DISCUSSION

A. NAPHTHALENE SCHIFF BASES

A. Naphthalene Schiff bases

There is a very delicate balance between the chemical constitution and liquid crystalline properties. A number of homologous series are synthesized constituting a p-phenylene unit to study the effect of chemical constitution on liquid crystalline properties. Normaly in a nematogenic homologous series first few members exhibit only nematic phases, middle members exhibit both smectic and nematic mesophases, whereas, last members of the series exhibit only smectic mesophases.

The introduction of a lateral substitution is normaly deterrent to all types of mesophases. The organic molecules having naphthalene moiety in place of the benzene moiety would generally increase the breadth of the molecules. Comparatively less mesogenic derivatives of naphthalene have been studied. Kast has reported some mesogenic naphthalene compounds (156). Wiegand (83) has reported mesogenic naphthalene Schiff base compounds. Gray and Jones (82) studied the mesomorphic behaviour in substituted naphthoic acid systems. Dave et al., studied anils comprising naphthalene moiety (85,157 - 160). Dave and Kurian (161,162) and Vora (163) studied the cholesteryl derivatives having naphthalene moiety. The introduction of naphthalene has two fold effect on mesomorphism i.e. it increases the breadth of the molecules which reduces the mesomorphic thermal stabilities and it enhances polarizabilities of the system which would increase the mesomorphic thermal stabilities. Generally the first effect is predominating.

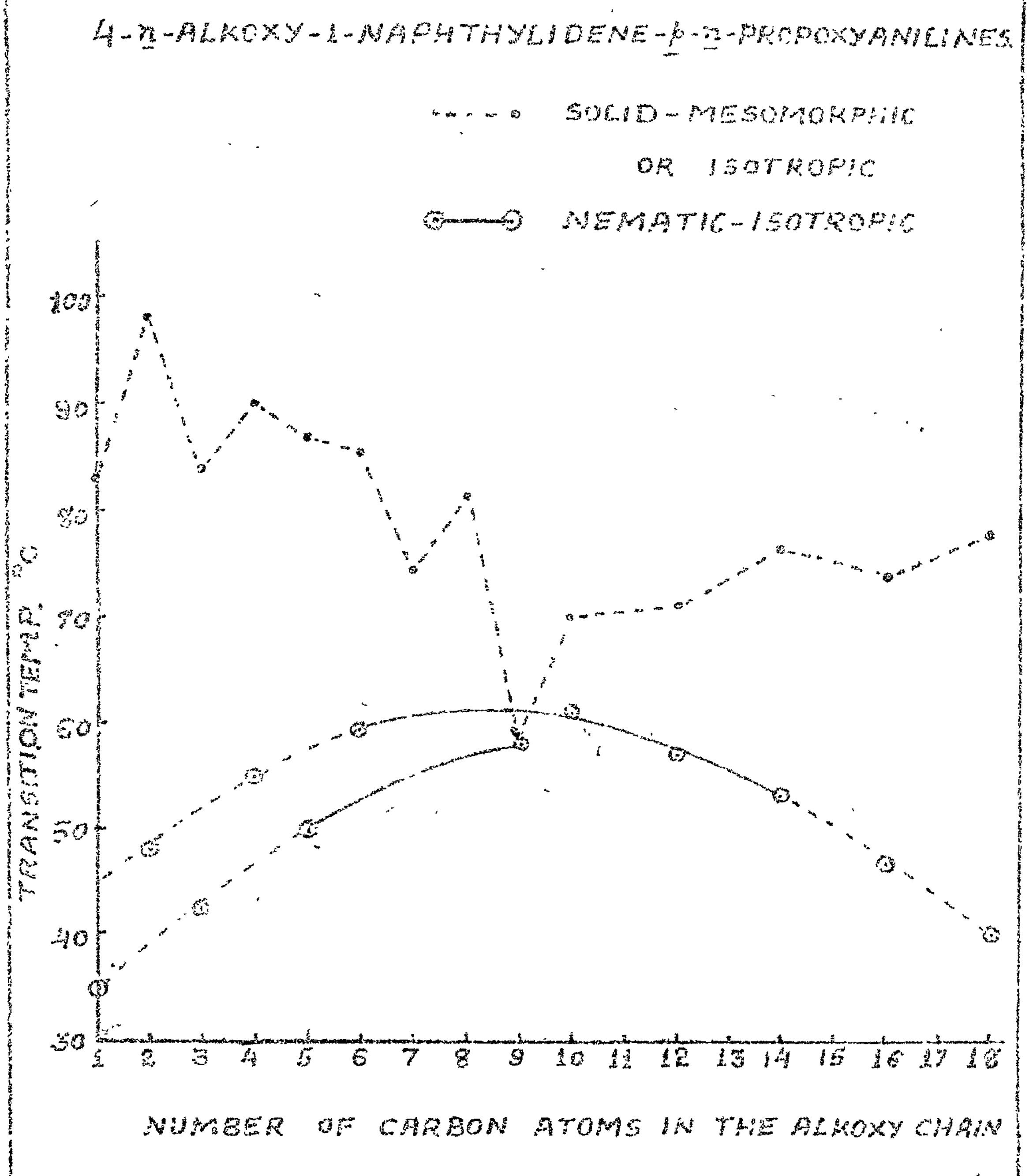
In the present study the following homologous series having a naphthalene moiety are synthesized and their mesomorphic properties discussed.

1. 4-n-Alkoxy-1-naphthylidene-p-n-propoxyanilines
2. 4-n-Alkoxy-1-naphthylidene-p-n-butoxyanilines
3. 4-n-Alkoxy-1-naphthylidene-p-n-amyloxyanilines
4. 4-n-Alkoxy-1-naphthylidene-p-i-amyloxyanilines

1. 4-n-Alkoxy-1-naphthylidene-p-n-propoxyanilines

Fourteen Schiff base compounds of the series 4-n-alkoxy-1-naphthylidene-p-n-propoxyanilines are obtained by condensing 4-n-alkoxy-1-naphthaldehydes with p-n-propoxyanilines. Their transition temperatures are summarized in Table 4.

Out of the fourteen derivatives synthesized, the pentyl, hexyl and nonyl to tetradecyl derivatives exhibit monotropic nematic mesophases while other derivatives are non-mesomorphic. The smectic mesophase is not observed even in the last member of the series. The plot of the nematic-isotropic transition temperatures against the number of carbon atoms in the alkyl chain, shows odd-even effect (Fig. 5.). It is interesting to


4-n-ALKOXY-1-NAPHTHYLIDENE-p-n-PROPOXYANILINES
SOLID-MESOMORPHIC OR ISOTROPIC
NEMATIC-ISOTROPIC
TRANSITION TEMP. °C
100
90
80
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1
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NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 5.

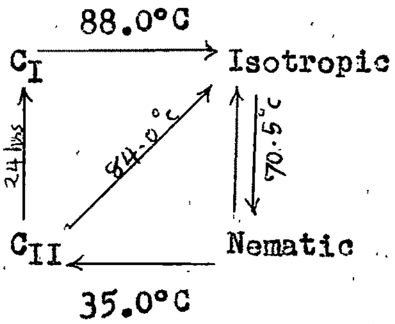
note that the plot of the odd members of the series shows as ascending tendency, whereas, the plot of the even members of the series initialy exhibit a little ascending tendency but later on it falls off as the chain length increases.

The first four members are non-mesogenic. Normaly 1,4-disubstituted naphthalene derivative joined to a phenylene unit by a bridge group like -CH=N- is not favourable for mesomorphism due to its decreased length to breadth ratio. The alkoxy chain length in the first four members are not sufficiently increased and their melting points are also comparatively high. These compounds could not also be supercooled much. These factors individually or collectively might be responsible for not imparting mesophases to these derivatives. The obscure values for the nematic-isotropic transition temperatures for all the four derivatives are obtained by extrapolating nematic-isotropic transition temperature curves and are recorded in Table 4. All the four derivatives crystallize much above these transition temperatures. In case of pentyl and hexyl derivatives the chain length is sufficiently increased eventhough mesophase is not observed on heating and solid melts to isotropic liquid directly. However, when isotropic melt is cooled the molecules align below their melting point and before crystallization commences, exhibiting monotropic nematic mesophases. Again the heptyl and octyl derivatives are non-mesogenic. This is quite surprising. Normaly one would expect them to be mesomorphic. The obscure transition temperatures obtained from the nematic-isotropic transition temperature curves for the heptyl and octyl derivatives are (55.0°C) and (62.5°C) respectively. The isotropic melt of both these compounds could not be supercooled up to these temperatures. The crystallization would always occur before these temperatures are reached. This suggests that the supercooling tendency of these two compounds deprive them to be non-mesomorphic. To confirm this, 1:1 mixture of heptyl and octyl derivatives was prepared. In the confirmation of above idea the mixture melts at 72°C and on cooling gives isotropic-nematic transition at 59°C. In many of the homologous series it is observed that first few members may be non-mesogenic, the mesophase appears as a monotropic phase in the middle members (70,164 - 166) and higher members are enantiotropic mesomorphic. In the present system nonyl to tetradecyl derivatives exhibit monotropic nematic mesophases. The alkyl chain length is sufficiently increased and the compounds have comparatively lower melting points eventhen they are monotropic nematic. This probably is due to the basic nature of the molecules, which possess a broad naphthalene moiety, due to which the lateral and end to end cohesive forces are not well balanced and melting does not occur in stages. However, as the molecules possess primary requirement of a mesogenic compound they supercool to exhibit mesomorphism. In the case of hexadecyl and octadecyl derivatives it seems that the increase of methylene unit higher than tetradecyl, again reduces the overall cohesive forces (74) of the system disallowing them to supercool to exhibit mesomorphism.

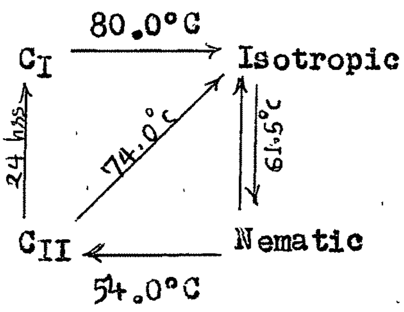
2. 4-n-Alkoxy-1-naphthylidene-p-n-butoxyanilines

Fourteen Schiff base compounds of the series 4-n-alkoxy-1-naphthylidene-p-n-butoxyanilines are obtained by condensing 4-n-alkoxy-1-naphthaldehydes with p-n-butoxyanilines. Their transition temperatures are summarized in Table 5.

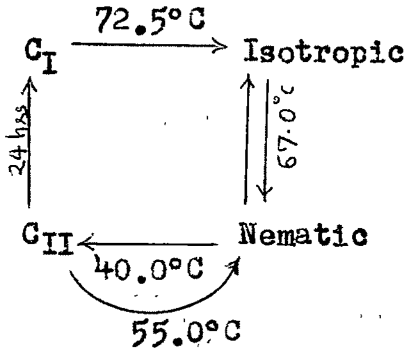
The series is purely nematic in nature. Methyl, hexadecyl and octadecyl derivatives are non-mesomorphic. All other derivatives are monotropic nematic except heptyl and dodecyl derivatives which are enantiotropic in nature. The ethyl, pentyl, nonyl and decyl derivatives exhibit two solid modifications. Stable solid modification (C_I) has a higher transition temperature than the other metastable modification (C_{II}), which is obtained by rapid cooling of the isotropic liquid phase. Ethyl and pentyl derivatives exhibiting stable modification (C_I) and the metastable modification (C_{II}) give monotropic nematic transitions. In the case of nonyl and decyl derivatives the stable modification (C_I) is monotropic nematic whereas the metastable solidmodification (C_{II}) exhibits enantiotropic nematic mesomorphism. The situation can be represented diagramatically as under :



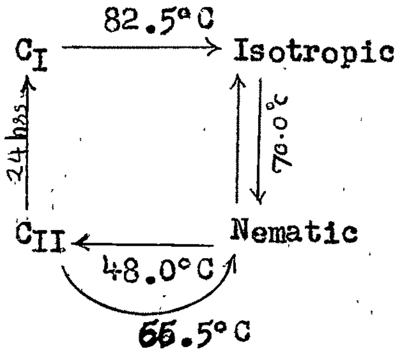
Ethyl derivative



Pentyl derivative



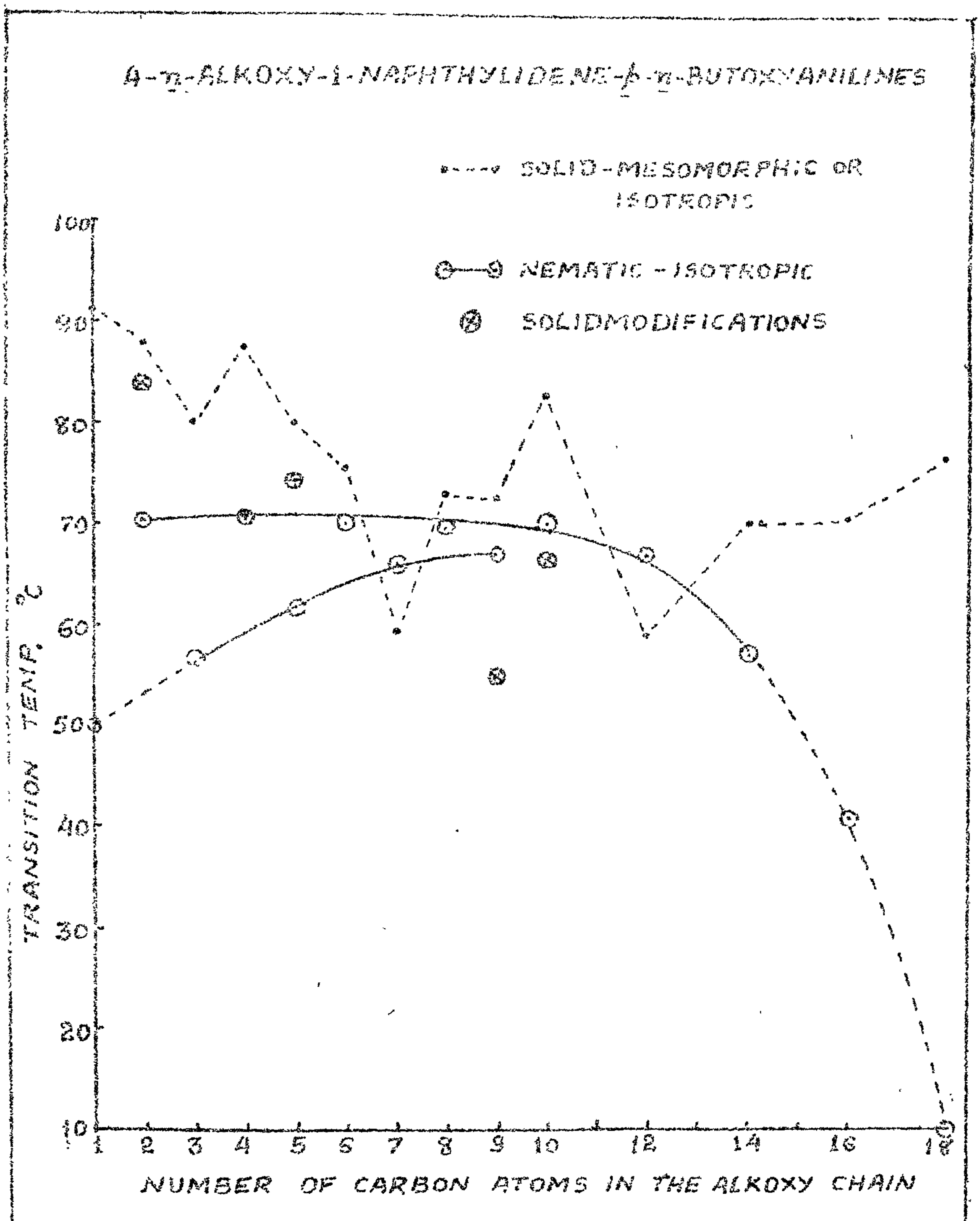
Nonyl derivative



Decyl derivative

Such examples of having more than one solid-modification are observed in a number of cholesteric compounds (125) and in aliphatic esters of cinnamic and α-methylcinnamicacid Schiff's base compounds (167). Dave and Vora have also reported the same type of behaviour in cholesteryl trans-p-methoxy-α-methyl cinnamate (168). When the transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, the nematic-isotropic transitions lie on two falling curves showing the odd-even effect (Fig. 6.). The even members occupying the upper curve as usual and shows the descending tendency as the chain length increases while the curve for the odd numbers exhibit an ascending tendency.

The higher melting points of methoxy derivative may be the reason for not exhibiting the mesophase. In the case of heptyl and dodecyl derivatives the enantiotropic mesophases are observed. This may be due to their low melting points. All other members exhibit monotropic behaviour. This is due to their melting points which are comparatively higher than heptyl and dodecyl derivatives. Hexadecyl and octadecyl derivatives have higher melting points and as discussed earlier the lateral and end to end cohesive forces would be much weaker in last two derivatives of the present system, which render these compounds non-mesogenic. The obscure nematic-isotropic transition temperatures for methyl, hexadecyl and octadecyl derivatives are obtained by the extrapolation of the nematic-isotropic transition temperature curves.


4-n-ALKOXY-1-NAPHTHYLIDENE-p-n-BUTOXYANILINES
SOLID-MESOMORPHIC OR ISOTROPIC
NEMATIC - ISOTROPIC
SOLIDMODIFICATIONS
TRANSITION TEMP. °C
100
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NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 6.

3. 4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-amyloxyanilines

Fourteen Schiff base compounds of the series 4-*n*-alkoxy-1-naphthylidene-*p*-*n*-amyloxyanilines are obtained by condensing 4-*n*-alkoxy-1-naphthaldehydes with *p*-*n*-amyloxy anilines. Their transition temperatures are summarized in Table 6.

In this series methyl, propyl, pentyl, hexadecyl and octadecyl homologues are non-mesomorphic. Butyl, nonyl, dodecyl and tetradecyl derivatives are enantiotropic nematic while others are monotropic in nature. Smectic mesophase is absent in the series. Ethyl and propyl derivatives exhibit two solid modifications, one is the stable modification (C_I) which has the higher transition temperature. The metastable solid form (C_{II}) is obtained by rapid cooling of the isotropic liquid phase. In the case of ethyl derivative both the solid forms give a monotropic nematic mesophase while in the case of propyl derivative both the forms are non-mesomorphic. These type of transitions have been discussed earlier in 4-*n*-alkoxy-1-naphthylidene-*p*-*n*-butoxyanilines series. The situation can be represented diagramatically as under :

$$\begin{tikzcd}
C_I \arrow[r, "81.5^\circ C"] & \text{Isotropic} \arrow[d, shift left, "61.5^\circ C"] \\
C_{II} \arrow[u, "24\ hrs"] \arrow[ur, "74.5^\circ C"] & \text{Nematic} \arrow[l, "55.5^\circ C"] \arrow[u, shift left]
\end{tikzcd}$$

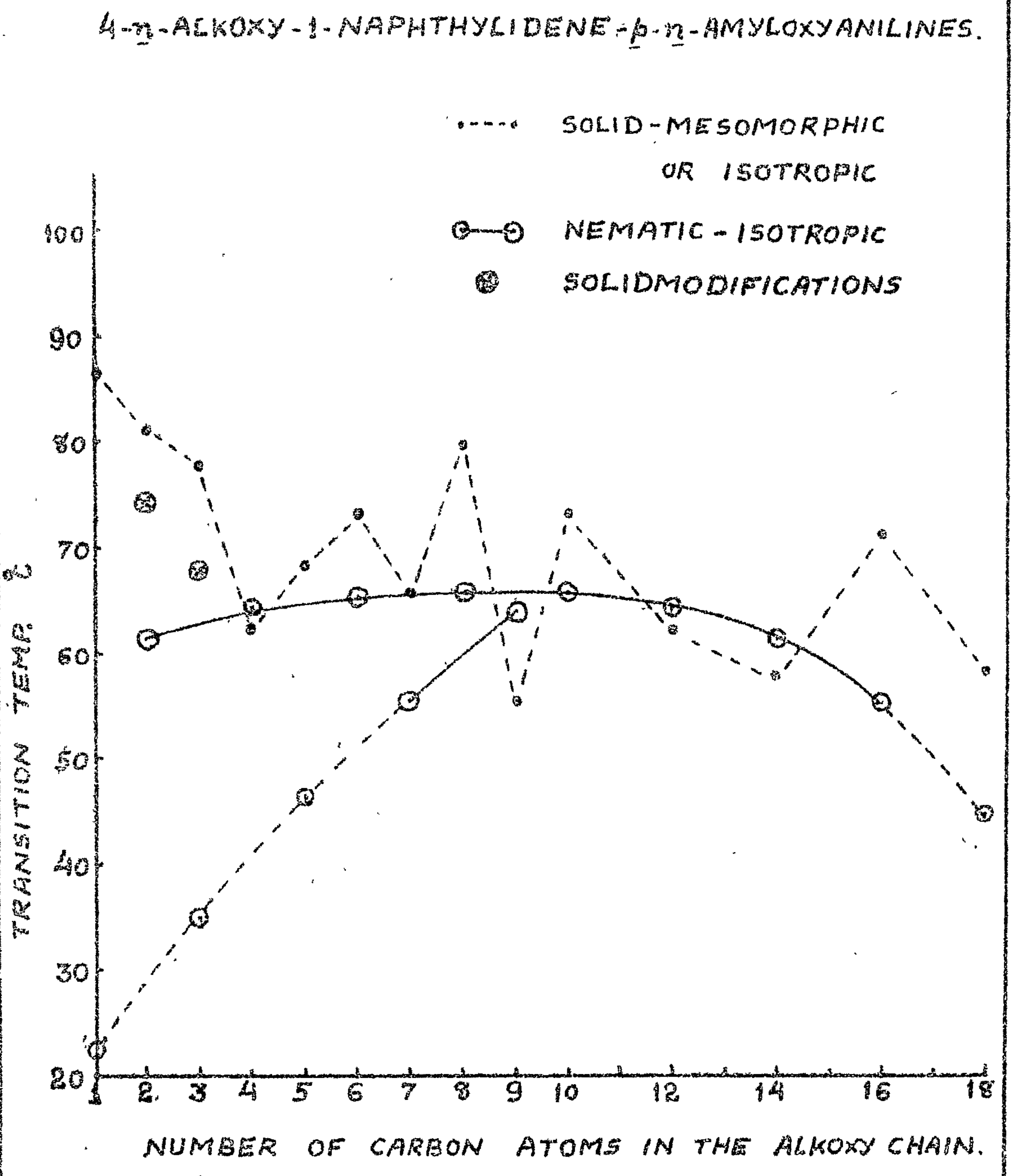
Ethyl derivative

$$\begin{tikzcd}
C_I \arrow[r, "78.0^\circ C"] & \text{Isotropic} \arrow[dl, shift right, "58.0^\circ C"'] \\
C_{II} \arrow[u, "24\ hrs"] \arrow[ur, shift right, "68.0^\circ C"'] &
\end{tikzcd}$$

Propyl derivative

When the transition temperatures are plotted against the number of carbon atoms in the alkoxy chain the nematic-isotropic transitions lie on two falling curves showing the usual odd-even effect from the hexyl member only (Fig. 7.). The odd-even effect for nematic-isotropic transition could not be observed as methyl, propyl and pentyl derivatives are non mesogenic. The obscure transition temperatures of these members obtained by extrapolation of the nematic-isotropic transition temperature curve are quite low. The extrapolated curve actually suggests that there is marked odd-even effect even in the initial members and therefore methyl, propyl and pentyl members are non-mesogenic. The obscure transition temperatures of these compounds are very low so they could not be supercooled upto these temperatures. Some of the members of this series are monotropic nematic and other are enantiotropic nematic. This depends on a number of factors and such behaviour is already discussed in the previous series. When lateral and end to end cohesive forces are weak, small alternation in crystal lattices or in supercooling tendency play their important role. All the naphthalene series discussed here have low lateral and end to end cohesive forces due to the decreased length to breadth ratio.

The non-mesomorphic tendencies of the last two members are similar to other two series discussed earlier.


4-n-ALKOXY-1-NAPHTHYLIDENE-p-n-AMYLOXYANILINES.
SOLID-MESOMORPHIC OR ISOTROPIC
NEMATIC - ISOTROPIC
SOLIDMODIFICATIONS
TRANSITION TEMP. °C
100
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NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN.

FIG. 7.

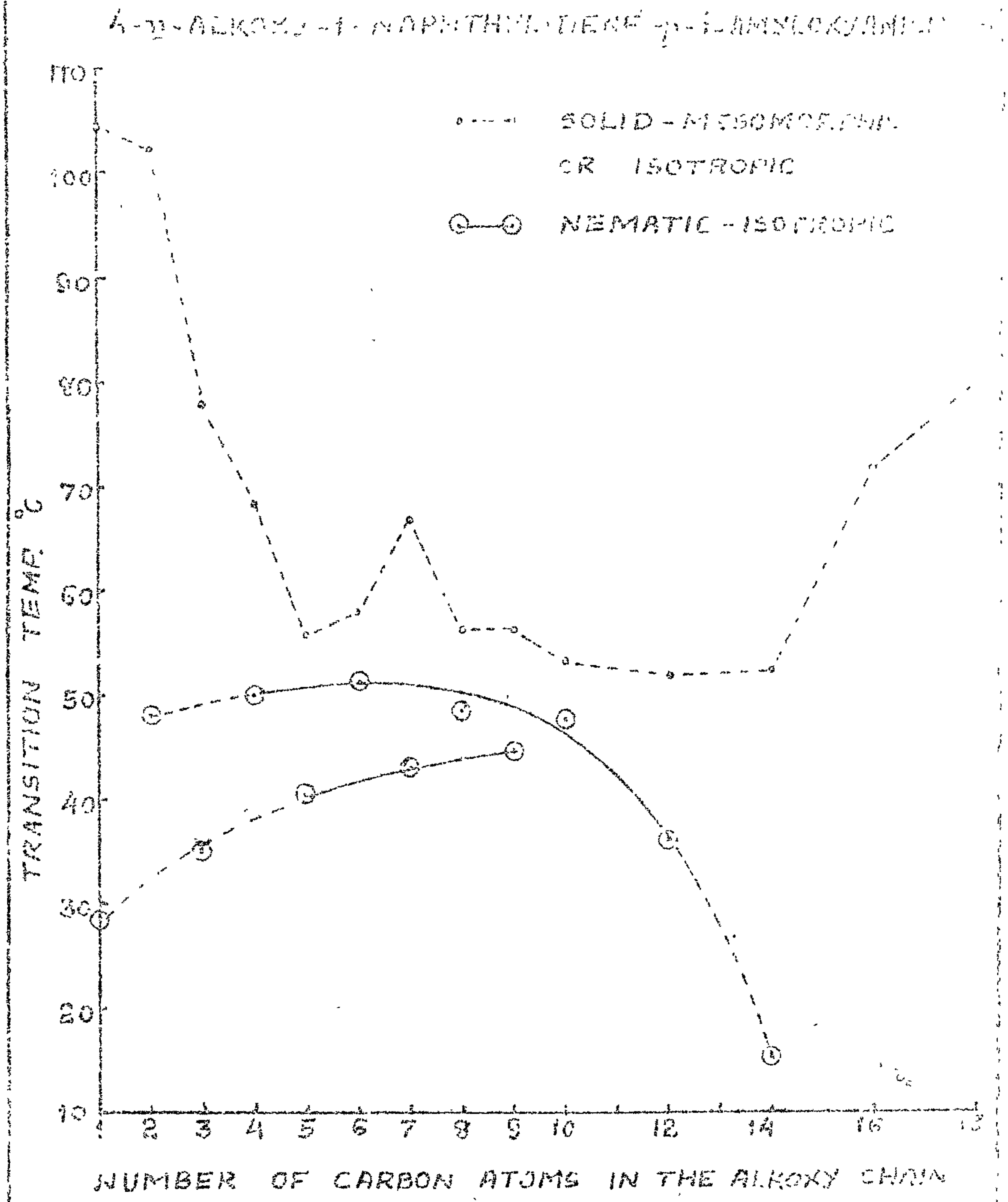
The molecular attractive forces weaken in such a way that they directly melt to isotropic liquid.

4. 4-n-Alkoxy-1-naphthylidene-p-i-amyloxyanilines

Fourteen Schiff base compounds of the series 4-n-alkoxy-1-naphthylidene-p-i-amyloxyanilines are obtained by condensing 4-n-alkoxy-1-naphthaldehydes with p-i-amyloxyaniline. Their transition temperatures are summarized in Table 7.

All the members of the series exhibit monotropic nematic mesomorphism except the methyl, ethyl, propyl, tetradecyl, hexadecyl and octadecyl derivatives which are non-mesomorphic. Smectic phase is absent in this series also. When the transition temperatures are plotted against the number of carbon atoms in the alkoxy chain the nematic-isotropic transitions show usual odd-even effect from the butyl member only (Fig. 8.). The absence of the odd-even effect in the initial members is because the methyl, ethyl and propyl derivatives are non-mesomorphic. The transition temperature curve for the even members rises to a maximum at the hexyl derivative and then levels off, whereas the transition temperature curve for odd members show an ascending tendency.

The first three members are non-mesomorphic. Structurally they should be expected to show mesomorphism but their melting points are high and when these temperatures


4-n-ALKOXY-1-NAPHTHYLIDENE-p-i-AMYLOXYANILINE
SOLID - MESOMORPHIC
OR ISOTROPIC
NEMATIC - ISOTROPIC
TRANSITION TEMP. °C
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NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 8.

are reached the thermal vibrations will be too great to allow an ordered arrangement of the molecules to persist and the compounds directly pass to the disordered isotropic liquid. These members even do not supercool enough to give a monotropic mesophase. In the case of butyl to dodecyl derivatives the compounds are having comparatively low melting points and their molecules possess the basic requirements for mesomorphism ; hence eventhough they melt to give an isotropic liquid, on cooling they give monotropic mesomorphism. In the case of hexadecyl and octadecyl derivatives the melting points are again increased and the isotropic liquid of these compounds do not supercool sufficiently to form the mesophase and hence they are non-mesomorphic. The obscure nematic-isotropic transition temperatures for the non-mesogenic derivatives are obtained by the extrapolation of the nematic-isotropic transition temperature curve ; however no such values could be obtained for C_{16} and C_{18} derivatives as the transition curve tends to bend sharply.

Common features of Series 1, 2, 3 and 4

All the four series have comparatively low melting points. Though most of the mesogenic compounds are monotropic in nature, some members are enantiotropic mesomorphic also. The number of compounds exhibiting enantiotropic mesophase goes on increasing as the alkyl chain length increases. In the case of series 4-n-alkoxy-

1-naphthylidene-p-n-butoxyanilines and pentyloxy anilines some of the compounds exhibit polymorphism i.e. they have two solid modifications. The careful scrutiny of these compounds could only reveal these polymorphic properties. In all the four series first few members are non-mesogenic, middle members are mesogenic (monotropic or enantiotropic) and the last members are again non-mesogenic. This behaviour suggests that these series are less mesogenic in nature. All the four series are purely nematic, the smectic mesophase is not observed even in the last members of the series. The nematic-isotropic transition temperature curves (Fig. 5-8.) in all the series exhibit odd-even effect, the even members always occupying the upper curve. It is interesting to note that both the curves exhibit ascending tendency and the nematic-isotropic transition curves for even members show a maximum. Generally the nematic-isotropic transition temperature curve in a normal homologous series falls smoothly with increase in the alkyl chain length. An ascending nematic-isotropic transition temperature tendency is also observed in other homologous series (169 - 175). Gray (171) attributed this type of behaviour found in laterally substituted biphenyl Schiff's bases to a decrease in the ratio of lateral to terminal interactions due to steric hindrance as found in these broadened molecules. Dietrich and Steiger (170) and Dave and Vora (166) attributed this phenomenon in the series

N(p-n-alkoxybenzylidene)-p'-n-alkylanilines and p(p'-n-alkoxybenzoyloxy)toluenes to their low intermolecular forces. This is indicated by their low transition points which are expected due to absence of strong permanent dipoles and shortness of the alkyl chains.

The mesogenic homologous series of the type N(p-n-alkoxybenzylidene)-p'-aminoacetophenone (173,174, 176) and propiophenones (177) also exhibit ascending tendency. These series possess a terminal carbonyl group conjugated with an aromatic system. Castellano et al., (174) have suggested that the acetyl group produces strong terminal attractions and this would result in a low ratio of lateral to terminal cohesions.

All the four series reported here possess broad naphthalene nucleus which would decrease the ratio of lateral to terminal interactions due to the steric hindrance. This suggests that the factors which operate in the substituted biphenyl series studied by Gray, also operates in naphthalene Schiff bases reported in the present series. This explains the ascending tendency of both the curves. The levelling off in the nematic-isotropic transition temperature curves in the case of even members can be attributed to the weakening of the terminal attractions, which begin to play their part in determining the temperature of the nematic-isotropic transition as the series is ascended. The molecules, forming liquid crystals usually consist of relatively rigid aromatic or alicyclic 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 (178). For the mesogenic homologous series Gray (179, 180) 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 attractions are overcome thus a nematic or cholesteric phase is formed. The molecules in the nematic or cholesteric melt are 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. 9.).

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 (74) 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 (74) and Maier and Baumgartner (181) 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. The lower homologues

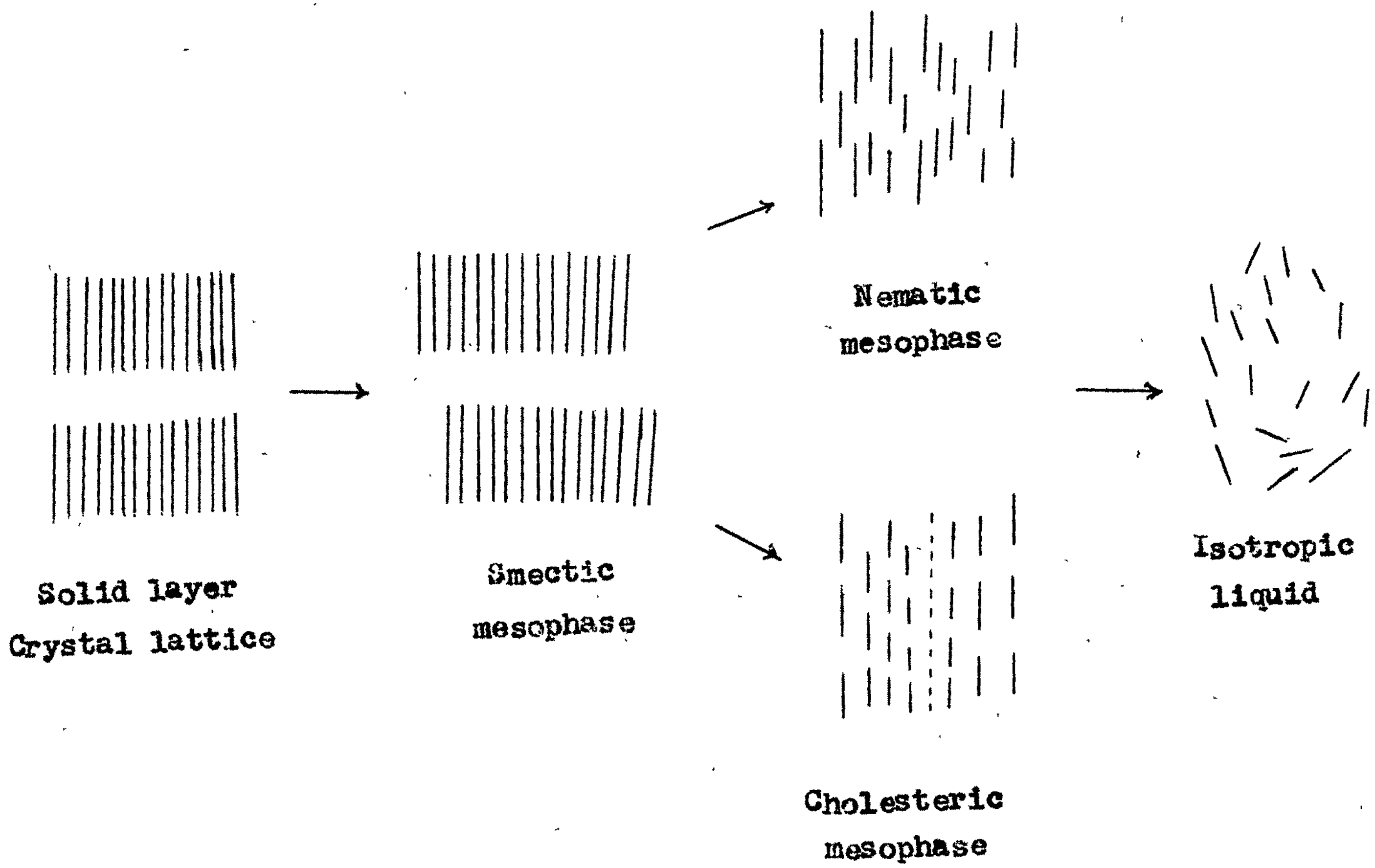

Solid layer
Crystal lattice
Smectic
mesophase
Nematic
mesophase
Cholesteric
mesophase
Isotropic
liquid

Fig. 9.

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 often 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 inter molecular 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. This type of behaviour has been reported by Gray et al., (182) for the series *p*-*n*-alkoxy-benzylidene aminofluorenones and 4-*p*-*n*-alkoxy-benzylideneaminobiphenyls having substitution in 2 or 3 position. Arora et al., (183) 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 weaking 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., (158 - 160) recently studied a number of naphthylidene Schiff bases and evaluated the effect of broad naphthalene nucleus. They have observed that in all these series even the last members are not purely smectic but exhibit a nematic phase in addition to the smectic 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 so arranged that on heating, the molecular layers slide over one another and do not get disrupted to the diordered 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 (74,163,184,185). 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 do not take place to give a smectic mesophase. The homologous series 4-n-alkoxy-1-naphthylidene-4'-amino-4"-methoxyazobenzene (185) and 4-n-alkoxy-1-naphthylidene-p-phenetidines (185) comprise of a naphthalene moiety and the mesogenic behaviour is similar to the present homologous series.

The 2,3 bridge substituent in the case of present series having a naphthalene moiety compared to benzene moiety would definitely increase the breadth of the molecule which in turn decrease the lateral cohesive forces. Forgoing discussion explains the general mesogenic behaviour but it does not explain the regular alternation in nematic-isotropic transition temperatures for odd and even members of carbon atoms.

Gray (179) has tried to explain such behaviour for nematic-isotropic transitions 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 :-

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

(2) The overall polarizability increases 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 forces apart polarizable centres in the molecules and decreases the residual terminal attractions.

Effect (1) and (2) would increase the nematic-isotropic transition temperatures and (3) and (4) would decrease the nematic-isotropic transition temperatures. Thus rising transition lines are obtained where the effects (1) and (2) predominate and vice versa. In keeping with this view the rising transition lines are found in series in which the transition temperatures are low and when the residual interactions are weak. Gray has explained 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 <u>n</u>-alkyl aryl ethers, such as the <u>p</u>-<u>n</u>-alkoxybenzoic acids. For short alkyl chains, if the chain extends strictly along its own axis (dotted line in Fig. 10.), 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 effect the energy of the system and account for an alternation of the transition temperatures.

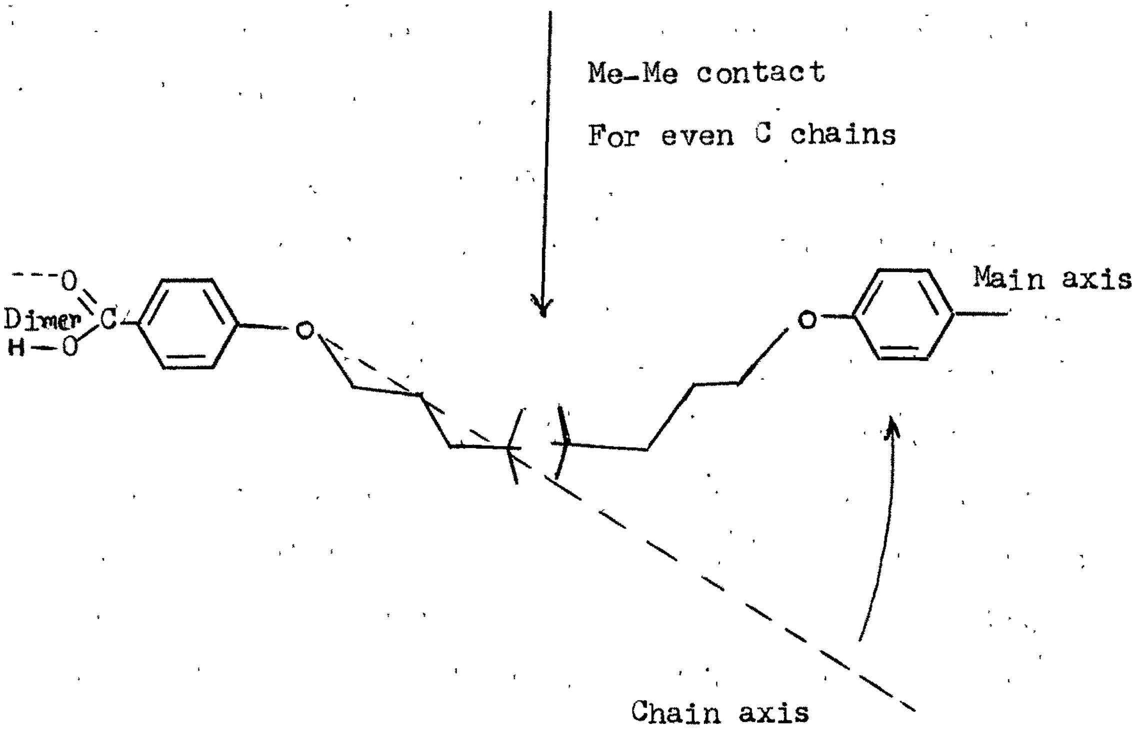


Fig. 10.

With the higher homologues the alkyl chain may be forced (curved arrow in figure 10.) 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 lateral interactions between the molecules, which would also play some role in determining the thermal stability of the nematic mesophase, has not been discussed.

Maier (186) and Maier and Baumgartner (181) also have tried to explain the alternation effect on the basis of their study of the dipole moment and dielectric anisotropies of a nematogenic homologous series.

Marcelja's (178) 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 unnoticeable. Pines et al., (187) 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 KH_z for the whole series throughout the nematic ranges.

Recently De Jeu and Van der Veen (188) 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.

There is a close relationship between mesomorphism and molecular constitution of organic compounds. Therefore, the thermal stability which is measure of mesomorphism can be correlated with the molecular constitution of the compounds. Table 24 summarizes the average nematic thermal stabilities of different mesogenic homologous series, viz.,

1. 4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-propoxyanilines A
2. 4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-butoxyanilines B
3. 4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-amyloxyanilines C
4. 4-*n*-Alkoxy-1-naphthylidene-*p*-*i*-amyloxyanilines D

and are compared with those of

5. *p*-*n*-Alkoxybenzylidene-*p*-phenetidines (189) E
6. *p*-*n*-Alkoxybenzylidene-*p*-*n*-propoxyanilines (164) F
7. *p*-*n*-Alkoxybenzylidene-*p*-*n*-butoxyanilines (164) G
8. *p*-*n*-Alkoxybenzylidene-*p*-*n*-amyloxyanilines (164) H
9. 4-*n*-Alkoxy-1-naphthylidene-*p*-phenetidines (185) I

The geometry of these series is given in Fig. 11.

Table 24

Average thermal stabilities in °C

Series	A	B	C	D	E	F	G	H	I
Nematic-Isotropic C_6-C_{10}, C_{12}	58.9 (C_6, C_9, C_{10}, C_{12})	68.3	63.6	45.2	118.6 (C_6-C_9)	107.2	114.5	112.3	71.8
Commencement of the smectic mesophase	-	-	-	-	C_9	C_9	C_8	C_7	-

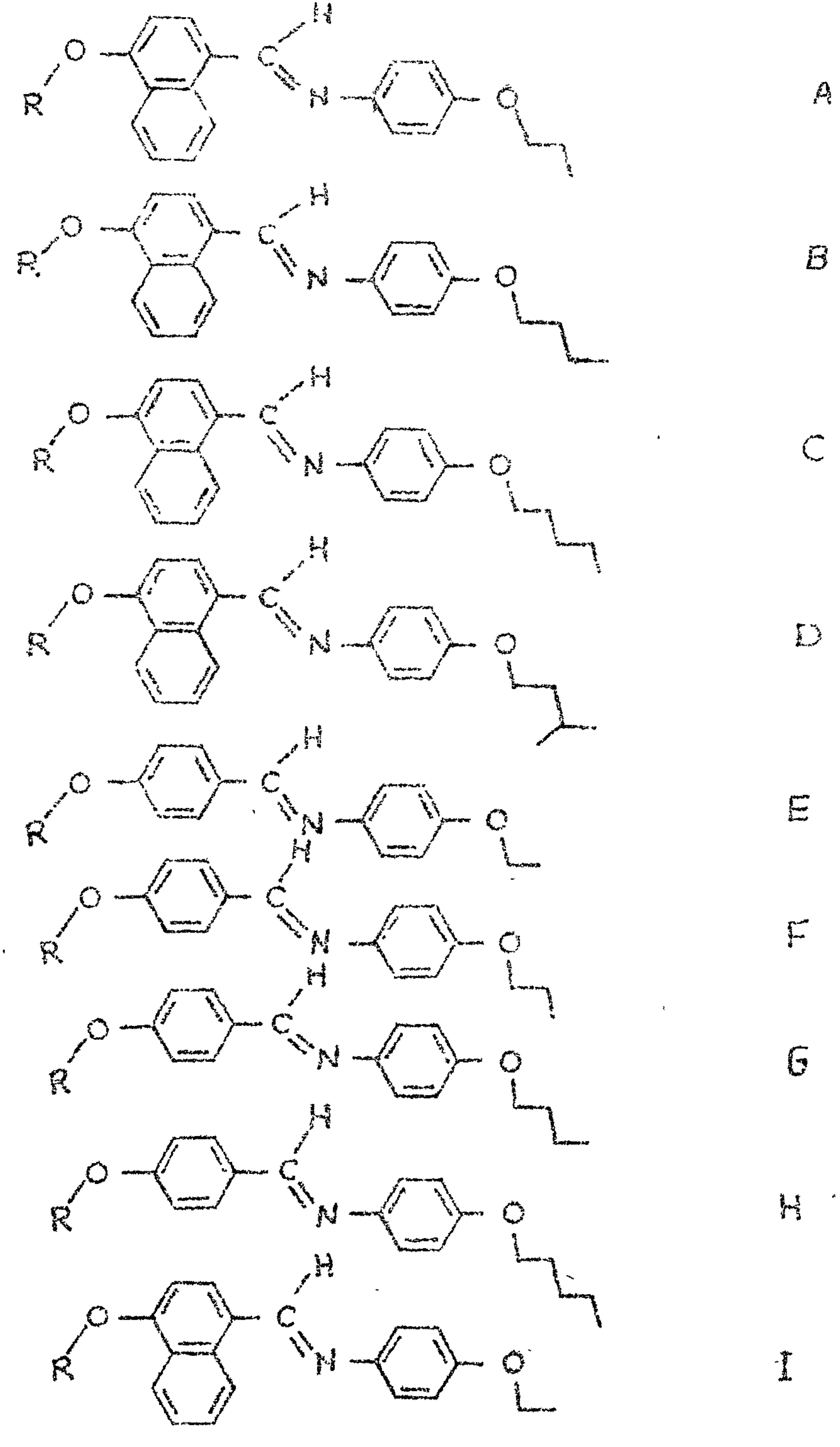


FIG. 11.

It can be seen from the table that the average nematic thermal stabilities of series A, B, C and D are less than those of series E, F, G and H. Series A to D and series E to H are almost similar except that in the case of series A to D the end phenelene groups are replaced by 1,4 substituted naphthalene unit.

A 1,4-substituted naphthalene nucleus can be considered as a bridge side substituent on the benzene ring at the 2,3-positions. Introduction of a substituent into the side position in the molecule of a mesomorphic compound has two opposing effects (179) :

(1) The substituent will decreases both the smectic and nematic thermal stabilities by increasing the separation of the long axes of the molecules, and

(2) the substituent will increase both the 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 the naphthalene nuclei in the molecules of series A, B, C and D increase the breadth as well as the polarizability of the molecules. The first effect predominates and overcomes the second effect which is evident from the lower thermal stabilities of all these series compared to those of series E to H.

An interesting correlation is found in the decrease of nematic thermal stabilities which is as under :-

Average nematic thermal stabilities of series

F - A = 48.6
G - B = 46.2
H - C = 48.7
E - I = 46.8

It can be seen that the difference in decrease is almost the same. This suggest that even in the case of homologous series having naphthalene moiety the increment of each methylene unit has the same effect on mesophase as in the case of p-phenelene derivatives.

Series I has an ethoxy end group whereas from series A to C there is an addition of methylene unit. It is discussed earlier that in a mesogenic homologous series the nematic-isotropic transition temperatures alternates as the alkyl chain length increases. Similarly if we extend same argument regarding the conformations of alkoxy chain than the average transition temperatures of series I, A, B and C should exhibit alternation. This is actually the case. The plot of average nematic-isotropic transition temperatures of series I, A, B and C against the increase in the alkoxychain (one side) does exhibit alternation (Fig. 12.) i.e. odd-even effect. In keeping with the earlier explanation odd-even effect goes on from ethoxy to amyloxy derivatives. Similar behaviour is also observed in the case of series E to H (Fig. 12.) reported by Weygand et al., (189) and Dave and Patel (164).

As mentioned earlier all the four series (A to D) are purely nematic whereas series E to H exhibit smectic mesophase along with nematic phase and the last members are purely smectic. From a study of a number of mesomorphic homologous series exhibiting smectic and nematic mesophases Gray (74) concluded that the increase in the breadth of the molecules reduces both nematic and smectic thermal stabilities but the effect is more pronounced on the smectic mesophase. 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 are ultimately dependent on the geometry, dipole moment and overall polarizability of the molecules. Gray (127) 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

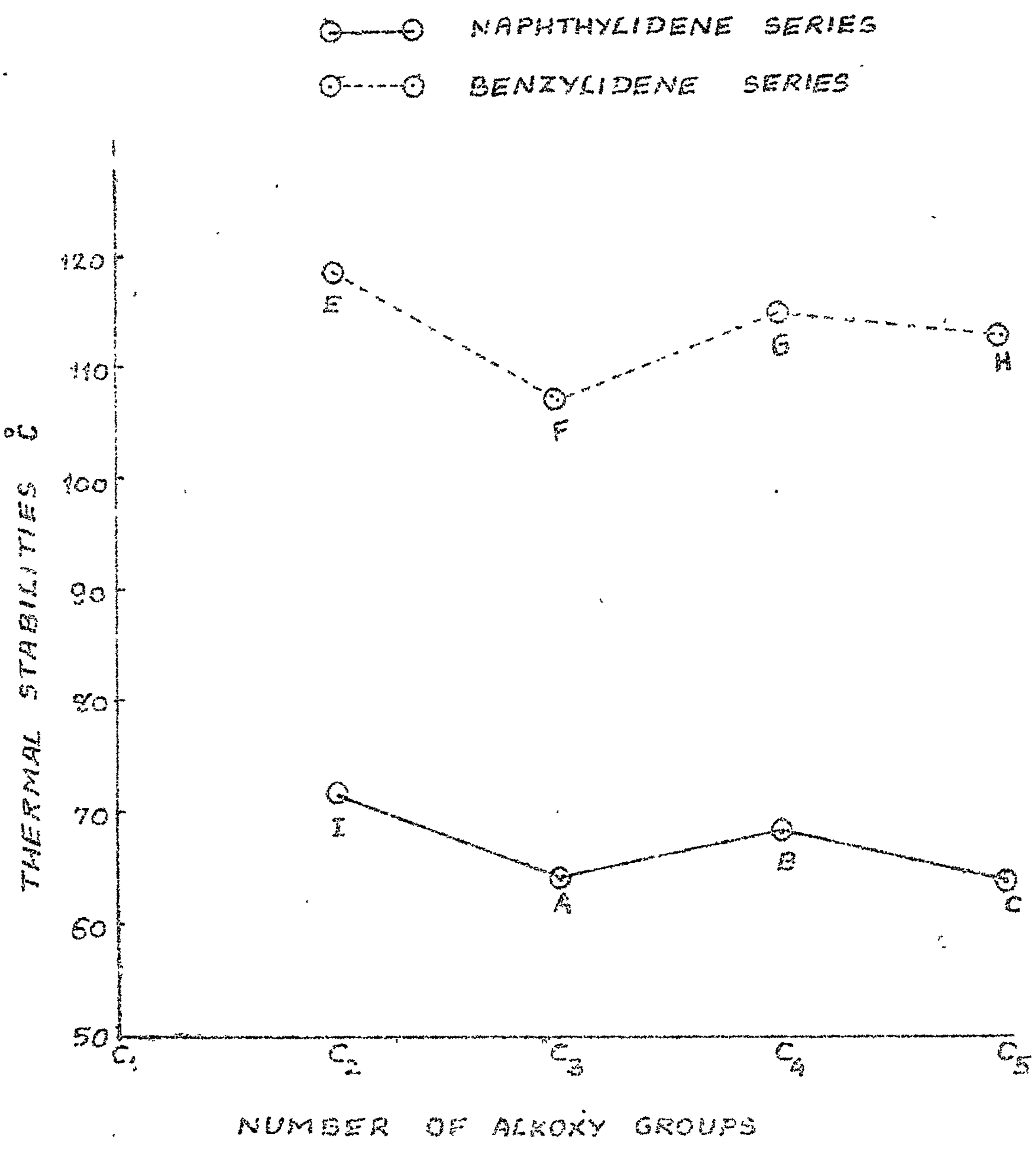

NAPHTHYLIDENE SERIES
BENZYLIDENE SERIES
THERMAL STABILITIES °C
120
110
100
90
80
70
60
50
E
F
G
H
I
A
B
C
C1
C2
C3
C4
C5
NUMBER OF ALKOXY GROUPS

FIG. 12.

the search for certain series where the appearance of smectic mesophase might be delayed so that low melting purely nematic or cholesteric substances could be obtained. A survey of homologous series and the points of commencement of smectic mesophase 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, i.e. it appears at C_{16} or C_{18} derivative. In the case of 4,4'-di-p-n-alkoxybenzylideneaminobiphenyls (182) 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 then the smectic mesophase can be eliminated from the homologous series. This explains the purely nematic nature of the series A to D. The molecules are short and have broad naphthalene nucleus, hence the increase in breadth is more pronounced i.e. length to breadth ratio is much lowered.

The average nematic-thermal stabilities of series D are lowest compared to series A, B and C. This is probably due to the branched iso-amyloxy group. Branching on the carbon atoms in the alkyl chain increase the breadth and causes steric hindrance which does not help the close packing of the molecules and in turn decrease the thermal stabilities. In the case of series A, B and C the effect of odd and even carbon is observed on thermal stabilities as discussed earlier and hence series A having propoxy group has lower thermal stabilities than those of series B having butoxy group which is again higher than those of series C having amyloxy group. The series I is similar in structure to present series. The short chain ethoxy group explains the higher thermal stabilities of series I. The group efficiency order obtained for the nematic thermal stabilities in the present study is as under :-

$$\underline{n}\text{-}OC_4H_9 > \underline{n}\text{-}OC_5H_{11} > \underline{n}\text{-}OC_3H_7 > \underline{i}\text{-}OC_5H_{11}$$

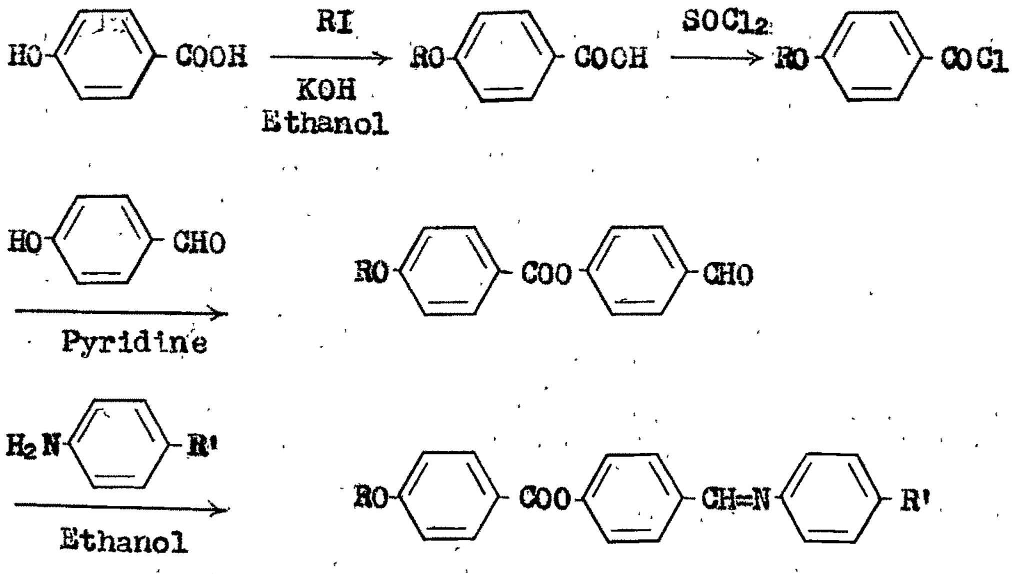
This order is similar to the one obtained for nematic phase by Dave and Patel (164). The tendency of these groups to give this type of the order is already discussed earlier.

B. p-PHENYLENE DERIVATIVES HAVING ESTER AND AZOMETHINE LINKAGES

I. Nematogenic Homologous Series

B. p-Phenylene derivatives having ester and azomethine linkages

Number of homologous series are known having either an ester or an azomethine linkages (70,164,167, 190). However, there are very few homologous series reported having both these groups in a single molecule (191,81). It would be quite interesting to study the effect of different end groups in such unsymmetrical molecular geometry. With this in view following six homologous series each having fourteen members were prepared by the following synthetic route and their mesomorphic properties studied.



R = n-alkyl (C_1 to C_{10}, C_{12}, C_{14}, C_{16} and C_{18})

R' = (5) $-C_2H_5$ (6) $-OC_2H_5$ (7) n-C_4H_9

(8) n-OC_4H_9 (9) $-CN$ (10) $-NO_2$

I. Nematogenic homologous series

5. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethylanilines
6. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethoxyanilines
7. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butylanilines
8. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butoxyanilines

II. Smectogenic homologous series

9. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-cyanoanilines
10. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-nitroanilines

I. Nematogenic homologous series

5. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethylanilines

The transition temperatures are summarized in Table 8. The lower homologues of the series are purely nematic. The smectic phase appears at the hexyl derivative as a monotropic phase and the heptyl to octadecyl derivatives are enantiotropic smectic and nematic.

6. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-phenetidines

The transition temperatures are summarized in Table 9. The lower homologues of the series are purely nematic. The smectic phase appears at the decyl derivative and persists up to the octadecyl derivative as an enantiotropic mesophase along with the nematic phase.

7. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butylanilines

The transition temperatures are summarized in Table 10. The lower homologues of the series are purely nematic. The smectic phase appears at the hexyl derivative and persists upto octadecyl derivative as an enantiotropic mesophase along with the nematic phase.

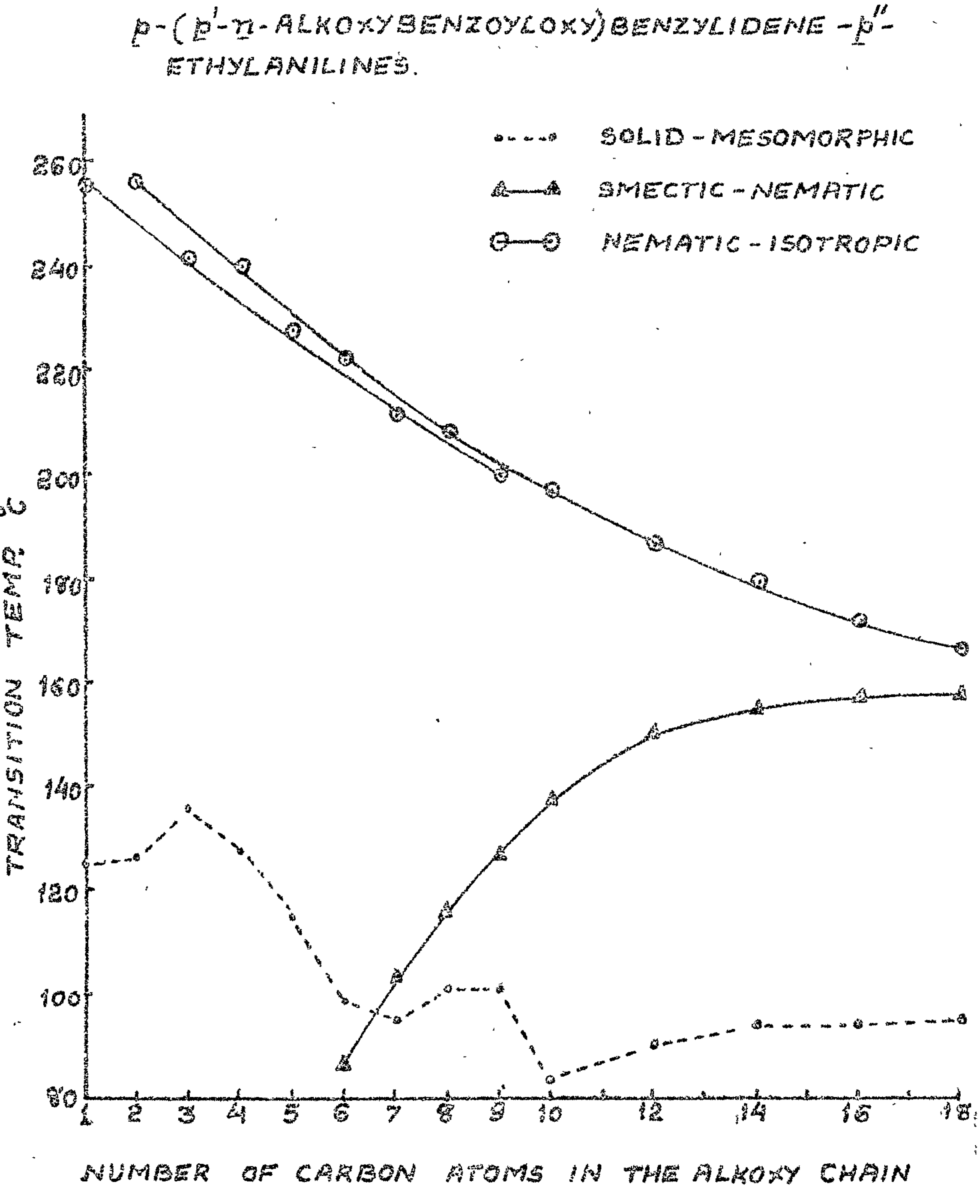
8. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butoxyanilines

The transition temperatures are summarized in Table 11. The lower homologues of the series are purely nematic. The smectic phase appears at the heptyl derivative and persists upto octadecyl derivative as an enantiotropic mesophase along with the nematic phase.

Common features of series 5, 6, 7 and 8

All the four series exhibit nematogenic behaviour, i.e. first few members are purely nematic and the smectic mesophase commences in the middle members. These series differ from normal nematogenic homologous series by exhibiting smectic and nematic mesophases in the last members. All these series have large mesophase ranges.

When the transition temperatures are plotted against the number of carbon atoms in the alkoxy chain (Fig. 13,14,15 and 16.) the nematic-isotropic transition temperatures exhibit alternations for odd and even members.



p-(p'-n-ALKOXYBENZOYLOXY)BENZYLIDENE -p''-ETHYLANILINES.

FIG. 13.

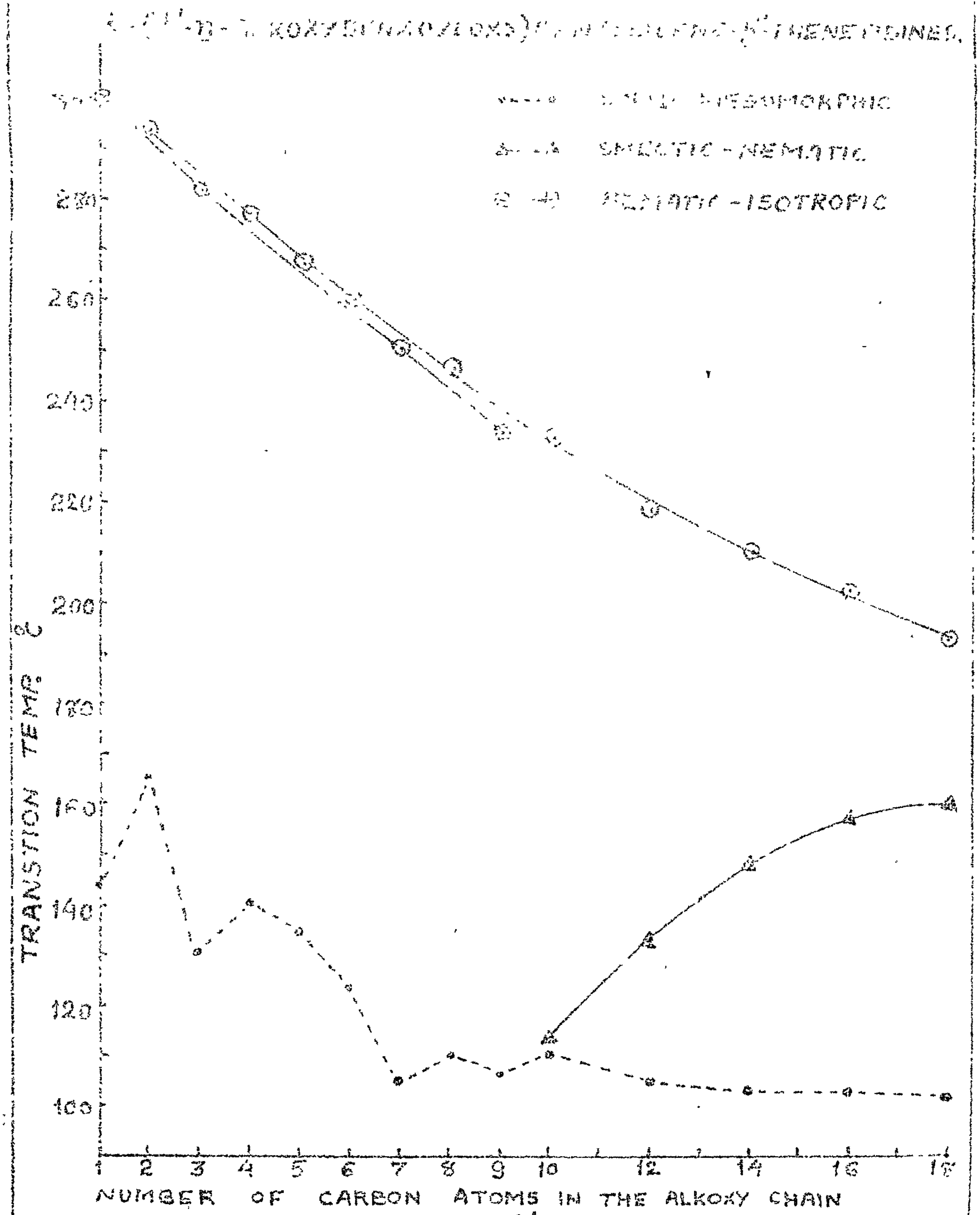

4-(4'-n-ALKOXYBENZOYLOXY)BENZYLIDENE-4'-PHENETIDINES.
SOLID-MESOMORPHIC
SMECTIC-NEMATIC
NEMATIC-ISOTROPIC
TRANSITION TEMP. °C
300
280
260
240
220
200
180
160
140
120
100
1
2
3
4
5
6
7
8
9
10
12
14
16
18
NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 14.

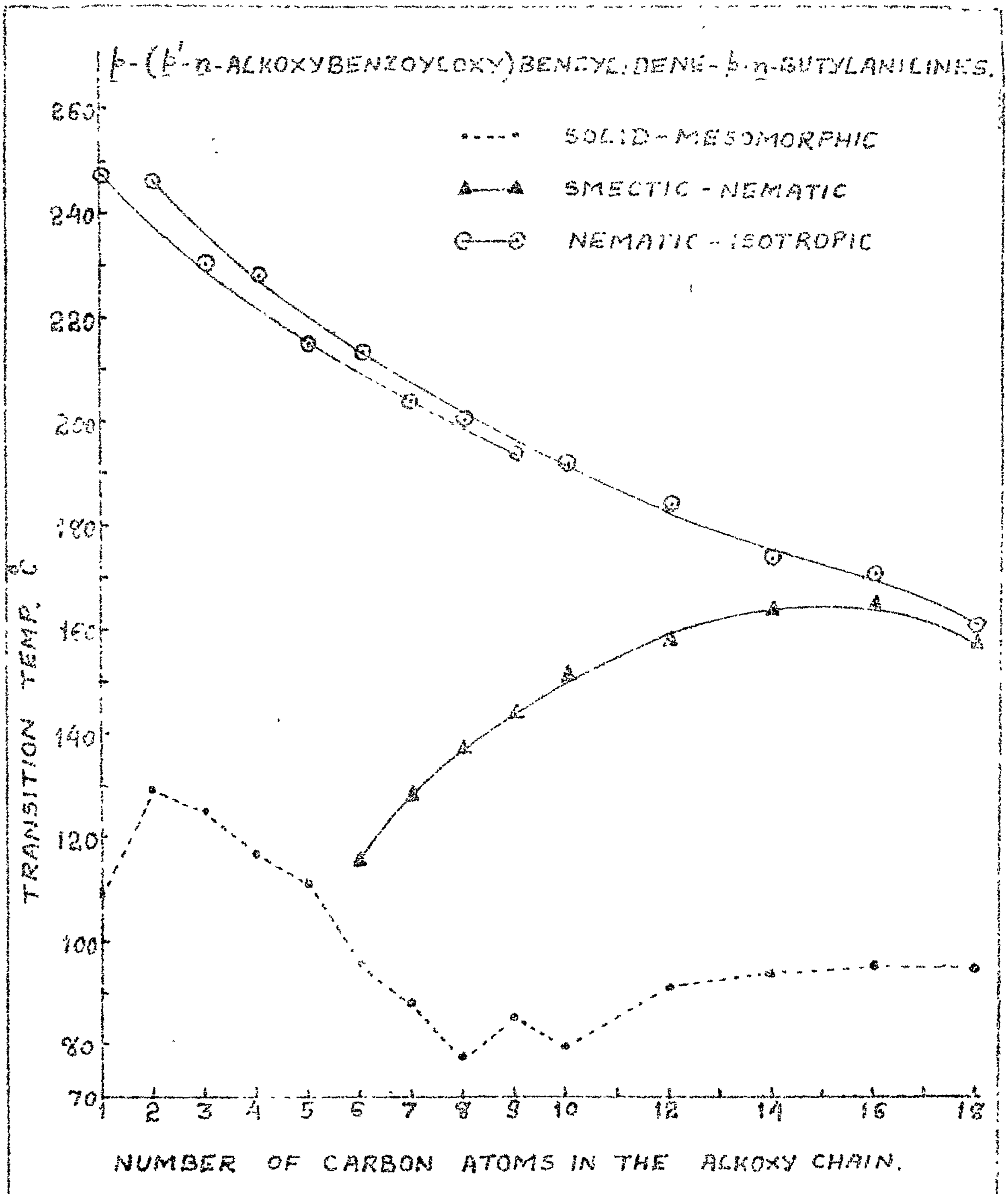

p-(p'-n-ALKOXYBENZOYLOXY)BENZYLIDENE-p-n-BUTYLANILINES.
SOLID - MESOMORPHIC
SMECTIC - NEMATIC
NEMATIC - ISOTROPIC
TRANSITION TEMP. °C
260
240
220
200
180
160
140
120
100
80
70
1
2
3
4
5
6
7
8
9
10
12
14
16
18
NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN.

FIG. 15.

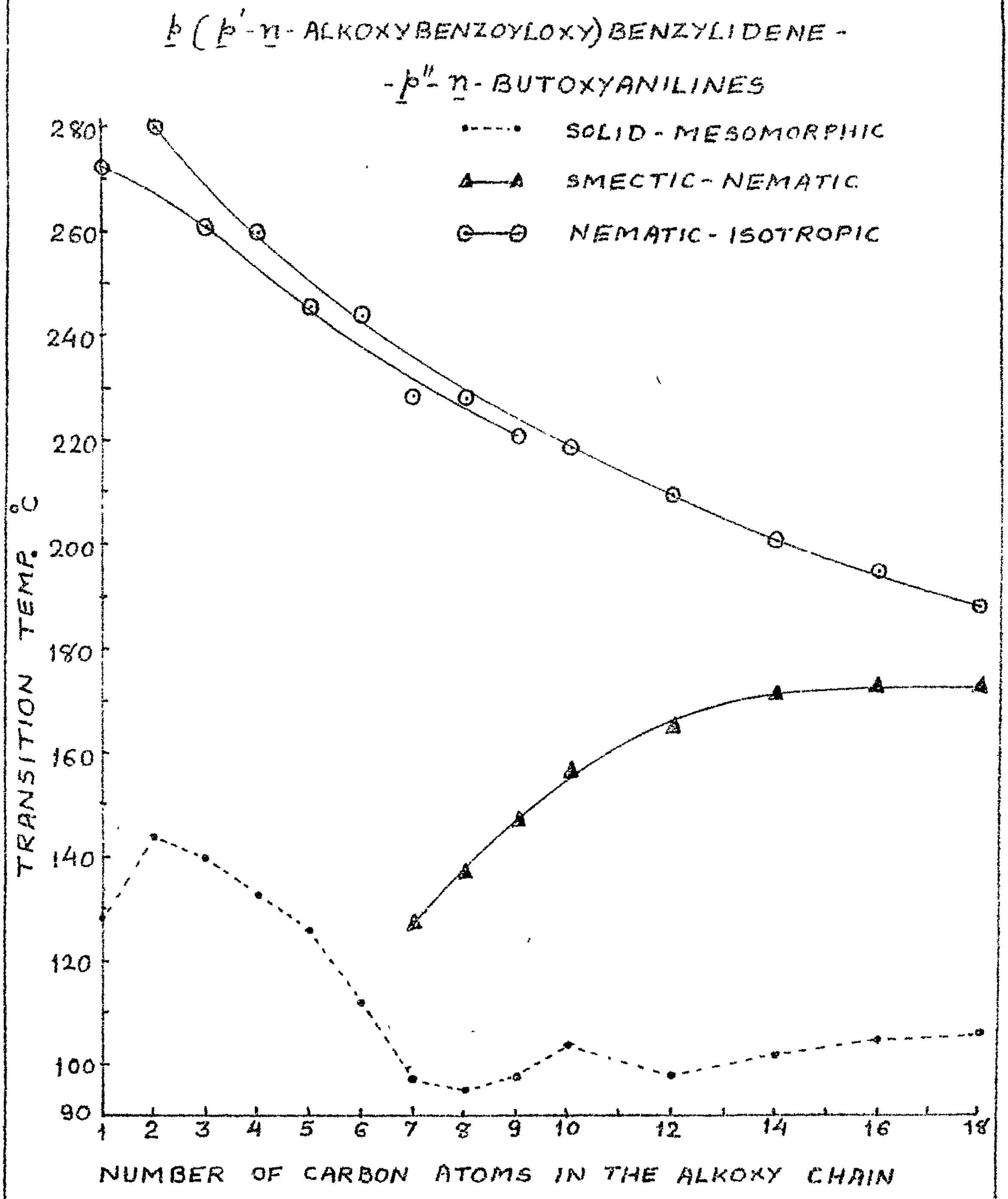

p (p'-n-ALKOXYBENZOYLOXY) BENZYLIDENE-
-p''-n-BUTOXYANILINES
SOLID - MESOMORPHIC
SMECTIC - NEMATIC
NEMATIC - ISOTROPIC
TRANSITION TEMP. °C
280
260
240
220
200
180
160
140
120
100
90
1
2
3
4
5
6
7
8
9
10
12
14
16
18
NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 16.

The even members occupy the upper curve as usual. The smectic-nematic transition temperature curve rises smoothly but do not merge with the falling nematic-isotropic transition temperature curve. However, in the case of series p(p'-n-Alkoxybenzoyloxy)benzylidene-p''-n-butylanilines the smectic-nematic transition temperature curve rises to the maximum and then levels off.

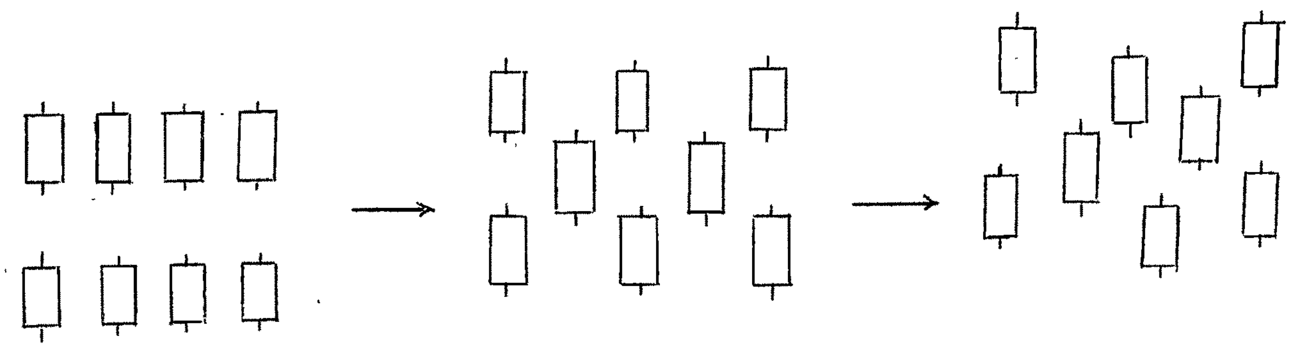
In all the cases the smectic mesophase exhibits focal conic texture, however many members of these homologous series exhibit homeotropic smectic mesophases. The type of the smectic mesophase is inferred as smectic A based on the focal conic texture.

The behaviour of the nematic-isotropic transition temperature curve is already discussed earlier. The nature of the smectic-isotropic transition and the different attractive forces operating in such mesophase are not discussed earlier as the previous four series were purely nematic. In series 5 to 8 the smectic mesophases are obtained and the smectic-nematic transition temperatures rise as series 5, 6, 7 and 8 are ascended and do not merge with the falling nematic-isotropic transition temperature curve.

The increase in the smectic-nematic transition temperatures with the increase in the alkyl chain can be explained by the overall increase in the polarizability of the molecules. This effect will increase the cohesive forces operating between the sides and planes of the molecules which are lying parallel to one another, with their ends in line, forming the smectic layers. Moreover increasing molecular weight tends to make it more difficult for the thermal vibrations to cause the sliding of the molecules out of the layers to give an imbricated orientation pattern of the nematic melt. It is rather difficult to comprehend the rising smectic-nematic transition temperature curve.

The intermolecular forces which operate between the ends of the molecules across the smectic strata are relatively weak since the layer 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 polarizable aromatic rings are represented by the ractangles 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. 17 (a).

As the chain lengthens,, the residual terminal



Smectic
(a)

Intermediate
(b)

Nematic
(c)

Fig. 17.

attractions become weaker and offer less resistance to interpenetration and 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. 17 (b) is formed where the ends of the molecules are still in line. As the temperature rises, the tendency for interpenetration of the chain grows, thus forcing apart the aromatic centres giving an imbricated nematic orientation to the melt as shown in Fig. 17 (c). The dislocation of the residual terminal intermolecular cohesions at the smectic-nematic transition is probably temporary. As the interpenetration of the layers becomes great and the normal imbricated arrangement of the molecules of the nematic melt is reached the ends of the molecules may once again become associated ; consequently the terminal interactions can again start to influence the thermal stability of the nematic melt as they do in purely nematic liquid crystals. As the alkyl chain lengthens, the increasing molecular mass and polarizability tend to increase the resistance to the gliding of the molecules from one stratum to another and also increase the tendency for interpenetration of the layers, thus causing the terminal attractions between them to become weaker. The role of these effects explains the shape of the smectic-nematic transition temperature curve and the levelling off of the curve and then the falling off.

Usually the smectic-nematic transition points lie on one smooth rising curve irrespective of odd or even members of the series. Gray (74), however, suggests that for many of the series it may not be easy to say conclusively that no alternation occurs, for, (a) smectic-nematic transitions do not occur for a sufficient number of the homologues and (b) when smectic-nematic transitions appears relatively early in the series the portion of the curve involving odd and even members of the series is rising steeply, such that the alternation would have to be very marked to be detectable. Gray and Harrison (167) have reported two nematogenic series wherein the smectic-nematic transitions clearly alternate to show an odd-even effect. Fishel and Patel (70), Patel (169) and Dietrich and Steiger (170) have also observed alternation of smectic-nematic transitions in the series studied by them. This behaviour of smectic-nematic transition curve may probably be due to the early origin of the smectic mesophase in the homologoues series. Dietrich and Steiger (170) argue that the determining factor for the course of transitions into the nematic mesophase and from the nematic mesophase into the isotropic phase should be the same. They attribute the regular alternation in the nematic-isotropic transitions found in many homologous series to the high cohesiveness of the molecules of these series due to close packing of the molecules for steric and polarity effects. Gray and Harrison (167) suggest that the understanding of the smectic-nematic transitions may be less easy to achieve and rather more speculative than might have been anticipated.

Forgoing discussion clearly suggests that it is rather difficult to understand smectic-nematic transitions and the different attractive forces playing their role. Generally in a normal nematogenic homologous series last members exhibit pure smectic mesophase. However as mentioned earlier, as this phenomenon differs in a number of cholesteric and nematogenic homologous series where steric factors operate. They exhibit both smectic and cholesteric or nematic mesophase even in the last member of the series.

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 the series having a naphthalene moiety or steric hindrance even the last members have such molecular arrangement that on heating, the layer slide over each other and do not give disruption to the disordered isotropic liquid. A nematic phase is thus obtained from the smectic phase and only on further heating is the isotropic liquid obtained. It is quite interesting that though series 5 to 8 do not possess any lateral substituent or a broad naphthalene moiety, the last members of all the series exhibit smectic-nematic transitions. It is rather difficult to explain this behaviour of the present homologous series. The molecules of all these series are unsymmetrical and acoplanar. Acoplanarity would increase the thickness and a fixed alkoxy or alkyl group at one end would not increase the residual lateral cohesive forces to the same extent as it would increase in the series where alkoxy group is present at both the ends of the molecule. These may probably be the reasons for comparatively weaker lateral cohesive forces so that the last members do not exhibit pure smectic mesophase.

The behaviour of the transition temperature curves of all the series have been explained and now will be discussed the chemical constitution and thermal stability behaviours of these series.

Table 25 summarizes the relative smectic and nematic thermal stabilities of the following present series.

1. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-ethylanilines A
2. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-phenetidines B
3. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-*n*-butylanilines C
4. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-*n*-butoxyanilines D

and are compared with those of

5. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-toluidines(191) E
6. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-anisidines(191) F
7. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-anilines (192) G
8. *p*(*p*'-*n*-Alkoxybenzoyloxy)benzylidene-*p*"-hydroxyanilines (81) H

The relative geometry of all the series are also drawn for the convenience to compare them (Fig. 18.). All the series have the same structural features except the end group on one side, which are different in all the series. As all these series have this feature a terminal group efficiency order for promoting smectic and nematic mesophases is obtained as under :-

Nematic : $OC_2H_5 > OCH_3 > \underline{n}\text{-}OC_4H_9 > CH_3 > OH = C_2H_5 > \underline{n}\text{-}C_4H_9 > H$

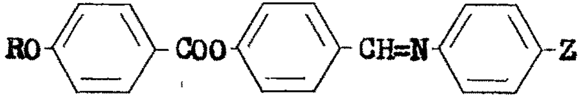
Smectic : $OH > \underline{n}\text{-}OC_4H_9 > \underline{n}\text{-}C_4H_9 > C_2H_5 \geqq CH_3 > OC_2H_5 > H > OCH_3$

The terminal group efficiency order deduced here broadly compare well with those of Dave and Dewar (90), Dave and Vora (91), Gray (74) and Dewar and co-workers (193).

From the terminal group efficiency order as well as from the relative thermal stabilities, it can be seen that the unsubstituted series having H-terminal group has least nematic thermal stabilities. The present series A and C having ethyl ($-C_2H_5$) and butyl ($-C_4H_9$) groups are also last in the nematic group efficiency order along with

Table 25

Average thermal stabilities in °C



Series End group Z=	A $-C_2H_5$	B $-OC_2H_5$	C $-C_4H_9$	D $-OC_4H_9$	E $-CH_3$	F $-OCH_3$	G $-H$	H $-OH$
Nematic-Isotropic (C_1-C_{18})	211.7	247.6	204.1	232.3	220.7	243.7	154.8 (C_1-C_{14})	212.0 (C_5-C_{14})
Smectic-Nematic or Isotropic (C_{12}-C_{18})	154.7	149.5	161.1	170.4	154.1	123.4	133.7	179.4
Commencement of the Smectic mesophase	C_6	C_{10}	C_6	C_7	C_7	C_{12}	C_7	C_{10}

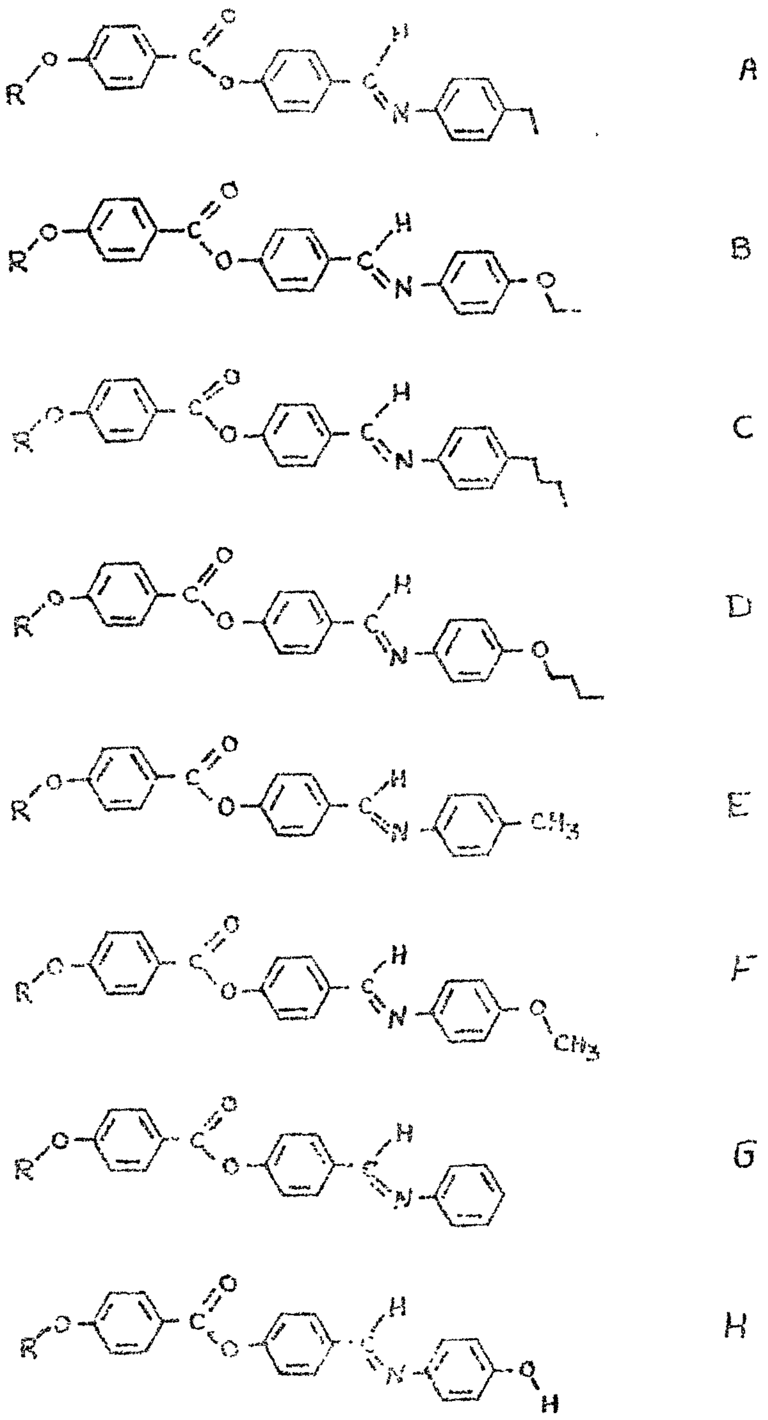


FIG. 18.

$-CH_3$ and -OH group. It is known that the alkyl groups are only polarizable groups hence the contribution to end to end cohesive forces is quite low, hence the lower nematic thermal stabilities in these series can be understood. The series B having the $-OC_2H_5$ group has the highest nematic thermal stability compared to series F and D having $-OCH_3$ and n-OC_4H_9 terminal groups. This suggest that terminal attractions increase from $-OCH_3$ to $-OC_2H_5$ and then again fall slowly as the chain length increases. The position of -OH group in the middle of the order cannot be explained on the simple end to end cohesive forces as this group would be increasing terminal cohesive forces by forming intermolecular hydrogen bonding. Vora and Gupta (194) have explained this behaviour by proposing a secondary structure due to the two types of intermolecular hydrogen bonding. One between two end hydroxy groups and the second between nitrogen of azomethine linkage and end hydroxy group.

Reference to the group efficiency order for the smectic mesophase suggests that it is totally different when compared to the one for nematic. This is understandable as the attractive forces playing their role in both these mesophases differ markedly. Here -OH $-OC_4H_9$ and $-C_4H_9$ groups are at the top. The -OH group increase both the terminal and lateral cohesive forces in the molecules and hence the smectic thermal stabilities are much more increased. In the case of n-OC_4H_9 and n-C_4H_9 groups the increased alkyl chain length provide increase in polarizability necessary for the stability of the smectic mesophase. n-C_4H_9, $-C_2H_5$ and $-CH_3$ groups are known as pro-smectic as they always induce smectic mesophase in a system. Here we see that $-OCH_3$ groups comes last in the group efficiency order for the smectic mesophase. Even -H promotes smectic more compared to $-OCH_3$ group. $-OCH_3$ group is known to induce nematic mesophase more due to high polarity and the shorter alkyl chain. This explains the different group efficiency orders obtained in the present study.

The smectic mesophase commences at hexyl derivative in series A and C, at heptyl derivatives in series D, E and G while it originates at decyl derivatives in series B and H and at dodecyl derivative in series F. The appearance is much delayed in the case of series F having $-OCH_3$ terminal group. As mentioned earlier it is difficult to predict exact commencement of the smectic mesophase in a homologous series. However, it can be seen that in the case of series having long alkyl chains, the commencement of the smectic mesophase is quite earlier compared to the one having short alkyl chains.

II. Smectogenic Homologous Series

II. Smectogenic homologous series

The mesogens with positive dielectric anisotropy has found uses in electrooptical display devices(136,195). Normally such property is exhibited by lath like organic compounds having a highly polar end groups like - NO_2 and -CN, whose dipole is working along the major axis of the molecule. A number of homologous series have been reported with positive dielectric anisotropy (95,96,196,197). In the present investigation two homologous series having $-NO_2$ and -CN end groups have been synthesized and their mesomorphic properties were studied.

9. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-cyanoanilines

The transition temperatures are summarized in Table 12. The series is purely smectic where all the members exhibit enantiotropic smectic mesophases.

10. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-nitroanilines

The transition temperatures are summarized in Table 13. The series is purely smectic where all the members exhibit enantiotropic smectic mesophases.

Common features of series 9 and 10

As discussed earlier, number of researchers have reported re-entrant nematic phase in the mesogenic compounds having -CN and $-NO_2$ terminal groups. However, re-entrant nematic phase is absent in both the series reported here. When the smectic-isotropic transitions are plotted against the number of carbon atoms both the series exhibit the normal odd-even effect (Fig. 19,20.). The even members occupy the upper curve as for the nematic-isotropic transitions.

This suggests that terminal intermolecular attractions are playing their part in determining the smectic-isotropic transition temperatures, just as they do for a nematogenic homologous series discussed in the preceding section. The descending nature of the smectic-isotropic transition curves in both the series can be explained as under.

Initially the molecules of these series would have very high residual lateral cohesive forces and end to end cohesive forces due to the presence of -CN and $-NO_2$ terminal groups. As the alkyl chain length increases the terminal attractions become weaker and allow inter-penetration of the layers to occur more easily, this explains the falling smectic-isotropic transition temperature curve for the higher homologues of the series.

Both the series would exhibit positive dielectric anisotropy as they have end $-NO_2$ and -CN end groups, whose dipole act along the long axis of the molecules.

There are certain end groups which are known to impart smectogenic tendencies to the system. An ester

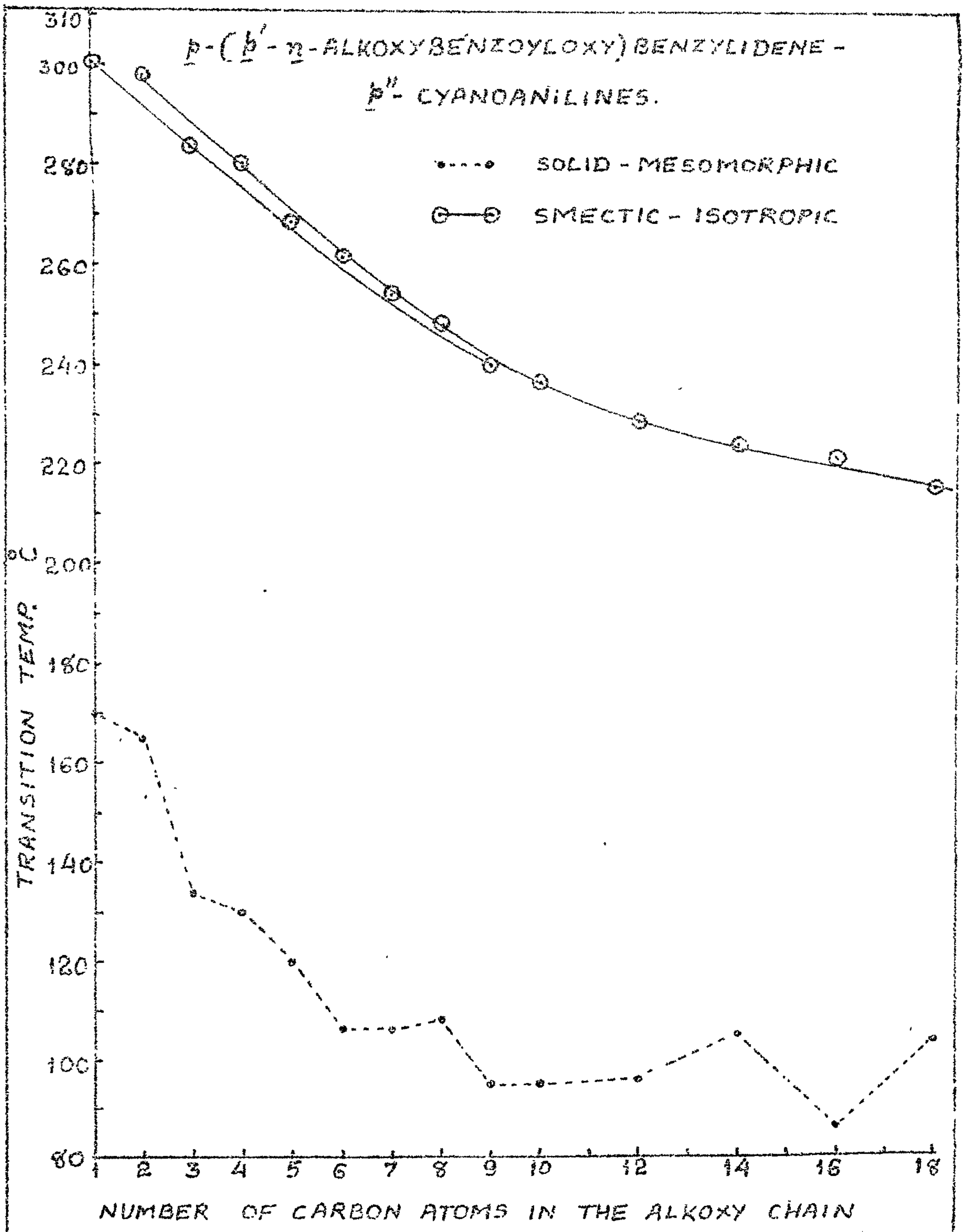

p-(p'-n-ALKOXYBENZOYLOXY)BENZYLIDENE-
p''-CYANOANILINES.
SOLID - MESOMORPHIC
SMECTIC - ISOTROPIC
TRANSITION TEMP. °C
310
300
280
260
240
220
200
180
160
140
120
100
80
1
2
3
4
5
6
7
8
9
10
12
14
16
18
NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 19.

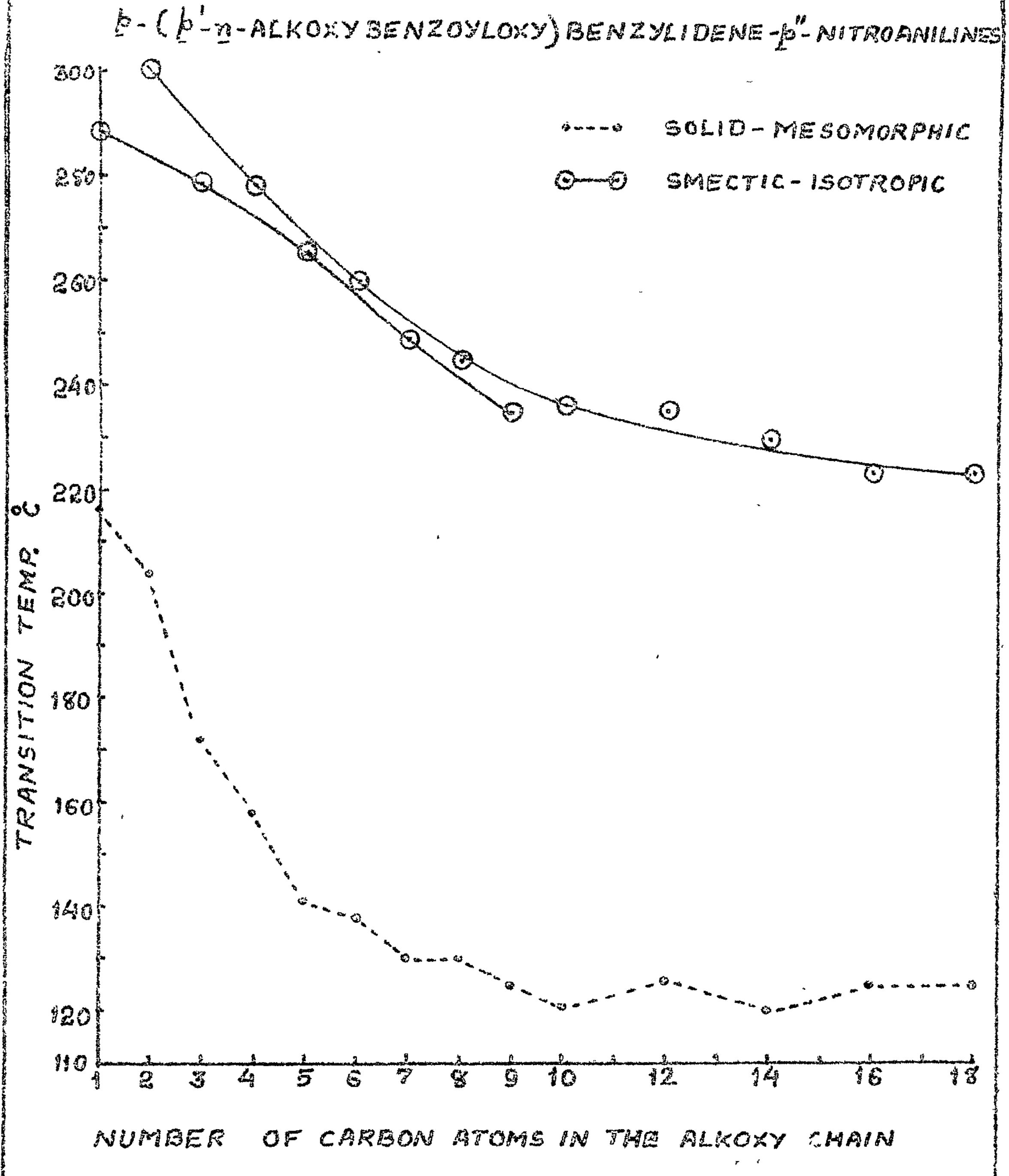

p-(p'-n-ALKOXYBENZOYLOXY)BENZYLIDENE-p''-NITROANILINES
SOLID-MESOMORPHIC
SMECTIC-ISOTROPIC
TRANSITION TEMP. °C
300
280
260
240
220
200
180
160
140
120
110
1
2
3
4
5
6
7
8
9
10
12
14
16
18
NUMBER OF CARBON ATOMS IN THE ALKOXY CHAIN

FIG. 20.

group whose dipole is acting across the major molecular axis generally imparts smectogenic tendencies i.e. the system becomes purely smectic. The halogen groups like Cl and Br also make the system smectogenic when present at the end of the molecule. The present study indicates that the presence of $-NO_2$ and $-CN$ as the end groups has changed the system from nematogenic to smectogenic. The reference to the smectic group efficiency order given by Gray (64) for the system 4-p-substituted-benzylideneamino-4'-n-octyloxybiphenyl (A) and racemic 2-methyl-butyl-4-p-substituted-benzylidene aminocinnamate (B) is as under :

(A) $NH.CO.Me > Ph > Br > Cl > F > NMe_2 > Me > H > NO_2 > OMe > CN$

(B) $Ph > NMe_2 > Me > OMe > H$

If the smectic group efficiency order derived in the preceding section is extended to both the present systems having $-NO_2$ and $-CN$ groups it would be represented as under :

$NO_2 > CN > OH > OC_4H_9 > C_4H_9 > C_2H_5 \backsimeq CH_3 > OC_2H_5 > H > OCH_3$

Looking to the position of $-NO_2$ and $-CN$ groups in promoting smectic mesophase in both the series, the group efficiency order shows a marked difference in the efficiency of both these groups. In the present series the $-NO_2$ and $-CN$ groups are at the top and they have comparatively greater smectic thermal stabilities. In discussing the smectic group efficiency order for the low efficiency of $-CN$ and $-NO_2$, Gray has attempted to relate it to the strong dipoles of nitro and cyano groups acting along the long molecular axis. Such dipoles can certainly be envisaged (179) as giving repulsions between molecules which lie parallel to one another, i.e., side by side, and prependicular to the layer planes of a smectic liquid crystals. However the result of the present study suggests quite opposing forces operating in the molecules. These two end groups increase the lateral cohesive forces of the present system to such an extent that system becomes smectogenic.

A number of homologous series are reported recently having a $-CN$ or $-NO_2$ end group but most of them are nematogenic in nature (95,96,196,197). The study of more such systems having $-NO_2$ or $-CN$ end groups can provide proper understanding and correlation of the different attractive forces operating in these molecules and their effect on smectic mesophase.

To understand the thermal stability behaviour and the molecular structure the relative thermal stabilities of the present series are compared with those of other related homologous series. Table 26 summarizes the smectic thermal stabilities of the following series :

1. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-cyanoanilines A
2. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-nitroanilines B

and are compared with that of

3. 1-(4-n-Alkoxybenzoyloxyphenyl)-2-(4'-cyanophenyl)-ethanes (76) C

The geometry of these series is given in Fig. 21.

The reference to Table 26 shows that the smectic thermal stabilities of series A and B are almost the same. There is hardly the difference of 4°C and if the average transitions for all the members are accounted the average thermal stabilities of both the series are same. This suggests that irrespective of little difference in dipole between $-CN$ and $-NO_2$, and even in size, the smectic mesophase thermal stabilities are not affected. This is quite interesting, because alkoxybiphenyl derivatives (95) having $-NO_2$ or $-CN$ group exhibit a difference in smectic thermal stabilities. The compounds are nematogenic in nature. In these series the octyloxy derivative having $-CN$ group has higher smectic thermal stability compared to the compound having $-NO_2$ group. The differencé in smectic thermal stabilities is 17.5°C.

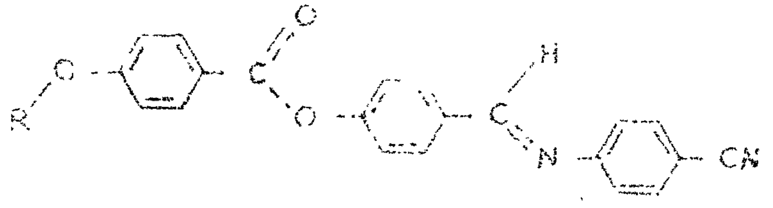
It can be seen from the forgoing discussion that eventhough the molecules of present series are unsymmetrical the change of end groups from $-NO_2$ to $-CN$ does not affect the average smectic transitions. Whereas in the case of symmetrical biphenyl compounds reported in the literature the change in the end group from NO_2 to CN effects the average smectic thermal stability.

Table 26

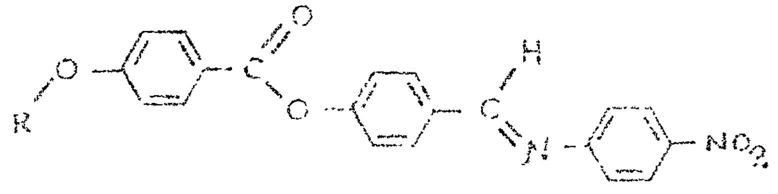
Average thermal stabilities (°C)

Series	A	B	C
Smectic-Isotropic (C_1, C_2, C_4, C_7, C_8)	276.1	272.2	182.4

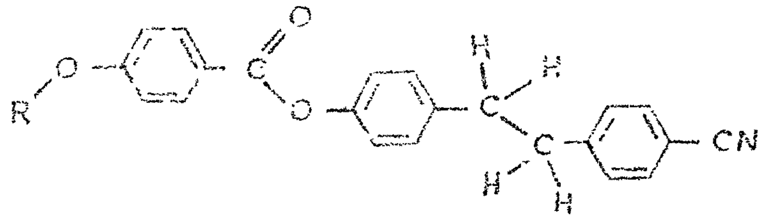
The smectic thermal stabilities of the present series A and B are quite higher than those of series C. This can be understood as the molecules of series C have a flexible $-CH_2-CH_2-$ bridge whereas the molecules of series A and B have a rigid polarizable $-CH=N$ bridge. The smectic mesophase is more ordered phase and flexibility introduced in the middle group would be definitely deterrent to the smectic mesophase. This explains the lower thermal stabilities of series C compared to those of series A and B.



A

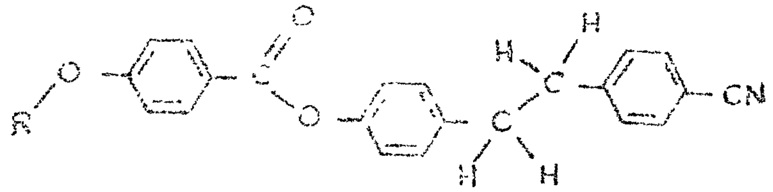


B



C

OR/AND



D

FIG. 21.

Calorimetric studies of all the compounds could not be carried out due to the non availability of Differential thermal analysis apparatus and Differential Scanning Calorimeter. However, on request some compounds could be analysed at the nearby university. Two representative thermograms are given in figure 22 and 23. The enthalpies of different phases are calculated and are as under :

	Compounds	ΔH KCal/mole		
		Solid	Smectic Nematic	Nematic-Isotropic
(1)	p(p'-n-Nonyloxybenzoyloxy) benzylidene-p"-phenetidine	6.37		0.3215
(2)	p(p'-n-Decyloxybenzoyloxy) benzylidene-p"-phenetidine	3.059	3.997	0.0622
(3)	p(p'-n-Pentyloxybenzoyloxy) benzylidene-p"-ethylaniline	4.154		0.0967
(4)	p(p'-n-Hexyloxybenzoyloxy) benzylidene-p"-ethylaniline	4.084		0.1319

The enthalpies for the monotropic smectic phase could not be calculated as the compound crystallized before the nematic-smectic transition temperature could be reached in the D.S.C. study.

p(*p*'-*n*-Nonyloxybenzoyloxy)benzylidene-*p*"-phenetidine

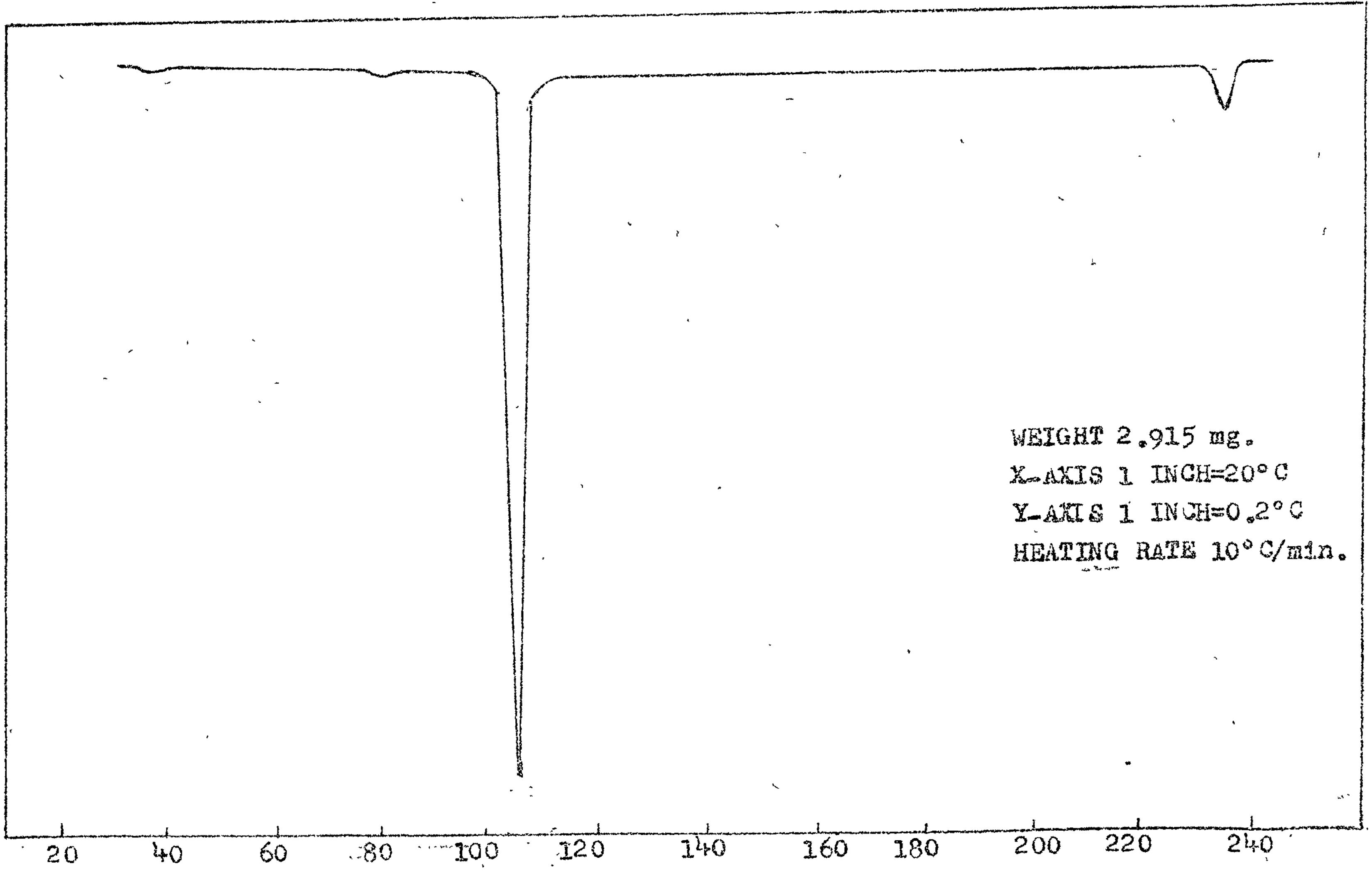


FIG.22.

p(*p*'-*n*-Decyloxybenzoyloxy)benzylidene-*p*"-phenetidine

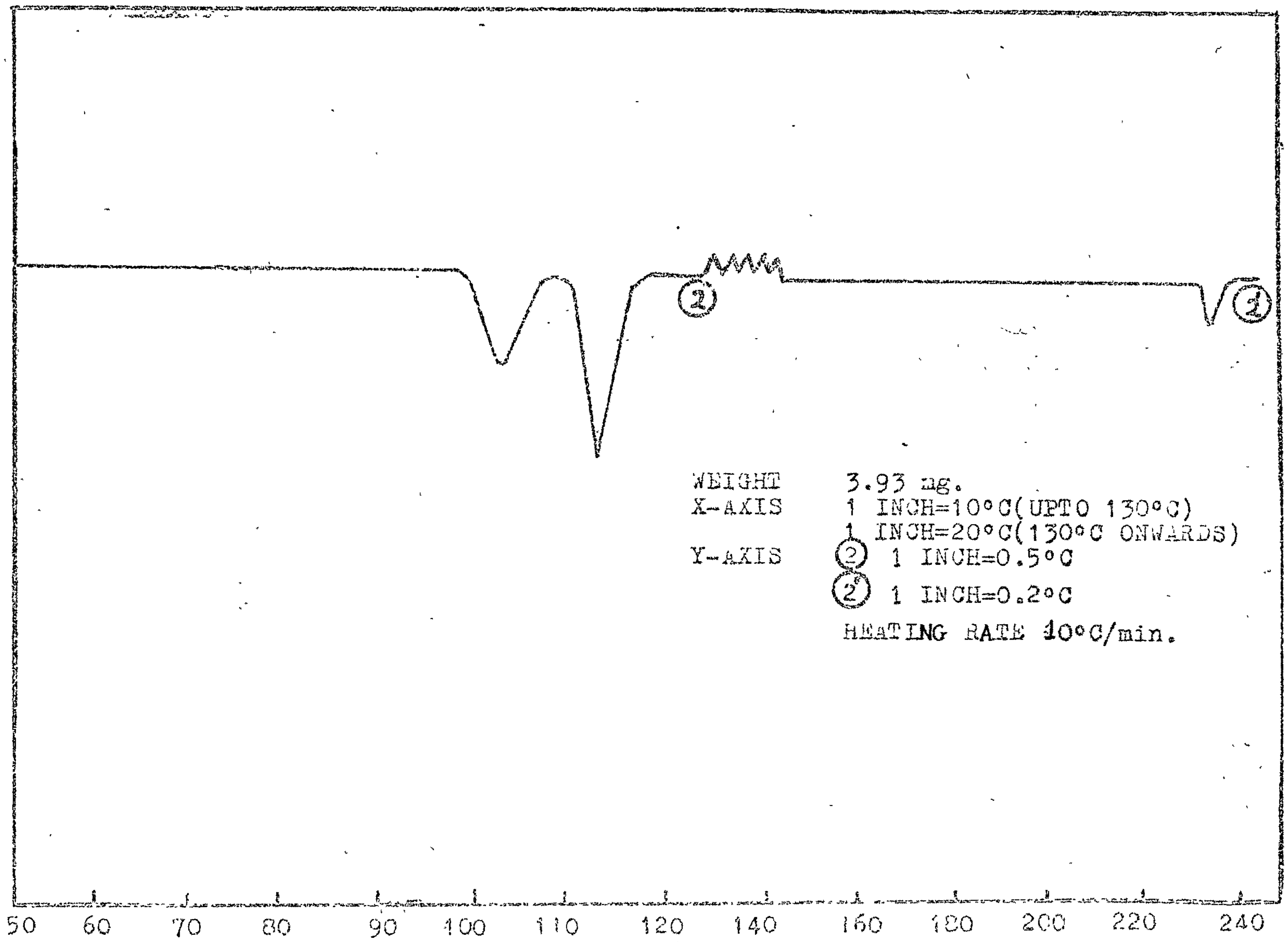


FIG. 25.

C. MESOGENIC MIXTURES

C Mesogenic Mixtures

As discussed earlier binary mixtures where both the components are mesomorphic have been studied less in number. Recent applications of liquid crystals have provided impetus to such studies. Bogojawlensky and Winogradow (87) and Dave and Lohar (198) have discussed the molecular forces operating and their effects on the binary phase diagrams where both components are mesogenic in nature. Recently Hirata et al., (199) and Szabo et al., (100) have studied the binary nematic mesophase systems and obtained phase diagrams. They have indicated the advantage of such mixtures over the pure individual components in the field of applications. Hsu and Johnson (200) have also reported some binary nematic mesophase systems. In the present study the low melting naphthalene nematogens prompted us to study some mixtures and observe the effect of melting points, mesogenic-isotropic transitions and the chemical constitution on mixed nematic mesomorphism. With this view three types of binary nematogenic systems were investigated.

System 1. Both components (A) and (B) exhibiting monotropic mesophases.

Component A : 4-n-Butoxy-1-naphthylidene-p-i-amyloxyaniline

K 68.5 I (50.0 N)

Component B : 4-*n*-Hexyloxy-1-naphthylidene-*p*-*i*-amyloxyaniline

K 58.0 I (51.5 N)

System II. Component (A) exhibiting monotropic nematic mesophase and component (B) exhibiting enantiotropic nematic mesophase.

Component A : 4-*n*-Dodecyloxy-1-naphthylidene-*p*-*n*-propoxyaniline

K 71.0 I (57.0 N)

Component B : 4-*n*-Dodecyloxy-1-naphthylidene-*p*-*n*-butoxyaniline

$$K \xrightarrow{59.0} N \xrightarrow{67.0} I$$

System III. Both components (A) and (B) exhibiting enantiotropic nematic mesophase.

Component A : 4-*n*-Nonyloxy-1-naphthylidene-*p*-*n*-amyloxyaniline

$$K \xrightarrow{55.0} N \xrightarrow{64.0} I$$

Component B : 4-*n*-Dodecyloxy-1-naphthylidene-*p*-*n*-butoxyaniline

$$K \xrightarrow{59.0} N \xrightarrow{67.0} I$$

The transition temperatures, mole percent concentration, eutectic composition and temperatures of system I, II and III are recorded in Tables 27, 28 and 29 respectively. The binary phase diagrams are

Table 27

Binary System :

4-n-Butoxy-1-naphthylidene-p-i-amyloxyaniline :

4-n-Hexyloxy-1-naphthylidene-p-i-amyloxyaniline

Mole of % of 4-n-Butoxy-1-naphthylidene-p-i-amyloxyaniline	Transitions	
	Solid-Isotropic °C	Mesomorphic-Isotropic °C
100.00	68.5	(50.0)
90.63	67.0	(49.0)
81.10	63.0	(47.5)
71.44	60.0	(47.0)
61.65	58.0	(46.5)
51.73	49.0	(45.0)
41.58	55.0	(45.0)
31.49	57.0	(48.0)
21.13	58.0	(48.0)
00.00	58.0	(51.5)

Values in parentheses indicate monotropy

Eutectic point

Mole % concentration of A	52.0
Temperature °C	49.0

Table 28

Binary system :

4-n-Dodecyloxy-1-naphthylidene-p-n-propoxyaniline :

4-n-Dodecyloxy-1-naphthylidene-p-n-butoxyaniline

Mole % of 4-n-Dodecyloxy--naphthylidene-p-n-propoxyaniline	Transitions	
	Solid-Mesomorphic °C or Isotropic	Mesomorphic-Isotropic °C
100.00	71.0	(57.0)
90.27	68.0	(55.5)
80.50	66.0	(56.0)
70.62	64.0	(59.0)
60.73	61.5	(58.5)
55.73	61.0	(58.0)
50.72	56.0	60.5
45.73	54.0	62.0
40.71	57.0	62.0
30.62	56.5	63.0
20.44	57.5	64.0
10.24	58.5	65.5
00.00	59.0	67.0

Values in parentheses indicate monotropy

Eutectic point

Mole % concentration of A	46.0
Temperature °C	54.0

Table 29

Binary system :

4-n-Nonyloxy-1-naphthylidene-p-n-amyloxyaniline :

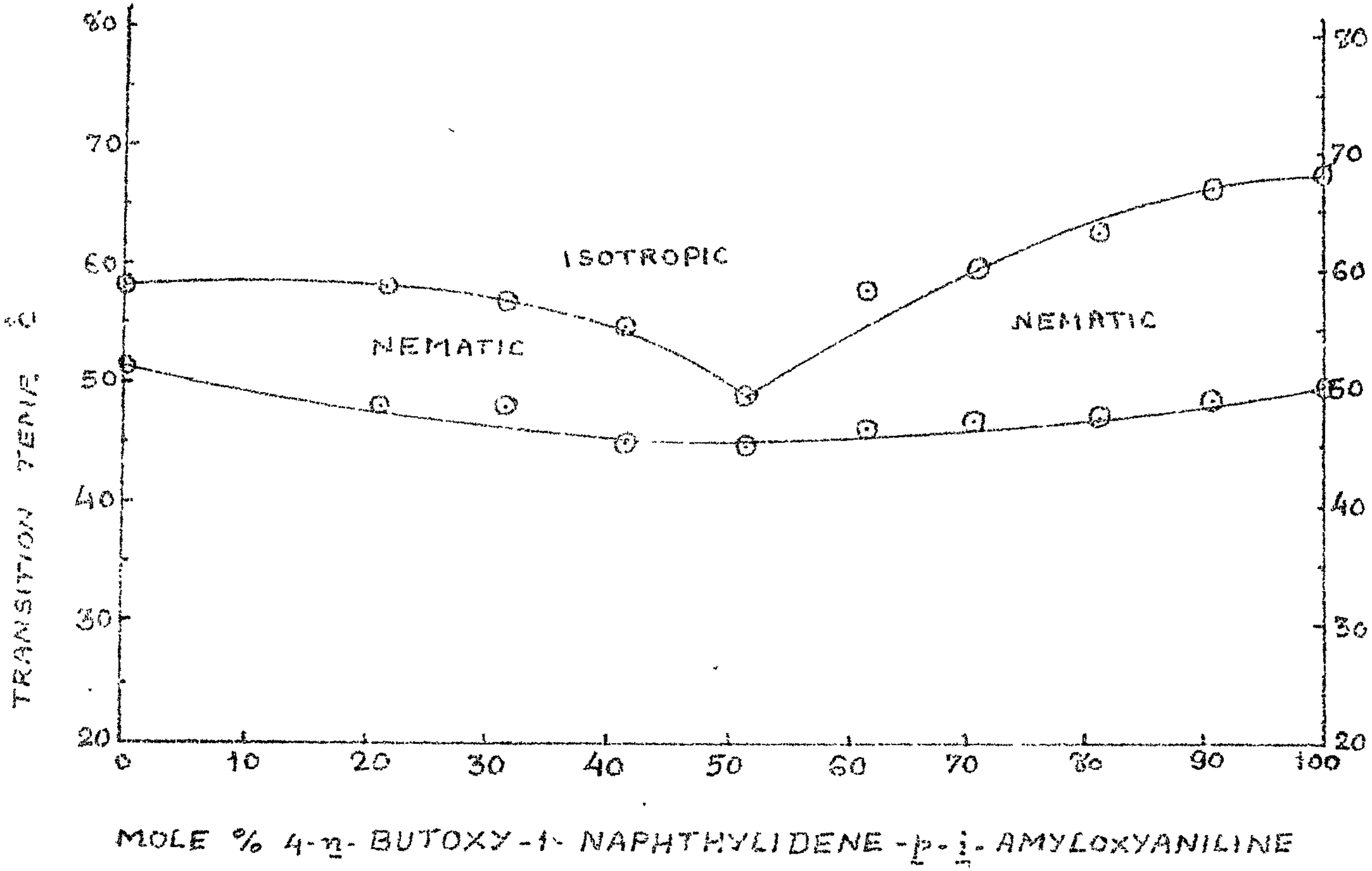
4-n-Dodecyloxy-1-naphthylidene-p-n-butoxyaniline

Mole % of 4-n-Nonyloxy-1-naphthylidene-p-n-amyloxyaniline	Transitions	
	Solid-Mesomorphic °C	Mesomorphic-Isotropic °C
100.00	55.5	64.0
93.53	49.0	64.0
80.94	44.5	63.5
71.22	44.0	63.5
61.41	43.0	64.5
51.58	44.5	64.5
41.53	45.0	65.5
31.33	48.0	65.0
21.04	52.0	65.5
10.58	55.0	66.0
00.00	59.0	67.0

obtained by plotting the transition temperatures against the mole percent concentration for all the three systems. To make the study simple the components selected for the mixture studies are isomorphous and having almost the similar structure except the difference in terminal alkoxy chain where also the difference is in the methylene units.

All the three systems show nematic behaviour over the entire composition range. Reference to Fig. 24, 25 and 26 suggests that system I and II are "simple-eutectic" type. The system III does not exhibit an eutectic point but shows a rounded minimum.

System I. This system exhibits monotropic nematic mesophase in all the compositions (Fig. 24.). Both the components of this system are monotropic nematic in nature and one would expect enantiotropic nematic mesophase in certain range of composition. Lohar (201) has obtained enantiotropic nematic mesophase in number of binary nematic systems, where both the components are monotropic nematic. However, he also observed monotropic mixed nematic mesophase throughout all the composition in one system and he is of the opinion that eutectic point and other associated aspects are responsible for the exhibition of enantiotropic mixed liquid crystallinity in such binary systems. In the present systems as both



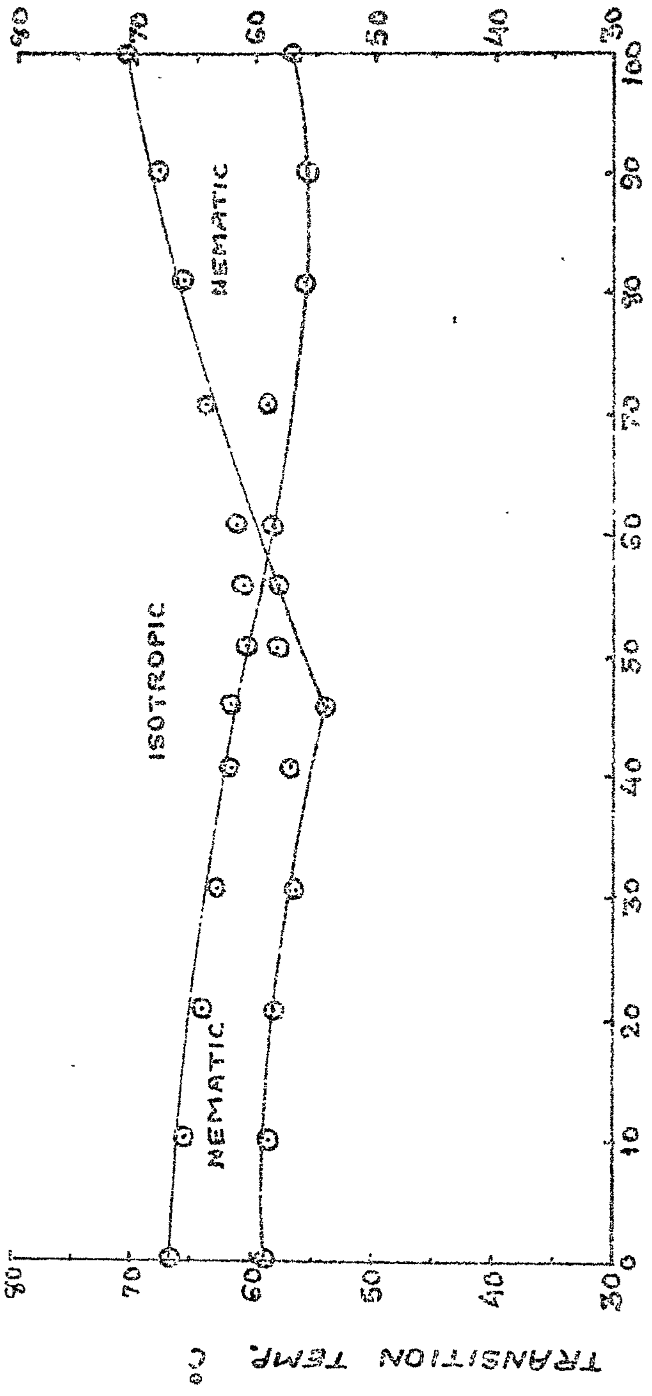
4-n- BUTOXY-1-NAPHTHYLIDENE -p-i- AMYLOXYANILINE:
4-n-HEXYLOXY-1-NAPHTHYLIDENE-p-i-AMYLOXYANILINE

FIG.24.

the components are isomorphous and have almost the same molecular geometries except the end alkoxy chain one would expect an ideal behaviour. However, it does not exhibit the ideal behaviour of exhibiting enantiotropic nematic mesophase which indicates that other forces would be operating in the present system.

The interesting result obtained in the system I is regarding the supercooling tendency of a mixture having 52 mole percent concentration of component A. It does not ~~supercool~~ Crystallized even at 0°C. In practice the binary mixture obtained by melting two components together does not solidify. As we are not having systematic cooling device we could not study the supercooling tendencies of all these mixtures. However, when the above mixture was allowed to stand for fifteen days at room temperature then it partly crystallized and we could determine the solid to isotropic temperature. All the mixtures have marked supercooling tendencies and crystallize well below their monotropic transitions.

System II. In this system no gain was observed either in lowering of solid-mesomorphic temperature or in increasing the supercooling tendencies of the system. The phase diagram (Fig. 25.) exhibits monotropic nematic mesophase on the ~~left~~ Right side of the eutectic and it cuts melting point curve at the 57.5 mole percent concentration



MOLE % 4-n-DODECYLOXY-1-NAPHTHYLIDENE-p-n-PROPOXYANILINE

4-n-DODECYLOXY-1-NAPHTHYLIDENE-p-n-PROPOXYANILINE;

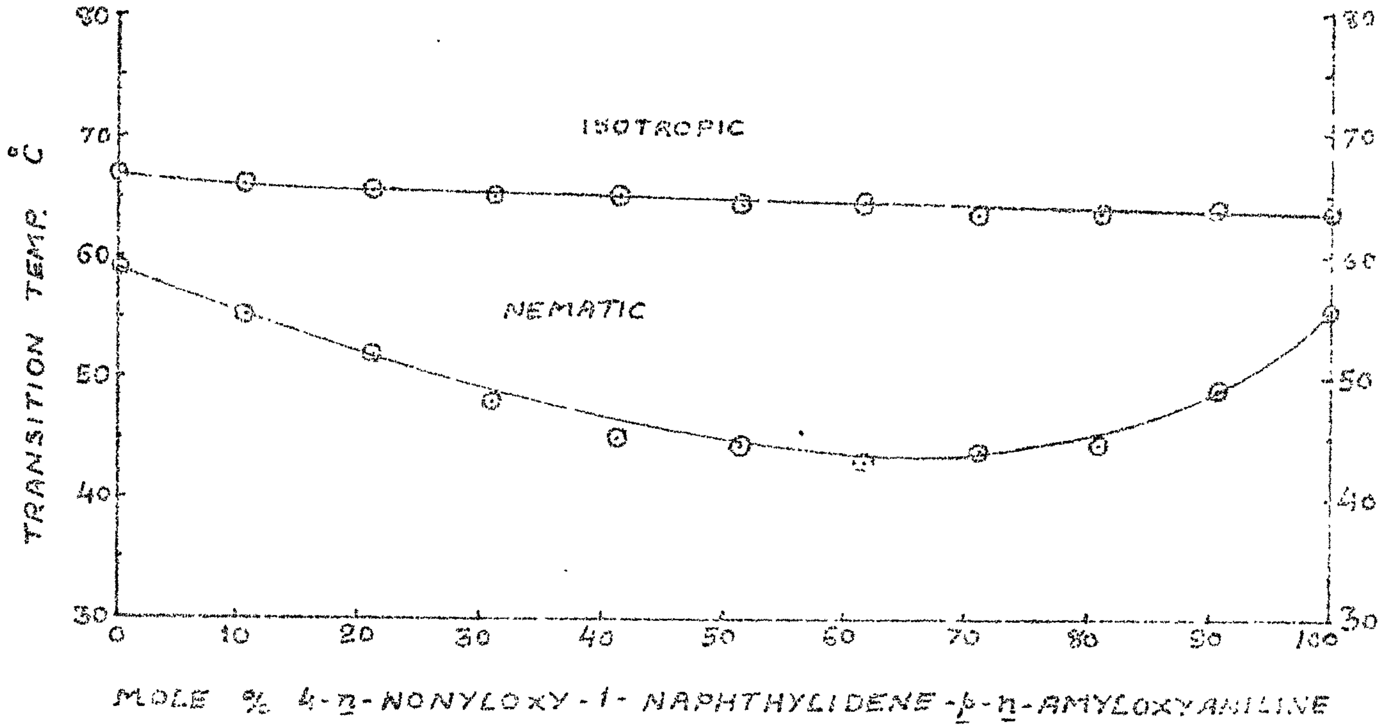
4-n-DODECYLOXY-1-NAPHTHYLIDENE-p-n-BUTOXYANILINE

FIG.25.

of the component A (enantiotropic) and becomes enantiotropic nematic.

<u>System III</u>. The binary mesogenic phase diagram itself suggests that the mixture has provided the advantage over the individual nematogenic components. Both the components are enantiotropic nematic. The nematic-isotropic transition temperature curve is a straight line indicating ideal behaviour of the mixtures in the mesogenic state (Fig. 26). The solid-nematic transition temperature curve exhibits a rounded minimum due to this tendency of solid-nematic transition temperature curve the maximum nematic temperature range obtained in this system is 43.5 to 64.5°C (21°C) at 61.5 mole percent concentration of component A. The individual phase length of component A and B is about 8.0°C whereas the maximum nematic range observed in the present study is 21.0°C as mentioned above. The solid mesomorphic temperature is lowered by 12-16°C compared to the component A and B. Additional advantage is obtained due to the marked supercooling tendencies of these mixtures. They do not supercool even when kept at room temperature for few days (22-26°C room temperature).

Hirata et al., (199) also have observed similar phase diagrams in their binary nematic mesophase system comprising two enantiotropic Schiff bases. The difference



4-n-NONYLOXY-1-NAPHTHYLIDENE-p-n-AMYLOXYANILINE;
4-n-DODECYLOXY-1-NAPHTHYLIDENE-p-n-BUTOXYANILINE

FIG.26.

between the two study is in getting lowering of solid-mesomorphic transitions. They could get much more lowering of the solid-nematic transitions due to the pronounced rounded minimum in solid-nematic phase transition curve. Components A and B of the present binary system have almost similar configuration whereas Hirata et al., (199) have taken two components where one of them has a lateral hydroxy substituent. This may probably be the reason in much more lowering of the solid-nematic transition temperature in the binary system reported by them.