D I S C U S S I O N

MESOMORPHISM IN HOMOLOGOUS SERIES

A. CHOLESTEROGENIC HOMOLOGOUS SERIES

Though the first mesomorphic substance reported was a cholesteric one (1), the effect of chemical constitution on this mesophase has not been studied in detail. Friedel (7), Lehmann (290), and Jaeger (291) studied the mesomorphic behaviour of the fatty acid esters of cholesterol. There is some disagreement about the transition temperatures and the number of mesophases in their results. Gray (59) studied the homologous series of fatty acid esters of cholesterol; he has reported modified transition temperatures for these compounds and some of the mesophases were identified which were missed in the previous work. Wiegand (287) tried to study the effect of side chain and modified sterol skeleton on the cholesteric mesophase by synthesizing a number of sterol derivatives. Recently some studies of homologous series exhibiting the cholesteric mesophase have been reported. These studies involved cholesteryl and stigmasteryl carbonates (292, 293) and cholesteryl thiocarbonates (294, 295). Pohlmann et al. (296) studied the structure dependence of the cholesteric mesophase in a number of cases by changing the position of the double bond, modifying the sterol skeleton and changing the aliphatic side chain in these compounds. Knapp and Nicolas (297) studied the cholesteric mesophases of triterpenes and sterols.

In all these studies the side chain was generally aliphatic. The main study was of the sterol skeleton and its effect on mesomorphism. It seems that no systematic attempt was made to correlate the effect of chemical constitution on the cholesteric mesophase with that on the nematic mesophase. In the present

study are synthesized the homologous series exhibiting cholesteric and smectic mesophases. In all the series, the sterol skeleton is the same, namely cholesterol; the side chain at the 3 β-position is changed. In the side chain are introduced different arene nuclei with such a geometry that the effect of these nuclei on the cholesteric mesophase can be compared with that on the nematic and smectic mesophases, as nematogenic and smectogenic compounds are known with these nuclei. The behaviours of all the homologous series exhibiting cholesteric mesophases are now discussed.

(1) Cholesteryl p-n-alkoxybenzoates :

Fourteen esters of cholesterol are synthesized by condensing p-n-alkoxybenzoyl chlorides with cholesterol and their melting points and transition temperatures are reported in table No. 17.

All the members of the series are enantiotropic mesomorphic. Wiegand (287) has reported the m.p. and t.p. of cholesteryl anisoate as 162.5 - 163°C and 236°C, respectively. Gray reports that it melts at 175°C and clears at 258.0°C with decomposition (67). In the present study the corresponding melting point and transition temperature observed for this compound are respectively 180°C and 268°C by microscopic examination. The slide was prepared by evaporating the solvent from the solution of the compound. Recently Barrall and Johnson (298) have reported the m.p. and t.p. as 181.5°C and 268.0°C, respectively.

The first six members of the series are enantiotropic cholesteric. The smectic mesophase commences at the heptyl derivative. The heptyl to octadecyl derivatives are polymesomorphic, i.e., they exhibit cholesteric and smectic

mesophases. In the corresponding n-alkanoates of cholesterol, the smectic phase commences with the heptanoate derivative as a monotropic phase. All the higher aliphatic esters of cholesterol studied also exhibit monotropic smectic phases except the myristate which is enantiotropic smectic. The smectic-cholesteric transition temperatures of the n-alkanoates of cholesterol increase only upto cholesteryl laurate and then fall steadily through the myristate, palmitate and stearate. In the cholesteryl p-n-alkoxybenzoate series, the cholesteric-isotropic transition temperatures change in a regular manner when the series is ascended as is the case with other mesomorphic series. The cholesteric-isotropic transition temperatures fall smoothly with a regular alternation between members with an odd and even number of carbon atoms in the alkyl chain. The smectic-cholesteric transition temperatures rise smoothly to a maximum at p-n-dodecyloxybenzoate and then fall steadily as the chain length increases through the tetradecyloxy-, hexadecyloxy- and octadecyloxy- benzoates. This is graphically represented in fig. 6 obtained by plotting the transition temperatures against the number of carbon atoms in the alkyl chain for the series. The smectic-cholesteric transition temperature curve does not coincide with the falling cholesteric-isotropic curve and does not give rise to direct smectic-isotropic transitions for the longest chain esters as is usually the case in other mesomorphic homologous series exhibiting the nematic mesophase. Cholesteryl n-alkanoates also behave in a similar manner.

In the polymesomorphic substances under investigation, first, on heating, the focal-conic smectic phase is obtained

which sometimes develops a homeotropic texture. This on further heating gives the focal-conic cholesteric phase. On cooling, the first twelve members of the series give the focal-conic cholesteric texture, just upto 1.5°C below the cholesteric-isotropic transition temperatures preceded by a blue phase. In all the cases the focal-conic cholesteric texture changes to the plane texture with only a slight disturbance in the melt. At the juncture of the cholesteric-smectic transition the plane texture displays different colours over a short temperature interval while cooling. Cholesteryl hexadecyloxy-and octadecyloxy benzoates cool to give a plane cholesteric texture 1°C below their cholesteric-isotropic transition temperatures preceded by a blue phase. These two members do not display any visible colour behaviour. On further cooling, the cholesteric phase changes to a homeotropic smectic phase.

(2) Cholesteryl trans-p-n-alkoxycinnamates :

Fifteen esters have been prepared and their melting points and transition temperatures are summarized in table 18.

All the esters studied here exhibit enantiotropic mesophases. The temperatures reported in the literature (36) for cholesteryl trans-cinnamate are 156.0°C for the solid-cholesteric transition and 197.0°C for the cholesteric-isotropic transition. In the present study the transition temperatures obtained are, 160.5°C for the solid-cholesteric transition and 215.0°C for the cholesteric-isotropic transition. This may be due to the purity of the sample and accuracy of the apparatus. Recently Barrall and Johnson (298) have

reported, 162.6°C and 214.5°C for the solid-cholesteric and cholesteric-isotropic transition temperatures, respectively.

The first nine members of the series are enantiotropic cholesteric. The higher members starting with cholesteryl trans-p-n-decyloxycinnamate exhibit polymesomorphism, i.e., they exhibit smectic and cholesteric mesophases. Cholesteryl trans-p-n-decyloxy-, dodecyloxy- and tetradecyloxy- cinnamates exhibit an additional smectic mesophase. When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (fig. 7) the transition points relating to the change cholesteric-isotropic lie on two falling curves, one representing the esters with an odd number of carbon atoms in the alkyl chain and the other representing the esters with an even number of carbon atoms in the alkyl chain. The latter curve lies above the former. The smectic$_I$-cholesteric transtion points lie on a smooth rising curve which rises to a maximum at the tetradecyloxy derivative and then falls off through the hexadecyloxy ester at 181.5°C and the octadecyloxy ester at 167.0°C, whereas in the cholesteryl p-n-alkoxybenzoates it rises to a maximum at the dodecyloxy ester and then falls off through the tetradecyloxy, hexadecyloxy and octadecyloxy esters. The smectic$_I$-cholesteric transition temperature curve does not coincide with the falling cholesteric-isotropic transition temperature curve. In all the acid esters series of cholesterol studied, the cholesteric mesophase persists upto the last member of the series.

In the polymesomorphic substances under investigation the decyloxy, dodecyloxy and tetradecyloxy derivatives, first,

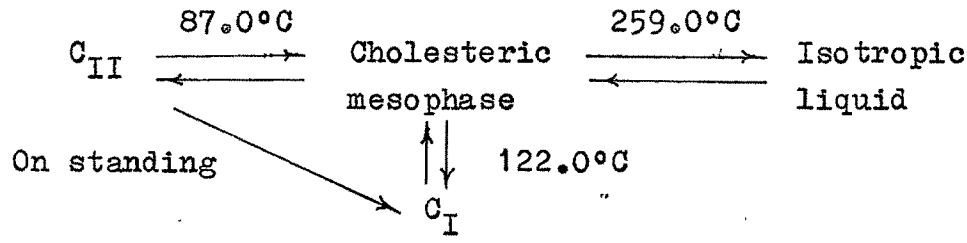
on heating, give the focal-conic smectic$_{II}$ phase which develops into a homeotropic texture except in the case of decyloxy derivative which gives a schlieren texture. On further heating a focal-conic smectic$_{I}$ phase is obtained, which on disturbance develops into a homogeneous texture. This on further heating gives a cholesteric focal-conic phase. In the case of last two members the solid, on heating directly gives a focal-conic smectic$_{I}$ phase which changes to a homeotropic texture. On further heating they give a focal-conic cholesteric phase. On cooling all the members give focal-conic cholesteric texture. The blue phase is not detected. In all the cases the focal-conic cholesteric texture changes to a plane texture with only a slight disturbance in the melt exhibiting vivid colours. At the juncture of the cholesteric-smectic transition the plane texture displays different colours over a short temperature interval while cooling. The last two members of the series also exhibit colour behaviour which is not the case with the n-alkanoates and p-n-alkoxybenzoates of cholesterol. This may be due to the trans -CH=CH- group present in the series. On further cooling the smectic$_{I}$ and smectic$_{II}$ phases are obtained, the behaviour of which is similar to that observed while heating.

(3) Cholesteryl trans-p-n-alkoxy-α-methylcinnamates :

Fifteen esters have been prepared by condensing trans-p-n-alkoxy-α-methylcinnamoyl chlorides with cholesterol. Their transition temperatures are recorded in table 19.

All the members of the series are enantiotropic mesomorphic. Cholesteryl p-methoxy-α-methylcinnamate has two solid modifications. Solid crystals (C_{I}) on heating melt

to give the cholesteric mesophase at 122.0°C becoming isotropic at 259.0°C. On cooling, the cholesteric phase crystallizes to another solid modification (C_{II}) which melts to give the cholesteric mesophase at 87.0°C becoming isotropic at 259.0°C. The crystalline modification C_{II} on standing changes to C_I and sometimes on heating, after allowing the solid to stand for a while, the two modifications C_I and C_{II} are observed to coexist side by side and melt at their respective transitions. The situation can be represented diagramatically as under :



Such examplesof having more than one solid modification are observed in a number of cholesteric compounds (235) and in aliphatic esters of cinnamic and α-methylcinnamic acid-Schiff's base compounds (299).

The first seven members of the series are purely cholesteric. Smectic mesophases commence at the octyloxy derivative. The octyloxy to octadecyloxy derivatives exhibit both smectic and cholesteric mesophases. The octyloxy derivative exhibits an additional smectic mesophase. When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain, the cholesteric-isotropic points lie on one curve generally falling and showing distinct odd-even effect only for the first five members (fig. 8). The

smectic$_I$-cholesteric transition temperature curve rises smoothly and exhibits a maximum at the tetradecyloxy derivative and then falls off smoothly through hexadecyl and octadecyl derivatives. This behaviour is analogous to the series cholesteryl trans-p-n-alkoxycinnamates. The smectic$_I$-cholesteric temperature curve does not coincide with the falling cholesteric-isotropic transition temperature curve. This series is similar to the cholesteryl trans-p-n-alkoxy-cinnamate series except that it has an α-methyl substituent.

In the polymesomorphic substances under investigation, the octyloxy derivative, first, on heating, gives a focal-conic smectic$_{II}$ phase which on disturbance gives a schlieren texture. On further heating a focal-conic smectic$_I$ phase is obtained, which on disturbance develops into a homogeneous texture. In the case of other polymesomorphic members, the solid on heating directly gives a focal-conic smectic$_I$ phase which changes to a homeotropic texture. Smectic$_I$ phase in all the cases, on further heating changes to a focal-conic cholesteric phase. On cooling all the members give focal-conic cholesteric texture. The blue phase is not detected. In all the cases the focal-conic cholesteric texture changes to a plane texture with only a slight disturbance in the melt exhibiting vivid colours. At the juncture of the cholesteric-smectic transition the plane texture displays different colours over a short temperature interval while cooling. The last two members of the series also exhibit colour behaviour. On further cooling smectic$_I$ and

smectic$_{II}$ phases are obtained, the behaviour of which is similar to that observed while heating. The solid-mesomorphic transition temperatures of these compounds are lower compared with those of the cholesteryl trans-p-n-alkoxy-cinnamates. This might be a function of the α-methyl substituent of the side chain.

(4) Cholesteryl-4-n-alkoxy-1-naphthoates :

Fourteen esters were prepared by condensing 4-n-alkoxy-1-naphthoyl chlorides with cholesterol. The melting points and transition temperatures are summarized in table 20.

All the members of the series exhibit cholesteric mesophases. The ethoxy to heptyloxy derivatives are monotropic cholesteric, the rest are enantiotropic cholesteric. Smectic mesophase commences at the decyloxy derivative as a monotropic phase and all the succeeding members are monotropic smectic. When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (fig. 9), the cholesteric-isotropic transition temperatures are found to fall on two falling curves, the upper one representing even numbers of carbon atoms, and the lower one representing odd numbers of carbon atoms in the alkyl chain. The smectic-cholesteric transition temperature curve rises smoothly exhibiting a maximum at the hexadecyloxy derivative and then falls off to the octadecyloxy derivative. In the case of the cholesteryl p-n-alkoxybenzoates the maximum is at the dodecyloxy derivative, and in the case of cholesteryl trans-p-n-alkoxycinnamates the maximum is at the tetradecyloxy derivative. The smectic-cholesteric transition temperature

curve does not coincide with the falling cholesteric-isotropic transition temperature curve.

Structurally, a compound having a long, narrow linear molecule with dipolar groups, contributing to intermolecular attractions, should be expected to exhibit mesomorphism. If the intermolecular attractions are too strong, selective weakening of the cohesive forces may not take place until high temperatures are reached and when the melting process begins, the thermal vibrations may be too great to allow an ordered arrangement of the molecules to persist. In the case of cholesteryl-4-methoxy-1-naphthoate, the melting point is not very high and the compound passes from solid to ordered mesophase and then to the isotropic liquid in stages during heating. In the case of the higher members, the compounds apparently form more stable crystal lattices; hence on heating, before they can exhibit a mesophase (ordered structure), the compounds become disordered to the isotropic liquid. The molecules however possess the basic requirements to exhibit mesomorphism and therefore, on cooling the melt the molecules align to give an ordered mesophase arrangement before solidification takes place. Hence, the ethyl to heptyl derivatives exhibit monotropic cholesteric mesophases. With the octyl derivative onwards, all the members exhibit enantiotropic cholesteric mesophases, as the crystal thermal stability and melting point are lower for these higher homologues.

Ethoxy to heptyloxy derivatives on heating directly

change to isotropic liquid and on cooling give a monotropic cholesteric phase with a focal-conic texture. Methoxy and octyloxy to octadecyloxy derivatives first, on heating, give a focal-conic cholesteric phase and on further heating change to isotropic liquid. On cooling these compounds give a focal-conic cholesteric phase, just upto 2°C below the cholesteric-isotropic transition temperatures. The blue phase is not detected. In all the cases the focal-conic cholesteric texture changes to the plane texture with only a slight disturbance in the melt. The last four members on further cooling give a monotropic focal-conic smectic phase which sometimes develops a homeotropic texture. At the juncture of the cholesteric-smectic transition the plane texture displays different colours over a short temperature interval while cooling. The last two members of the series also exhibit colour behaviour.

General characteristics of series 1, 2, 3 and 4 :

The general behaviour is similar for all the series. For instance, the cholesteric-isotropic transition temperatures fall on two falling curves, one representing odd and the other even numbers of carbon atoms in the alkyl chain, and the latter curve lies above the former.

Mesomorphic-isotropic transition temperatures generally change regularly in a mesomorphic homologous series. In the case of mesomorphic compounds, the melting process occurs in stages. The mesomorphic compound on heating passes through one or more ordered intermediate stages before the increasing thermal agitations give rise to the isotropic liquid. When a poly-mesomorphic compound is heated, at the solid-smectic

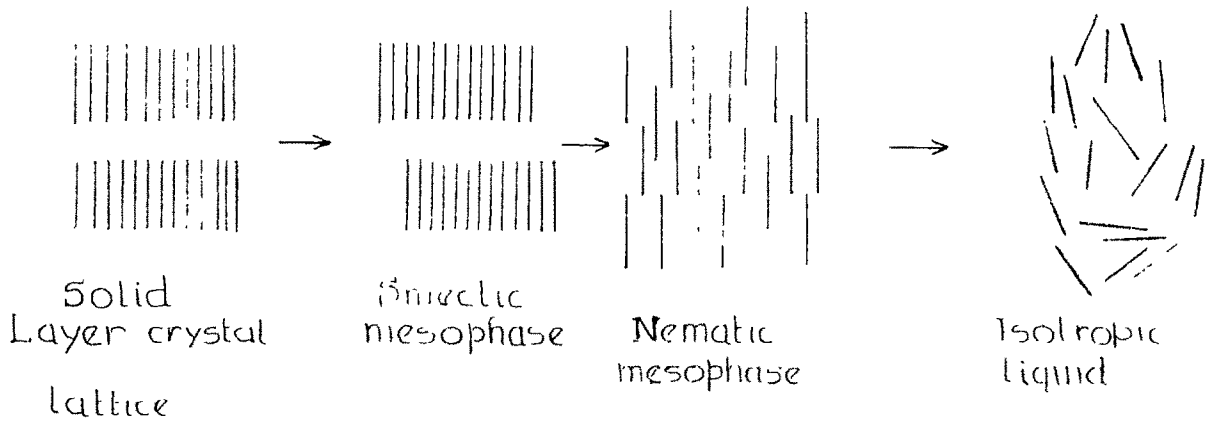

Solid
Layer crystal
lattice
Smectic
mesophase
Nematic
mesophase
Isotropic
liquid

Fig. 13

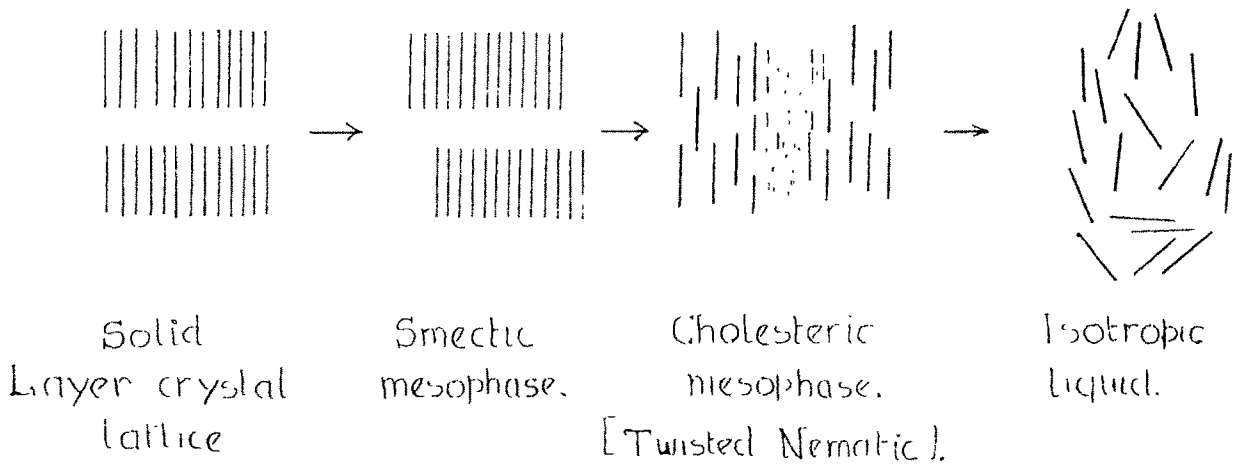

Solid
Layer crystal
lattice
Smectic
mesophase.
Cholesteric
mesophase.
[Twisted Nematic].
Isotropic
liquid.

Fig. 14

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 eventually become great enough to overcome the strong lateral intermolecular attractions and the molecules are no longer maintained in their layer arrangement. Consequently the smectic-nematic or smectic-cholesteric change takes place and the molecules are arranged in a parallel orientation but not in strata. Thus a nematic or cholesteric mesophase is formed. The parallel arrangement of the molecules in the nematic or cholesteric melt is maintained by the residual lateral and terminal cohesions, the weaker of these two determining the nematic-isotropic or cholesteric-isotropic transition temperature. On further heating, the molecules pass to a disordered isotropic liquid state. The change can be represented tentatively as shown in fig. 13 and 14.

In a homologous series exhibiting mesomorphism, as we ascend the series the increment of each $-CH_2$ group brings about regular changes in the transition temperatures for the series. Gray (67) has tried to explain this behaviour of homologous series. 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, Gray (67) and Maier and Boumgartner (300) have suggested that the addition of each methylene group simultaneously increases the overall polarizability of the molecules and so the lateral

intermolecular attractions may also increase with the growing chain length. In this way the behaviour of the homologous series can be explained. The lower homologues are only purely nematic, i.e., for the shorter chain compounds, the separation of the aromatic nuclei is at a minimum and the terminal cohesions are strongest. Smectic properties are often observed to commence for the middle members of a series; because with the increase in the alkyl chain the lateral cohesive forces also increase and the molecules maintain themselves in the layer arrangement before they give a nematic mesophase. That is, the tendency of a compound to be nematic should decrease as the alkyl chain is lengthened, and at the same time, its tendency to exhibit smectic properties should increase. One would therefore expect a stage to be reached in a homologous series at which no nematic properties would be shown and the system would be purely smectic in behaviour. At this stage, the smectic mesophase will pass directly to the isotropic liquid, presumably because the terminal intermolecular attractions are inadequate to maintain the parallel molecular orientation required for the nematic mesophase. This is the general pattern for a number of homologous series, involving simple rod-shaped molecules, exhibiting nematic and smectic mesophases.

There are a number of other homologous series which do not behave exactly as discussed above. Especially in the case of cholesteryl homologous series, the behaviour is only similar

up to the middle member compounds. Those compounds having short alkyl chains exhibit only cholesteric mesophases because of the relatively strong terminal cohesive forces. The middle members are smectic and cholesteric, because with the increase in the alkyl chain the lateral cohesive forces are again increasing and the molecules may maintain themselves in the layer arrangement before they give the cholesteric mesophase at higher temperatures. Cholesteryl homologous series differ only in the last stage. In a nematogenic system, generally the last members are purely smectic, whereas in a cholesterogenic system, the last members exhibit a smectic phase along with the cholesteric phase. Cholesterol is a broad and flat molecule, and the effect of chemical constitution on the behaviour of such nematogenic systems has not been studied in detail. Hence some of the properties of cholesteric compounds may not easily be understood. This type of behaviour has also been observed with some nematogenic systems (107, 301). Recently Arora *et al.* have reported a nematogenic system where the last members are not purely smectic, but also exhibit a nematic mesophase along with the smectic mesophase (302). The striking feature of these particular homologous series is that they are comprised of broad molecules. In support of this can be cited the study of Dave *et al.* (108a) evaluating the effect of the broad naphthalene nucleus on mesomorphism. In homologous series of anils prepared from *p*-phenylenediamine or *p*-aminobenzoic acid with 4-*n*-alkoxy-1-

naphthaldehydes, they observed differences compared with the corresponding anils prepared from alkoxybenzaldehydes. In the case of the p-phenylenediamine analogues, all the members are monotropic mesomorphic and the last members exhibit a smectic mesophase along with the nematic mesophase. In the case of the analogous p-aminobezoic acid series, the last members again exhibit a smectic mesophase along with the nematic mesophase. The series of N,N'-di(4-n-alkoxy-1-naphthylidene) p-azoanilines and 4-n-alkoxy-1-naphthylidene-p-aminoazobenzenes also behave in a similar manner (108b). There are also a number of nematogenic homologous series which do not show any smectic mesophase even in the last members of the series (67). All the members exhibit only nematic mesophases. This indicates that irrespective of the mesophase type, if the molecule is broad and the length to breadth ratio is decreased considerably, the normal behaviour of the homologous series is changed. Complementarily, this is a further illustration that cholesteric and nematic mesophases are essentially similar.

This can be explained, as increase in breadth reduces lateral cohesive forces, and for a compound to exhibit only a smectic mesophase the lateral cohesive forces should be much higher than the terminal cohesive forces. In such a series, even in the last members, the molecules are arranged in such a way that on heating, the layers slide over each other and do not give disruption to the disordered isotropic state. A cholesteric or nematic phase is thus obtained from the smectic phase and only on further heating is the isotropic liquid obtained. It should be noted that a nematic or

cholesteric mesophase cannot give rise to a smectic mesophase at higher temperatures. The smectic mesophase is a more highly organised state and therefore represents a system of lower kinetic and potential energy than the nematic and cholesteric phases. A nematic-smectic or cholesteric-smectic transition occuring with rising temperature is therefore impossible as it would necessitate a change from a higher to a lower energy system with increasing temperature. This discussion explains the general behaviour of the present homologous series, but it does not explain the regular alternation in cholesteric-isotropic transition temperatures for odd and even members of carbon atoms as the series is ascended.

Gray originally explained this behaviour on the basis of a cog-wheel rather than a zig-zag conformation of the carbon chains (67). He also tried to explain why a cog-wheel, rather than a zig-zag conformation of the alkyl chain might be presumed to occur in these systems. However, he states in his recent paper (303) that the preliminary results of X-ray studies of the crystalline state of some liquid crystalline compounds now make this unlikely and show that the zig-zag conformation is favoured for the carbon chain. He then goes on to explain the trends in transition temperatures and the alternation effect in terms of the arrangements outlined below.

As the chain length increases, it will have a number of effects, and the transition temperature from nematic to isotropic will be determined by those effects which

predominate in the molecule. (1) Higher members of the series will be less readily rotated out of the ordered state due to the increased length of the molecule. (2) The overall molecular polarizability will increase with each added methylene unit. (3) The frequency with which readily polarizable aromatic parts of the molecules lie next to one another in the fluid nematic melt will decrease, i.e., the residual lateral attractions will tend to decrease. (4) Each methylene unit will also force apart the polarizable centres in the molecules, and will decrease the residual terminal attractions. The first two effects would increase the nematic-isotropic transition temperatures, whereas the last two effects would decrease the nematic-isotropic transition temperatures as the series is ascended.

The alternation of nematic-isotropic transition temperatures cannot be easily dealt with on the basis of a zig-zag alkyl chain conformation. Gray has tried to explain this by a diagramatic representation of the possible relative orientations of terminal methyl groups in an end-to-end packing of the molecules of n-alkyl aryl ethers such as the p-n-alkoxybenzoic acids.

For short alkyl chains, the chain extending strictly along its own axis (dotted line in fig. 15), the terminal methyl groups will present different faces to one-another or to other end groups in the molecule depending on whether the chain is even or odd. The different attractive forces resulting could affect the energy of the system and account for an alternation of the transition temperatures. With the higher

homologues, the alkyl chain may be forced (curved arrow in fig. 15) into line with the main axis defined by the more rigid aromatic parts. The methyl to other end group contact would then gradually become the same in nature for odd and even carbon chains and can explain the petering out of the alternation as the series is ascended.

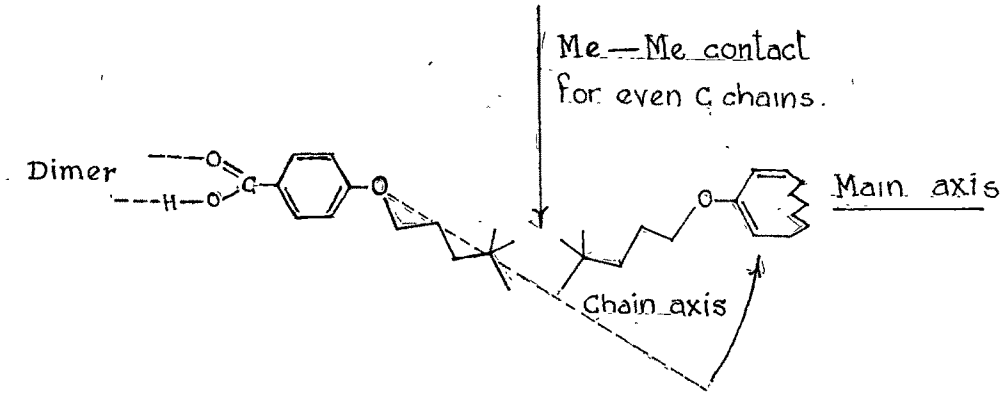


Fig. 15

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 attractions between the molecules, which also play some part in determining the thermal stability of the nematic mesophase, has not been taken into account. In a potentially nematogenic homologous series, 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, making more difficult the disruption of the weaker residual terminal attractions which are responsible for the nematic-isotropic transition temperature. This increase in the residual lateral attractions reduces the rate of decrease in the nematic-isotropic transtion temperatures as the series is ascended causing ultimate levelling off in the nematic-isotropic curve for the longer chain homologues for which residual lateral attractions may be the strongest.

To explain the alternation in nematic-isotropic transition temperatures Maier and Baumgartner (300, 304) carried out experiments for measuring the dipole moment and dielectric anisotropies of the lower homologues in the series 4,4'-di-n-alkoxyazoxybenzenes. They concluded that the dielectric constant and, therefore, the polarization is greater at right angles to the major axes of the molecules and advocated that it is the difference in the polarization effects between the sides of the molecules containing even and odd numbers of carbon atoms in the alkyl chains that explains the alternation effect. However, Gray argues that the important factor is the polarizability of the alkyl chain 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 interactions 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 discussion explains the alternation of nematic-isotropic transition curves for odd and even numbers of carbon atoms in the alkyl chain.

This explanation for the behaviour of nematic-isotropic transition temperature curves can be extended to the cholesteric-isotropic transition temperature curves obtained in the present study. It has been mentioned earlier that other properties of this mesophase are similar to those of the nematic mesophase. It would be natural then to assume that the forces which determine the nematic-isotropic change should be operative at the cholesteric-isotropic change. The cholesteric-isotropic transition temperature curve behaves analogously to the nematic-isotropic transition curve. Odd-even effects are also observed in all the cholesteric homologous series. However, in some of the cholesteric series two distinct curves, one for odd and the other for even members of the series, are not observed, (295). Difficulties in obtaining some cholesteryl compounds in a highly pure state may explain these deviations from a regular odd-even effect.

The smectic-cholesteric transition temperature curve rises smoothly to a maximum and then falls off in all the four series. It does not merge in any case with the falling cholesteric-isotropic transition temperature curve to give pure smectic mesophases in the last members.

The increase in the smectic-cholesteric or 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 or cholesteric melt. Of course, it is difficult to comprehand the rising smectic-nematic or smectic-cholesteric curve andalso the merging of the smectic-nematic curve with the falling nematic-isotropic curve, resulting in a falling smectic-isotropic transition temperature curve. The behaviour of smectic-nematic curves in some nematogenic systems and of smectic-cholesteric curves in cholesterogenic systems in which the falling nematic-isotropic or cholesteric-isotropic curve does not merge at all has been discussed earlier.

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. These residual

attractions may 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. If the highly polarisable aromatic rings are represented by the rectangles and the two end alkoxy groups are represented by small lines, then the molecular arrangement in the smectic melt may be as shown in fig. 16a.

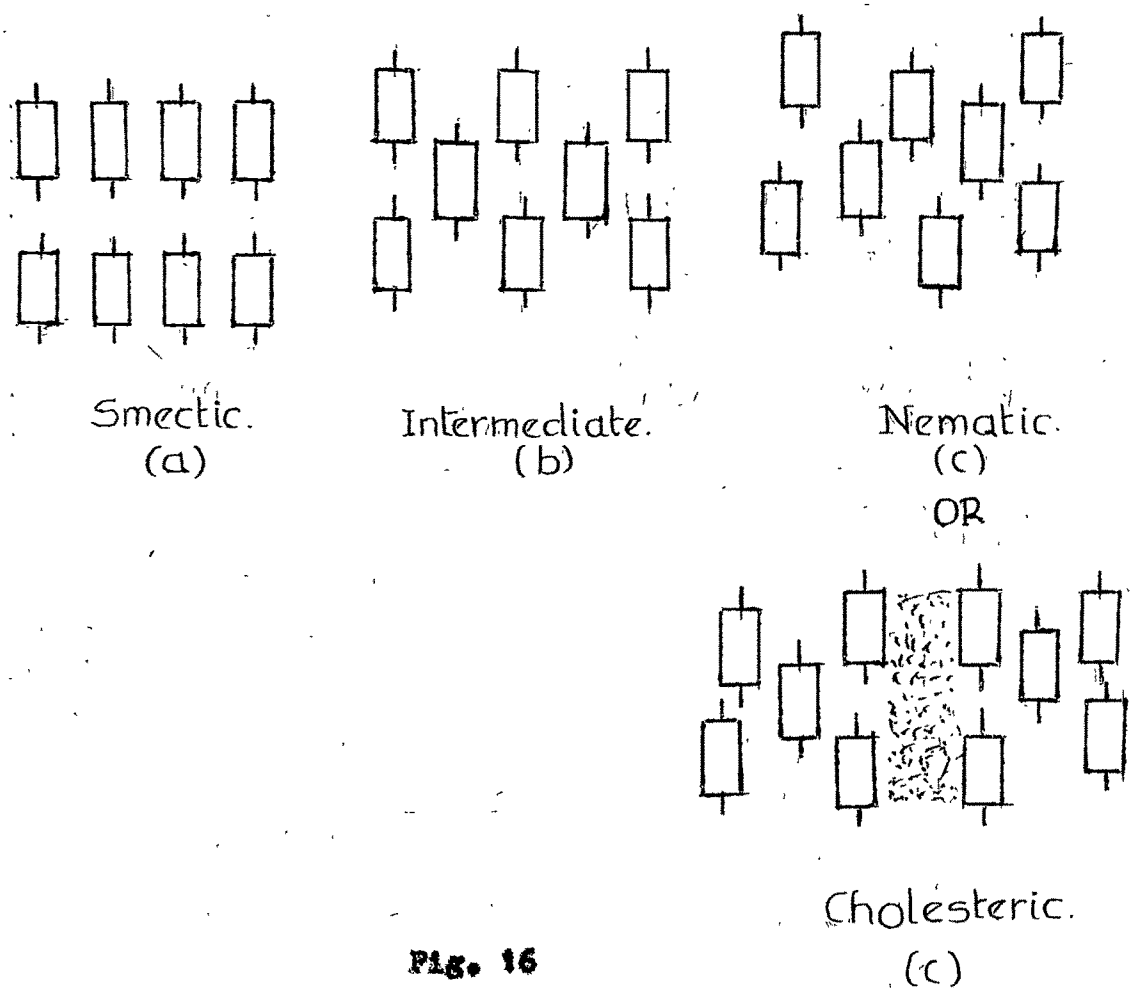


Fig. 16

As the chain lengthens, the residual terminal attractions become weaker and offer less resistance to interpenetration, the distortion of individual bonds in the alkyl groups necessary to achieve interpenetration becoming less. Therefore, an intermediate state of the type shown in fig. 16b is formed where the ends of the molecules are still in line. As the temperature rises, the tendency for interpenetration of the chains grows, thus forcing apart the aromatic centres giving an imbricated nematic or cholesteric orientation to the melt as shown in fig. 16c. The dislocation of the residual terminal intermolecular cohesions at the smectic-nematic or smectic-cholesteric transition is probably temporary. As the interpenetration of the layers becomes great and the normal imbricated arrangement of the molecules of the nematic or cholesteric 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 or cholesteric 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 shape of the smectic-nematic transition temperature curve and the smectic-cholesteric transition temperature curve, i.e., the levelling off of the curve and

then the falling off. In the case of the smectic-nematic transition temperature curve it usually merges with the falling nematic-isotropic curve at the C_{12} or C_{16} derivative where the alkyl chain is reasonably long, the residual terminal cohesions being quite weak and sufficiently unable to maintain nematic order. Hence, the smectic mesophase passes directly, into the isotropic liquid. Naturally in the higher homologues like C_{16} or C_{18}, 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.

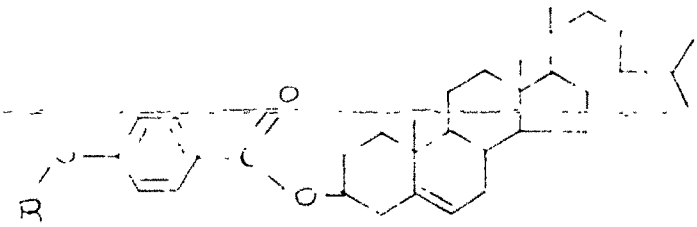
A point worth taking into consideration is that all the smectic-cholesteric or smectic-nematic transition points lie on one smooth rising curve irrespective of odd or even members of the series. It was pointed out earlier that the alkyl chain conformation is zig-zag in the mesomorphic compound. This easily explains the absence of odd-even effects in the smectic-cholesteric or smectic-nematic transition temperature curve, because, with the alkyl chain adopting a zig-zag conformation, the addition of each methylene unit does not affect the lateral attractions differently, whether the chain is even or odd, provided that the chain axes are normal to the layer interfaces. Recently some cases of odd-even effect in the smectic-nematic transition curve have however been observed (299, 305).

The behaviours of the transition temperature curves of all the series have been discussed and now will be discussed the thermal stabilities of these series.

Table 24 summarizes the average thermal stabilities of the cholesteric and smectic mesophases and the point of commencement of the smectic mesophases in these series, viz., (1) cholesteryl p-n-alkoxybenzoates (A), (2) cholesteryl trans-p-n-alkoxycinnamates (B), (3) cholesteryl trans-p-n-alkoxy-α-methylcinnamates (C), and (4) cholesteryl 4-n-alkoxy-1-naphthoates (D) and these are compared with those of the (5) cholesteryl n-alkanoates (59) (E), (6) cholesteryl 4-n-alkoxy-1-naphthylidene p-aminobenzoates (306) (F) and (7) cholesteryl 6-n-alkoxy-2-naphthoates (306) (G).

Reference to table 24 indicates that the thermal stabilities of series A are higher than those of series E. This is as expected. Series E contains an aliphatic side chain at the 3β-position, whereas in series A, the side chain consists of a benzene ring with an alkoxy group in the para position, both of which contribute to the length and polarizability of the molecule; the presence of the phenyl ring in the series will also cause a little increase in the breadth of molecules of series A. Increase in length and polarizability are known to increase nematic and smectic thermal stabilities in a mesomorphic compound, whereas breadth increase has just an opposite effect. The higher cholesteric and smectic thermal stabilities of the series A can be explained on this reasoning.

A



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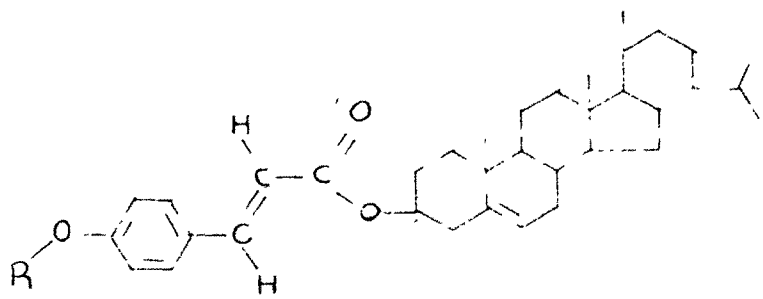
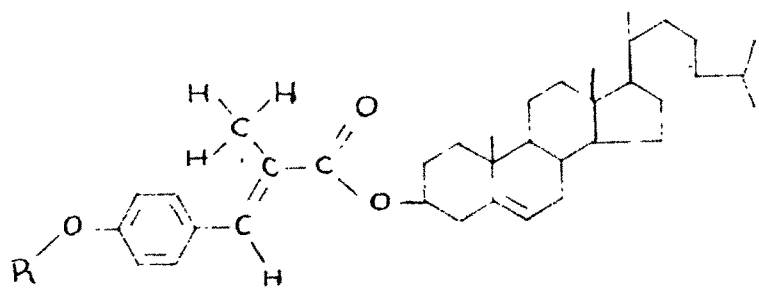
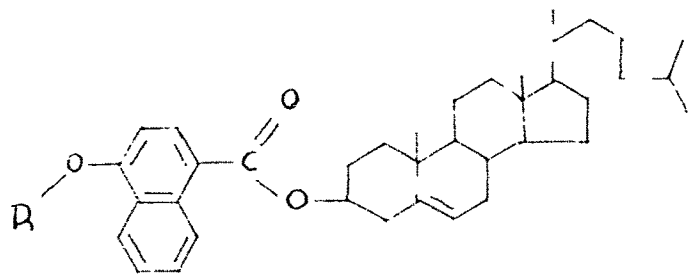


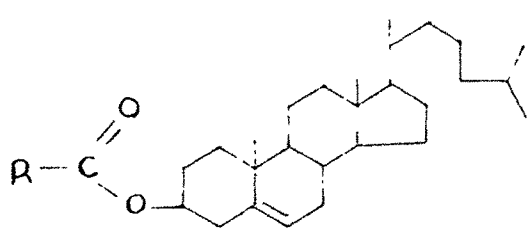
C



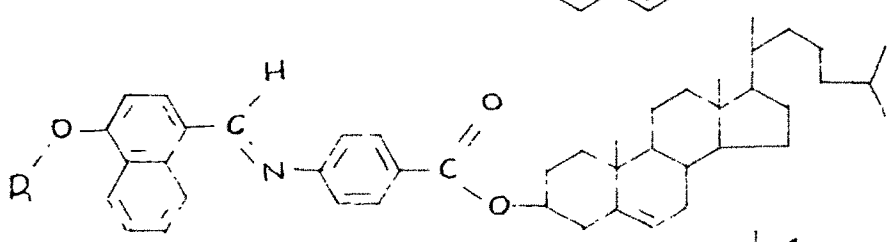
D



E



F



G

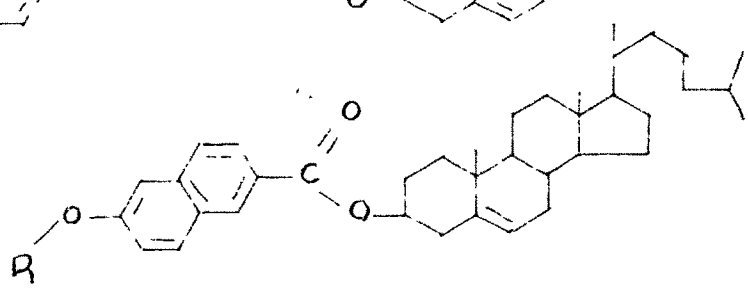


Table 24

Relative thermal stabilities.

Transition temperatures °C.	A	B	C	D	E	F	G
Smectic-Cholesteric (C_{10}-C_{18})	174.0	176.1	164.0	98.9	80.0 (Monotropic) (C_{10}, C_{11}, C_{13} C_{15}, C_{17})	176.0 (C_{16}, C_{18})	221.2
Cholesteric-Isotropic (C_1 - C_{18})	222.4	246.8	221.0	157.7	76.3 (C_1-C_{10}, C_{11}, C_{13}, C_{15}, C_{17})	284.5	268.8
Commencement of the smectic phase	heptyloxy	decyloxy	octyloxy	dodecyloxy	heptanoate	hexadecy-loxy	pentyloxy

From the study of a number of homologous series, Gray (67) has concluded that increase in breadth reduces nematic and smectic thermal stabilities, but the decrease is more pronounced in the smectic thermal stability than the nematic.

If the cholesteric mesophase is considered nematic in type, then molecular breadth will have a less pronounced effect on this mesophase than on the smectic mesophase. If, however, the arrangement of the molecules in the cholesteric mesophase is similar to that in the smectic mesophase, the effect of the breadth should be same on cholesteric and smectic mesophases.

The cholesteric and smectic thermal stabilities of series A are higher by 146°C and 94°C respectively than those of series E. The stability increases are appreciable in both the cases, but the increase is greater in the cholesteric phase than in the smectic phase. This shows that the breadth increase has a more pronounced effect on the smectic mesophase.

The thermal stabilities of series B are much higher than those of series E. This increase in the thermal stabilities of series B is due to the phenyl ring and the -CH=CH- (trans) group, which contribute to an increase in the polarizability and the length of the molecule which in turn increase the thermal stabilities of the mesophases. Here also the presence of phenyl ring and -CH=CH- (trans) group will cause a little increase in the breadth of molecules of series B. The increase in cholesteric thermal

stability of series B is 170.5°C, whereas the increase in the smectic thermal stability is 96.1°C which is less than the former one. This shows that molecular breadth has less effect on the cholesteric mesophase and a more pronounced effect on the reduction of the smectic mesophase.

The cholesteric thermal stability of series B is higher than that of series A. This is not surprising, as series B is longer by a -CH=CH- (trans) group and more polarizable than series A. However, the smectic thermal stabilities of both the series are almost the same. This can be attributed to the increased breadth of series B due to the -CH=CH- (trans) group, compared with series A.

The cholesteric thermal stability of series C is lower than that of series B and coincides with that of series A, whereas, the smectic thermal stability of series C is a little lower than that of series B and A. Series C is essentially series B, having an α-methyl group. Naturally series C would be broader compared with series B resulting in lower cholesteric and smectic thermal stabilities. Trans-p-n-alkoxycinnamic acid series and trans-p-n-alkoxy-α-methyl-cinnamic acid series differ by α-methyl group but the nematic thermal stability of the series of trans-p-n-alkoxy-α-methylcinnamic acid is much decreased and the smectic mesophase is eliminated from this series compared with the other series. In the case of series C and B, differences in thermal stabilities are not so great as observed in above nematogenic series.

The effect of α-substitution on mesomorphism is not

clearly known. Gray (299) studied the effect of methyl substitution in the alkyl chain of alkyl 4-p-substituted benzylideneaminocinnamates. He points out that when the carbon atom at which branching occurs is next to the oxygen atom of the carbonyl group in the molecule, the 1-methyl group will occupy such a position in the molecule that it minimises the steric effect and in doing so hinders most the parallel arrangement required for the nematic mesophase. In the smectic mesophase it may be fitted in such a way that it does not interfere with layer arrangement to any considerable extent and does not decrease the smectic mesophase thermal stability to any great extent. Possibly the α-methyl substituent in series C may be behaving in a similar manner but may not be operating to its fullest breadth effect due to the broad and flat cholesterol nucleus.

The molecules of series C are more polarizable and little longer than series A, and as discussed above the α-methyl group does not operate to its fullest breadth effect. Consequently the cholesteric thermal stability of series C and A almost coincide and the smectic thermal stability of series C is decreased a little.

The thermal stabilities of series D are less than those of series A, B, C, F and G. Series D is essentially series A having a bridge substituent at the 2,3-positions, which increases the breadth of the molecule. Gray (303) has pointed out that lateral substituents increase the molecular breadth and will affact the mesomorphism in the following ways :-

(a) by broadening the molecule. This will tend to decrease the thermal stabilities of the smectic and nematic states as a result of the increased lateral separation and the decreased lateral attractions;

(b) by increasing the polarity and polarizability of the molecule. This will tend to increase the smectic and nematic thermal stabilities because of the resulting increase in lateral attractions.

Of these two opposing effects, the first always predominates, unless the substituent does not exert its full breadth increasing effect.

In cholesterogenic compounds also a similar behaviour is observed. As can be seen from the geometry of these molecules, those of series D are broader than those of series A, B and C, and hence it is natural that the first effect will predominate reducing the cholesteric and smectic thermal stabilities of series D. The thermal stabilities of series D are also lower than those of series F though the breadth of both the series is almost the same. This is because of the increased length of the molecules of series F, due to the extra phenyl ring and the azomethine group. This will increase the length to breadth ratio, resulting in higher thermal stabilities of the mesophases. The lower thermal stability of series D compared with series G can also be explained. The molecules of series D are broader due to 1,4-substitution in the naphthalene nucleus, whereas 2,6-substitution imparts linearity which increases the length resulting in the higher thermal stabilities of

series G. Gray (101) has observed that 4-n-alkoxy-1-naphthoic acids are non-mesomorphic, whereas 6-n-alkoxy-2-naphthoic acids are mesomorphic. In the present case because of the cholesterol moiety, the cholesteryl-4-n-alkoxy-1-naphthoates are mesomorphic, but less so compared with the cholesteryl-6-n-alkoxy-2-naphthoates.

The thermal stabilities of series D are higher than those of series E. Here it can be seen that the molecules of series D contain a naphthelene nucleus and are longer than for series E. The polarizability and length increase predominate over the increased breadth in series D compared with series E, resulting in higher thermal stabilities of series D.

The thermal stabilites having been discussed and explained, it is interesting to discuss now the point of commencement of smectic mesophases in these homologous series.

The appearance of smectic properties in a series is influenced by the melting points of the compounds and/or by the supercooling tendencies of the melts. Both these factors are related to the crystal structures of the compounds, which ultimately are dependent on the geometry, dipole moment and overall polarizability of the molecule. Gray (67) is of the opinion that the appearance of the smectic mesophase in a homologous series has little significance. Knowledge about the point of appearance of the smectic mesophase may, however, help in the search for certain series where the appearance of smectic mesophases might be delayed so that low melting purely nematic or cholesteric substances would be

obtained. A survey of homologous series and the points of commencement of smectic mesophases indicate that the appearance of the smectic mesophase is influenced by the geometry of the molecule. If the molecules of the series are long, straight, rod-shaped and polarizable, smectic mesophases commence early in the series. If the molecules are short and linear, smectic mesophases appear, at the middle members of the series, but in homologous series where breadth is increased, the commencement of the smectic mesophase is always delayed. Sometimes it appears very late in the series, i.e., at the C_{16} or C_{18} derivative.

In the N,N'-di(p-n-alkoxybenzylidene) benzidene (107) series smectic mesophases appear at the butoxy derivative, whereas in the N,N'-di(4-n-alkoxy-1-naphthylidene) benzidine (105) series smectic phases appear late in the series, i.e., at the nonyloxy derivative. Similar behaviour is observed in the two series of N,N'-di(p-n-alkoxybenzylidene) p-phenylenediamines (107) and N,N'-di(4-n-alkoxy-1-naphthylidene) p-phenylenediamines (106a). In the former case smectic mesophases appear at the pentyloxy derivative, whereas in the latter case they appear at the hexadecyloxy derivative. The difference in the above series is in the breadth of the molecules, for the length of the molecules is the same. However, although it is difficult to postulate the exact point of commencement of the smectic mesophase in a homologous series, it may be possible to anticipate the probable point of commencement of the smectic mesophase in

a series from the geometry of the molecules. Dave and Patel observed that in the p-n-alkoxybenzylidene-p-n-alkoxy anilines (307), by the addition of a $-CH_2$ group in the aniline alkoxy chain, the point of commencement of the smectic mesophase is enhanced by one member, i.e., in p-n-alkoxybenzylidene-p-n-propoxyanilines it commences at the nonyloxy derivative, whereas in the butoxyanilines it commences at the octyloxy derivative and in the pentyloxy anilines it commences at the heptyloxy derivative.

Smectic mesophases commence earlier in series G, A and E than in the other series. This is because the molecules of series G, A and E are less broad compared with other series. In the case of series B, smectic mesophases commence at the decyloxy derivative which is later than in series G, A, E and C. The molecules of series B are broader than those of series G, A and E. In the case of series C, the molecules are arranged in such a way that smectic mesophases commence earlier than in series B which is difficult to explain. However the solid-mesomorphic transition temperatures of series C are lower compared with series B, and this might be the reason for the early commencement of smectic mesophases in series C. In series D, smectic mesophases commence at the dodecyloxy derivative, which is late in the series. It can be seen from the geometry of the molecules that series D is broader than series A, E, B, C and G and naturally the commencement of the smectic mesophase would be delayed. In the case of series F, the commencement of the smectic mesophase is further delayed. This also should be

due to the increased breadth of the molecules of series F. Apparently there is little difference in the breadth of series F and series D. However, the smectic phase appears later in series F. This may possibly be due to the -CH=N- group in series F, which due to its lack of coplanarity is likely to cause difficulty in the packing of the molecules, resulting in the delayed commencement of the smectic mesophase (67, 163, 302, 307, 308).

From all this discussion, it is apparent that the effect of chemical constitution on the cholesteric mesophase is very similar to that on the nematic mesophase. This strengthens the view that the cholesteric mesophase is nematic in type. The properties which are specific to the cholesteric mesophase and not observed in the nematic mesophase are due to the asymmetry of the molecules in the cholesteryl compounds.

(5) Substituted benzoates of cholesterol :

Gray (67) studied the effect of substitution on mesomorphism in the para- position in cholesteryl benzoates and obtained an efficiency order for the substitution. Dave and Dewar (219, 220) obtained an order for the group efficiency in the para- position in their study of mixed liquid crystals. It seems however that the data available to study the effect of substitution on cholesteric mesomorphism are rather limited. Therefore, different substituted benzoates of cholesterol were prepared and their melting points and transition temperatures are reported in table 21.

All the ortho- and para- derivatives exhibit enantiotropic cholesteric mesomorphism. In addition to the cholesteric mesophase, cholesteryl o-nitrobenzoate exhibits a monotropic smectic mesophase. Sandquist and Gorton (288) do not report any monotropic smectic mesophase for this compound. They report the melting point and transition point of this compound as 150.9°C and 156.9°C, respectively. In the present study, the solid-cholesteric and cholesteric-isotropic transitions for this compound are found to be 147.0°C and 155.0°C, respectively. The monotropic smectic phase is obtained on cooling at 98.5°C. Vorlander also reports it to be monotropic smectic, but transition temperatures are not mentioned (289). In the case of the meta- derivative, except for cholesteryl meta-nitrobenzoate which is enantiotropic cholesteric, all the compounds studied exhibit monotropic phases. Examination of table 21 will show that whereas para- substitution in the parent compound increases the mesophase thermal stability, substitution in ortho- and meta- positions decreases the mesophase thermal stability of the parent compound. The order of thermal stability is found to be

para > parent compound > meta > ortho
(cholesteryl benzoate)

The higher thermal stability and enantiotropic mesomorphism of the para- substituted compounds can be easily understood, the molecules being linear and polar at the ends. In the case of the meta- substituted compounds, the substituent increases the breadth of the molecule, resulting in decreased

mesophase thermal stability. This will cause difficulty in packing of the molecules and the compound melts directly to the isotropic liquid, although the melting point of the meta- compound will be less than that of the para- compound. On cooling, the molecules align together and exhibit monotropic phases before crystallisation takes place.

NO_2- group is known to enhance the mesophase thermal stability and the enantiotropy of the meta-NO_2- substituted compound may be due to the very high polarity of the group; the NO_2- group exhibits similar behaviour in other mesomorphic compounds (67, 219, 220, 257, 258).

In the case of the ortho- compounds, although the breadth increase effect is there, because of the lowering in the melting point of the compound as a result of the groups being in the ortho- position, mesomorphism is not destroyed and the ortho- compounds are enantiotropic cholesteric.

The substituent groups are arranged in the orders of group efficiency in promoting liquid crystalline properties and these are compared with similar orders obtained by other workers (67, 219, 220, 303).

Cholesteric mesophase :

1. MeO > NO_2 > Br ≥ Cl > I > Me > H (para-substituted benzoates of cholesterol, present work.)

2. Phenyl > NO_2 > MeO > Cl > Me > H (para-substituted benzoates of cholesterol- Gray)(67).

3. $H > NO_2 > Cl > Br \geqslant Me > I$ (ortho-substituted benzoates of cholesterol, present work.)

4. $H > NO_2 > Cl > Br > Me > I$ (meta-substituted benzoates of cholesterol, present work.)

Nematic mesophase :

1. $NO_2 > MeO > NMe_2 > Me \geqslant Cl > Br > H$ (Dave and Dewar) (219, 220).

2. $MeO > NO_2 > Cl > Br > NMe_2 > Me > H$ (4-p-substituted benzylideneamino-4'-methoxybiphenyls-Gray) (303).

3. $MeO > NO_2 > NMe_2 > Me > H$ (4-p-substituted benzylideneamino-4'-n-octyloxybiphenyls-Gray) (303).

Smectic mesophase :

1. $Br > Cl > F > NMe_2 > Me > H > NO_2 > MeO$ (4-p-substituted benzylideneamino-4'-n-octyloxybiphenyls-Gray) (303).

It can be seen that the group efficiency orders for the cholesteric phase in the present work are broadly similar to the group efficiency order of Dave and Dewar (219, 220) for the nematic mixed liquid crystal formation and the group efficiency order of Gray (303) for the nematic mesophase. Gray (67) has also given a similar order for the cholesteric phase for para- substituted compounds, which is similar to the one obtained in the present work. It can be seen that the group efficiency order for the smectic phase does not agree with the group efficiency order for the cholesteric phase. This shows that

the mode of behaviour of the cholesteric phase is more akin to that of the nematic phase than the smectic phase.

B. NEMATOGENIC HOMOLOGOUS SERIES

A large number of nematogenic compounds and homologous series of different molecular structures have been prepared, for the systematic study of the effect of chemical constitution on mesomorphism in organic compounds. The important nematogenic systems which exhibit mesomorphism are Schiff's base compounds, aromatic carboxylic acids and aliphatic esters of aromatic carboxylic acids. Generally the homologous series comprising Schiff's base compounds or aromatic carboxylic acids exhibit the normal behaviour of a nematogenic series. The first few members are purely nematic, the middle members are smectic and nematic and the last members exhibit pure smectic mesophases. The aliphatic esters of aromatic carboxylic acids generally exhibit pure smectic mesophases. Recently Arora et al.(302) and Dewar et al. (309, 310) have reported the mesomorphic properties of the arene diesters of aromatic carboxylic acids. These esters exhibit the normal behaviour of nematogenic series. In the present study are synthesized the homologous series, biphenyl 4-p-n-alkoxybenzoates and biphenyl 4-trans-p-n-alkoxycinnamates, trans-p-n-alkoxy-α-methylcinnamic acids. Their mesomorphic behaviour is now discussed.

I. Biphenyl 4-p-n-alkoxybenzoates :

Fifteen esters were prepared by condensing p-n-alkoxybenzoyl chlorides with 4-hydroxybiphenyl (p-phenylphenol). Their melting points and transition temperatures are reported

in table 22. Biphenyl 4-benzoate is non-mesomorphic. The methyl to pentyl derivatives are monotropic nematic, smectic mesophases commence at the nonyl derivative, and the nonyl to tetradecyl derivatives are polymesomorphic, exhibiting smectic and nematic mesophases, the nonyl derivative being monotropic smectic. The hexadecyl and octadecyl derivatives are purely smectic. When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (fig. 10), the transition points relating to the change nematic to isotropic lie on two falling curves, one representing the ethers with odd numbers of carbon atoms in the alkyl chain and the other representing the ethers with even numbers of carbon atoms in the alkyl chain. The latter curve lies above the former. The smectic-nematic transition points lie on a smooth rising curve coinciding with the falling nematic-isotropic transition point curve at the hexadecyl ether which exhibits a purely smectic mesophase analogous to other normal mesomorphic homologous series.

Biphenyl 4-benzoate does not exhibit mesomorphism, whereas the methoxy derivative is mesomorphic. Generally, for a compound to exhibit mesomorphism, its molecules should be elongated and rectilinear, containing dipolar groups and should be highly polarizable (67). The methoxy derivative has a methoxy group at one end, whereas biphenyl 4-benzoate has no terminal susbtituent at that end and hence its non-mesomorphism is not surprising.

The first five members are monotropic nematic. The

melting points of these compounds are high. Due to the high melting points when the melting process begins, the thermal vibrations will be too great to allow an ordered arrangement of the molecules to persist and the compound directly passes to the disordered isotropic liquid. However, these molecules possess the basic requirements for exhibiting mesophases and so on cooling, the molecules align together to give a monotropic nematic mesophase before crystallization occurs. With the hexyl derivative onwards the melting points are low and the alkyl chain being reasonably long, as discussed earlier, the higher homologues behave as in other normal nematogenic series.

Some of the compounds give homeotropic nematic and smectic mesophases. The smectic mesophase in other cases gives a fan-type texture.

II. Biphenyl-4-trans-p-n-alkoxycinnamates :

Fifteen esters were prepared by condensing p-n-alkoxycinnamoyl chlorides with 4-hydroxybiphenyl (p-phenylphenol). Their melting points and transition temperatures are summarized in table 23.

All the derivatives exhibit enantiotropic mesomorphism except biphenyl-4-trans-p-n-heptyloxycinnamate, which exhibits a monotropic smectic mesophase. Biphenyl-4-trans-cinnamate is non-mesomorphic. The methyl to hexyl derivatives are purely nematic, the heptyl to tetradecyl derivatives are polymesomorphic, i.e., they exhibit smectic and nematic mesophases and the hexadecyl and octadecyl derivatives are purely smectic. When the transition points are plotted against

the number of carbon atoms in the alkyl chain (fig. 11), the transition points relating to the change nematic to isotropic fall on two falling curves, one representing the ethers with odd numbers of carbon atoms in the alkyl chain and the other representing the ethers with even numbers of carbon atoms in the alkyl chain. The latter curve lies above the former. The smectic-nematic transition points lie on a smooth rising curve coinciding with the falling nematic-isotropic transition point curve at the hexadecyl ether which exhibits a purely smectic mesophase. The general behaviour is therefore analogous to other normal mesomorphic homologous series.

Biphenyl-4-trans-cinnamate does not exhibit mesomorphism whereas the methoxy derivative is enantiotropic mesomorphic. Here also, as in the case of the previous series, the methoxy group is essential for a mesophase to arise.

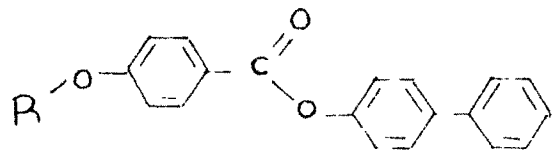
General characteristics of series I and II :

The transition temperature curves behave similarly in both the series. The alternation for odd-even carbon chains has already been explained in detail. The smectic-nematic curve rises smoothly and joins the falling nematic-isotropic curve to give a pure smectic phase at the C_{16} derivative. The behaviour of the smectic-nematic transition curve has also been explained in detail earlier. The thermal stabilities of the series are now compared with other series.

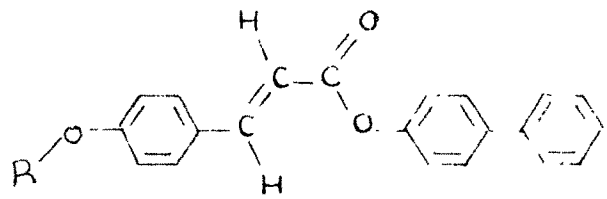
Table 25 summarizes the thermal stabilities of the nematic and smectic mesophases and the point of commencement of the smectic mesophases in these series, viz., (1) biphenyl-

4-p-n-alkoxybenzoates A, (2) biphenyl 4-trans-p-n-alkoxycinnamates B, and these are compared with (3) p-n-alkoxybenzoic acids C (101), (4) trans-p-n-alkoxy-cinnamic acids D (281), (5) 4-p-n-alkoxybenzylideneamino-biphenyls E (107) and (6) 1,4-phenylene bis-(4'-n-alkoxy-benzoates) F (302, 309, 310).

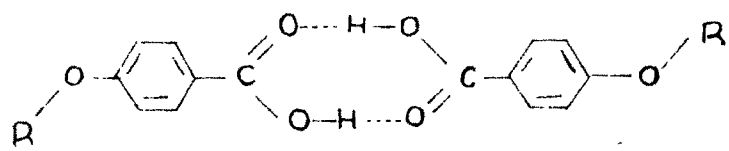
The thermal stabilities of series A are lower than those of all the series compared in the table. The lower thermal stabilities of series A compared with those of series B can be easily explained, as the molecules of series B are a little longer and more polarizable than those of series A. In the case of series C and D, their molecules are more linear and have alkoxy groups at both the ends, whereas, the molecules of series A would be less coplanar and have alkoxy groups at one end only. According to Arora *et al.* (302) in such a molecular geometry the oxygen atoms of the carbonyl group will be bumping into the non-bonded sides of the adjacent hydrogens of the aromatic ring thereby causing considerable strain on the molecule. They are of the opinion that in order to avoid this situation, some twist around the C-O bond will occur. This twist, however small it may be, will force the aromatic ring together with the ester linkage out of the plane of the biphenyl ring, thus reducing the coplanarity of the molecule. This will reduce the mutual conjugation along the entire molecule resulting in the decrease in the polarizability of the molecule and consequently in the decrease of the thermal stabilities of the mesophases. This explains the higher



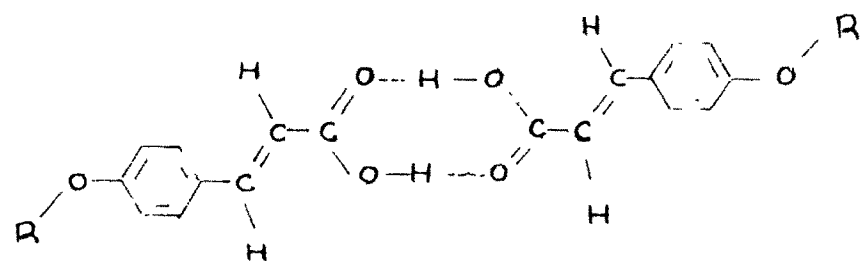
A



B



C



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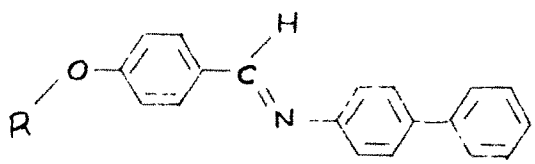
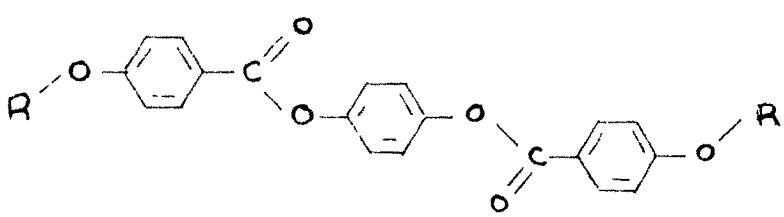


E



F

Table 25

Relative thermal stabilities.

Transition temperatures °C.	A	B	C	D	E	F
Smectic-Nematic or Isotropic (C_9 - C_{18})	115.0	152.8	126.3	153.6	153.0	150.0 (C_9-C_{16}) (302)
Nematic-Isotropic (C_1 - C_{10})	136.9	189.8	149.5 (C_3 - C_{10})	181.2	169.2	232.0 (C_1-C_4, C_6-C_8, C_{10}) (310)
Commencement of the smectic phase	nonyl	heptyl	heptyl	nonyl	pentyl	heptyl

thermal stabilities of series C and D compared with those of series A.

Series E and series A differ only in the middle group, series A having -C(=O)-O- and series E having -CH=N- as the middle group. In the case of series E, the same effect as discussed above will operate. Van der Veen and other workers (163, 302, 308) have shown that the molecules of Schiff's bases are non-coplanar due to the twist in the molecules, but since the hydrogen atom is smaller than the oxygen atom, it would be reasonable to assume that the twist in the case of series E would be smaller than the corresponding twist in the case of series A. Thus the molecules of series A would be a little more non-coplanar than the molecules of series E, resulting in more anisotropic polarizability of series E compared with that of series A, and hence, the thermal stabilities of series E are higher than those of series A.

The molecules of series F possess two ester groups and have alkoxy groups at both the ends; thus compared with series A, the molecules of series F will be longer and more polarizable. Hence, naturally the thermal stabilities of series F are higher than those of series A.

Reference to table 25 shows that the nematic thermal stability of series B is higher than that of series C, D and E. Although compared with series B, the molecules of series C and D are more linear and have alkoxy groups at both the ends, the molecules of series B contain a more polarizable trans CH=CH-C(=O)-O group and a biphenyl ring. As discussed

earlier, though there would be a twist in the molecules of series B, the effect of the polarizability of the molecules of series B will overweigh and the net result will be that the molecules of series B will be more polarized compared with the molecules of series C and D resulting in the higher nematic thermal stability of series B.

The difference between series B and E is in the middle group; series B has a trans -CH=CH-C(=O)-O as the middle group whereas, series E has the -CH=N- middle group. As discussed earlier the twist will be operating in both the series and will be a little more in the case of series B. However, series B contains a more polarizable trans -CH=CH-C(=O)-O group and therefore the conjugation must be more in series B than in series E, resulting in a higher polarizability of the molecules of series B. The nematic thermal stability of series F is very high. This is not surprising as not only the length of the series F is more, but it also contains two -C(=O)-O groups which may contribute to the overall polarizability of the molecules.

The smectic thermal stabilities of series B, D, E and F are almost the same, although the nematic thermal stability of series B is higher than that of series D and E. In the case of series B, due to the presence of the -CH=CH-C(=O)-O group and the biphenyl ring the conjugation would be transferred from one end of the molecule to the other compared with the acid dimer of series D where the hydrogen bond will not transfer the

effect of conjugation in the two dimer units and thus the polarizability of the molecules of series B would be more in the direction of long axis. Further, it has been discussed earlier that the molecules of series B are less coplanar. This will increase the thickness of the molecules and will affect the smectic thermal stability of series B. In these terms it is possible to explain that, though the nematic thermal stability of series B is higher, its smectic thermal stability is not increased.

In the case of series E, though conjugation is possible, the molecules will be less broad and thick compared with those of series B, which contain a trans -CH=CH-C(=O)-O group. Due to this increase in breadth and thickness of the molecules of series B, the smectic stability is not increased, as molecular thickness and breadth have more pronounced effects on the smectic mesophases than on the nematic mesophases.

In the case of series F, the nematic thermal stability is very high but the smectic thermal stability is almost the same as for series B. Series F contains one more ester group and a middle phenyl ring which may contribute more to the axial polarizability of the molecules. Lateral cohesive forces may be reduced by cancellation of the cross dipoles if the molecules adopt a trans configuration. These factors would result in a lower smectic thermal stability. Further, Arora *et al.* (302) have suggested that in such a trans configuration the coplanarity of the molecule will be reduced resulting in an effective thickness of the molecule. This

also will affect the smectic thermal stability of the molecule.

The smectic thermal stability of series C is less than that of series B. Although series C has the same molecular geometry as series D, compared with series D the molecules of series C are short and less polarized due to the absence of two -CH=CH- groups. This will easily explain the lower thermal stability of series C.

Having discussed and explained the thermal stabilities it will be of interest to review the point of commencement of the smectic mesophases.

As has been said before, the point of the commencement of the smectic mesophase in a homologous series depends on a number of factors, and a survey of homologous series indicates that increase in the breadth generally delays the commencement of the smectic mesophases.

Smectic mesophases commence at the heptyl derivative in series B, which is earlier than in series A and D and coincide with those of series C and F. As has been said before, the molecules of series B are broad; compared with this the molecules of series C are linear. This may be the reason for the coincidence of the point of commencement of the smectic mesophases of the two series. In the case of series F, as discussed earlier, the molecules will be a little more broad than the molecules of series B; this may be the reason for the delay in the point of commencement of smectic mesophase in series F and its coincidence with that of series B. The earlier commencement of smectic mesophases in series B than in series A might be due to the increased length of series B as other

factors are common in both the series. In the case of series D its molecules will be more broad than those of series B due to the presence of two trans -CH=CH- groups in series D. This may be the reason for the delay in the point of commencement of the smectic mesophase in series D.

In series E the smectic mesophase commences at the pentyl derivative, which is earlier than that in series B. As discussed earlier the molecules of series B will be thick and broad compared with those of series E. This may be the reason for the delay in the point of commencement of the smectic mesophase in series B.

Trans-p-n-alkoxy-α-methylcinnamic acids :

Fourteen trans-p-n-alkoxy-α-methylcinnamic acids have been prepared and their melting points and transition temperatures are reported in table 8. The first member of the series is non-mesomorphic. The ethyl and octadecyl derivatives are monotropic nematic and the propyl to hexadecyl derivatives are enantiotropic nematic. Smectic mesophases do not appear even in the last member of the series, which is rather unusual compared with other normal homologous series. All the members of the series are purely nematic.

When the transition points are plotted against the number of carbon atoms in the alkyl chain (fig. 12) the transition points relating to the change nematic to isotropic lie on two falling curves, one representing the ethers with odd numbers of carbon atoms in the alkyl chain and the other represnting the ethers with even numbers of carbon atoms in the alkyl chain. The latter curve lies above the

former.

The behaviour of the nematic-isotropic transition temperature curve has been explained earlier in detail. As has been said before, structurally, a compound having a long, narrow, linear molecule with dipolar groups contributing to intermolecular attractions would be expected to exhibit mesomorphism. If the intermolecular attractions are too strong, selective weakening of the cohesive forces may not take place until high temperatures are reached, and when the melting process begins, the thermal vibrations may be too great to allow an ordered arrangement of the molecules to persist, as is the case with the methyl derivative, which is non-mesomorphic. In the case of the ethyl derivative, though the polarizability and the chain length are increased, the melting point is not decreased. Hence it directly gives the isotropic liquid on heating, but on cooling, because of the greater length and polarizability compared with the methyl derivative the molecules align to give a monotropic nematic mesophase before crystallization occurs. As the chain length increases, there will be a progressive reduction in the overall molecular polarizability with consequent reduction in the melting point; thus, the propyl to hexadecyl derivatives are enantiotropic nematic. In the case of the dctadecyl derivative, before the molecules could align to give a mesophase, they pass to the disordered isotropic liquid because of the reduction in the terminal intermolecular cohesions due to increase in chain length, but on cooling,

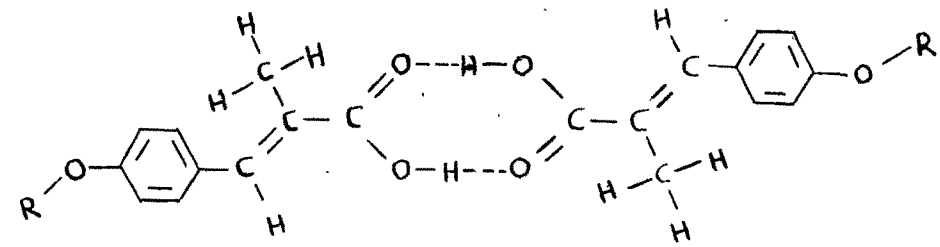
presumably due to the longer alkyl chain and overall molecular polarizability, the molecules align to give a monotropic nematic mesophase.

As discussed earlier, it is difficult to postulate the exact point of commencement of the smectic mesophase in a homologous series. In the p-n-alkoxybenzoic acid series (101), the smectic mesophase commences at the heptyl derivative. In the case of the trans-p-n-alkoxycinnamic acid (281) series it commences with nonyl derivative, possibly because the molecules of the trans-p-n-alkoxycinnamic acid series are a little broader than those of the p-n-alkoxybenzoic acid series. In the trans-p-n-alkoxy-α-methylcinnamic acid series, the α-methyl substituent increases the breadth of the molecules to such an extent that they do not exhibit smectic mesophases. This is due to the increase in the breadth of the molecule which makes it more difficult for the molecules to pack economically side by side in a parallel arrangement to give a smectic mesophase, because of the reduced intermolecular cohesions. In the case of 4,4'-di-p-n-alkoxybenzylideneaminobiphenyls (107) the smectic mesophase commences at the heptyl derivative whereas 4,4'-di(p-n-alkoxybenzylideneamino)-2,2'-, 2,5- and 2,6-substituted biphenyls exhibit only nematic mesophases. This indicates that if the breadth is increased considerably the smectic mesophases can be eliminated from the homologous series.

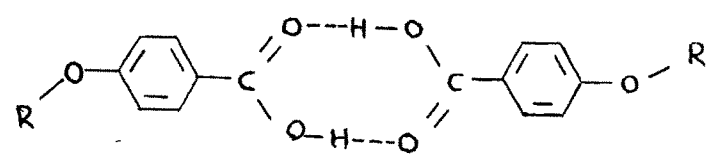
Table 26 summarizes the thermal stability of series (1) trans-p-n-alkoxy-α-methylcinnamic acids (A) and this is compared with (2) p-n-alkoxybenzoic acids (B), and trans-p-n-

Table 26
Relative thermal stabilities.

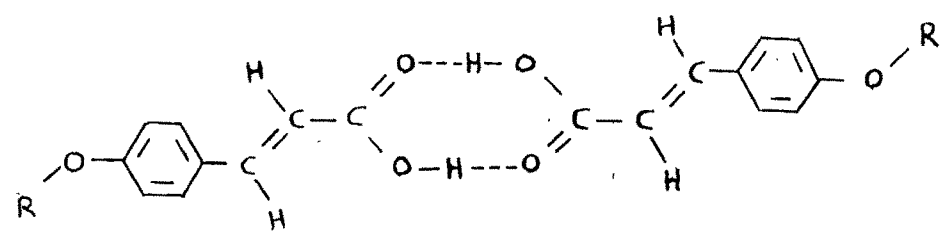
Transition temperatures °C.	A	B	C
Smectic-Nematic or Isotropic (C_9-C_{18})	-	126.3	153.6
Nematic-Isotropic (C_3- C_{14})	125.7	148.1	184.3



A



B



C

alkoxycinnamic acids (C).

Reference to table 26 shows that the nematic thermal stability of series A is lower than that of series B and C. This can be expected from the molecular geometry of these series. Though series A is a little longer and more polarizable than series B, since it is broader due to the $-CH=\underset{\displaystyle CH_3}{\overset{|}{C}}-$ group, breadth predominates resulting in reduction of its thermal stability. In the case of series A and C, the molecular geometry is the same, except for the α-methyl group. In the acid dimer of the series A, other things being common, there will be an increase in the breadth of the molecule due to α-methyl group. Because of this, the nematic thermal stability of series A is much less than that of the series C. It can be seen from the table that compared with series B and C, the smectic phase is completely absent in series A, although it has comparatively a good nematic thermal stability. As said before the molecules of series A are comparatively broader than those of series B and C and the breadth has a more pronounced effect on the smectic mesophase than on the nematic mesophase. Further, as discussed earlier (see page 160) it may be possible that some twist may also be operating in the molecule of series A due to the steric effect caused by the α-methyl group, resulting in the decrease of the coplanarity of the molecule. This effect along with the breadth of the molecule may be responsible for the complete elimination of the smectic mesophase in series A.

In the case of cholesteryl trans-p-n-alkoxy-α-methyl-cinnamates and cholesteryl trans-p-n-alkoxycinnamates, the

difference in mesomorphic behaviour is not as great as it is between series A and C. This can be attributed to the long and broad molecule of cholesterol and the geometry of the acyl group in cholesteryl compounds. In the case of series A, it can be seen from the geometry that in the dimer two ∝-methyl groups exert their full breadth increasing effect. This type of behaviour is observed in cholesteryl 4-n-alkoxy-1-naphthoates. 4-n-Alkoxy-1-naphthoic acids (101) are non-mesomorphic because in the acid dimer the breadth increase is to the fullest extent, whereas in the case of the corresponding cholesteryl esters, though they are less mesomorphic, they do exhibit mesomorphism due to the increased length to breadth ratio and the geometry of the molecule.