# DISCUSSION

## DISCUSSION

The influence of molecular structure on the properties of smectic, nematic and cholesteric liquid crystals, notably on their thermal stabilities has been studied by many workers in the field. A large number of mesogenic 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. Many compounds which form nematic mesophases contain a para substituted benzene ring as the central group. The contribution of this ring to mesophase stability appears to lie in its rigidity, linearity and polarizable $\pi$ electron density. The important nematogenic systems which exhibit mesomorphism are Schiff's base compounds, aromatic carboxylic acids, and aliphatic esters of aromatic carboxylic acids. Recently a number of heterocyclic Schiff bases are reported which exhibit nematogenic character (103,104). The smectogenic systems are mainly exhibited by the alkyl esters of aromatic acids comprizing azomethine, azo or azoxy linkages.

The cholesteric systems are mainly comprised of aliphatic and aromatic esters, thioesters and carbonates of cholesterol. A Number of optically active nematogenic compounds are reported which exhibit cholesteric mesophase.

Generally in a nematogenic system~~s~~ the first few members are purely nematic, the middle members are smectic and nematic and the higher members are purely smectic in nature. The cholesterogenic systems differ from this general behaviour. In the case of a cholesterogenic system the first few members are purely cholesteric whereas all the higher members exhibit a smectic mesophase alongwith the cholesteric mesophase. However, there are nematogenic systems which exhibit behaviour similar to cholesterogenic systems in which the higher members exhibit both smectic and nematic mesophases(112,222,223).

A change in the molecular structure by introducing a lateral substituent may bring about appreciable changes in the general behaviour and the system may become purely nematic (224,225) whereas introduction of alkyl ester linkage or halogens at the end group may make it purely smectic(226,58).

The recent upsurge of activity in the field of liquid crystals is undoubtedly a prelude to the synthesis of new mesomorphic compounds of varied structures. Low melting cholesteric and nematic thermotropic liquid crystal synthesis have aroused considerable interest because of the potential use of the materials in display devices and as temperature indicators. Mesogenic compounds to be used for display devices should satisfy basic requirements; they should possess a suitable mesomorphic range, should be chemically, photochemically and electro-chemically stable, colourless and safe to handle. Although a number of such nematogens have recently become available, only a few satisfy all these requirements, Champa(227), Fishel and Patel (104), Dietrich and Steiger(228), Patel(229) van der Veen and Grobben(230) and Gardlund et. al(231) have reported low melting schiff bases.

Gray et. al.(232) synthesized a number of biphenyl mesogens exhibiting low mesophases. Canceill et.al.(233) and Jacques et. al(234) have reported disubstituted fluorenes and 9,10 dihydro phenanthrenes and substituted tolanes, young et al.,(235) studied low melting substituted stilbenes. Steinsträsser(236), van Meter and Klandermann(237) and Dave and Vora(238) have reported low melting phenyl benzoates.

Schiff bases are prone to hydrolysis and oxidation; Tolanes and stilbenes are colourless but are chemically and photochemically unstable. Biphenyls are the best of the lot as they do not have the central linkage with which these problems are usually associated(232). However the ease with which Schiff bases can be synthesized prompted more research around stabilizing mesogenic Schiff base compounds. Good number of esters are synthesized having low melting behaviour. Some homologous series are reported comprising an azo group(239-242). However, the report that the coloured azomesogens would not be suitable for display devices did not give much impetus for the synthesis of azomesogens.

Heilmeier and coworkers(156) reported the orientation of certain nematogenic host compounds by external dielectric fields which could be used to orient pleochroic dye molecules(guest).

Later on the work of Heilmeier(243), Morita(244) and Taylar(245) and Uehida et.al(246) created a ground of guest-host type colour display devices. The guest-host type cell with excellent character for colour switching has good features over other liquid crystal display devices(247) which are summarized as follows:

(a) Non-uniformity of the electrode spacing of a liquid crystal layer does not harm uniformity of the display colour.

(b) Viewing angle is very wide

(c) Transmittance is high.

(d) Hue and chroma can be controlled by selecting a guest dye.

Uchida et.al. have summarized that the long, rod-like molecules of azodyes give overall good response. These results again provided impetus for the synthesis of new azomesogens and the study of guest-host interactions of mesogenic and non-mesogenic azodyes(157,158).

In the present study the following homologous series have been synthesized and their mesomorphic properties studied:

I 4-(4'-n-Alkoxy-2'-methylphenylazo)-benzoic acids.
II Methyl 4-(4'-n-alkoxy phenylazo)- benzoates.
III Ethyl 4-(4'-n-alkoxy phenylazo) benzoates.
IV n-Propyl 4-(4'-n-alkoxyphenylazo) benzoates.

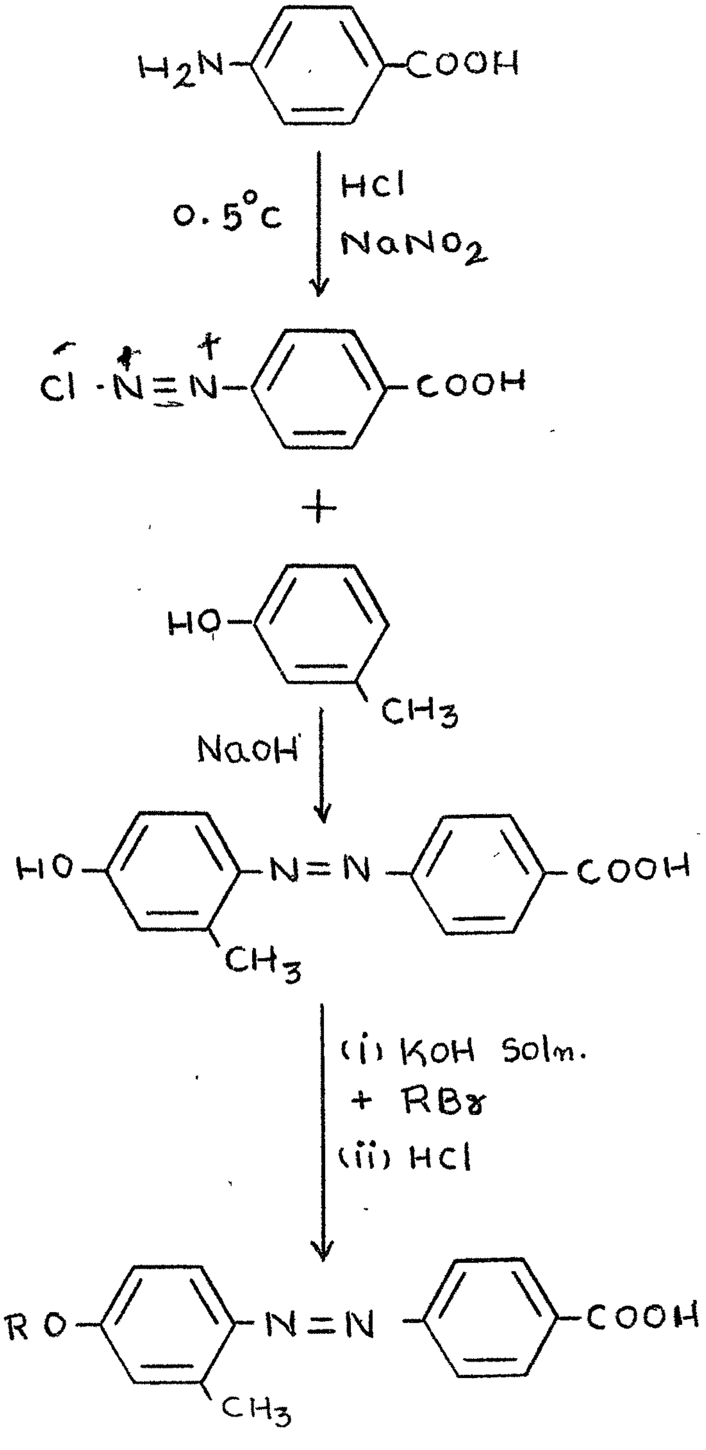
## I 4-(4'-n-Alkoxy-2'-methylphenylazo) benzoic acids.

A homologous series of thirteen acids has been studied. These compounds were prepared by the synthetic route as shown in scheme-1.

The melting points and transition temperatures are recorded in Table 5.

All the members of the series are mesomorphic and exhibit only a nematic mesophase. When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (Fig.5) the nematic-isotropic transition temperatures lie on two falling curves, one representing the ethers with odd number 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 one. As the first member decomposed, the curve is joined with dotted lines. The odd even effect is observed only upto the third member of the series.

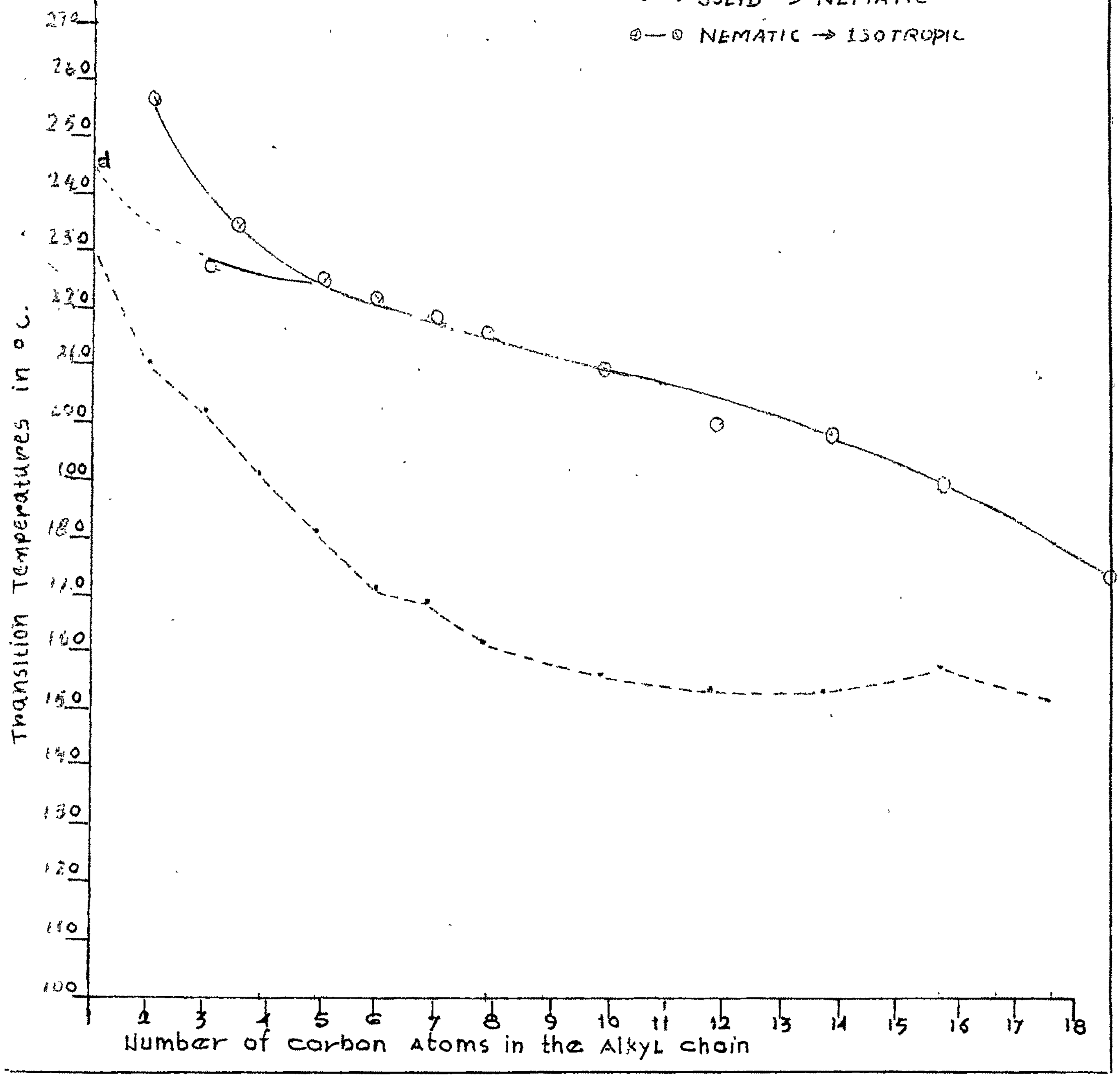
Homologous series are usually studied to correlate molecular features with properties of the mesomorphic state, Within a given homologous series, systematic variation of transition temperatures indicate that the end chains actually


H₂N
COOH
0.5°C
HCl
NaNO₂
Cl
N≡N
COOH
+
HO
CH₃
NaOH
HO
N=N
CH₃
COOH
(i) KOH Soln.
+ RBr
(ii) HCl
RO
N=N
CH₃
COOH

SCHEME-1

Fig. 5

4-(4'-n-ALKOXY 2'-METHYL PHENYL AZO) BENZOIC ACIDS.



take an active part in the anisotropic interactions.

The molecules, forming liquid crystals usually consist of relatively rigid aromatic or aliphatic rings with alkyl chains attached to one or both ends. Within the isotropic or the nematic phase, different regions of each molecule are continuously in contact with parts of the neighbouring molecules. The energy of the system depends on different conformations of molecules, London-van der Waals dispersive forces between the neighbouring molecules and on steric repulsion between different molecules(248).For the mesogenic homologous series Gray(55,249) has successfully used concepts of molecular arrangement and complex molecular interactions with lateral and terminal attractions between neighbouring molecules. These ordering forces, which are strongly dependent on molecular separations, have to compete with disordering thermal fluctuations.

Due to the presence of balancing lateral and terminal cohesions and long lath like molecules,mesogenic compounds melt in stages. They pass through one or more ordered intermediate stages before changing to isotropic liquid. The molecular layer structure of the smectic phase occurs in temperature regions where lateral attractions dominate while the parallel molecular arrangement of nematic phase occurs in a temperature interval with predominant terminal attractions. Thus at the solid-smectic transition the primary terminal cohesions of the molecule are overcome and at the smectic-nematic or smectic-cholesteric change the strong lateral intermolecular attractions are overcome and a nematic or cholesteric phase is formed. The molecules in the nematic or cholesteric melt are thus maintained by the residual lateral and terminal cohesions. On further heating all these van der Waals forces are again broken down and the molecules pass into randomly arranged isotropic liquid state. These changes can be represented schematically as shown in the figure(Fig.6).

In a mesomorphic homologous series,usually the mesomorphic-isotropic transition temperatures change in a regular manner. The increment of each methylene group brings about regular changes in the transition temperatures for the series. Gray(58) has tried to explain this behaviour of the homologous series. As the methylene chain is lengthened, the separation of the aromatic centres which are highly polarizable and which carry permanent dipolar substituents is increased; consequently there should be a decrease in the strength of the terminal intermolecular cohesions. However, Gray (58) and Maier and Baumgartner(250) 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 a homologous series can be explained.

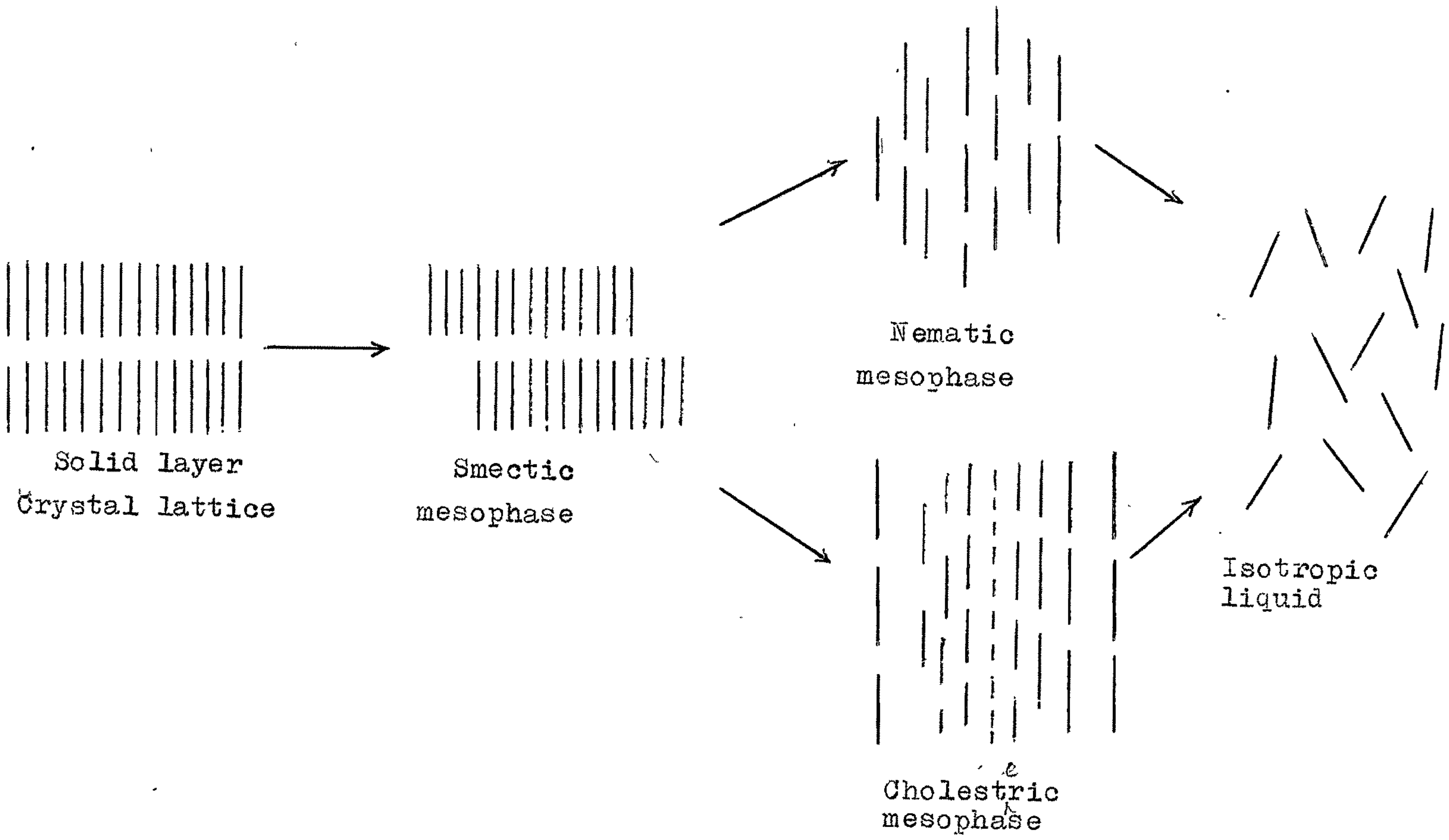

Solid layer
Crystal lattice
Smectic
mesophase
Nematic
mesophase
Cholesteric
mesophase
Isotropic
liquid

Fig. 6

The lower homologues are only purely nematic, i.e, for the short-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 from 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. Thus with the increase in the alkyl chain length, the tendency of a compound to be nematic should decrease, and at the same time, its tendency to exhibit smectic properties should increase. Therefore, in a homologous series a stage would be reached when no nematic properties would be shown and the system would be purely smectic in behaviour. At this stage the smectic mesophase will pass directly into 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 similar rod-shaped molecules, exhibiting nematic and smectic mesophases.

A number of other homologous series, however, do not behave exactly as discussed above. In the cholesteric homologous series the initial members with shorter alkyl chains are only cholesteric, the higher members being both smectic and cholesteric. In the initial members the terminal cohesive forces are relatively strong and with the increase in the alkyl chain length the lateral cohesive forces increase and the molecules maintain themselves in the layer arrangement before they give rise to a cholesteric mesophase at higher temperature. However, the cholesteric systems differ from the nematogenic systems. The last members in the cholesterogenic systems exhibit the smectic phase along with the cholesteric phase, whereas in nematogenic systems generally, the last members are purely smectic. This may presumably be due to the broad and flat cholesterol molecule. However, this type of behaviour has been observed with some nematogenic systems. Gray et. al. found that p-n-alkoxybenzylideneaminofluorenones and 4(p-n-alkoxy-benzylidene) aminobiphenyls having substitution in 2 or 3 position show this type of behaviour(223). Arora et. al. (251) have also reported this type of behaviour in 2-methyl-1,4-phenylene bis(4'-n-alkoxybenzoates). In all these cases the effect of the steric influence is to increase the thickness of the molecules. This should make it more difficult for the molecules to pack economically side by side in a parallel arrangement and should result in a weakening of the lateral intermolecular cohesions. Thus even at the octadecyl derivative the smectic-nematic curve does not merge with the nematic - isotropic curve. Dave et.al., recently studied a number of naphthylidene Schiff bases and evaluated the effect of broad naphthalene nucleus (112). They have observed that in all these series pure smectic mesophase is not observed and the last members of the series exhibit a smectic phase along with the nematic phase. This can be explained as the 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 systems even in the last members, the molecules are arranged in such a manner that on heating, the molecular layers slide over one another and do not get disrupted to the disordered isotropic state but pass to the nematic or cholesteric state. A cholesteric or nematic phase is thus obtained from the smectic phase and on further heating the disruption is complete to give the isotropic liquid. However, there are also a number of purely nematogenic homologous series wherein the last members of the series do not exhibit any smectic mesophase(58,224,225). All these series contain a lateral substituent which increases the breadth of the molecules to such an extent that the economical packing of the molecules does not take place to give a smectic mesophase. This discussion explains the general behaviour of the present homologous series, but it does not explain the regular alternation in nematic-isotropic transition temperatures for odd and even numbers of carbon atoms as the series is ascended.

Gray(249) has tried to explain such behaviour for nematic-isotropic transition in terms of the conformation of the alkyl chain. He has considered the zig-zag conformation for the alkyl chain, as evidenced from the X-ray studies of crystalline state of some liquid crystalline compounds.

As the chain length increases, it will have the following effects and the nematic-isotropic transition temperatures will be determined by those effects which predominate:

(i) The longer molecules will be less readily rotated out of the ordered state.

(ii) The overall polarizability increases with each added methylene unit.

(iii) 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.

(iv) Each methylene unit forces apart polarizable centres in the molecules and decreases the residual terminal attractions.

(i) and (ii) would increase the nematic-isotropic transition temperatures and (iii) and (iv) would decrease the nematic-isotropic transition temperatures. Thus rising transition lines are obtained where the effects(i) and (ii) predominate and vice versa. In keeping with this view the rising transition lines are found in a series in which the transition temperatures are low and when the residual interactions are weak. Gray has tried to explain this alternation of nematic-isotropic transition temperatures 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, if the chain extends strictly along its own axis(dotted line in Fig.7), then the terminal methyl groups present different faces to one another or to other end groups in the molecules 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.

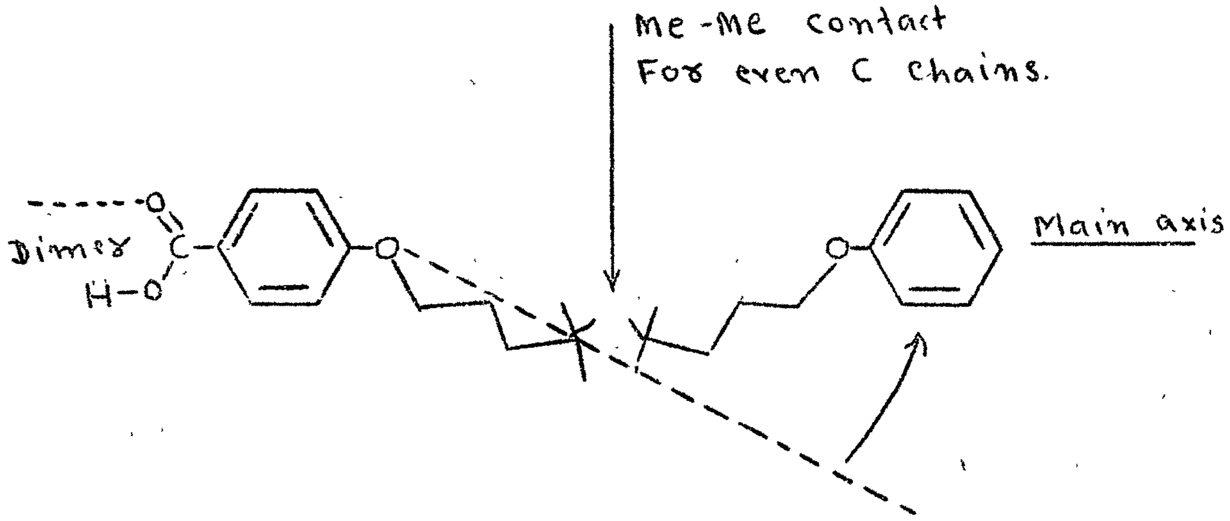


Fig 7

With the higher homologues the alkyl chain may be forced (curved arrow in figure 7) into line with the main axis defined by the more rigid aromatic parts. Gradually the end groups contact would 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. So far, the effects of changes in terminal attractions between the molecules on the nematic-isotropic transition temperatures have been considered, but the effect of residual later interactions between the molecules, which should also play some role in determining the thermal stability of the nematic mesophase, has not been discussed.

Maier (252) and Maier and Baumgartner(250) also have tried to explain the alteration effect on the basis of their study of the dipole moment and dielectric anisotropies of a nematogenic homologous series.

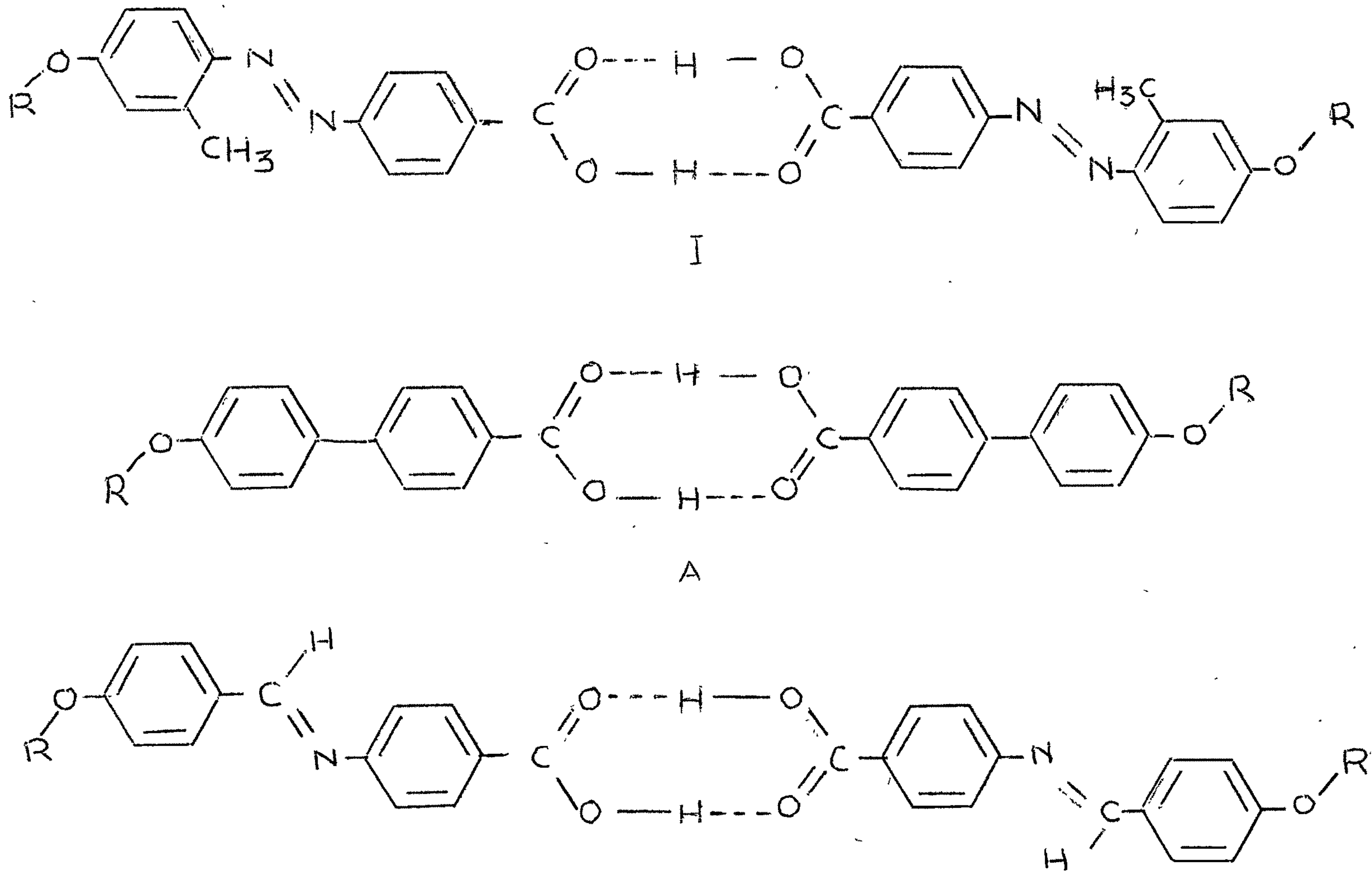
Marcelja's(248) theory explains the even-odd effect in isotropic-nematic transition temperatures and entropies. From the geometry of p,p'-di-n-alkoxy-azoxybenzenes they have shown that the addition of carbon atoms $C_2$ increases the anisotropy of the molecule and helps the ordering process, subsequent addition of atoms $C_3$ hinders the ordering, atoms $C_4$ helps again, and so on. As the chains become longer, their flexibility makes the effect progressively smaller until, for long end chains, it becomes unnoticable.

Pines et. al.,(253) have measured order parameters in a series of nematic liquid crystals p-alkoxy azoxybenzenes, by $^{13}C$ NMR. The ordering exhibits an even-odd alternation along the series. They conclude that the benzene rings rotate or flip about the para axes at a rate greater than 1 KHz for the whole series throughout the nematic ranges.

Recently De Jeu and Van der Veen(254) have reviewed some experimental results on the variation of the nematic-isotropic transition temperatures $T_{NI}$ and evaluated molecular structure with the aid of expressions for $T_{NI}$ from molecular-statistical theories.

In the case of homologous series with higher transition temperatures, with increase in end-chain length a decrease is observed. In this case, the anisotropic interaction between the rigid structures of the molecule is rather strong and the addition of end chains decreases the average anisotropic interaction(248). This explains the decrease of nematic-isotropic transtion temperatures in the case of present series.

There is a close relationship between mesomorphism and molecular constitution of organic compounds. Therefore, the thermal stability which is a measure of mesomorphism can be correlated with the molecular constitution of the compounds. Table 9 summarizes the average nematic thermal stabilities of the present series. The geometry of all the three series is given in Fig. 8.



I

A

B

Fig. 8

Table 9

Relative Thermal Stabilities

| Transition temperatures °C | I | A | B |
|---|---|---|---|
| Nematic-Isotropic $C_2 - C_8$ , $C_{10}$ | 227.3 | 275.8 | 262.3 |
| Commencement of smectic mesophase | - | Pentyloxy | Hexyloxy |

4-(4'-n-Alkoxy-2'-methylphenylazo) benzoic acids (I) and these are compared with those of

4'-n-alkoxybiphenyl-4-carboxylic acids(A) (255)

4'-n-alkexoy benzylidene-4-aminobenzoic acids (b) (256)

Reference to table 9 indicates that the nematic thermal stabilities of series I are less compared to those of series A & B. molecules of series A and B do not have any lateral substituent whereas molecules of series A contain a lateral methyl substituent and in a dimer of the acid two methyl groups would be in the trans position, which would be more favoured. The introduction of a substituent into a side position in the molecule of a mesomorphic compound has two opposing effects(249):

(i) the substituent will decrease both the smectic and nematic thermal stabilities by increasing the separation of the long axes of the molecules, and

(ii) the substituent will increase both smectic and nematic thermal stabilities because of its polarization effects which will enhance the intermolecular cohesions. Of the two opposing effects, the first always predominates unless the substituent does not exert its full breadth increasing effect. The presence of two trans methyl groups in the molecules of series I would exert a predominant breadth increasing effect which is evidenced by its lower nematic thermal stabilities compared to those of series A and B. Compared to series A and B, the decrease of the nematic thermal stabilities in series I is 48.5° c and 35.0°c, respectively. Biphenyl derivatives have no middle linkage which makes it more linear, and compared to the phenyl ring, biphenyl ring is more polarizable, hence the difference in decrease of nematic thermal stability is observed.

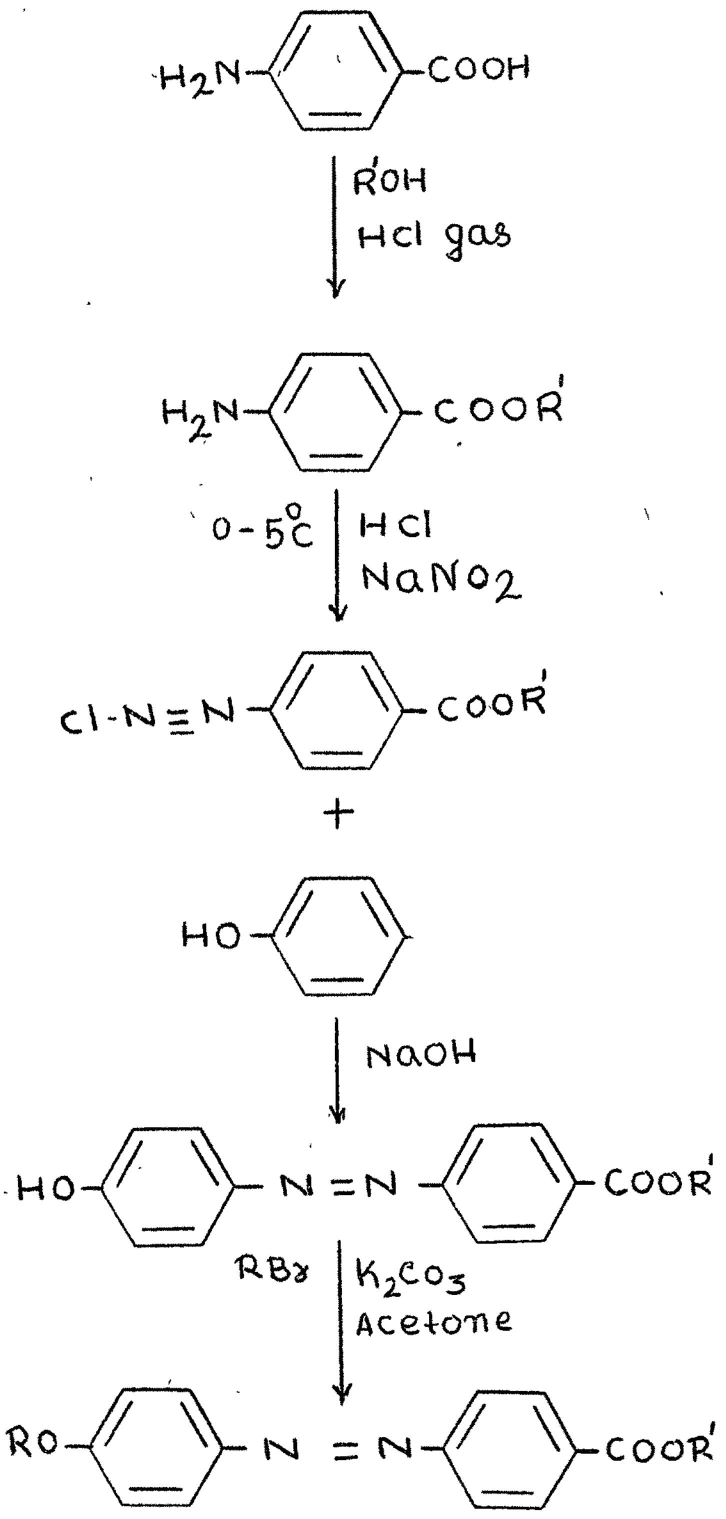
Vora(224) has studied the effect of lateral methyl substituent on trans p-n-alkoxy cinnamic acids and observed that the nematic thermal stabilities of the substituted series was decreased by 58.6°c. Here also two methyl groups are in the trans position but are in the side chain, and not on the aromatic ring as is the case with series I.

This indicates that a lateral substituent decreases the nematic thermal stabilities. But the series I is purely nematic, no smectic mesophase is observed even in the last member of the series.

The appearance of smectic properties in a series is influenced by the melting points of the compound and/or by the supercooling tendences 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 molecules. Knowledge about the appearance of the smectic mesophase may help in the search for certain series where the appearance of smectic mesophases might be delayed so that purely nematic or cholesteric substances would be obtained. A survey of the nematogenic homologous series and the point of commencement of the smectic mesophase indicates that the appearance of the smectic mesophase is influenced by the geometry of the molecules. If the molecules of the series are long, straight rod-shaped and polarizable, the smectic mesophase commences early in the series. If the molecules are short and linear the smectic mesophase appears 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 $C_{18}$ derivatives. If the breadth increasing effect is very great, smectic mesophases may not appear in homologous series. This explains the absence of smectic mesophase in series I. Nematic thermal stabilities of series I are not much decreased, compared to those of series A and B, but the smectic mesophase does not commence even in the last members of the series. Such observations are explained by Gray(58). The increase in the breadth decreases both, the smectic and nematic thermal stabilities, but the effect is more pronounced on smectic mesophases compared to the nematic mesophase.

Series II, III and IV

Compounds of series II, III and IV are synthesized by the route given in scheme 2.



II $R' = CH_3$, III $R' = C_2H_5$, IV $R' = n\text{-}C_3H_7$.

SCHEME-2

## II. Methyl 4-(4' -n-Alkoxyphenylazo)- Benzoates :

Mesomorphic properties of thirteen members of this homologous series are studied. The melting points and transition temperatures are recorded in Table 6.

The smectic mesophase commences at the heptyl derivative as a monotropic phase, heptyl, octyl, decyl and dodecyl members exhibit monotropic smectic mesophases. Lower members of the series are non-mesomorphic. When the smectic-isotropic transition temperatures are plotted against the number of carbon atoms in the alkyl chain (Fig.9), the smectic-isotropic transition temperature curve rises a little and then levels off. No odd-even effect is observed as there is only one ($C_7$) odd member, which fits in the single curve of the even members.

## III. Ethyl 4-(4'-n-Alkoxyphenylazo) Benzoates :

Mesomorphic properties of thirteen members of this homologous series are studied. The melting points and transition temperatures are recorded in Table 7.

The smectic mesophase commences from the pentyl derivative as a monotropic phase. Hexyl to octadecyl derivatives exhibit enantiotropic smectic mesophases.

When smectic-isotropic transition temperatures are plotted aganist the number of carbon atoms in the alkyl chain (Fig.10), the smectic-isotropic transition temperature curve rises to a maximum and then levels off. The odd-even effect is not observed in the homologous series.

### IV. n-Propyl 4(4'-n-Alkoxyphenylazo) Benzotaes :

Mesomorphic properties of thirteen members of this homologous series are studied. The melting points and transition temperatures are recorded in Table 8.

The smectic mesophase commences from the butyl derivative. Butyl to octadecyl derivative exhibit enantiotropic smectic mesophases.

When the smectic-isotropic transition temperatures are plotted against the number of carbon atoms in the alkyl chain (Fig.11), the smectic-isotropic curve shows the odd-even effect. The smectic-isotropic transition temperature curve for odd and even members rises to the maximum and then falls off. for even members,

### General characteristics of series II, III and IV :

All the three series are smectogenic in nature and exhibit smectic mesophases. The transition temperature curves in the case of series II and III do not show any odd-even effect; whereas in the case of series IV odd-even effect is observed. In all the three series the transition temperature curves rise to a maximum and then levels off.

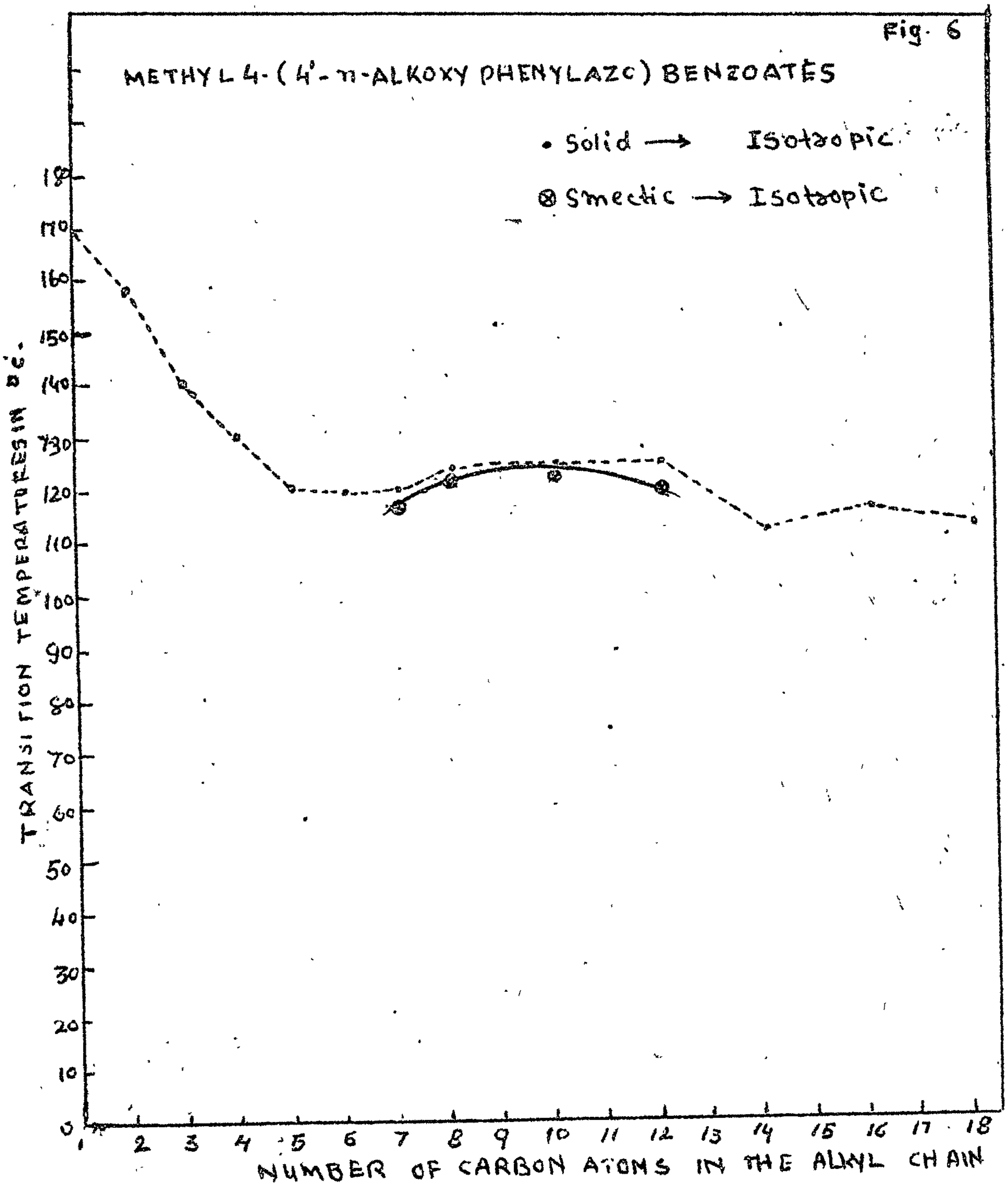


Fig. 6

METHYL 4-(4'-n-ALKOXY PHENYLAZO) BENZOATES

Fig.no-10

Ethyl 4-(4'-n-Alkoxy phenylazo) Benzoates.

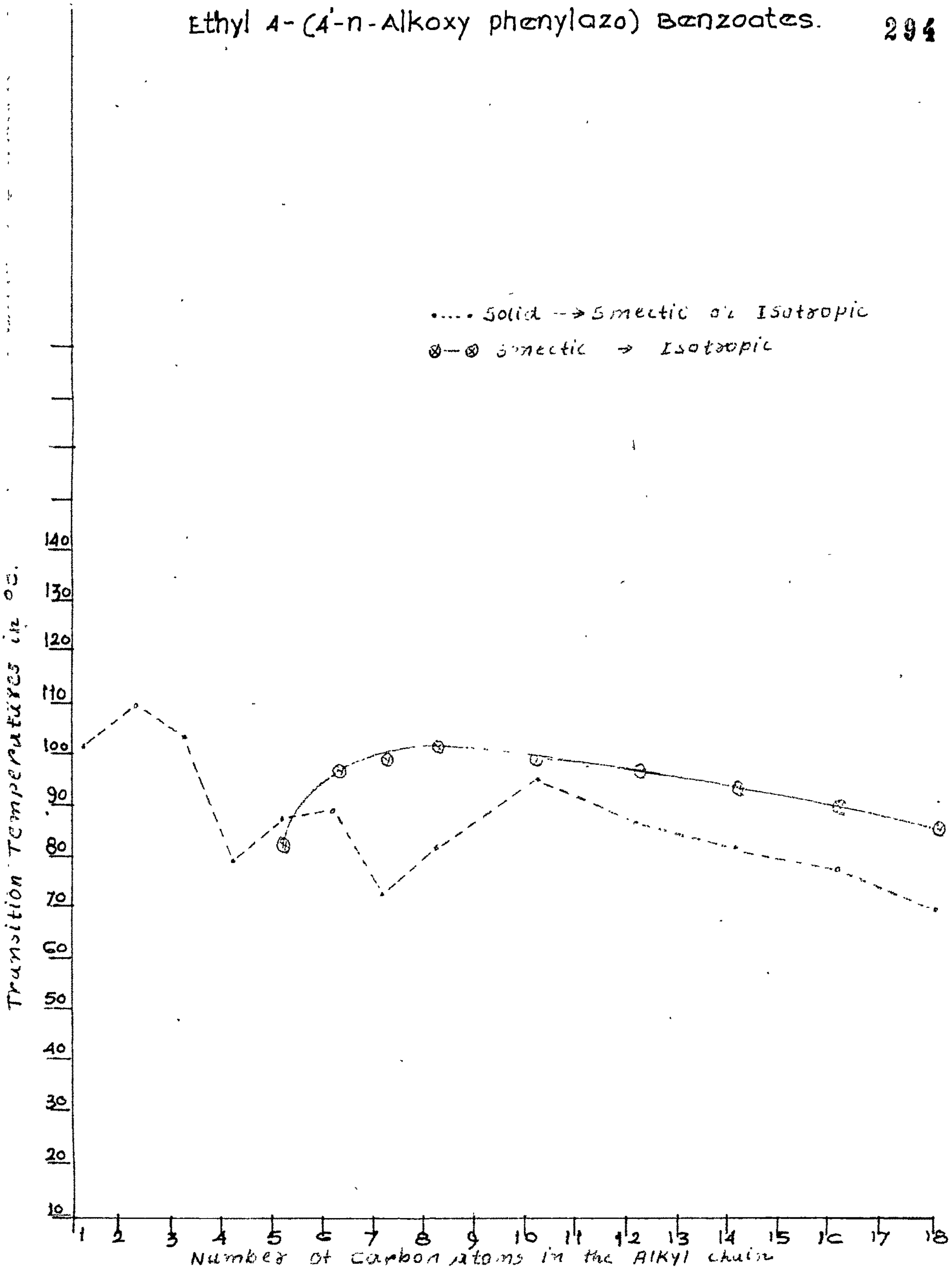
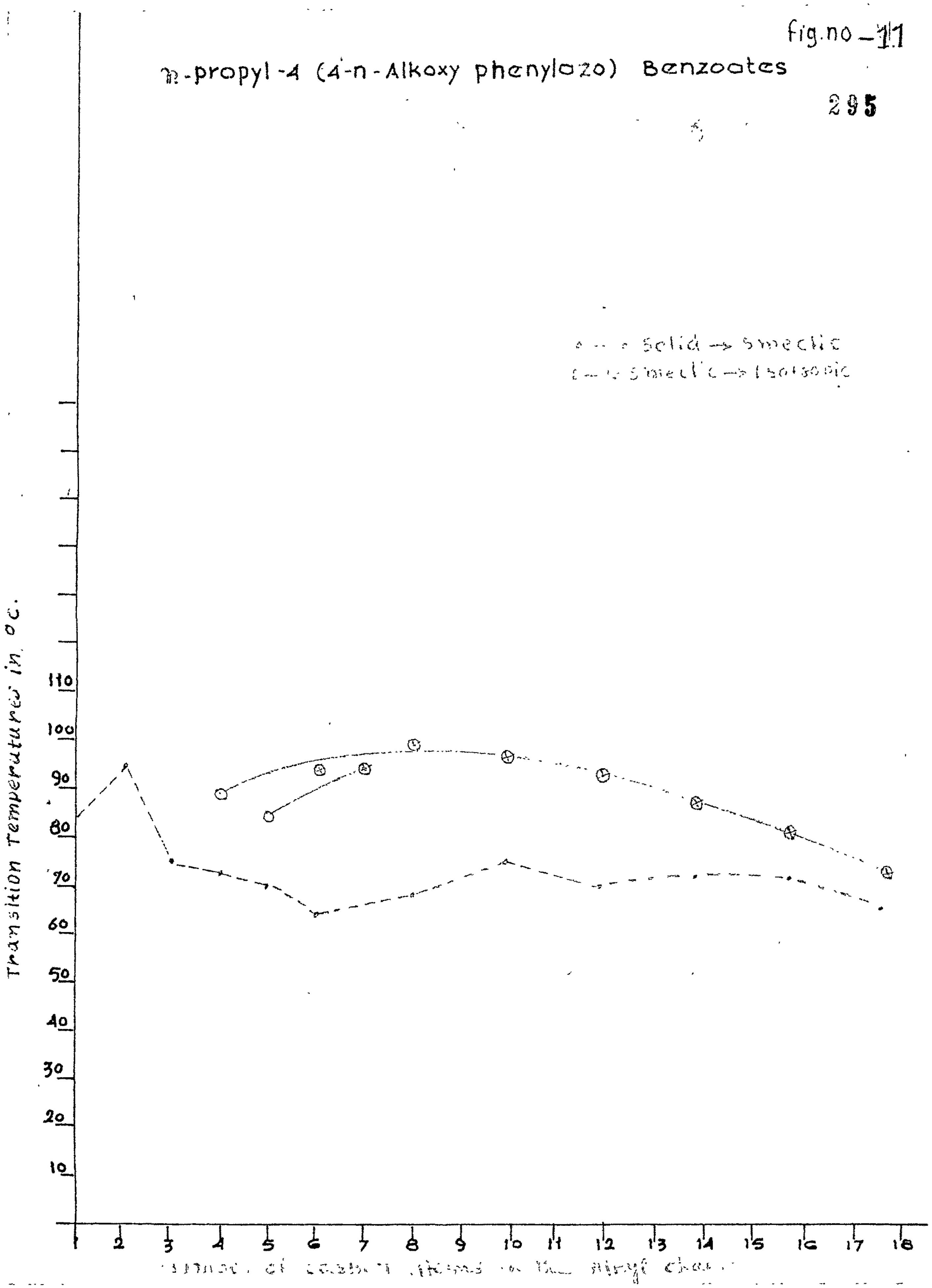


fig.no-11

n-propyl-4 (4'-n-Alkoxy phenylazo) Benzoates



It is worth noting that series II and III do not show any odd-even effect whereas series IV exhibits odd-even effect. The difference in these series is of $-CH_2-$ units only.

Gray(58) has explained the rising and levelling off in the smectic-isotropic transition curves.

In such homologous series, only members of the series which give increasing smectic-isotropic transition temperatures as the alkyl chain lengths, the terminal intermolecular attractions will be at their strongest, but the lateral intermolecular attractions will be at their weakest. The smectic-isotropic transition temperatures of the first members of the series must therefore be determined by the weak lateral attractions. These attractions will increase as the chains grow longer, and the smectic mesophases will increase in thermal stability, but only upto a point, for as the alkyl chains lengthen still further, the terminal cohesions grow weaker and the probability of interpenetration of the smectic strata at a lower temperature increases. For the higher homolog~~ous~~ues therefore, the weakening terminal cohesions determine the thermal stabilities of the smectic mesophases, and explain the subsequent fall in the smectic-isotropic transition line as the series is ascended.

The alternation of smectic-isotropic transition temperature curve in series IV can be explained as in purely smectic series the smectic-isotropic transition exhibits an alternation between the odd and the even carbon chain homologues. This suggests that intermolecular attractions are playing their part in determining the smectic-isotropic transition temperatures just as they do for normal homologous series, exhibiting nematic and smectic mesophases.

Even though overall structural parameters in series II, III, and IV are the same, absence of the odd-even alternation of smectic-isotropic transition in series II and III suggests that the additional methylene unit present in alkyl side chain must be playing some role in the alternations of these transitions. Gray(249) has explained the alternation by assuming zig-zag conformation of the alkyl chain in the molecule. The absence of alternation in the smectic-nematic transition temperatures are explained by stating that in such a conformation the added methylene group does not affect the lateral transitions differently whether the chain is even or odd provided that the chain axes are normal to the interfaces. However, recently some homologous series are reported by Gray and Harrison(257) and by Fishel and Patel(104) where odd-even effect is observed for smectic-nematic transition temperatures. Gray and Harrison(257) also observed high alternation for the nematic-isotropic transition temperatures in the $\omega$-substituted alkyl arene esters. They report that smectic-nematic and smectic-isotropic transition temperatures alternate less markedly and in some systems, the alternation is negligible, and the smectic-nematic and smectic-isotropic transition temperatures fit in a single curve. From the above discussion it is reasonably evident that transition temperature changes in mesogens are a delicate balance of several factors such as molecular shape, conjugation, resonance conformational preference of alkoxy chain, size and position of dipole etc. This is further supported by some recent studies. In the case of p-(p'-n-alkoxybenzoyloxy)-p'-aminoacetophenones(258), odd-even alternation is observed for the smectic-isotropic transition temperatures, whereas in the series p-(p'-n-alkoxybenzylidene)-p'-aminoacetophenones(254) no such alternation is observed for the smectic-isotropic transition temperatures. The difference between the two series is only in the middle group. Recently Vora(226) has also reported the absence of odd-even effect in the smectic-isotropic transition temperature curve of series p-n-alkoxybenzylidene-p-bromoanilines.

# Table 10.

## Relative Thermal Stabilities

| Transition temperatures °C | II | III | IV | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|---|
| Smectic-Isotropic | 121.0 | 98.0 | 91.7 | 130.3 | 107.7 | 100.8 | 119.0 | 95.6 | 54.0 |
| | $C_7, C_8$<br>$C_{10}, C_{12}$ | $C_5-C_8$,<br>$C_{10}-C_{18}$ | $C_4-C_8$<br>$C_{10}-C_{18}$ | $C_7, C_8$,<br>$C_{10}, C_{12}$ | $C_5-C_8$<br>$C_{10}-C_{18}$ | $C_4-C_8$<br>$C_{10}-C_{18}$ | $C_7, C_8$<br>$C_{10}, C_{12}$ | $C_5-C_8$<br>$C_{10}-C_{14}$ | $C_4-C_8$<br>$C_{10}-C_{16}$ |
| Commencement of Smectic mesophase | $C_7$ | $C_5$ | $C_4$ | $C_6$ | $C_5$ | $C_2$ | $C_4$ | $C_2$ | $C_2$ |

The average smectic-isotropic thermal stabilities and molecular geometry of the following series viz. :

II Methyl 4(4'-n-alkoxyphenylazo) benzoates,
III Ethyl 4(4'-n-alkoxyphenylazo) benzoates,
IV n-Propyl 4-(4'-n-alkoxyphenylazo) benzoates

are compared with those of :

C Methyl 4'-n-alkoxydiphenyl-4-carboxylates(255).
D Ethyl 4'-n-alkoxydiphenyl-4-carboxylates(256).
E Propyl 4'-n-alkoxydiphenyl-4-carboxylates
F Methyl p-n-alkoxybenzylidene-p-aminobenzoates(256).
G Ethyl p-n-alkoxybenzylidene-p-aminobenzoates(104).
H Butyl p-n-alkoxybenzylidene-p-aminobenzoates(104).

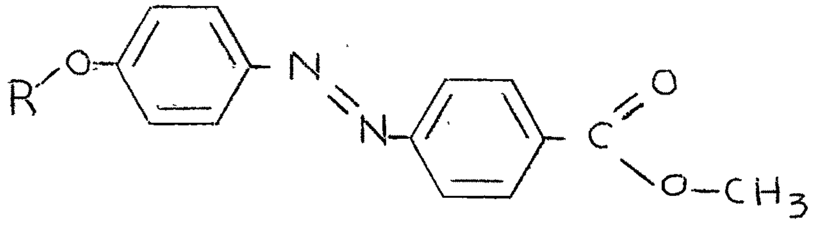
The geometry of all these series is given in Fig.12.

Reference to Table 10 indicates that the average smectic-isotropic thermal stabilities of series II are almost the same as series F whereas, they are lower than those of series C. The decrease of the smectic thermal stabilities in series II, compared with those of series C is of 9.5°C only. This is expected as series C is linear compared to series II. In the case of series II and F, there is the difference in middle groups only. Series II contains azo middle group, whereas, series F has azomethine group. This suggests that the change of these groups do not affect smectic thermal stabilities. However the geometry of all these series is given in Fig.12.

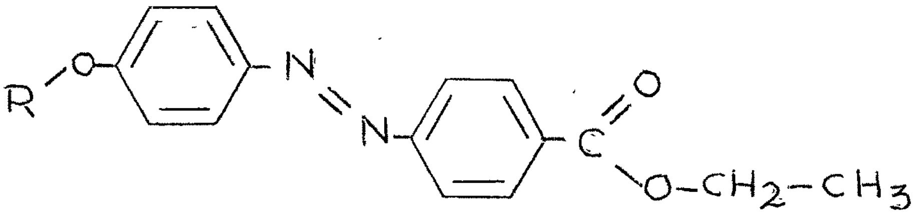
~~The~~ Reference to the Table 10 indicates that the smectic thermal stabilities of series II, III and IV are lower than those of series C, D and E respectively. Series C, D and E are alkyl 4'-n-alkoxydiphenyl-4-carboxylates, without any central linkage, hence there would not be any deviation from linearity, whereas molecules of series II, III and IV will have less linearity compared to those of series C, D, and E, due to the presence of central azo linkage. It is quite interesting to note that the difference in decrease of smectic thermal stabilities between series II and C, III and D, and IV and E is almost the same and is of the order of 9.0°C.

The smectic thermal stabilities of series II, III and series F and G are the same. This again suggests that the role played by azo or azomethine group in determining the smectic-isotropic transition temperatures is almost the same.

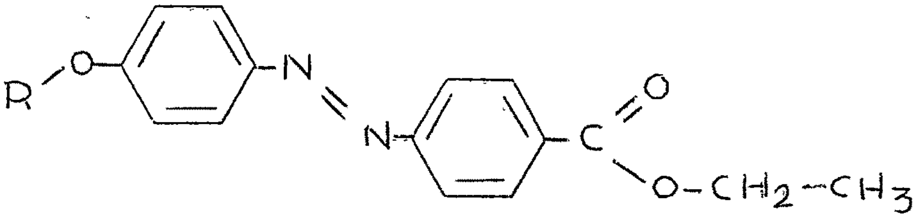
The smectic thermal stabilities of series IV is higher than those of series H. ~~The~~ Reference to Table 10 indicates that the thermal stabilities of alkyl esters decrease~~s~~ as we go from lower alkyl to higher alkyl group. This explains the lower thermal stabilities of series H which has n-butyl



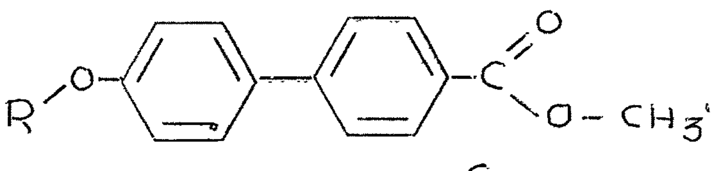
II



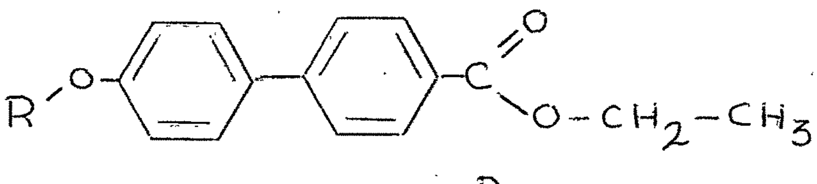
III



IV

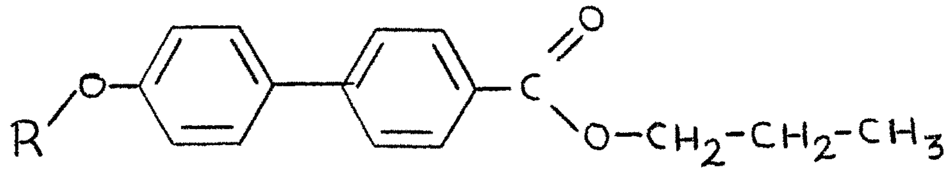


C

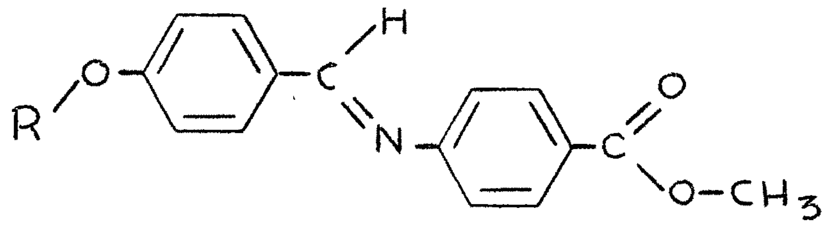


D

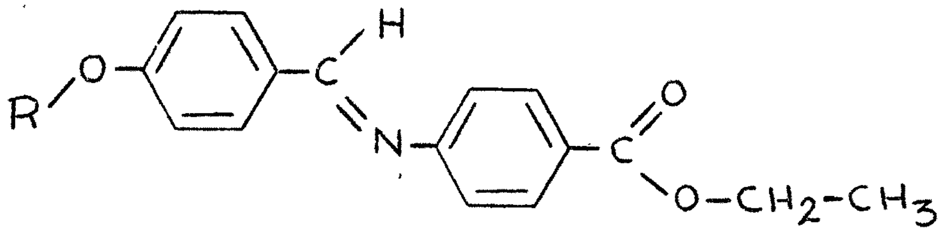
Fig-12



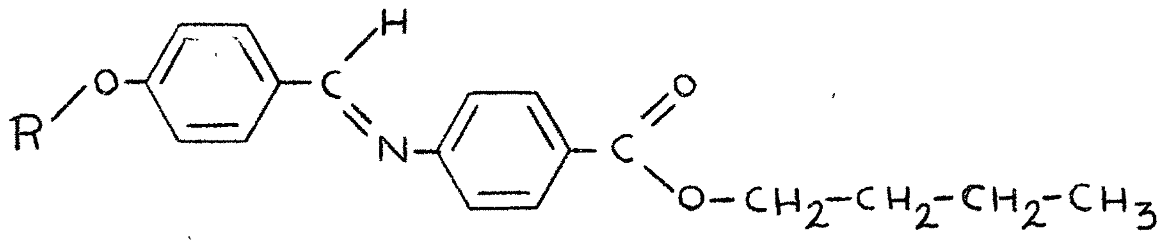
E



F



G



H

Fig. 12 (cont.)

alkyl chain as an ester linkage which is longer than the n-propyl alkyl chain of series IV.

Another interesting point worth noting is that when we go down from methyl to ethyl esters the decrease in the smectic thermal stabilities is large. This difference of smectic thermal stabilities between series

II and III = 23°C
C and D = 23°C
F and G = 23°C

In the similar manner if we calculate the thermal stabilities differences between ethyl and propyl esters, the difference is small and equal. The Difference of smectic thermal stabilities between series :

III and IV = 6.5
C and D = 6.3

The Above discussion suggests that the addition of each $-CH_2$ unit in the side chain has a different effect on the stability of the smectic mesophases. Another point worth taking note is that the molecular geometry of the present series, the diphenyl series and the Schiff base series are not the same and polarizability of all the three series also would differ, eventhough the changes brought about in the decrease in thermal stabilities by the addition of a $-CH_2$ unit are of the same order and shows the same trend.

Reference to Table 10 shows the commencement of the smectic mesophase in different series. Eventhough smectic thermal stabilities of series II, III and IV are equal to those of series F and G, the commencement of the smectic mesophase is early in the series F and G compared to that in series II and III. This suggests that minor geometrical differences and polarizability differences may not change thermal stabilities to a greater extent, but the mesogenic nature of series may differ as evidenced in the presentstudy.

The commencement of the smectic mesophases in series II, III, C and D coincides. Here, even though thermal stabilities of the two series differ, the commencement of the smectic mesophase coincides.

It is apparent from the above discussion that when there are minor difference in geometry, molecular length and polarizability, it is difficult to correlate the commencement of the smectic mesophase with thermal stabilities between these series.

The smectic mesophases observed in all the three homologous series were characterized from their fan-shaped textures as smectic A phases.

In the absence of the DTA or DSC facilities the studies of smectic phases could not be correlated by comparing calorimetric data and optical observations.

Recently the study of guest-host interaction is being taken up as a research project at the Leeds University by using different dyes(260).

The pure smectogenic series, studied so far, are less in number compared to the nematogenic series. The results of the present study of the three smectogenic series would help to understand the effect of chemical constitution on smectic mesophases.