chlorobenzylidene-p-aminobenzoate shows enantiotropic mesomorphism between 66.0-100.0 mole per cent of liquid crystalline component while methyl p-nitrobenzylidene-p-aminobenzoate exhibits similar mesomorphism between 73.5-100.0 mole per cent of the smectic component. Similarly ethyl p-chlorobenzylidene-p-aminobenzoate exhibits enantiotropic mesomorphism between 49.0-100.0 mole per cent of the smectic component while ethyl p-nitrobenzylidene-p-aminobenzoate displays similar mesomorphism between 70.0-100.0 mole per cent of ethyl p-azoxybenzoate. But the behaviour of p-nitrobenzylidene-p-phenetidine and p-chlorobenzylidene-p-phenetidine in their binary mixtures with ethyl p-azoxybenzoate is not the same; the nitro-compound exhibits enantiotropic liquid crystallinity between 29.0-100.0 mole per cent of the smectic component

while the chloro-compound exhibits the same mesomorphism between 40.0-100.0 mole per cent of the smectic component. The tendency of showing maximum by the nitro mixtures may not be attributed to the high melting points of nitro-compounds because the melting points of p-nitrobenzylidene-p-phenetidine (123.5°C), p-nitrobenzylidene-p-toluidine (124.0°C) and the smectic-isotropic transition temperature of ethyl p-azoxybenzoate (122.5°C) are almost the same and the maximum smectic-isotropic transition temperatures showed by p-nitrobenzylidene-p-phenetidine and p-nitrobenzylidene-p-toluidine are 147.5°C and 133.5°C respectively when studied individually in binary mixtures with ethyl p-azoxybenzoate. It will, therefore, be presumptuous from this limited data to postulate the role of the terminally situated groups and their dipole moments on the smectic characteristics of the mixtures, till more detailed studies are carried out.

It was also proposed to deduce the slope of the transition curves in these binary mixtures comprising a smectic compound and a non-mesomorphic compound, similar to the study carried out by Dewar, Dave and Lohar in the nematic solutions. However, this is not possible as the transition curves in these smectic mixtures are almost all curved and no order for the tendency of the terminal polar groups present in the non-mesomorphic component can be derived. The study indicates that the anisotropic smectic mixed liquids are in all cases homogeneous one-phase mixed liquid crystals. However, in the course of microscopic observations it was found that the mixed smectic phase at the smectic-isotropic transition was disappearing or reappearing

over a range of 0.5° to 1.0°C but such is not the case when the mixtures are studied by the usual optical method where the sample is stirred continuously.