XoX

RESULTS AND DISCUSSION

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CHAPTER - 4

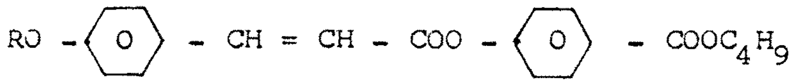
RESULTS AND DISCUSSION

PART I - NEW MESOGENS

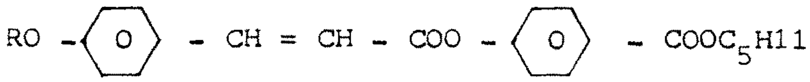
There are certain molecular factors which almost governs or dictates the characteristics of mesogens. The increased utility value in the field of application has given a lot of attention towards the synthesis of low melting mesogens. The present investigation has been inspired with the desire to search new mesogens that may be endowed with specific characteristics.

The following new homologous series have been synthesized. On the basis of previous studies their structures are also depicted -

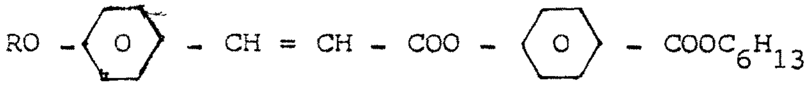
(1) n - Butyl (p'- n' -alkoxycinnamoyloxy) benzoate



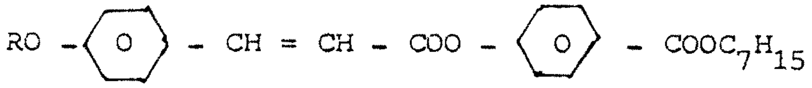
(2) n - Amyl p -(p' - n' - alkoxycinnamoyloxy) benzoate



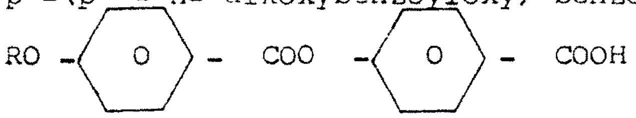
(3) n - Hexyl **p** -(p' - n' - alkoxycinnamoyloxy) benzoate



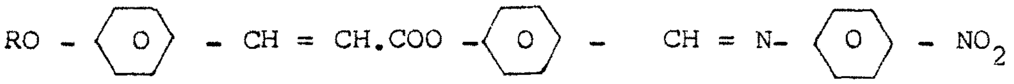
(4) n - Heptyl p - (p' -n' - alkoxycinnamoyloxy) benzoate



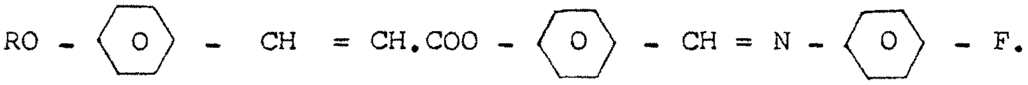
(5) p -(p' - n- alkoxybenzoyloxy) benzoic acid



(6) p -(p'-n-alkoxycinnamoyloxy) benzilidene p" nitroaniline



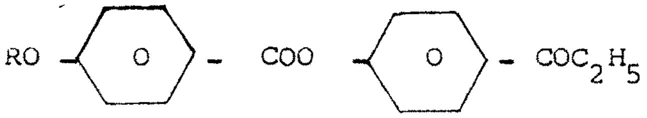
(7) p -(p' -n-alkoxycinnamoyloxy) benzylidene -p" -fluoroaniline



Each of the above series consists of twelve compounds with alkoxy groups from methoxy to octyloxy and decyloxy, dodecyloxy, tetradecyloxy and hexadecyloxy the total number of compounds being eighty four.

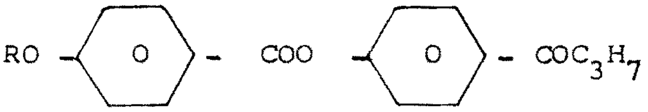
Some members of already reported series (323) of p (p' - n- alkoxybenzoyloxy) propiophenone and p (p'- n -alkoxybenzoyloxy) butyrophenone are also synthesized in a view to complete the entire series.

(8) P (p' - n - alkoxybenzoyloxy) propiophenone



The newly synthesized members are -

(9) p (p' - n - alkoxybenzoyloxy) butyrophenone



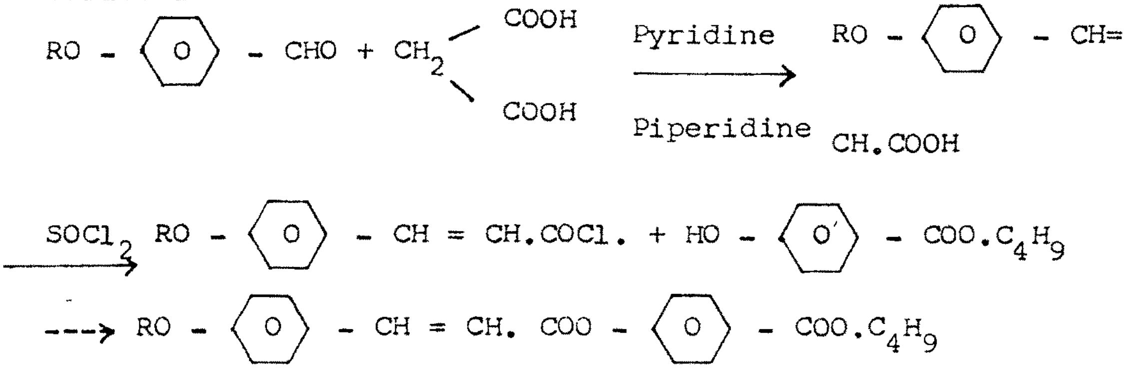
The new members are - C_{12}, C_{14} and C_{16}

Most of the newly synthesized members are mesogens and show mesomerphism at a wide range of temperatures.

Mesomorphic characteristics of various Homologous Series

1. n - Butyl p - (p' - n' - alkoxycinnamoyloxy) benzoate

The route followed for the synthesis of this series is -

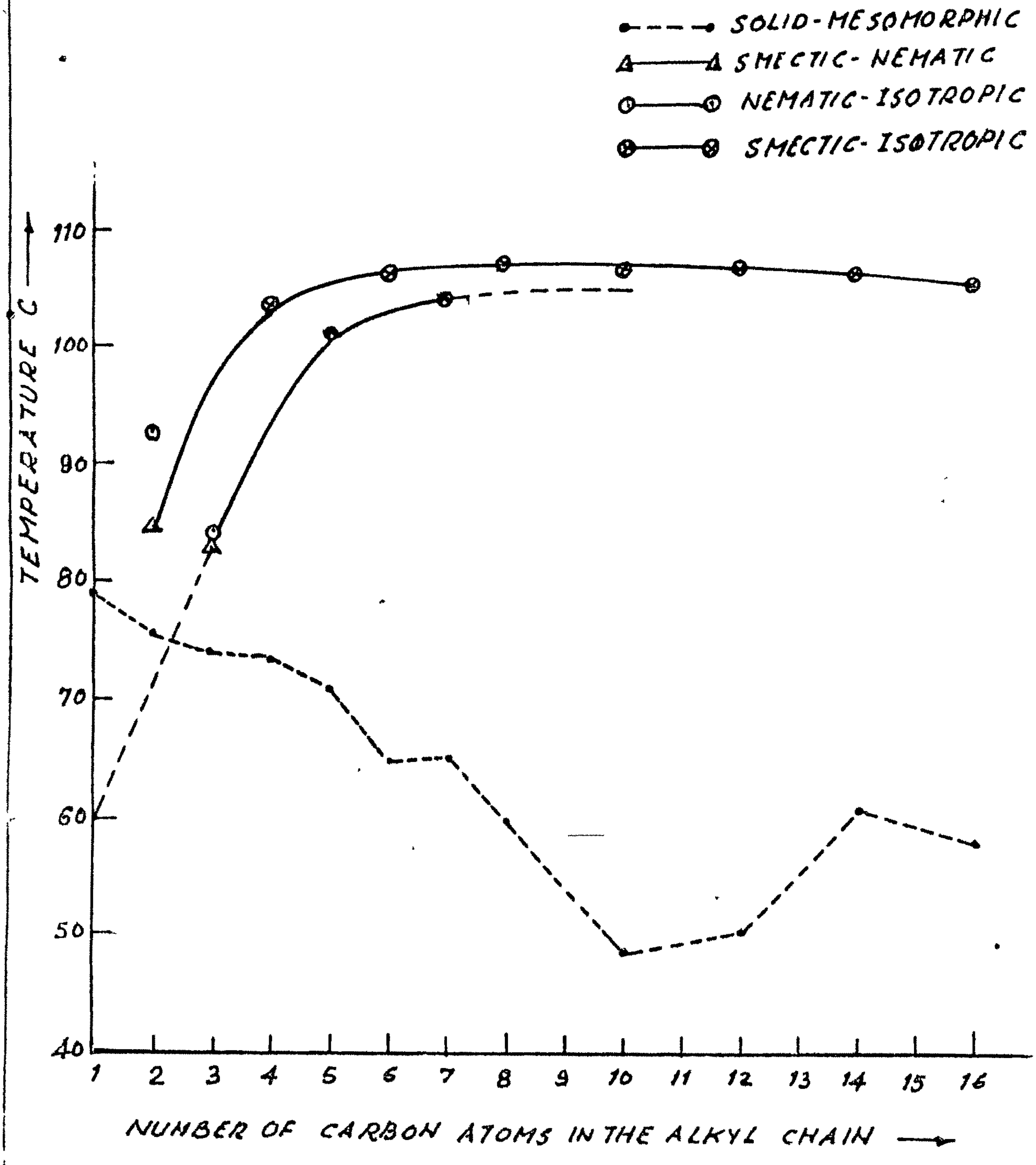


R = n - alkoyl group.

Transition temperatures of all members are recorded in Table - 5. The plot of these transitions versus the number of carbon atoms in the alkyl chain is given in fig. 8. All but methyl-members of this series show mesomorphism. Polymemomorphism is also exhibited by two

FIG. 8

p-n-BUTYL (p'-n'-ALKOXYCINNAMOYLOXY) BENZOATE



members viz. second and third holoques. The appearance of smectic mesophase is marked by odd-even effect. The two curves (Fig. 8) one for odd members and the other for the even members, show a steep rise as the series is ascended, but after the sixth homologue, the curves run parallel to the absicssa line. The even-curve then follows a plateau-like shape upto the tenth member after which a slow but definite fall is observed upto the octa-decyloxy homologue as the series is ascended.

Extapolation of the odd smectic-nematic curve towards the methyl homologue indicate a monotropic smectic/nemetic transition at about 62° but all efforts to observe such an observation under microscope were failed.

The solid-mesomorphic transitions plot shows an alternating effect of the odd-even type. The curve rises and falls between the first and seventh members alternatively and from eighth member, the curve exhibits a definite but slow descending tendency as the series is ascended.

This series of n-butyl p - (p'-n' alkoxycinnamoyloxy) benzoate esters show mesomorphism at lower temperatures. The nematic mesophase is that of threaded type while the smectic texture is of focal conic fan shaped type belonging to smectic A variety.

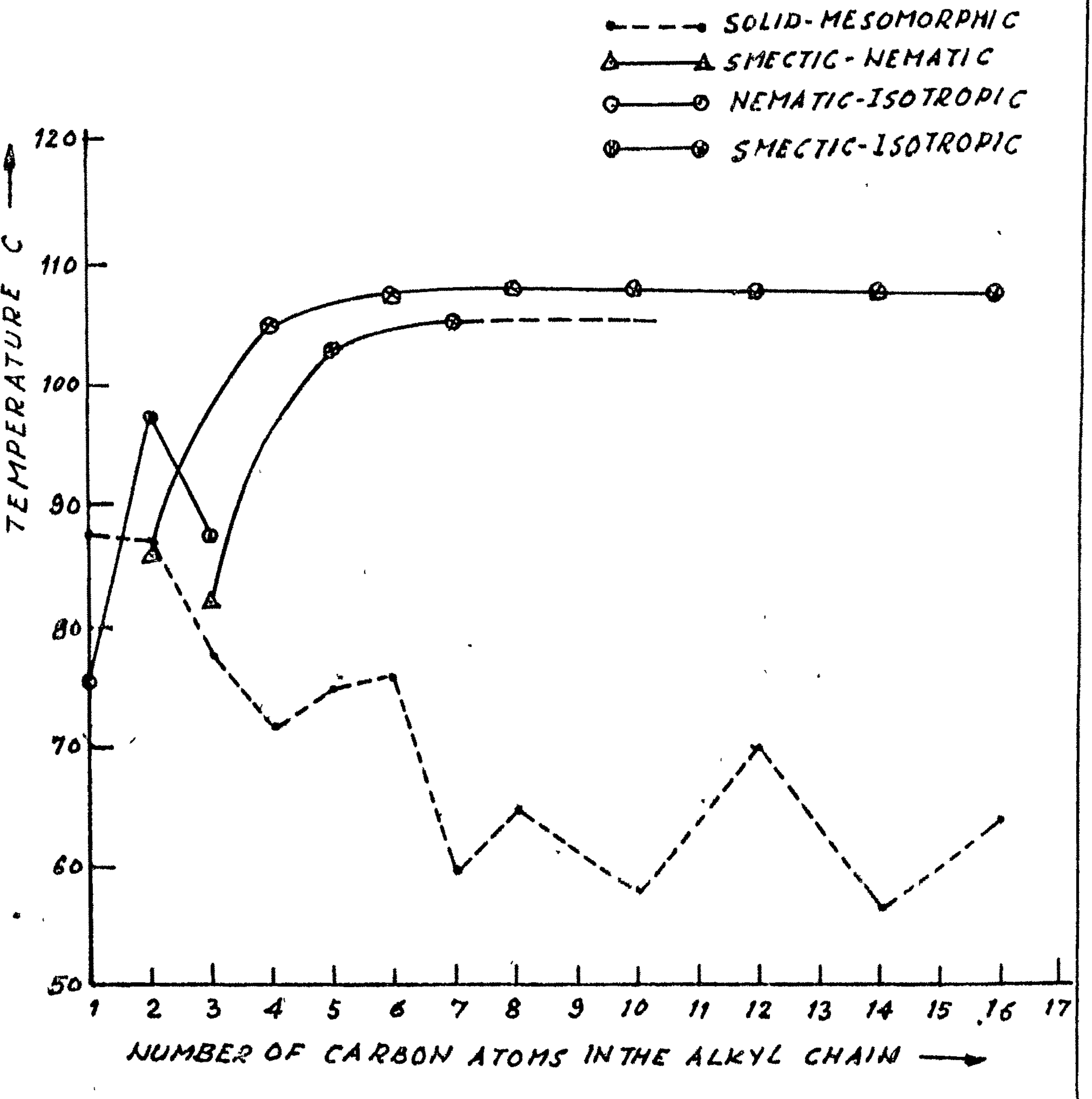
2. n - Amyl o - (p'- n' - alkoxycinnamoyloxy) benzoate

This entire series, unloke the series 1 shows mesomorphic characteristics though the first member shows only monotropic mesophase (Fig - 9). The transitions of this series are slightly higher than those of the first one. The solid-isotropic or solid-mesomorphic curve shows a fall initially upto the fourth homologue then rises a little upto seventh homologue and then shows a continuous zig-zag structure right upto sixteenth homologue.

Nematic mesophase is exhibited upto third homologue, though the first member shows it in monotropic condition only. All the other members are purely smectogens, though the second member shows monotropic smectic phase. Since polymesomorphism commences from the third homologue with simultaneous exhibition of the smectic mesophase prior to nematic property, the homologous series is predominantly smectogenic. From butyl to hexadecyl member, the range of smectic mesophase is quite good. The smectic isotropic curve also shows alternation effect very clearly which persists right upto the seventh member. Both these odd and even curves first rise steeply upto fourth members respectively. Then both the curves run almost parallel to

FIG. 9.162

p-n-AMYL (p'-n'-ALKOXYCINNAMOYLOXY) BENZOATE



abscissa line. The upper limit and lower limit for upper and lower transition curves are 108° and 58° respectively. The series can be regarded as low-melting type.

The nematic mesophase shows threaded texture whereas smectic mesophase exhibits focal conic fan shaped textures of smectic A variety.

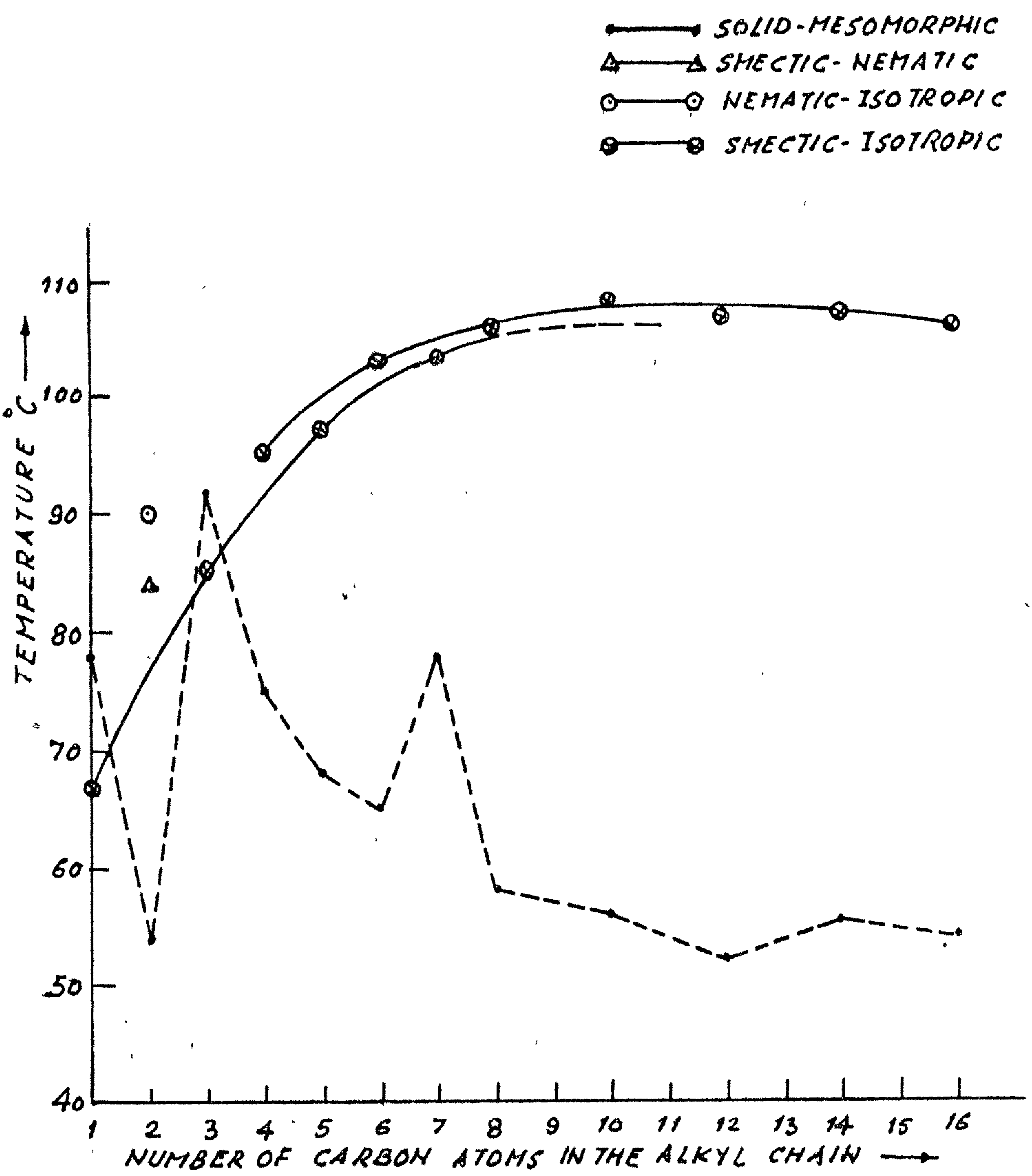
3. n - Hexyl p - (p' - n' - alkoxycinnamoyloxy) benzoate

This entire series of esters of n-Hexyl p - (p'- n' - alkoxycinnamoyloxy) benzoate shows mesomorphism, though first and third members show only monotropic mesomorphism. The solid-mesomorphic curve (Fig -10) shows almost zig-zag course of rising and falling transitions but it also shows an overall tendency of decreasing transitions (solid-mesomorphic) as the series is ascended. The initial steep rising tendency of S-M curve is responsible for the first and third member showing smectic mesophase in monotropic condition, while the relatively steep falling tendency may be taken as responsible for second member showing both nematic and smectic mesophases in enantiotropic conditions.

The nematic mesophase is exhibited by second member only. So there is no transition curve for this in the diagram (fig. 10). The smectic-isotropic transitions

FIG. 10.

p-n-HEXYL (p'-n'-ALKOXYCINNAMOYLOXY) BENZOATE



clearly show alternation effect. Both the smectic-isotropic curve, one for odd members and the other for even members show a initial rise but the rising effect peters off at seventh and eighth members, respectively after which there is a slight but definite falling tendency upto the last member studied. The series is purely smectogenic in character, its overall smectic mesophase length is quite good. The series should be taken as belonging to a low melting type.

The nematic texture is of threaded type while the texture of smectic mesophase is of focal conic fan shaped variety belonging to smectic A type as discussed by microscopic studies.

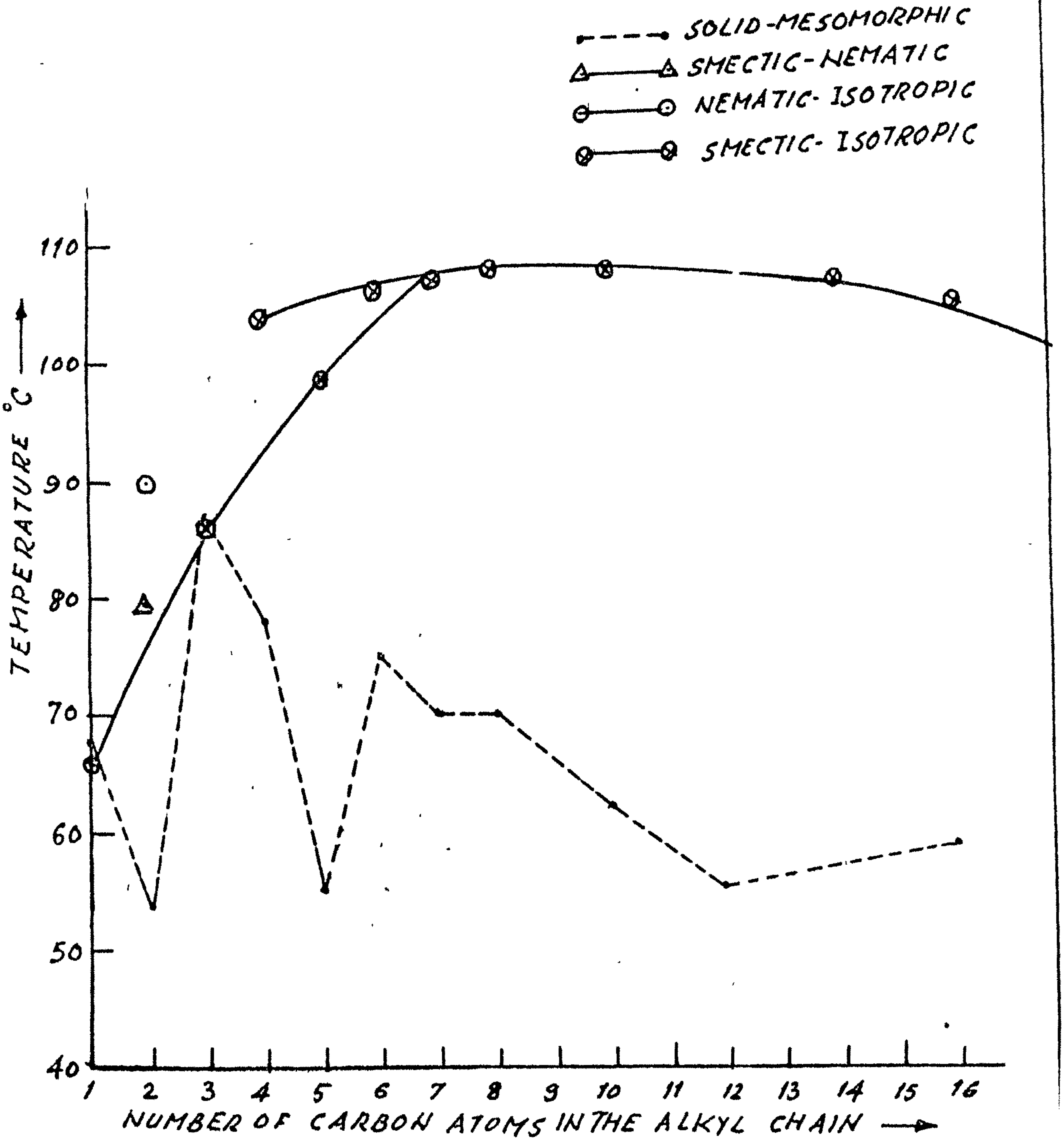
4. <u>n - Heptyl - p (p' -n' - alkoxycinnamoyloxy) benzoate</u>

This homologous series behaves quite strangely. All the members of the series show mesomorphism though the first and third members show mesomophism only in monotropic condition. Only second member shows polymesomorphism. All the other members are purely smectogens.

The solid-mesomorphic transition curve (fig.11) is typically zig-zag, showing an alternate rise and fall upto the seventh member. Then the curve runs almost parallel to abscissa line upto the eighth member then falls steeply upto the twelveth member. The curve shows again a rising tendency

FIG. 11.

p-n-HEPTYL (p'-n'-ALKOXYCINNAMOYLOXY) BENZOATE



upto the last member studied.

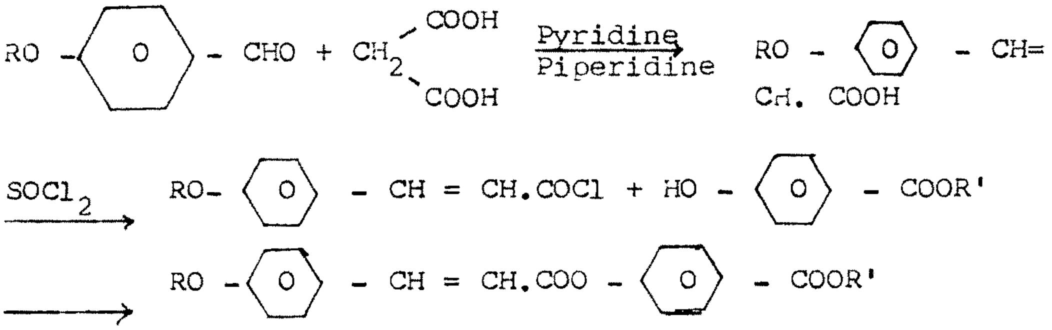
Since nematic properties is exhibited by only second homologue, there is no transition curve for this in the diagram (fig. 11). Some of the initial homologues show a very clear alternation effect in the case of smectic-isotropic transitions but the smectic isotropic curve for odd members merges with that of even member at the seventh homologue after which the curve shows a slight but gradual falling tendency upto the last member studied. The overall mesomorphic range is quite good in all the homologues showing enantiotropic mesophase.

The nematic texture is of threaded variety while the smectic mesophase exhibits fan shaped focal conic textures of smectic A variety. The series is of low melting type.

General characteristics of the homologous series 1,2,3 & 4.

All these four series viz. n-butyl p - (p'- N' - alkoxycinnamoyloxy) benzoate, n-amyl p - (p' -n' - alkoxycinnamoyloxy) benzoate, n-hexyl p -(p'-n'-alkoxycinnamoyloxy) benzoate and n-heptyl p - (p'-n'-alkoxycinnamoyloxy) benzoate are synthesized by the same route i.e. esterification of trans-p-n-alkoxycinnamic acid with n-butyl, n-amyl, n-hexyl and n-heptyl p-hydroxy benzoates respectively.

The route can be depicted as -



where R = n - alkyl group

R' = n - C_4H_9, C_5H_{11}, C_6H_{13} or C_7H_{15}

Several other homologous series with this core structure are known to exhibit mesomorphic characteristics. The molecular forces which in their peculiar combinations affect the mesomorphic properties are polarity, polarisability, length to breadth ratio, steric hindrance caused by certain groups attached to the molecules, planar nature, electron density etc. (324).

Besides several other factors are also considered to be sufficiently important in deciding mesomorphic characteristics of the molecules. With the above core structure excluding the terminal groups the basic length due to two benzene rings and central linking unit, aeromaticity of the molecules and electron density of the central bridge are the constant unchanging features. So the display of molecular forces on account of these with remain the same for all the four series.

The homologous series have their changing parts at both terminals but in a sequential manner. Naturally the variations in mesomorphic behaviour can be traced to this specific alterations in the terminal group. It can be observed that as a methylene unit $-CH_2$ is added to the R terminal group of the various homologues of the same series, the other terminal group R' remain fixed. This R' alkyl group changes from series 1 to 4 in a step wise alterations in the two terminal groups of the homologous series from 1 to 4 should be taken into account to evaluate the series.

It can be observed (Tables 5,7, 9 and 11) that the addition of a methylene unit $- CH_2$ does not affect the transition to a larger extent. It is possible that with addition of a methylene unit, the increased chain length of the terminal group will have a bearing on the overall polarity across the molecule but as the polarizability also gets enhanced, the ratio of polarity to polarizability is not greatly altered.

A glance at these fig. 5,7,9 and 11 also brings out another interesting variation. In the homologous series No.1 and 2, n-butyl p- (p'-n'-alkoxycinnamoyloxy) benzoate and n-amyl p- (p'-n'-alkoxycinnamoyloxy) benzoate, the nematic mesophase is exhibited by second and third members whereas in the series no. 3 and 4, n-hexyl p- (p'-n'-alkoxycinnamoyloxy) benzoate and n-heptyl p-(p'-n'-alkoxycinnamoyloxy) benzoate, the nematic mesophase is exhibited by second member only.

The smectic-isotropic curves in all the four series have alternating effects which has not been explained well (325). Perhaps this alternation can be explained assuming that shorter alkyl chain extends strictly along an axis determined by the tetrahedral bond angles (fig.39). The nature of the contact between terminal methyl groups of molecules arranged end to end will then differ for even and odd homologues.

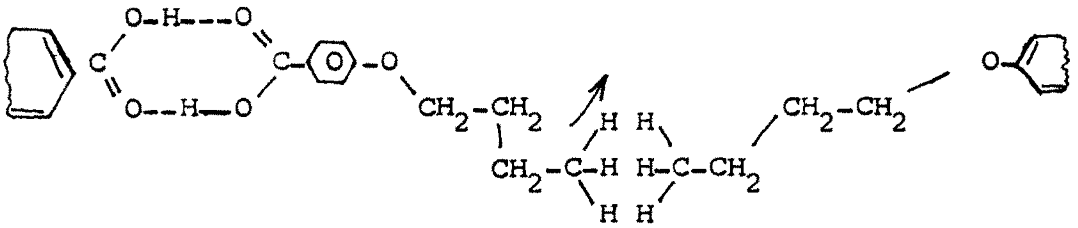


Fig. 39

End to end relationship between molecules with terminal substituents consisting of n-alkyl chain

This would affect the terminal interactions between molecules and explain the alternation of the transition temperatures. The longer alkyl chain of higher homologues may be constrained (shown by arrow in fig. 39) to lie in the line with the major axis of the core, giving the same end to end contact for odd and even homologues. Thus the alternation would diminish with increasing tendency of alkyl chain to bend.

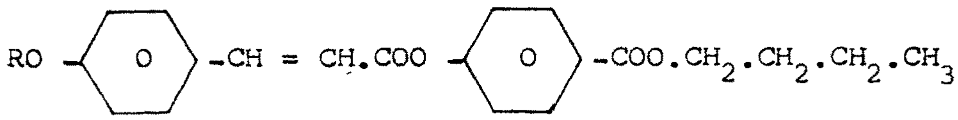
An alternative explanation is that the contribution of each new carbon-carbon bond to the polarizability of the molecules in the direction of long axis is different i.e. greater in short alkyl chains (fig. 39). The polarizability effect is greater on passing from odd to even homologues compared with from even to odd homologues. This terminal intermolecular interaction should therefore alternate as the series is ascended. However, the longer n-alkyl chains bend and come into line with the molecules long axis, so the contribution of every newly added carbon-carbon bond to the polarizability isthe same diminishing the alternation effect.

The shape of smectic-isotropic curve for all the four series are almost same with slight deviations.

The termal stabilities when compared, often offer interesting information leading to molecular characteristics. Since these homologous series 1,2, 3 and 4 have all other molecular structure the same excepting the carboxylate terminal group R' which varies from butyl to heptyl it is the alkyl chain length that increases with every addition of a methylene unit. The variations in the thermal stabilities of the four series are also linked with the variations in chain length and its associated characteristics of the terminal carboxylate group of the homologous series. Another interesting characteristic is that the smectic-isotropic transitions of four series again show alternation effect in their thermal stabilities with the increase in chain length. Thus smectic-isotropic thermal stabilities for series 2 and 4 are higher than those for series 1 and 3. This may be again due to increase in polarizability with the lengthening of alkyl chain.

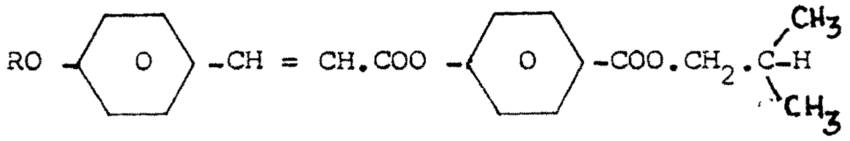
These homologous series are compared with other homologous series. The series 1 is compared with homologous series iso-butyl p-(p'-n-alkoxycinnamoyloxy) benzoates (326), which differ only in the right terminal group. In the present investigation, the alkyl chain at the right terminal end has a straight linking while the iso-butyl p-(p'-n-alkoxycinnamoyloxy) benzoate has iso-dispositioned linking (fig. 40).

A.



n-butyl p-(p'-n'-alkoxycinnamoyloxy) benzoates

B.



iso-butyl p- (p'-n-alkoxycinnamoyloxy) benzoates

FIG. 40

The core geometry is same for both the series but in series (b) the overall length is shortened as breadth of the molecule is increased by one $-CH_3$ unit assuming iso-linking in space (fig. 40).

Now, with shorter length and wider breadth, the transition temperatures of series B should be low, or the homologues of series A are expected to exhibit a little higher transition temperatures. The different values are given in Table 44. With the branched iso-linking of the right alkyl chain, the breadth has increased sufficiently to cause somewhat odd fitting of the molecules, throwing apart the molecules, consequently they need less thermal agitation to break down partially so as to give rise to mesomorphism. But then the total range of mesomorphism is also not much as the molecules break down finally to give rise to isotropic liquid easily. But in the present series, though the molecules in the right alkyl chain are linked straight, a comparatively lower transition temperatures are observed. It can be stated that though the molecules are loosely fitted in iso-disposition, due to increased breadthness of the alkyl chain, at right terminal, the homologues resist the forces of thermal breakdown well enough to exhibit mesophase or yield an isotropic liquid at a higher temperature, when the thermal energy is sufficient enough to break down then partially.

TABLE - 44

No.of carbon atoms in the left alkyl chain	Upper Transitions (mesomorphic-isotpic)		Difference in the transition temperatures (°C)
	Series A :	Series B	
5	101.0	108.0	7.0
6	106.0	113.0	7.0
7	104.0	110.5	6.5
8	107.0	110.0	3.0
10	106.5	108.0	1.5
12	106.5	107.0	0.5
14	106.0	104.0	2.0

Secondly, somewhat surprising though, the nematic property is almost eliminated with the n-linking taking place of the iso-linking. In case of iso-butyl p-(p'-n-alkoxycinnamoyloxy) benzoate, the nematic mesophase is exhibited upto the seventh homologue with the usual odd-even effect. In a striking contrast the present homologous series n-butyl p- (p'-n'-alkoxycinnamoyloxy) benzoate with just one terminal linkage changed, only second and third homologues exhibited nematic mesophase. It appears that the terminal interactions are not sufficiently strong enough to induce nematic property, but the overall polarizability of the molecule is sufficient to cause a layered smectic mesophase to appear. The later homologues of both series under comparison, however show mesomorphic-isotropic transitions almost at comparable temperatures indicating that for higher members, the effect of n-linkage at right terminal of the present homologous series is on the lower solid-mesomorphic transitions only.

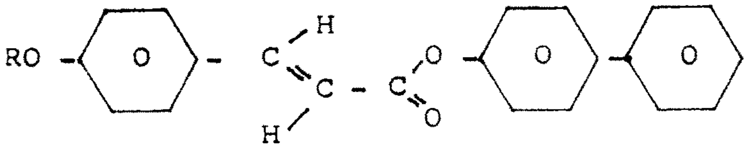
These contrasting features are quite important as these alternations are caused by a slight change i.e. n-linking of the right terminal alkyl chain. But before a generalization is attempted, it would be worthwhile to have some more comparisons made.

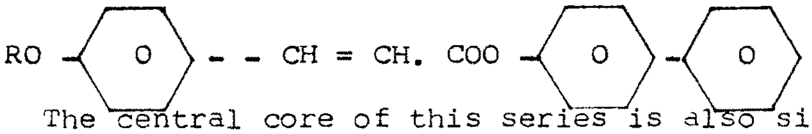
TABLE - 44 (a)

THERMAL STABILITIES

Average Transition Temperature	1	2	3	4	A.	B.	C.
Smectic- Isotropic	106.5 $C_8 - C_{14}$	107.6 $C_8 - C_{14}$	106.9 $C_8 - C_{14}$	107.0 $C_8 - C_{14}$	107.2 $C_8 - C_{14}$	100.2 $C_8 - C_{14}$	148.4 $C_8 - C_{18}$
Nematic-Isotropic	92.5 $C_2 - C_3$	92.5 $C_2 - C_3$	90 C_2	90 C_2	108.7 $C_3 - C_6$	-	206.0 $C_1 - C_4$
Commencement of Smectic mesophase	C_2	C_2	C_1	C_1	C_2	C_1	C_7

Another comparison of interest is with series (C)- Diphenyl 4-trans p-m-alkoxycinnamate (327).





The central core of this series is also similar to that of series under present investigation, but the aromaticity of this series is increased by one more benzene ring which replaces the -COOR' moiety of the series 1, 2, 3 and 4.

The thermal stabilities of this series compiled in Table 44, are quite high. As the increased aromaticity and increased polarizability of a biphenyl ring provides a greater lateral adherence power, the nematic-isotropic stability is increased to a large extent.

In all these homologous series, a common feature is the early commencement of smectic mesophase. As the alkyl chain length is increased with the addition of methylene -CH_2 unit, the smectic mesophase appears quite early as in series 1, it appears at the second member, in series 2, it commences at the third member, in series 3 it commences at second member and the same order is maintained in the other series under comparison. This is in keeping with the generalization that with enhanced polarizability and a typical ratio of terminal to lateral attractions would induce an early beginning of the smectic mesophase.

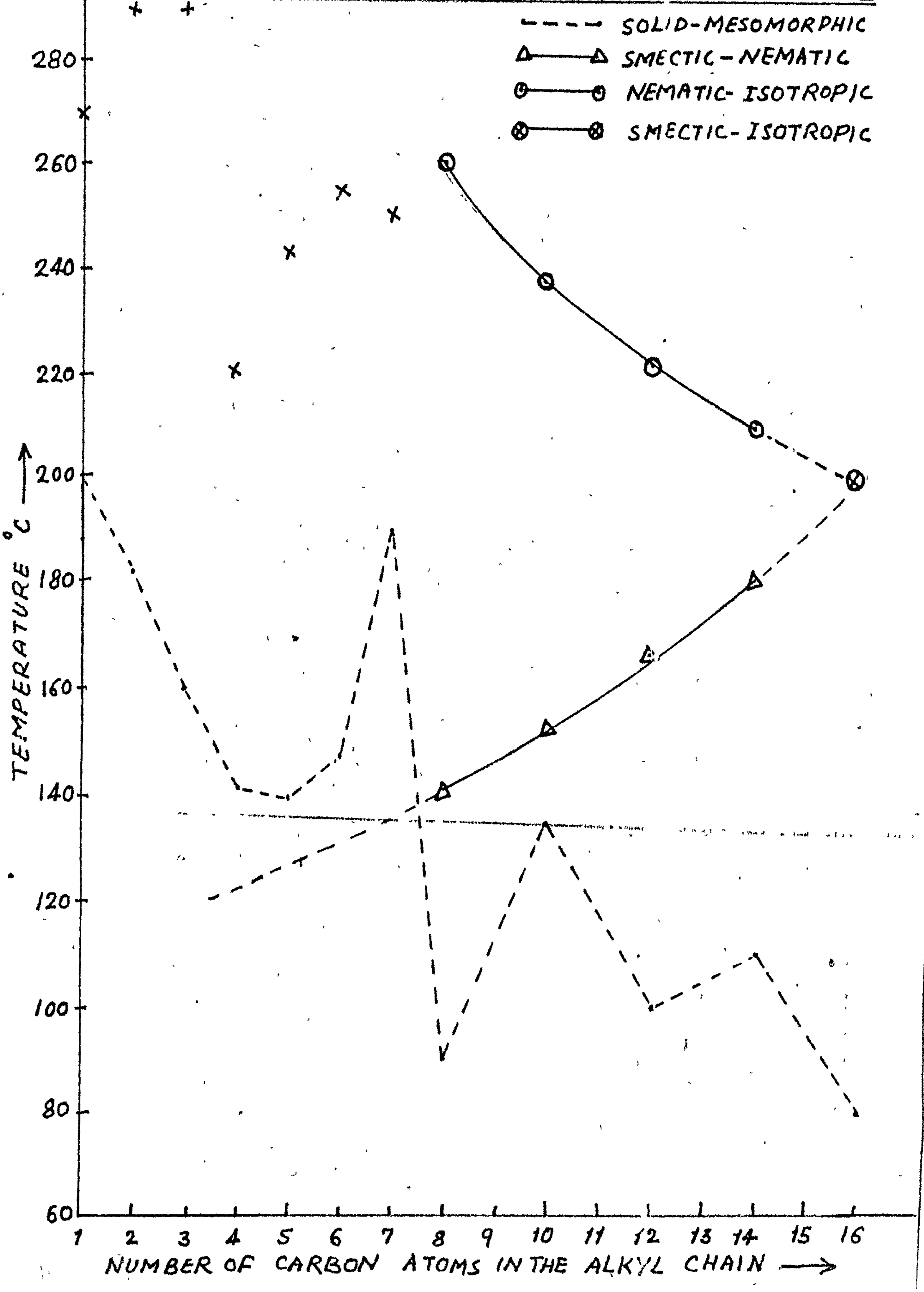
5. P (p'-n-alkoxybenzoyloxy) benzoic acid

This new homologous series of mesogens is indeed typical in several respects. Though some members of this homologous series were prepared as intermediate compounds (328), a detailed account of their transition temperatures and mesomorphic characteristics was not available. All the homologues of this series are having very high transitions obviously the series belongs to the high melting class of homologous series of mesogens. All the homologues of this series exhibit mesomorphism. The various transitions are recorded in Table - 13 and are plotted versus the number of carbon atoms in the alkyl chain (fig. 12).

The solid - mesomorphic curve shows an initial steep fall upto the fifth homologue then curve rises upto seventh homologue after which it follows a course of falling and

FIG 12.

P-(P'-n-ALKOXYBENZOYLOXY)BENZOIC ACID



rising of temperatures in a zig-zag manner right upto the last member studied. The solid-mesomorphic curve shows an overall falling tendency in a good measure as the series is ascended. This tendency is responsible for the widening of the range of mesomorphism upto the last. At the tetradecyl member the mesomorphic range is doubled than what it is at the first member. Still, it is difficult to find out the maximum mesomorphic stage because of the abnormal tendency of most of the homologues of this homologous series to decompose at higher temperatures making it impossible to have smooth transition to the isotropic liquid.

It appears that characteristic dimerization of the acid molecules renders the dimer molecules too long to sustain the high thermal vibrations and rule out any probability of a smooth transition to isotropic liquid. But with the sufficient increase in the alkyl chain length at left terminal end, the lateral attractions induce sufficient resistance to the forces of thermal breakdown of the molecules thus the tenth, twelvth, fourteenth and sixteenth homologues do not decompose but undergo a smooth transition to isotropic liquid.

Other series showing the dimerization of the acid molecules are (i) p-n-alkoxybenzylidene-p'-amino-benzoic

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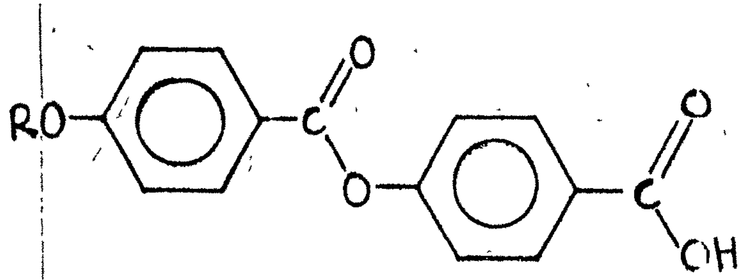
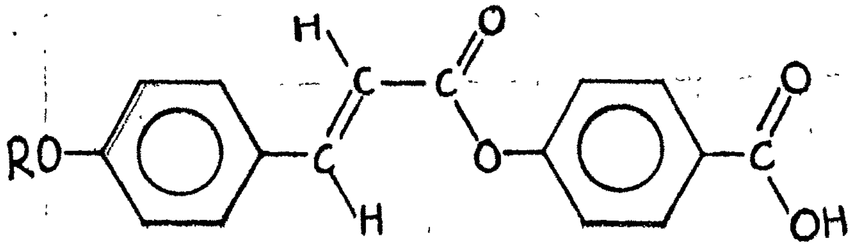


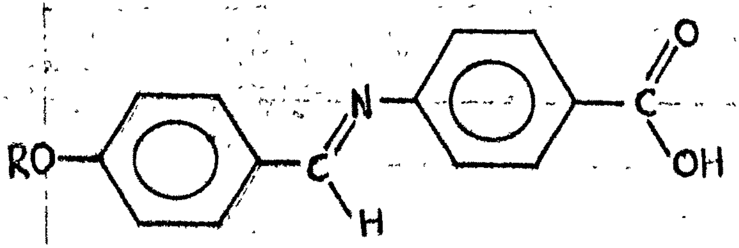
P-(p'-n-Alkoxybenzoyloxy) benzoic acid

(i)



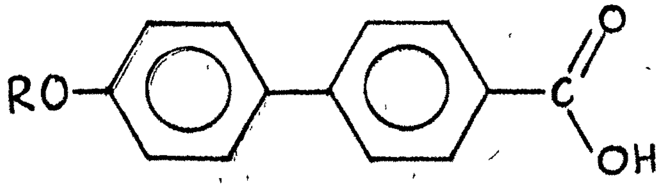
P-(p'-n-Alkoxycinnamoyloxy) benzoic acid (331)

(ii)



P-n-Alkoxybenzylidene-p'-aminobenzoic acid (329)

(iii)



P-n-Alkoxydiphenyl-p'-carboxylic acid (330)

FIG - 44

acid (329), (ii) p-n-alkoxydiphenyl-p'-carboxylic acid (330) and (iii) p- (p'-n'-alkoxycinnamoyloxy) benzoic acid (331). All the three series are mesogenic, the series (i) and (ii) are of high melting nature which show smooth mesomorphic - isotropic transition at such high temperatures as about 290°or 300°, but not a single homologue of these series undergo decomposition whereas all the homologues of series (iii) p-(p'-n-alkoxycinnamoyloxy) benzoic acid decompose at high temperatures without transforming into isotropic liquid. Now the homologues of all the three series under reference would be forming dimer molecules with sufficient length, but the striking feature is that in case of p-n-alkoxybenzylidene-p'-aminobenzoic acid, the central bridge is azomethine - CH = N - group, in p-n- alkoxydiphenyl-p'-carboxylic acid, the central bridge is totally eliminated and in p- (p'-n'-alkoxycinnamoyloxy) benzoic acid the central bridge is quite large. i.e. vinyl caroboxy-CH = CH.COO - group in comparison to only carboxy -COO - group of the present homologous series p- (p'-n- alkoxybenzoyloxy) benzoic acid. It appears, therefore, that an abnormal length due to dimer formation alone may not have brought in the decomposing nature had it not been strengthened with the proper proportionately larger central bridge. The nematic-isotropic curve shows an ascending tendency a characteristic of high melting mesogenic series.

The polymesomorphism commences from the eighth homologue with the appearance of the smectic mesophase at a lower temperature. It should be clear that from the first to the seventh member only nematic mesophase is exhibited which disappears on decomposition of the molecules at higher temperatures. From the octyl homologue to hexadecyl homologue both smectic and nematic mesophases are exhibited. The smectic-nematic transitions are sharp and smooth. The rather late appearance of smectic mesophase could be due to insufficient lateral attractions in relation to terminal attractions until sufficient chain length at octyl level and beyond could be acquired to enhance the lateral attractions in due proportions. High thermal stability of this series may also be attributed to the high ratio of the molecular attractions which would offer abnormal resistanceto the thermal vibrations.

The smooth extrapolation of the smectic - nematic transition curve on left side, indicates that monotropic smectic nematic transition could be obtained for heptyl, hexyl and amyl derivatives of this homologous series at 135.00, 130.5 and 127° respectively, but the transitions are well below the solid - mesomorphic curve and could not be obtained due to early crystallising nature of the homologues.

The texture of the mesophase is homeotropic. Homeotropic textures apparently being indistinguishable from isotropic nature does not give rise to birefringence. However, at the stage of nematic-isotropic, smectic-nematic or smectic-isotropic transition temperatures, the fields become birefringent as bright spots appear which makes the detection of these transitions quite reliable. On cooling as well the birefringence is observed at isotropic-nematic, nematic-smectic or isotropic-smectic for a moment but soon the homeotropic texture change occurs and prevails thereon.

SERIES : 6

P (p'-n-alkoxycinnamoyloxy) benzilidene -p' -nitroaniline

The homologous series 6 viz. p- (p' - n - alkoxycinnamoyloxy) benzylidene - p" - nitroaniline meets all the general requirements of exhibition of liquid crystallanity. The all homologues of the series are mesomorphic though the isotropic points are very high but the mesomorphic range and thermal stabilities are quite wide. The molecular structure of this series may be depicted as below :

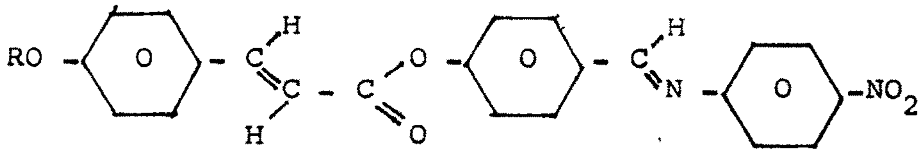
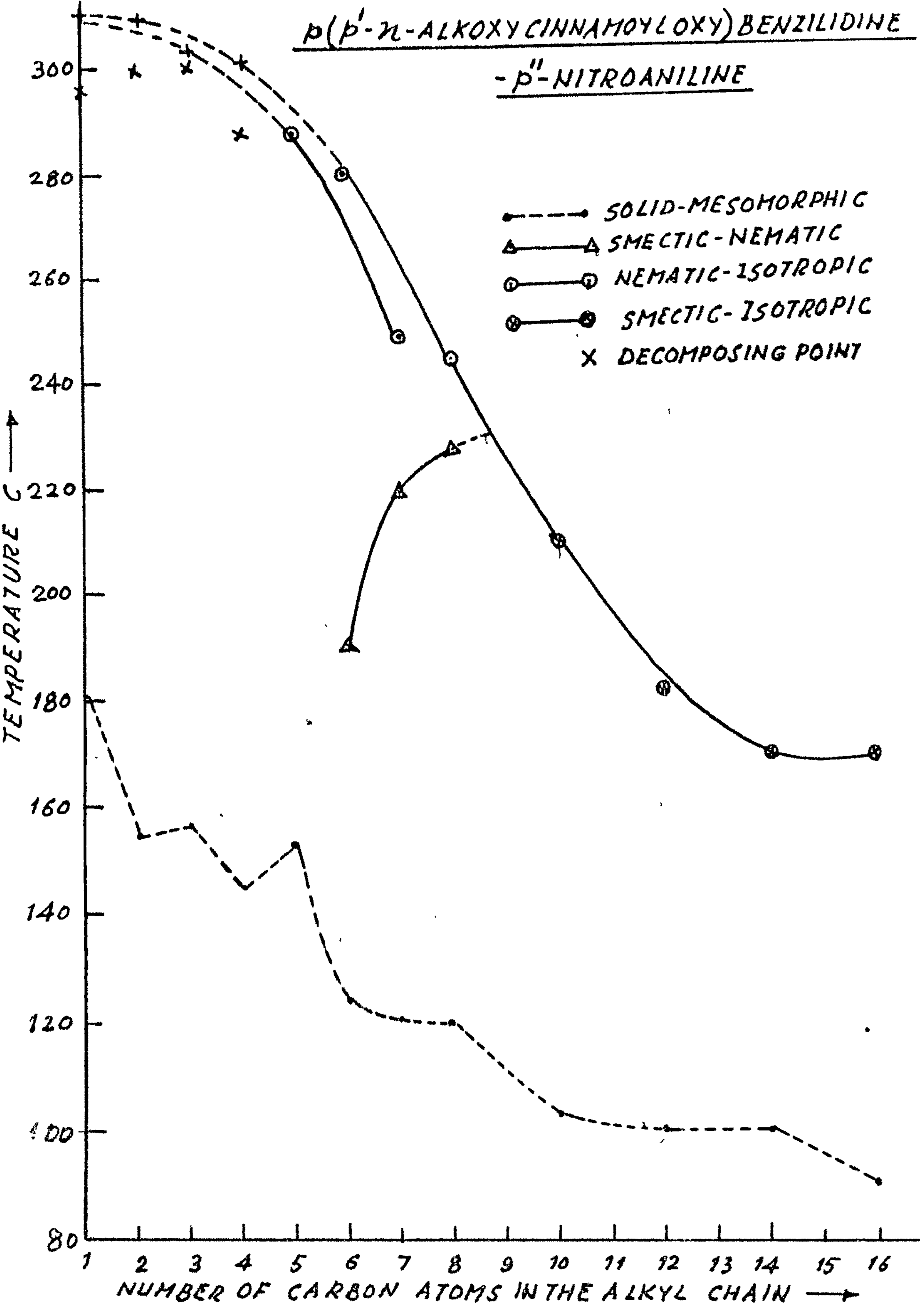


Fig. 41

The solid-mesomorphic transition plot versus the number of carbon atoms in the alkyl chain of the alkoxy end shows an alternation of rise and fall upto the sixth member from the seventh member, the falling tendency continues upto the hexadecyl member of the homologous series (Fig-13).

Only nematic mesophase is exhibited upto the fifth member. The sixth, seventh and eighth members show

FIG. 13.



p(p'-n-ALKOXY CINNAMOYLOXY) BENZILIDINE -p''-NITROANILINE polymesomorphism. The tenth member shows only smectic mesophase which persists thereafter upto the hexadecyl homologue. As is evident from fig. 13, the first four members of this series exhibit mesomorphic range of about 120 - 130° then decomposes before reaching mesomorphic-isotropic point the first at 290.5°, the second at 300°, the third at 300.5° and the fourth at 285°. It appears that molecules cannot resist the high thermal vibrations received at such a high temperature as about 300° and break down all of a sudden instead of following a smooth transition to isotropic liquid.

The nematic-isotropic curve shows the usual odd-even effect. The two transition curves, one for odd members and the other for even members, are very near each other. These curves show a steep fall as the series is ascended, an usual characteristic of high melting series. These two curves on extrapolation toward the left side, indicate the temperatures of nematic-isotropic transitions for the odd and even mebers,respectively, had they not decomposed beforehand. These extrapolated nematic-isotropic transitions are 310°, 310°, 302° and 300.5° for methyl, ethyl, propyl and butyl derivatives, respectively.

Exhibition of only nematic mesophase initially upto the amyl homologue is rather justified as the terminal attractions due to polar ends are high enough in comparison to lateral forces. The stratified layers of smectic mesophase do not get formed due to insufficient lateral adhesions. Both smectic and nematic mesophases are exhibited from the sixth homologue, the increased chain length of the alkyl group affects considerably the ratio of lateral to terminal attractions so as to allow strata formation to take place at relatively low temperatures of 122° giving rise to smectic mesophase in case of hexyl member of the homologue series. The nematic mesophase persists from 190° to 280°, which is a very wide range. The smectic-nematic transition curve from the hexyl member shows a steep rise towards heptyl member then a smooth rise towards the octyl member. On account of the falling nature of one transition curve and the rising nature of the other transition curve, the nematic mesophase narrows down while the smectic mesophase widens up from the heptyl member. As the smectic-nematic transition curve crosses the upper transition curve between eighth and ninth member, the nematic mesophase disappears after the octyl hologue. The nonyl member has not been studied in this investigation and even if the nonyl derivative has been prepared it would have shown only smectic mesophase. The nematic mesophase range of about 90° at the hexyl homologue gets reduced to about 14° at the octyl level while the range of smectic mesophase increases from about 62° at hexyl member to 110° at octyl derivative, the range decreases again as both solid-mesomorphic curve and smectic-isotropic curve show a falling tendency. At the hexadecyl member the range of smectic mesophase narrows down to about 80°. This behaviour of varying ranges of polymesophases can be attributed to the enhanced polarizability due to lengthening of the alkyl chain as the series is ascended added to the lateral attractions emanating from the π electrons of the two central bridges besides the contribution to it on account of an additional benzene ring.

An attempt to locate the monotropic smectic mesophase for the amyl member of the homologous series by smoothly extrapolating the smectic-nematic transition curve to the left hand side is rendered impossible due to extremely steep nature of the said curve between the sixth and seventh member.

The texture of nematic mesophase was threaded and the stratified smectic mesophase assumes focal conic fan-shaped structure of smectic A variety.

SERIES NO. 7

p-(p'-n-alkoxycinnamoyloxy) benzylidene - p"-fluoroaniline

All the members of the series p -(p'-n-alkoxycinnamoyloxy) benzylidene- p" - fluoroaniline show mesomorphism over a wide range of temperatures. Its general molecular geometry may be depicted as follows -

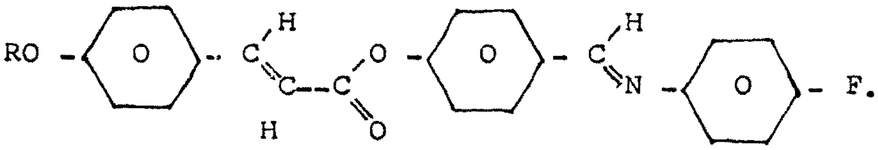


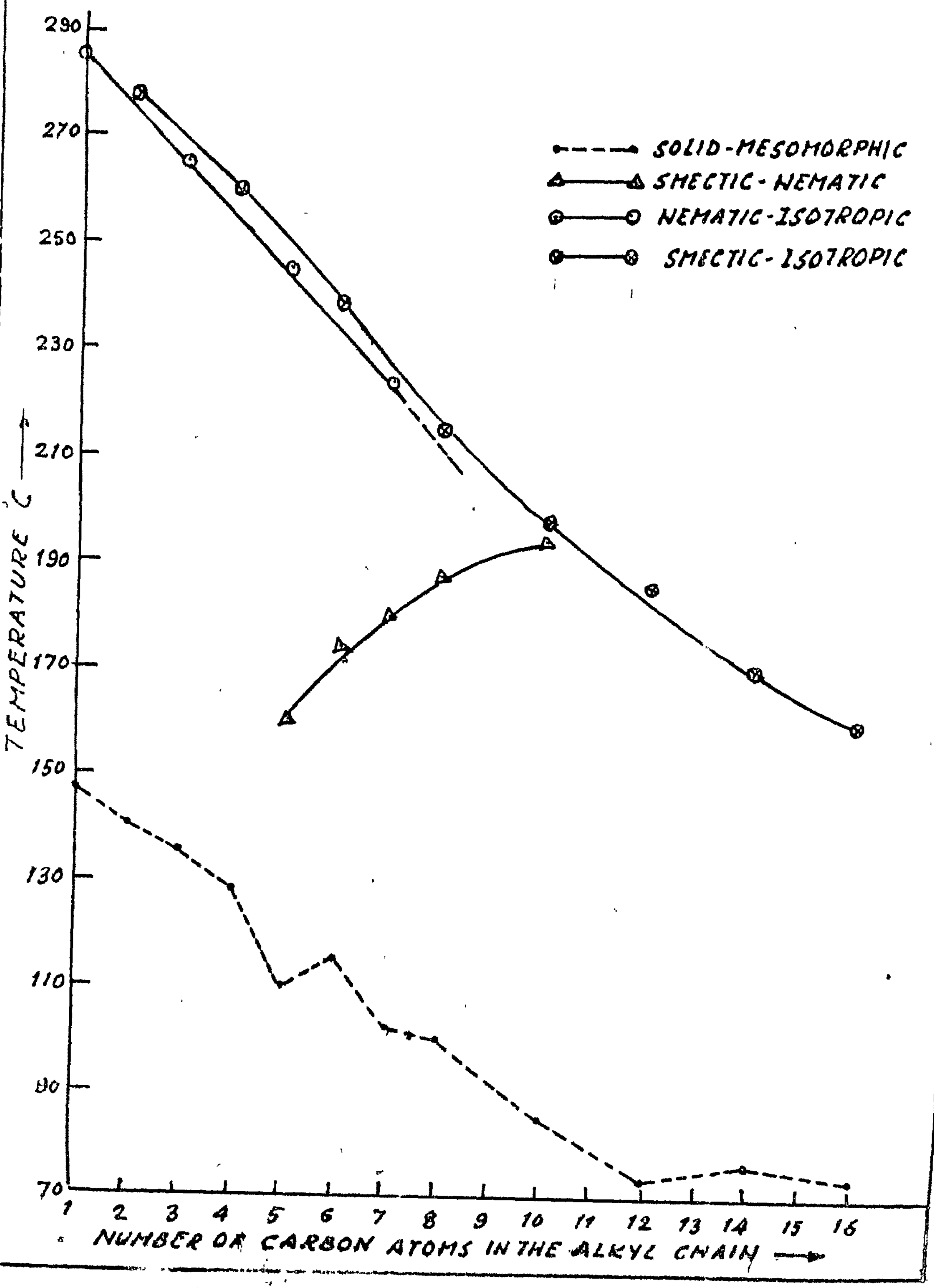
Fig. 42

The solid-mesomorphic versus the number of carbon atoms in the alkyl chain of the alkoxy end shows a continuous falling tendency. Only the fifth member behaves different and shows an upward trend towards the sixth member otherwise the falling tendency continues right upto the dodecyl homologue after which the curve levels off with negligible variations upto the hexadecyl member of the homologous series.

The nematic-isotropic transitions show the usual odd-even effect in a marked manner upto the seventh member. The general nature of the slope of both these curve is of falling nature as the series is ascended. This falling nematic-isotropic transition curve seems to be continuous

FIG. 14.

p-(p'-n-ALKOXYCINNAMOYLOXY) BENZYLIDENE-p''-FLUORANILINE



with the pure smectic-isotropic curve obtained for the last three homologues.

On account of the nematic-isotropic or smectic-isotropic curve showing almost a parallel falling tendency with the solid-mesomorphic curve upto the twelvth homologue, the mesomorphic range is almost maintained unchanged, the levelling off tendency of the solid-mesomorphic curve thereafter reduces the range by about 20° at the tetradecyloxy homologue.

The smectic-nematic transition begins from the fifth homologue with the advent of polymesomorphic region which continues upto the tenth homologue of the series. The smectic-nematic curve rises smoothly as the series is ascended without showing any maximum transition and seems to be merging with the smectic-isotropic transition curve at the eleventh homologue which is not studied in this investigation. The range of smectic mesomorphism is maximum at tenth homologue about 115°.

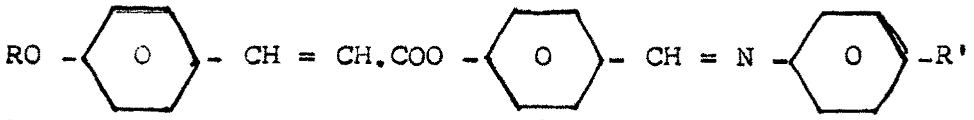
The extrapolation of the smectic-nematic curve to the left side indicates 142° and 117° for the latent smectic-nematic transitions for the fourth and third member respectively. But for the high crystallizing tendency, the monotropic smectic mesophase could not be observed.

Though the homologous series p-(p'-n-alkoxycinnamoyloxy) benzylidene - p" - fluoroaniline is a high melting series, no homologue of this series shows decomposition at high temperatures.

The nematic texture is of threaded variety. The smectic mesophase shows focal conic fan shaped smectic A texture.

General comparative study of series 6 and 7

These two homologous series are very much similar in their molecular geometry, the two central bridges, varying alkoxy group with changing number of carbon atoms in alkyl chain at one end and three benzene rings are the common features of the molecules of these two series. The molecules differ in one respect only i.e. the substitution in the right end. The general molecular geometry of series 6 and 7 may be depicted as below -



R = n.alkyl chain

R' = $-NO_2$ Series 6

= -F Series 7

Fig. 43

Both these series are having high transition temperatures in comparison to those of series 1, 2, 3 and 4. These high transition temperatures are attributed to the introduction of one more benzene ring, which not only increases the aromaticity of the mesogens but also polarizability. The nematic-isotropic transitions of both the series 6 and 7 show a steep fall. This descending nature of the nematic-isotropic curve can be explained as under:

Initially the molecules of these series would have very high residual cohesive forces and end to end cohesive forces due to the presence of highly polar - NO_2 and -F terminal groups at the right, but as the alkyl chain length at the left terminal increases, these terminal forces become weaker and allow interpenetration of the layers to occur more easily lowering the transition temperature.

The nematic-isotropic transition of both the series show usual odd-even effect and the two transition curves, one for odd and other for the even members do not seem to merge together.

With the increase in alkyl chain length, the polarizability of the molecule also increases. This effect will increase the cohesive force operating between the sides and planes of the molecule which are lying parallel to each other thus introducing the smectic mesophase. This smectic mesophase appears at the sixth member in series 6 and at the fifth member in the series 7. But still increasing polarizability due to increase in alkyl chain length tends to make it more difficult for the thermal vibrations to cause the sliding of the molecules out of the layer to give an imbricated nematic pattern. That is why the nematic mesophase gradually disappears, at tenth member in series 6 (the nonyl member was not studied in this investigation but the plot clearly indicates the disappearance of nematic mesophase before nonyl member) and at twelvth member in series 7 (here again the plot clearly indicates the disappearance of nematic mesophase even before the eleventh member also).

The smectic-nematic transitions of both these series do not show any alternation effect. Though some nematogenic series have been reported (332 - 335) wherein the smectic-nematic transitions clearly alternates but in all these series the smectic-nematic transitions appear relatively early. Though it is rather difficult to understand smectic-nematic transitions, it may be suggested that as the lateral cohesive forces become weakened with the increase in alkyl chain length, and as the transition temperatures are not rising steeply, the cohesive forces do not affect the smectic-nematic transitions. So markedly to give a detectable alternation effect.

To understand their nature more explicitely these series are compared with following series :

Series 6 - p(p'-n-alkoxycinnamoyloxy) benzylidene - p" - nitroanilines is compared with -

6-(i) p-(p'-n-alkoxycinnamoyloxy) nitrobenzenes (336)

6-(ii) p-(p'-n-alkoxybenzoyloxy) benzylidene - p" - nitroaniline (337)

6-(iii) p- (p'-n-alkoxybenzoyloxy) m - methoxybenzylidene- p" - nitroanilines (338)

6-(iv) p- (p'-n-alkoxybenzoyloxy) m-chloro-p"-nitroazobenzene (339)

Series 7 p (p'-n-alkoxycinnamoyloxy) benzylidene - p"-fluoro-aniline is compared with -

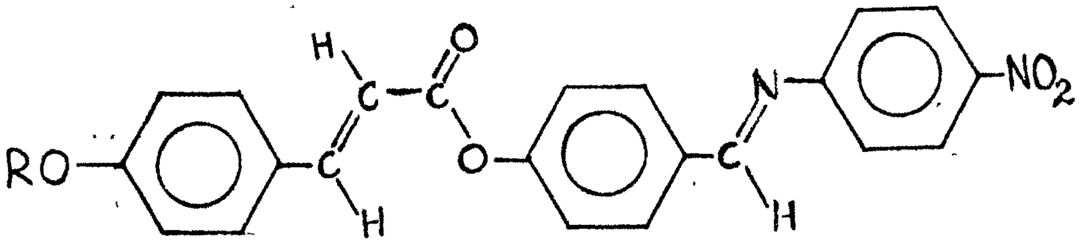
(v) p- (p'-n-alkoxycinnamoyloxy) benzylidene - p" - chloro-anilines (336)

(vi) p- (p'-n-alkoxycinnamoyloxy) benzylidene - p"-bromo-anilines (336)

(vii) p- (p'-n-alkoxycinnamoyloxy) benzylidene anilenes (336)

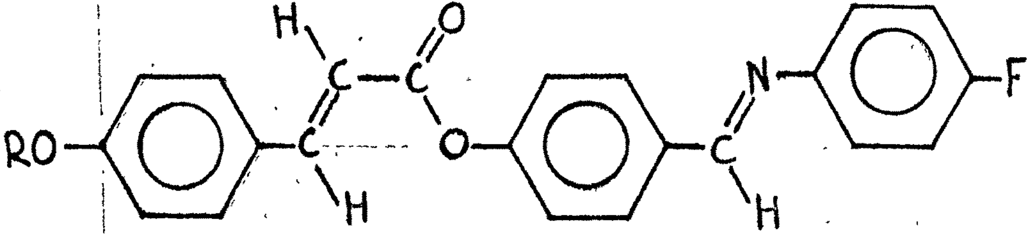
(viii) p- (p'-n-alkoxybenzoyloxy) benzylidene - m - fluoro anilines (339)

6.



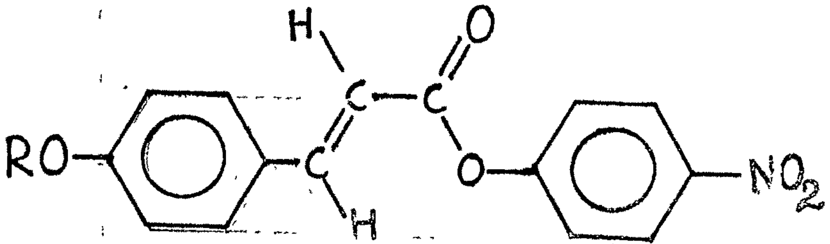
P- (p'-n-Alkoxycinnamoyloxy)benzylidene-p''-nitroaniline.

7.



P- (p'-n-Alkoxycinnamoyloxy)benzylidene-p''-fluoroaniline.

(i)

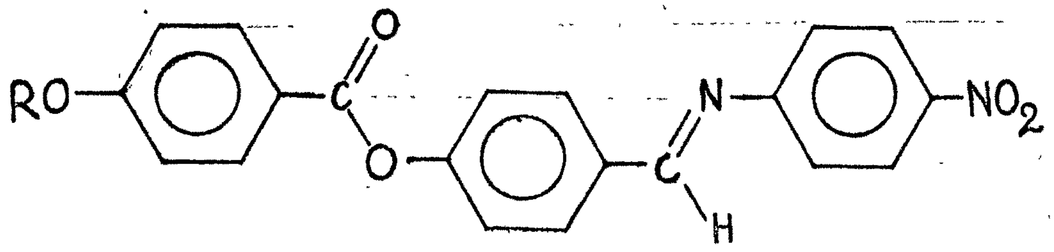


P- (p'-n-Alkoxycinnamoyloxy) nitrobenzene (336)

FIG - 45

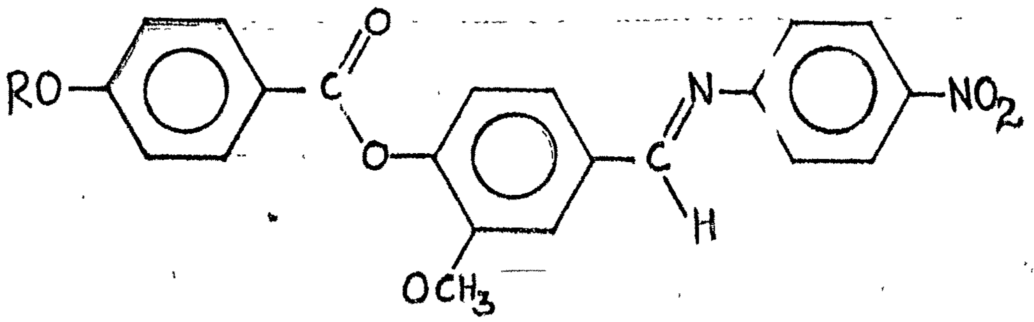
contd.

(ii)



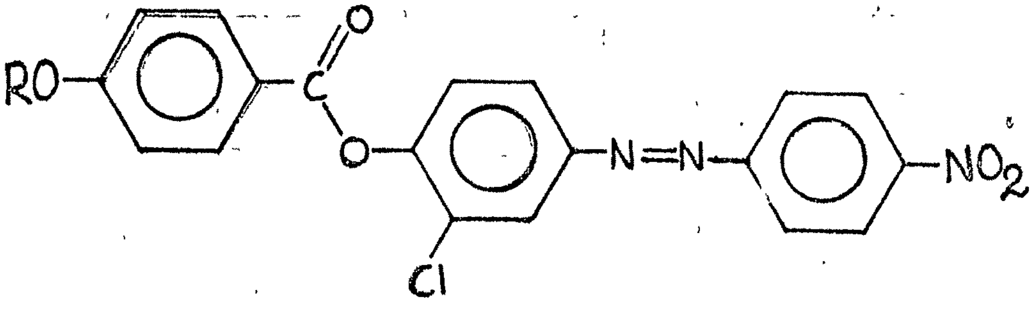
P-(P'-n-Alkoxybenzoyloxy) benzylidene-p''-nitroaniline (337).

(iii)



P-(P'-n-Alkoxybenzoyloxy)-m-methoxybenzylidene-p''-nitroaniline (338)

(IV)

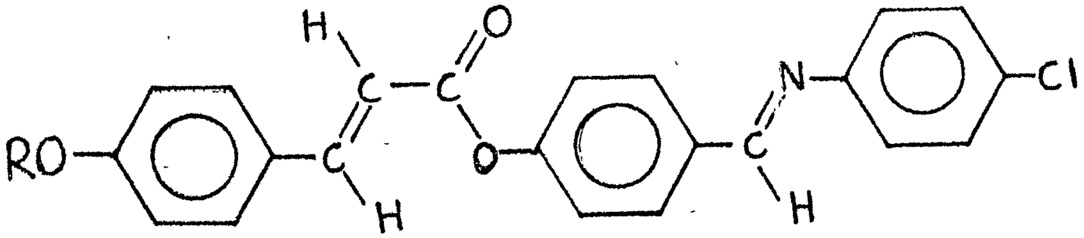


P-(p'-n-Alkoxybenzoyloxy)-m-chloro-p''-nitroazobenzene. (339)

FIG 45

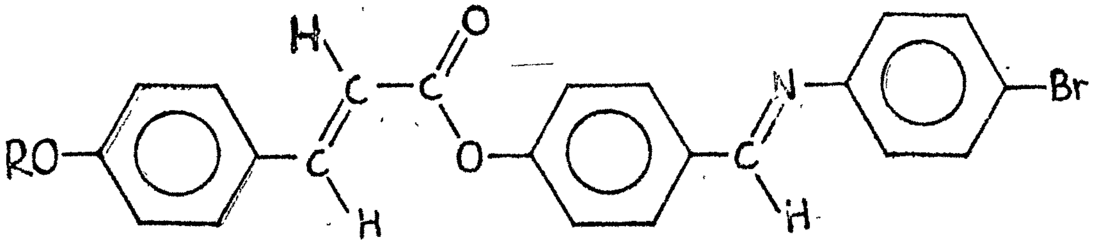
contd.

(V)



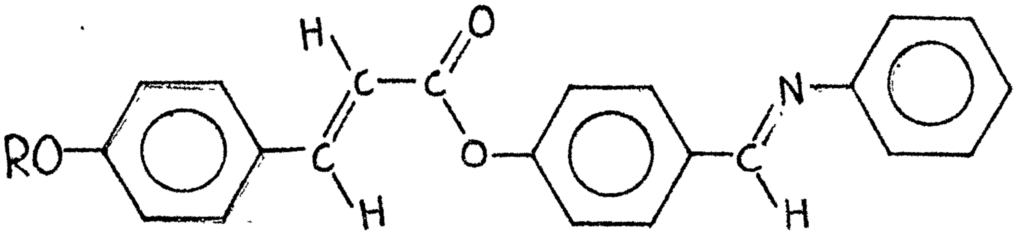
P-(p'-n-Alkoxycinnamoyloxy) benzylidene - p''- chloroaniline (336)

(VI)



P-(p'-n-Alkoxycinnamoyloxy) benzylidene - p''- bromoanilines (336)

(VII)



P-(p'-n-Alkoxycinnamoyloxy) benzylidene - anilines (336)

FIG 45.

The molecular geometry of these Series is depicted in fig. ~~44 and~~ 45.

All these series under comparison have three benzene ring and are almost equally coplaner. Thus the two terminal groups and two central bridges, which vary should account for the variations in their general behaviour.

The series 6 and the (i), (ii), (iii) and (iv) all are having $-NO_2$ group at the right terminal end, but their comparative thermal stabilities (Table 45) reveal a large variation. The average thermal stability for nematic-isotropic and smectic isotropic transitions for series (i) are the lowest in all the four series under comparison. But it is most expected as one benzene ring and one central bridge of azomethine $-CH = N -$ group is absent in this series. So, while the overall breadth of molecules of series 6 and (i) remains the same, the aromaticity and length consequent to azomethine group will be more in series (6) and the molecules of this series will be more coplaner. While the magnitude of terminal attractions remaining almost the same due to same polarity, with more length, more aromaticity, more length to breadth ratio, more polarizability, and more coplaner nature, the upper transition temperatures are increased by about 130° for the homologues of series 6. The lower transitions are

TABLE - 45

THERMAL STABILITIES

AVERAGE TRANSITION TEMPERATURES	6	(i)	(ii)	(iii)	(iv)
Nematic-Isotropic	258.00 C6-C8	121.3 C5-C7	-	164.6 C6-C8	205.5 C6-C8
Smectic - Nematic or Smectic - Isotropic	171.6 C12-C16	134.1 C12-C16	226.6 C12-C16	143.3 C12-C16	159.6 C12-C16
Commencement of Smectic mesophase	C6	C6	C1	C10	C10

also increased within a range of about 30° to about 10°. The overall mesomorphic range is also quite low for series (i) only 40° at the eighth homologue whereas it is 122° for series 6 at the eighth homologue. All homologues of the series 6 are mesogenic whereas the first two members of series (i) e.g. methyl and ethyl do not show mesomorphism at all.

Now, if the absence of an aromatic ring and a central azomethine group is responsible for the comparatively low transitions temperatures of series (i), the absace of vinyl -CH = CH - group also affects considerably the transitions of the homologue of Series(ii). The Series (ii) is purely smectogenic though the transition temperatures are quite high. With the elimination of - CH = CH - linkage, the molecules of Series (ii) will become more non-coplaner in comparison to serie 6 and with the shorter central bridge, the length and breadth ratio will also be changed raising the transition temperatures. It seems that with a changed breadth and length ratio, the highly polar terminal nitrogroup affects the molecules to such an extent that the series exhibits only smectic mesophase.

The higher thermal stabilities of series 6 in comparison to that of Series (iii) and (iv) may also be attributed to the changed breadth and length ratio due to not only the presence of - CH = CH - linkage but also the absence of a lateral methoxy and chloro groups respectively. The methoxy group at meta position in series (iii) increases the breadth of the molecule. Thusthe end to end cohesive forces due to terminal nitro substituent are much weaker in this series. The absence of -CH = CH- linkage also shorten the length of molecule, thus the thermal stabilities of smectic isotropic and nematic-isotropic transitions are considerably decreased. In Series (iv) the breadth of the molecule is increased in comparison to Series 6 by adding one chloro group at meta position, the overall length is decreased by the elimination of -CH = CH- central bridge and the - CH = N- linkage is replaced by -N = N-group. The higher thermal stabilities of Series 6 are, therefore expected as the molecules of this Series are comparatively longer and more polarizable due to the presence of -CH = CH linkage.

The present homologous series 7 differs from the (v), (vi) and (vii) series in its terminal end while the varying alkyl chain at the other end and the main central bridge remains unchanged. In series 7, the right terminal substituent is fluoro (-F) group whereas in series (v), (vi) and (vii), these ends are chloro -Cl, bromo-Br and -H group, respectively. Most of the variations in the mesophase nature can be attributed to these terminal substituents.

All the four homologous series are of comparatively high melting nature. The nematic-isotropic transition curves show a remarkable falling tendency, as the series are ascended. A close observation though reveal that the initial slope of nematic - isotropic transition curve shows a gradation which may find a link with the terminal substituent at the right end. The falling tendency is much steep in case of series 7 which becomes less steep in series (v) and (vi) and it is least within the four series in series (vii). It can be stated that the effect of terminal group on account of varying polarizability and polarity will be contributing towards the steepness or otherwise the falling mesomorphic - isotropic curve. The molecules of present series 7 do not show any decomposing tendency but pass through smooth isotropic transition showing usual odd-even effect but the first four members of series (v) and (vi) decompose abruptly at higher temperatures. The -Cl and -Br groups are broader than the -F group. It seems that with increased breadth, their molecules cannot resist the high thermal vibrations received at such high temperatures and ultimately break-down without passing through smooth isotropic transitions. The odd-even effect shown in nematic-isotropic transitions in series 7 can be explained by assuming zig-zag conformation of Gray (319).

All the four series 7, (v), (vi) and (vii) show polymesomorphism. The first four members of series 7, three each from (v) and (vi) and five member of series (vii) are only nematogens thereafter polymesomorphic character sets in with the advent of smectic mesophase. The members continue exhibiting polymesomorphism upto the tenth member in series 7, (v) and (vi) and upto twelvth member in series (vii), then nematic mesophase gets eliminated endowing the molecules with more smectogenic character. The predominating smectogenic character of halogen groups in various series is well known (340 - 343).

All the four series show quite a good mesophase range. The Table - 46 provides a comparative account of maximum mesophase range in all the series.

TABLE - 46

MAXIMUM MESOPHASE LENGTH

5th member of the homologous series	Maximum mesophase length
7	135.0
(v)	151.5
(vi)	146.5
(vii)	82.0

The Table -46 provides an interesting trend, the mesophase length for present series 7 is quite lower than those of series (v) and (vi). The comparatively weak terminal attractions due to smaller fluoro group should explain the lower phase length.

A comparison of smectic mesophase length suggests that the series 7, (v), (vi) and (vii) are more smectogenic in character.

TABLE - 47

SMECTIC PHASE LENGTH

Series No.	Alkyl member of the homologous series	Phase length
7	12	113.0
(v)	12	125.5
(vi)	12	117.0
(vii)	14	80.0

The large smectic mesophase range clearly confirms that the halogen substituted molecules are more likely to have smectogenic character (340).

Comparison of thermal stabilities (Table -48) of these series provides an interesting study, as molecular geometry and forces play significant role in the thermal stabilities of the homologues. The thermal stability of present series 7 are lower than the thermal stabilities of series (v) and (vi). Though the Fluoro group is more polar and the magnitude of its polarity is much more than that of chloro and bromo groups. It is comparatively smaller in size than chloro and bromo group, so it does not contribute much towards the axial polarizability and is not capable of strong conjugative interactions. Naturally, the homologues of the series 7 are relatively less polarizable, enhancing the ratio of lateral to terminal attractions. With relatively less overall polarizability, the thermal stability is also considerably reduced. This explains the lower thermal stability for series 7. In this manner, the thermal stability of present series p- (p'-n-alkoxycinnamoyloxy) benylidene -p" - fluoraniline are more comparable with p- (p'-n-alkoxycinnamoyloxy) benzylidene - m" -chloroaniline (344). The shift of chloro group from p- to m- position increases the breadth of the molecule and the steric hindrance and lateral adhesion are also increased. The balancing of these two factors seems to be responsible for the lowering of thermal stability of this series to the comparison level with series 7, where the thermal stability is lowered due to less terminal forces associated with fluoro group.

In Series (vii), the therminal substituent is -H group, other core structure is similar to that of series (7). Now, the size of -H group of Series (vii) and -F group of Series (7) is quite comparable. But though they are almost equal in size, the fluoro-group is more polar in nature than -H group, promoting the nematic properties. It is evident (Table - 48) as the smectic

TABLE - 48

Thermal Stabilities

Average transition temperatures	(7)	(V)	(VI)	(VII)	(VIII)
Nematic-Isotropic	226.0 C6-C8	266.0 C6-C8	266.2 C6-C8	195.0 C6-C8	129 C6-C8
Smectic-Nematic or Smectic- Isotropic	170.0 C12-C16	232.2 C12-C16	232.5 C12-C16	168.2 C12-C16	108.2 C12-C16
Commencement of Smectic Mesophase	C5	C4	C4	C6	C8

thermal stabilities of both these series are quite comparable e.g. 170.0° for series 7 and 168.2 for series (vii), but the nematic thermal stability of series 7 is much higher i.e. 226.0° when compared to nematic thermal stability of series (vii) which is 195.0°.

The thermal stabilities of series (7) are much higher than that of series (viii). This can be explained as below. In the series (7), the fluoro group is located at the terminal end, which increases end to end cohesive forces and lateral cohesive forces, whereas the shifting of fluoro group at ortho position in series (viii) will bring its detrimental effect on overall mesophase length as it increases the breadth of the molecule. Thus, the terminal position of fluoro substituent and one additional -CH = CH - linkage at the central bridge results in higher nematic and smectic thermal stabilities in series (7).

Series - 8 :

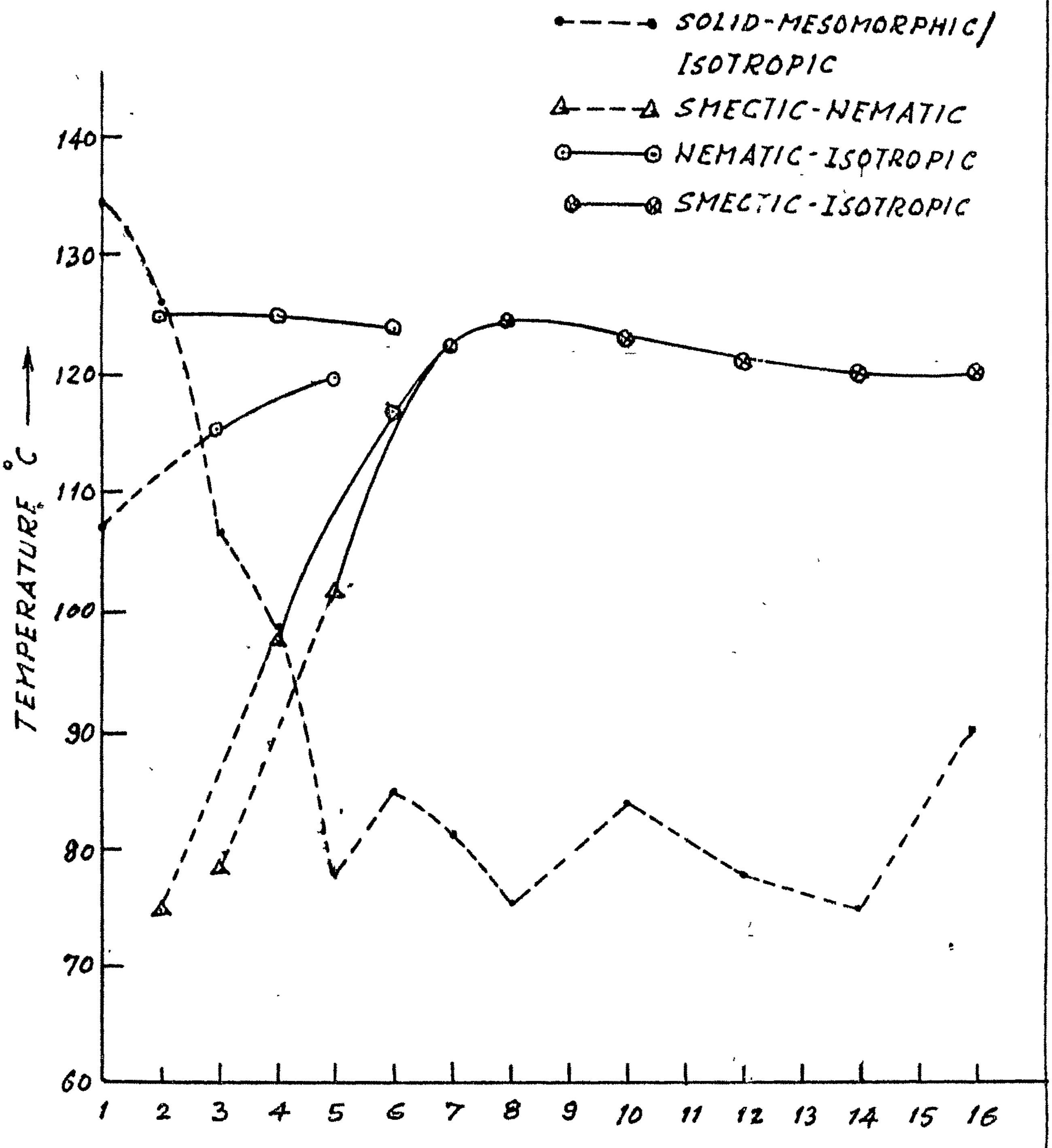
P-(p'-n-alkoxybenzoyloxy) propiophenones

Though some members of the series are reported earlier (323), other members of this series are synthesized to complete the series. As the transition temperature are quite low some binary mixtures are also studied.

It can be observed (fig. 15) that the entire series show mesomorphism, though the first three members shows

FIG. 15.

p-(p'-n'-ALKOXY BENZOYLOXY) PROPIOPHENONE



only monotropic mesomorphism. It seems that these members are unable to resist the strong thermal vibration set on heating and yield an isotropic liquid. While cooling this isotropic liquid, supercooling occurs sufficiently below the solid-isotropic liquid point and molecules, possessing all the prerequisites of mesomorphic behaviour, get the chance of setting themselves to threaded orientation giving rise to monotropic nematic mesophase.

The solid-mesomorphic curve shows a steep fall upto the fifth member. It rises again for sixth member then falls for seventh and eighth member. The curve rises again for tenth member but shows a downward tendency again for twelfth and fourteenth member. The value of this transition is again higher for sixteenth member. This falling tendency of solid-mesomorphic curve provides a broad range of mesomorphism.

Enantiotropic nematic mesophase is exhibited by fourth and fifth and sixth member only and as these members also exhibit smectic mesophase no other member is polymesomorphic as from heptyloxy onwards upto hexadecyloxy member only smectic mesophase is exhibited.

The plot of transition temperatures versus the number of carbon atom in alkyl chain (fig.15) shows the usual odd-even effect. The upper curve corresponds to even members and the lower curve corresponds to the odd members.

The nematic-isotropic curve for odd members shows an initial rising tendency but this curve for even members exhibits a slight falling tendency. The series is a medium melting series. The smectic-isotropic curve shows a rising tendency followed by a slight downward slope towards the sixteenth member.

The two transition curves for the odd and even carbon atoms of the alkyl chain do not seem to be mergingsince the difference in the temperature range between them is somewhat greater than expected.

A smooth extrapolation of the smectic-nematic curve, shown along the dotted ring (fig.15) indicates a temperature of 75° for second member of the homologous series at which a monotropic smectic phase should have been visible but for the high crystallizing tendency of these homologues, the monotropic smectic mesophase could not be observed.

The nematic texture exhibited by the homologues of this series of p- (p'-n-alkoxybenzoyloxy) propiophenone is of threaded varied and the smectic mesophase exhibited focal conic fan shaped texture of Smectic A type.

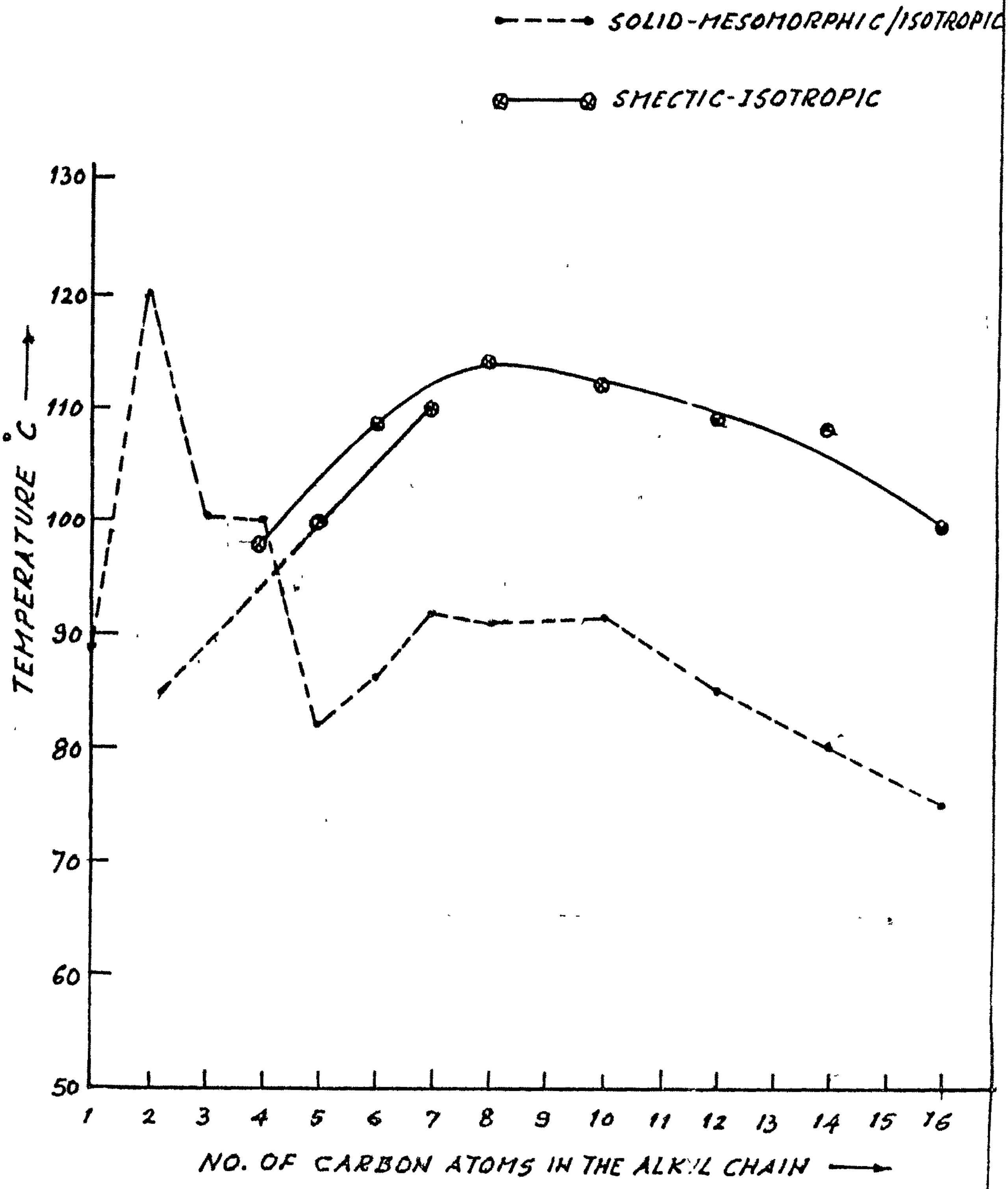
Series - 9

P- (p'-n-alkoxybenzoyloxy) butyrophenone

Some members of this series are also reported (323) earlier but the complete series hasbeen synthesized again to study the behaviour of later homologues. The behaviour of this series of p-(p'-n-alkoxybenzoyloxy) butyrophenone is quite strange. First three members of this series do not exhibit mesomorphism unlike the previous series where it begins from the very first member. Fourth homologue exhibits mesophase in monotropic condition only. None of homologue of this series exhibited polymesomorphism.All the homologues exhibiting mesomorphism are smectogens only. The solid-mesomorphic or solid-isotropic curve shows a continuous falling tendency, though solid-isotropic transition for seventh, eighth and tenth member are slightly higher. The falling trend is predominent right upto the last homologue studied. The smectic-isotropic curve exhibits the alternation for odd and even homologues. These curves show an ascending tendency as the series is ascended but after the eight homologue the curve shows a definite falling tendency giving the a dome shaped structure. If the smectic-isotropic

FIG. 12·15

p-(p'-n-ALKOXYBENZOYLOXY) BUTYROPHENONE



transitions are extrapolated smoothly towards the left side, it will indicate the temperatures (as shown by dotted line in (fig. 16) at which propyl, ethyl and methyl homologues can exhibit a monotropic smectic phase. These extrapolated temperatures are 90°, 82° and 76.5° for propyl, ethyl and methyl homologues, respectively. A careful investigation was made but monotropic mesophase could not be observed as the sudden crystallization of the melt just below its isotropic point could not be prevented.

The mesophase range in the case of series p- (p'-n-alkoxybenzoyloxy) butyrophenone is quite wide though not of the order of the one given by the corresponding propiophenone series.

The texture of the smectic mesophase indicates that it is of Smectic A type.

General characteristics of Series 8 and 9

The series of p-(p'-n-alkoxybenzoyloxy) propiophenones and p-(p'-n-alkoxybenzoyloxy) butyrophenones are synthesized by esterification of p-n-alkoxybenzoic acid with corresponding hydroxy phenone. The p-n-alkoxybenzoic acids are high melting mesogens and their

GENERAL STRUCTURE may be depicted as -

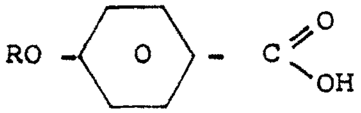
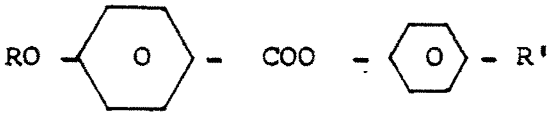


Fig. 46

The transition temperatures are given in Table-2.

High transition temperatures have been interpreted to be so because of hydrogen bonding that occurs on formation of dimers of these p-n-alkoxybenzoic acid molecules. Esterification of these acids eliminates hydrogen bonding yielding p-substituted benzoic acid esters with lower mesophase stability. Both the series may be represented structurally as -



R' = - COC_2H_5 (Series 8) and -COC_3H_7 (Series 9)

Fig. 47

It can be seen that both the series 8 and 9 possess the same core structure and differ in their R' structure as the series 9 is having one more methylene unit at right terminal, the differences in the behaviour of both the series can be attributed to this increased lateral alkyl chain length only. It has been generated by taking into consideration a zig-zag nature of the alkyl chain (350) that when the lateral attractions between the molecules are high, the effect of increased lateral attractions arising from lengthening of the alkyl chain are relatively small. The overall polarizability is also increased with each added methylene unit for the smectic mesophase, lengthening of the alkyl chain affects the thermal stability in two opposing ways - one due to enhancing of primary lateral attractions and the second on account of softening of layer surfaces.

The most striking feature is the total elimination of nematic mesophase in the series 9. With every new methylene unit, the polarizability of the molecule increases thus decreasing the residual lateral attractions, simultaneously decreasing the tendency of molecule lying next to one another.

The behaviour of these series 8 and 9 can well be explained by comparing them with following series.

Series -8 : p-(p'-n-alkoxybenzoyloxy) propiophenone
Series -9 : p-(p'-n-alkoxybenzoyloxy) butyrophenone

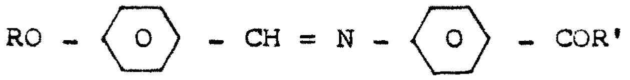
A. P- (p'-n-alkoxycinnamoyloxy) propiophenones (351)

B. P- (p'-n-alkoxycinnamoyloxy) butyrophenone (351)

C. P- (p'-n-alkoxybenzoyloxy) acetophenones (352)

A comparative account of thermal stabilities of these series is shown in Table -49. The smectic and nematic thermal stabilities for Series 8 are higher than that of Series 9 or C which have odd number of carbon atoms in the alkyl chain in the ketonic moity of the molecules. This alternation effect in the thermal stabilities as viewed on the basis of the number of carbon atoms of the alkyl chain in the ketonic portion is quite striking and may be attributed to the same reasons as for the odd-even effect arising from the alkoxy groups at the other end. This alternation is also marked for the thermal stabilities for the nematic - isotropic transition.

The mesomorphic characteristics of substituted benzylidene anilines (353) are also studied. Their general structure is as follows -



Where R and R' stand for alkyl chains.

The following Table shows three mesogens where R is methyl group and R' is ethyl or propyl group.

TABLE 49

THERMAL STABILITIES

Average Transition Temperatures	8	9	A	B	C
Smectic - Nematic or Smectic - Isotropic	120.9 $C_8 - C_{16}$	108.5 $C_8 - C_{16}$	152.5 $C_6 - C_{18}$	146.2 $C_8 - C_{18}$	83.0 $C_8 - C_{16}$
Nematic - Isotropic	122.8 $C_3 - C_6$	-	163.0 $C_5 - C_6$	143.3 $C_1 - C_4$	-
Commencement of Smectic Mesophase	C_4	C_4	C_4	C_3	C_6

The first members of Series (8) and (9) of the present investigation have the same bearings.

TABLE - 50

Substituted Benzylidene Anilines (353)

Compound	R	R'	Smectic Range 0°	Nematic Range °C
1	CH_3	C_2H_5	-	115 - 132
2	CH_3	C_3H_7	-	101 (96) *

* = monotropic

As those mentioned in the table where R is methyl and R' is ethyl or propyl group with the change in central bridge. The substituted benzylidene anilines have -CH = N - Central group whereas those present compounds have -COO- group. Their mesomorphic temperatures are given in Table -51.

TABLE - 51

Ketonic Compound

Compound No.	R	R	Smectic Range	Nematic Range
1	CH_3	C_2H_5	-	134 - 107.5 *
2	CH_3	C_3H_7	-	89° (a)

* monotropic

(a) non-mesomorphic

A comparison of these two Tables 50 and 51 shows that the change in central group greatly affects the mesonophic characteristics. The thermal stabilities are greatly lowered for Series (8) and (9) because the oxygen atom of the central carboxy group in the molecules will be bumping into the non-bonded sides of the adjacent hydrogens of the aromatic ring which will cause considerable strain on the molecule. Consequently a twist ground C-O bend will occur forcing the benzene ring out of the plane of molecule, reducing the co-planarity of the molecule to some extent making them thick. Though the hydrogen atom of the azomethine group -CH=N- will also behave in the same way bringing about a twist in the molecules, but the twist in this case will be less than that brought about by bumping of the oxygen atom of carboxy group. Naturally the molecules of Series (8) and (9) are less co-planer than the molecules of that series. Thus the series thermal stabilities of Series (8) and (9) are decreased.

Evaluation of the characteristics of the new series of Mesogens

All the new homologous series answer the basic requirements for exhibiting mesomorphism. But the variations in the polar nature of the terminal groups besides the additional ring and middle group in the sixth and seventh series along with the shifts in the overall polarizability of the mesogens displays a corresponding changing pattern in the extent and variety of mesomorphism.

The corresponding homologues of the first four series differ only in the terminal groups of the ester sector of the molecule which are (i) butyl $-COOC_4H_9$ (ii) amyl $-COOC_5H_{11}$ (iii) hexyl $-COOC_6H_{13}$ and (iv) Heptyl $-COOC_7H_{15}$. These terminal groups are in the increasing order of chain length as methylene $-CH_2$ units are added as well as of polarizability as the chain length increases. The fifth series has a carboxylic -COOH group at the other end with a comparatively shorter central bridge of carboxy -COO-unit only. The sixth and seventh series have an added phenylene unit through an additional middle bridge alongwith the main vinyl carboxy -CH = CH.COO-central bridge ending with more polar terminal groups viz. nitro $-NO_2$ and fluoro -F group.

In order to obtain an efficiency order, thermal stabilities of series 1, 2, 3 and 4 are compared. All other molecular aspects being common and the difference being that of the other terminal or lateral substituent, an order for the terminal or lateral substituent can be derived by taking into consideration their average thermal stabilities which are presented in Table .

The order for smectic thermal stabilities derived from series 1 to 4 is given as under:

Smectic Order (decreasing sequence)

$COOC_5H_{11} > COOC_7H_{15} > COOC_6H_{13} > COOC_4H_9$

Nematic Order (decreasing sequence)

$COOC_5H_{11} = COOC_4H_9 > COOC_7H_{15} = COOC_6H_{13}$

As only one member each from series 3 and 4 exhibited nematic mesophase, the generalization is not reliable.

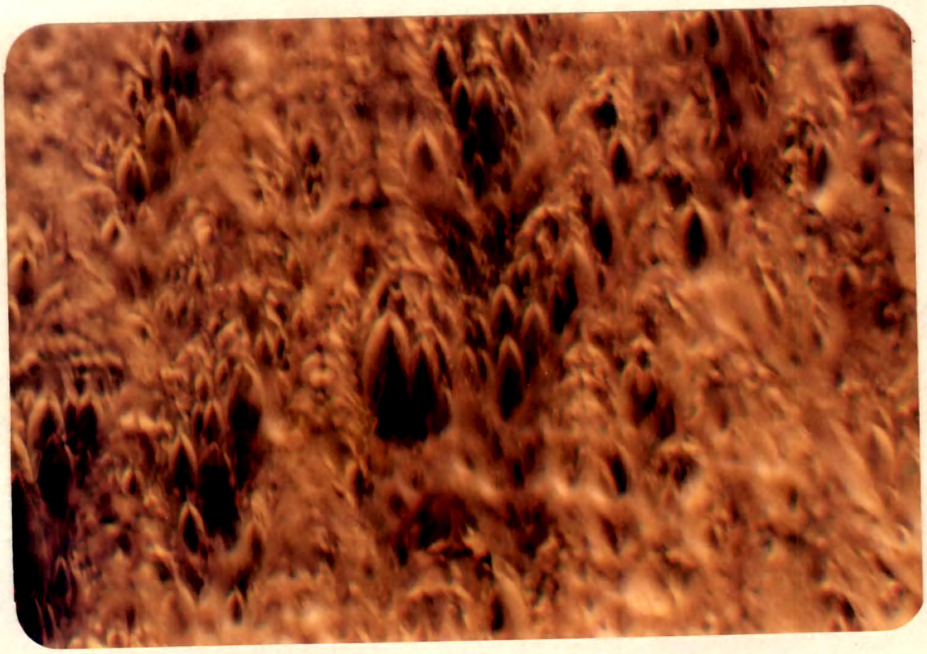
Identification of Smectic Mesophases

Most of the compounds investigated in the present study exhibit smectic mesophases. The identification of smectic mesophase is usually done by miscibility studies (30, 31, 345) as like phases are miscible with each other in all proportions whereas the unlike phases are only partially miscible. The technique is used by a number of workers in the field (31, 345 - 347) and is quite reliable. However, the calorimetry (348) and X-ray (348 -349) analysis can finally confirm the types of smectic mesophases.

In the present study, the mesophases are inferred from the textures observed under polarizing microscope, but it is not possible to identify the various forms of smectic mesophases under this microscope, as the textures of various forms of smectic mesophases are quite similar, showing only a little deviation of usual focal conic textures.

An attempt to study the smectic mesophases exhibited by the homologues of new mesogenic series is also made by means of miscibility method. Following lebelled compounds were used for characterization -

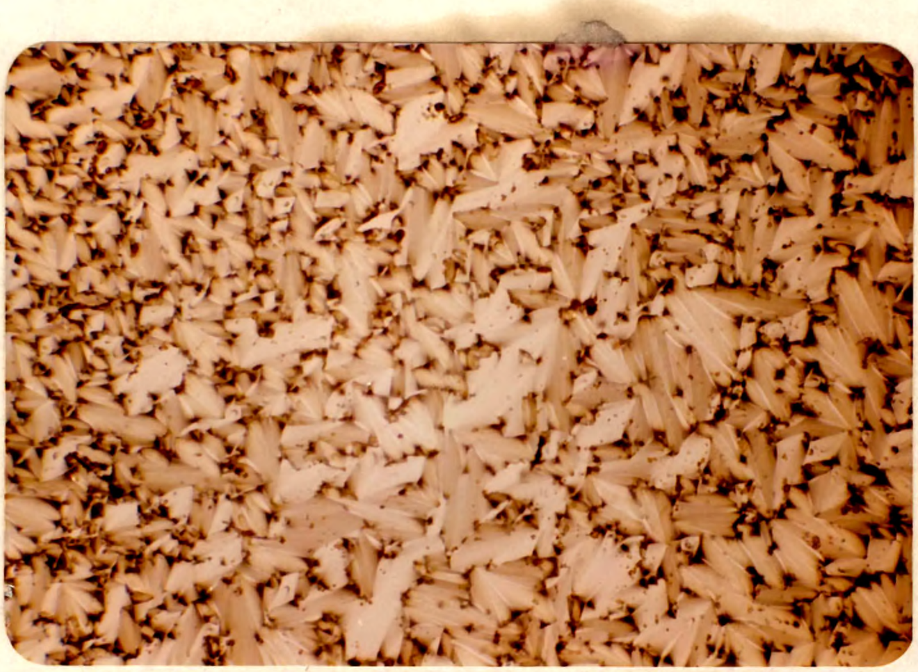
SMECTIC MESOPHASE.



SMECTIC A - FOCAL CONIC TEXTURE OF n-BUTYL p-(p'-n'-OCTYLOXYCINNAMOYLOXY) BENZOATE AT 101°C (HEATING). FILM BETWEEN CROSSED POLARIZERS. MAGNIFICATION X 96.

FIG. 48.

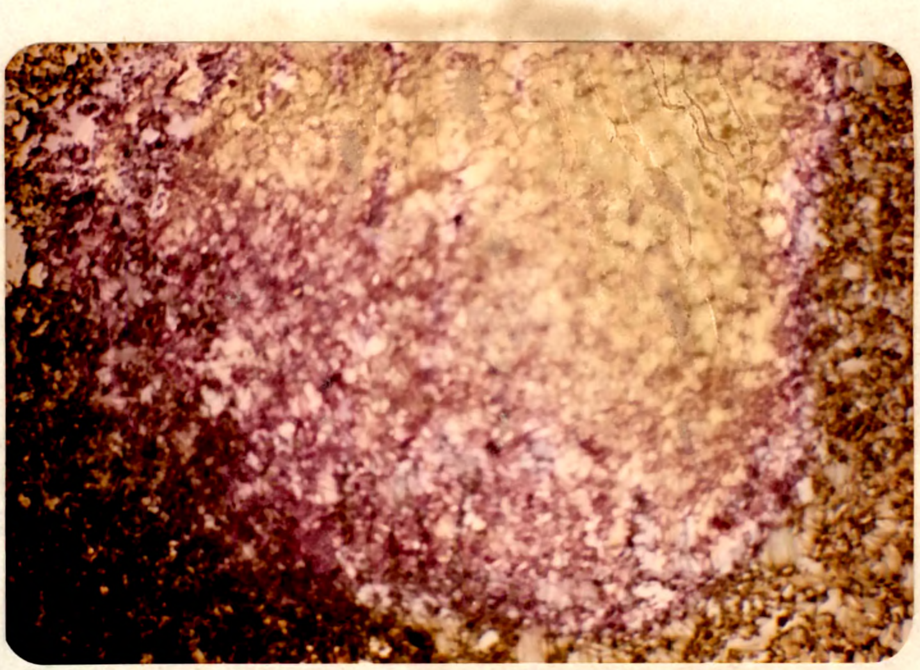
SMECTIC MESOPHASE.



SMECTIC A - FAN SHAPED TEXTURE OF n-AMYL p-(p'-n'-HEXYLOXYCINNAMOYLOXY) BENZOATE AT 107°C (COOLING). FILM BETWEEN CROSSED POLARIZERS. MAGNIFICATION X 96

FIG - 48.

SMECTIC MESOPHASE.



SMECTIC MESOPHASE OF n-AMYL P-(P'-n'-HEXYLOXYCINNAMOYLOXY) BENZOATE AT 77°C (HEATING). FILM BETWEEN CROSSED POLARIZERS. MAGNIFICATION X 96.

FIG - 48.

(A) Smectic A lebelled compounds.

(i) P- Propyl phenyl ester of p-n-amyloxy benzoic acid

$$C \xrightarrow{92.5^\circ} SA \xrightarrow{110^\circ} N \xrightarrow{118^\circ} I$$

(ii) ISO - Butyl P-(p'n-amyloxycinnamoyloxy)benzoate

$$C \xrightarrow{79.0^\circ} SA \xrightarrow{102^\circ} N \xrightarrow{108^\circ} I$$

(B) Smectic C levelled compounds.

(i) p.n.Dodecyloxy benzoic acid

$$C \xrightarrow{95.0^\circ} Sc \xrightarrow{129.0^\circ} N \xrightarrow{137.0^\circ} \text{Isotropic liquid}$$

(ii) p.n. Hexadecyloxy cinnomic acid

$$C \xrightarrow{117.5^\circ} Sc \xrightarrow{159^\circ} I$$

The following homologues of series were characterized :

Series 1 n. Butyl P- (p'-n'-alkoxycinnamoyloxy) benzoate

Smectogens - n-propoxy to n-hexadecyloxy derivative

Series 2 n.Amyl P-(p'-n'-alkoxycinnamoyloxy) benzoate

Smectogens n- propoxy to hexadecyloxy derivative.

Series 3 : n-Hexyl p-(p'-n'-alkoxycinnamoyloxy) benzoate
Smectogens n - propoxy to hexadecyloxy derivative

Series 4 : n -Heptyl p-(p'-n'-alkoxycinnamoyloxy)benzoate
Smectogens n-octyloxy to hexadecyloxy derivative

Series 6 : P(p'-n-alkoxycinnamoyloxy) benzylidene p" - nitroaniline

Smectogens n-hexyloxy to hexadecyloxy derivative

Series 7 : P(p'-n-alkoxycinnamoyloxy) benzylidene p"-fluoroaniline
Smectogens n-amyloxy to hexadecyloxy derivative

First the inter-miscibility of above homologues within the series is studied. The study indicated that the smectic mesophases exhibited by homologues of a particular series are completely miscible with each other. Then one homologue each from all the series is studied with lebelled compounds as mentioned above.

The texture observed in polarizing microscope (fig.48) indicates that the texture of smectic mesophase is focal conic fan shaped texture of smectic A variety.

The miscibility study also confirmed that the smectic mesophase exhibited by the homologues studies is of smectic A variety.

Infra-red spectroscopy

Some of the hemologues of the Series P- (p'-n-Alkoxycinnamoyloxy) benzylidene -p"- flueroaniline have been characterized by the infra-red spectroscopy. The phenyl ring vibrations are observed in the region 800 cm^{-1}, 1200 cm^{-1} and 1600 cm^{-1}. The carbonyl group vibrations are observed in region 1700 - 1800 cm^{+} and - CH = N- group vibrations and alkyl vibrations are obtained at 3000 cm^{-1}. The -F substitution vibrations are at 1000 - 1400 cm^{-1}.

The infra-red spectra, therefore, confirms the molecular structure assigned to the hemologues of this series.

MIXED MESOPHASES

The transition temperatures of pure mesogens are lowered by the presence of any foreign substance. The presence of such substances also cause more or less readjustment of molecules in the domain structure, thus affecting its physical and chemical properties. The extent of these variations in mesomorphic properties depends upon the characteristics of mesomerphic component and the molecular disparities of the mixed component as well as its mixing tendency with the mesogen.

The mixed mesomorphic systems could be classified as binary, ternary and so on. While selecting the homologues as components, the only aspect that was predominant was the extent of lowering of mixed transitions and obtaining a lower range of mixed mesomorphism. While this objective is not satisfactorily fulfilled the mixed study nevertheless has presented very interesting features with probabilities for further investigations. The work has been carried out with extremely small quantities of the materials, any detailed and perfect determinations have been ruled out as beyond the scope of present investigation. Again, the DTA and DSC techniques of investigating mixtures might have proved more fruitful but the limitations under which the present investigation has been carried out are too obvious to feel apologetic.

Most of the binary mixtures, studied for this investigation, were mainly comprising components, both of which were mesogens, the components, being the member of same homologous series, have the same molecular structure. So the molecules of both the components have an identical domain structure, also forming a homogeneous mixed liquid crystal. Binary mixtures where one or both the components are monotropic mesogens are also investigated from the point of view new of studying the characteristic traits condusive to exhibition of enantiotropic mesomorphism.

TABLE - 52

The binary systems studied are -

GROUP A:- A non-mesomorphic compound -n-Butyl p-(p-methoxycinnamoyloxy) benzoate mixed with.

(1) -n-Butyl p-(p'-ethoxycinnamoyloxy) benzoate

(2) -n-Amyl p-(p'-methoxycinnamoyloxy) benzoate

(3) -n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate

GROUP B :- Monotropic smectogen but enantiotropic nematogen -n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate mixed with

(4) -n-Amyl p-(p'-methoxycinnamoyloxy) benzoate

(5) -n-Amyl p-(p'-n'-propoxycinnamoyloxy) benzoate

(6) -n-Amyl p-(p'-n'-butoxycinnamoyloxy) benzoate

(7) -n-Amyl p-(p'-n'-amyloxycinnamoyloxy) benzoate

GROUP C :- Both the components show enantiotropic smectic mesophase.

p-n-Butyl p-(p'-n'-butoxycinnamoyloxy) Benzoate mixed with

(8) p-n-Butyl p-(p'-n'-amyloxycinnamoyloxy) benzoate

(9) -n-Amyl p-(p'-n'-butoxycinnamoyloxy) benzoate

-n-Amyl p-(p'-n'-amyloxycinnamoyloxy) benzoate mixed with

(10) -n-Amyl p-(p'-n'-butoxycinnamoyloxy) benzoate

(11) -n-Butyl p-(p'-n'-amyloxycinnamoyloxy) benzoate

GROUP D :- One component shows polymesomorphism.

p-n-Butyl p-(p'-ethoxycinnamoyloxy) benzoate mixed with

(12) -n-Butyl p-(p'-n'-propoxycinnamoyloxy) benzoate

(13) -n-Butyl p-(p'-n'-butoxycinnamoyloxy) benzoate

(14) -n-Butyl p-(p'-n'-amyloxycinnamoyloxy) benzoate

(15) p-n-Amyl (p'-ethoxycinnamoyloxy) benzoate and
p-n-Amyl (p'-n'-propoxycinnamoyloxy) benzoate
mixed with

(16) p-n-Butyl (p'-n'-propoxycinnamoyloxy) Benzoate

(17) p-n-Amyl (p'-n'-butoxycinnamoyloxy) benzoate

A few binary mixtures comprising the homologues of another ester series are also studied. These are as follows -

(18) p-(p'-n-propoxybenzoyloxy) propiophenone mixed with
p- (p'-n-methoxybenzoyloxy) butyrophenone.

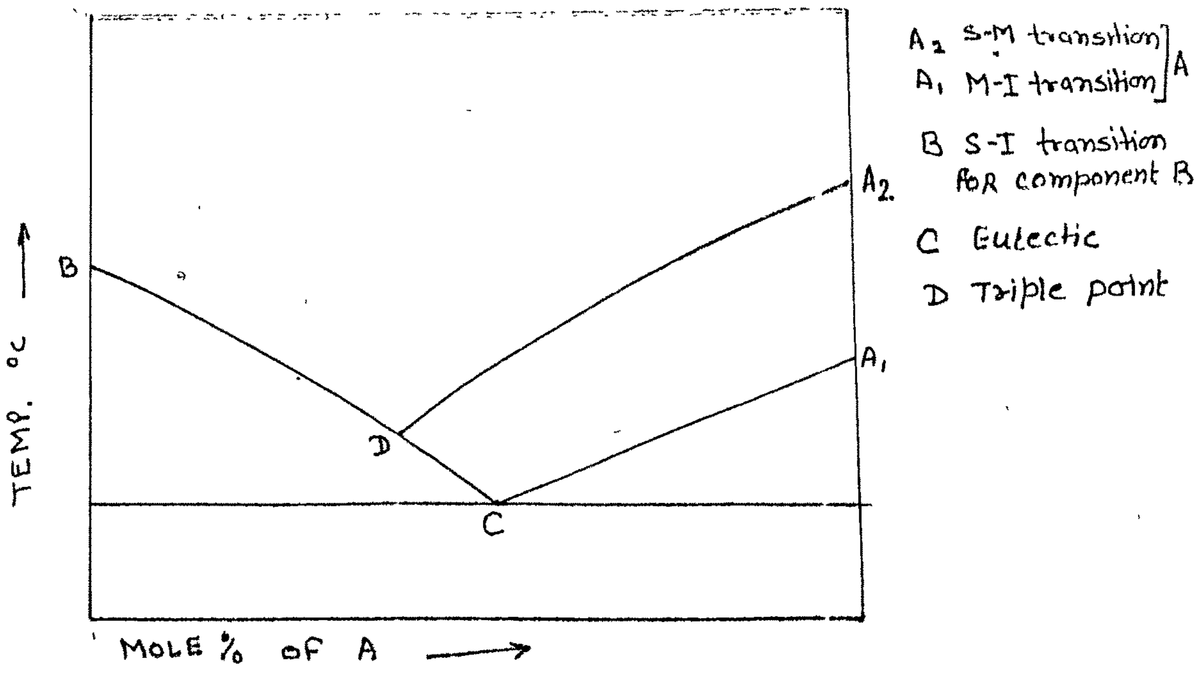
(19) p-(p'-n-ethoxybenzoyloxy) propiophenone mixed
with p-(p'-n-propoxybenzoyloxy) propiophenone.

(20) p- (p'-n-Ethoxybenzoyloxy) propiophenone mixed
with p-(p'-n-Butoxybenzoyloxy) propiophenone.

(21) p- (p'-n-Amyloxybenzoyloxy) butyrophenone.

PHASES CHARACTERISTICS

The work of earlier researchers in the field of mixed mesomorphism viz. that of Bogojawlensky, Winogradow, Varlander, Walter, de Cock etc. is of classical importance and some of their conclusions still hold their ground. The recent reports work was revived by Dave and Dewar (262) and was intensively followed up by Lohar(263) Vasanth (264), Shroeder (363), Goldberg (364) etc.



BINARY SYSTEM 11:B.

Fig 47A.

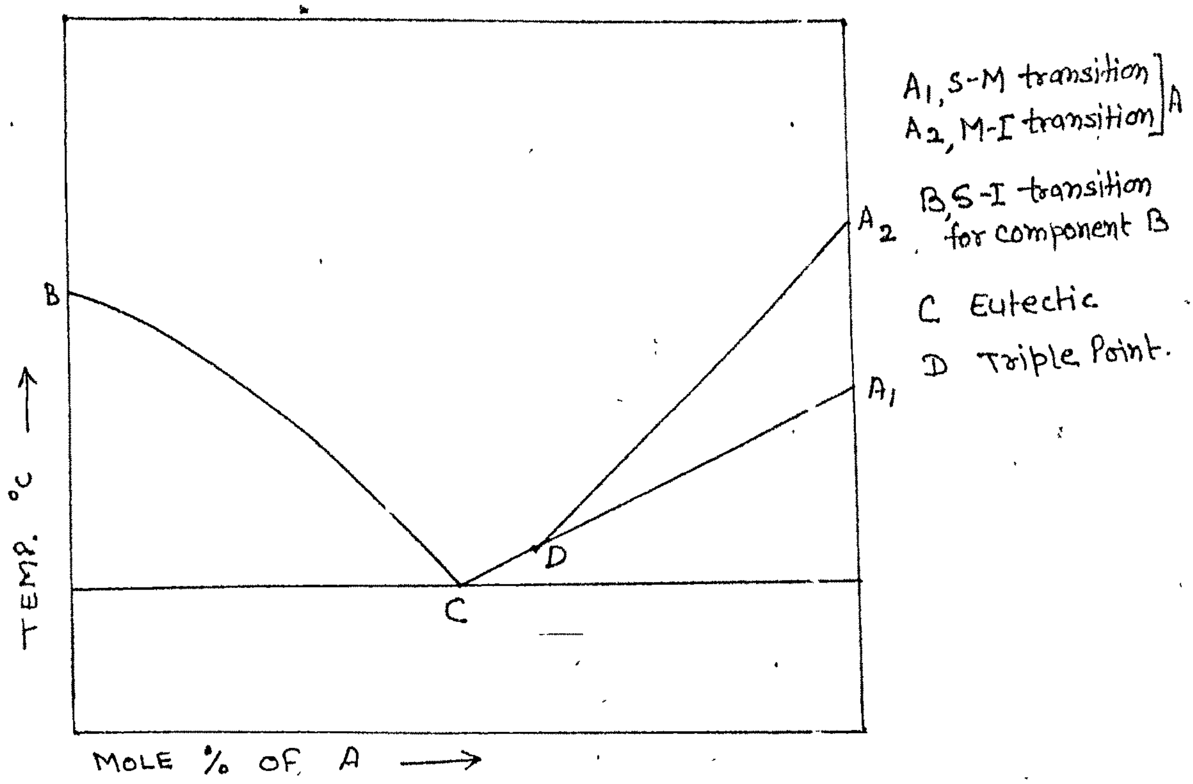


Fig 47 B.

BINARY SYSTEM A: B.

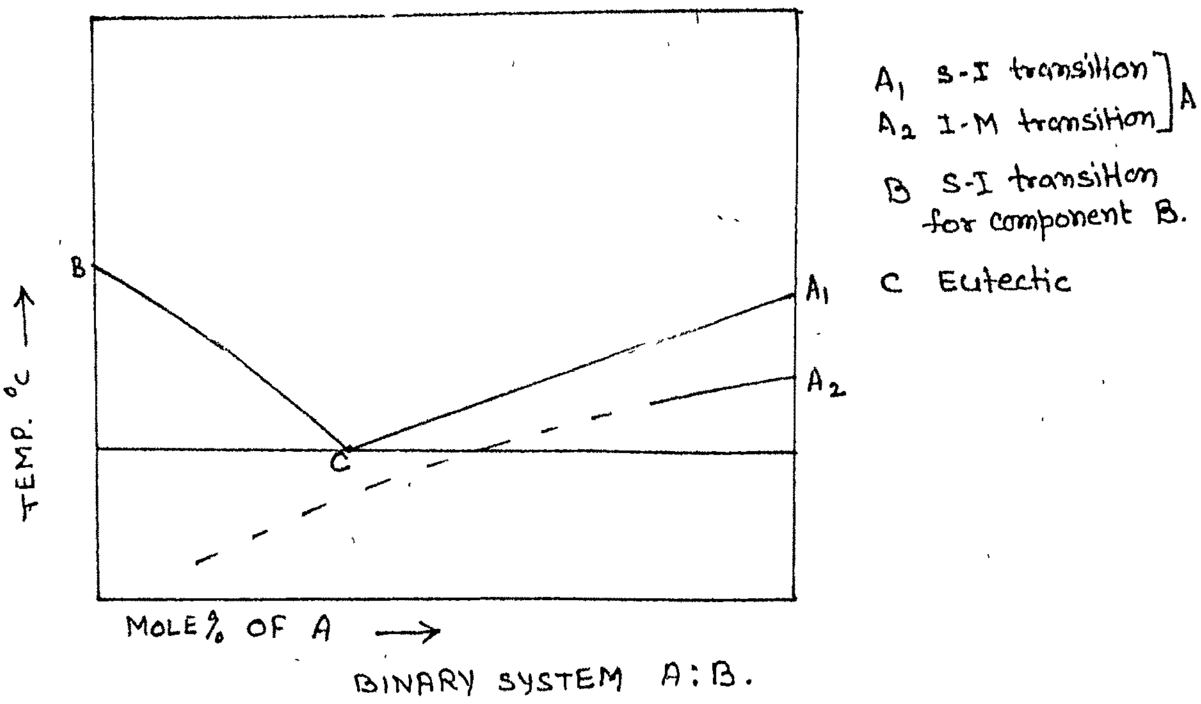


Fig 47C.

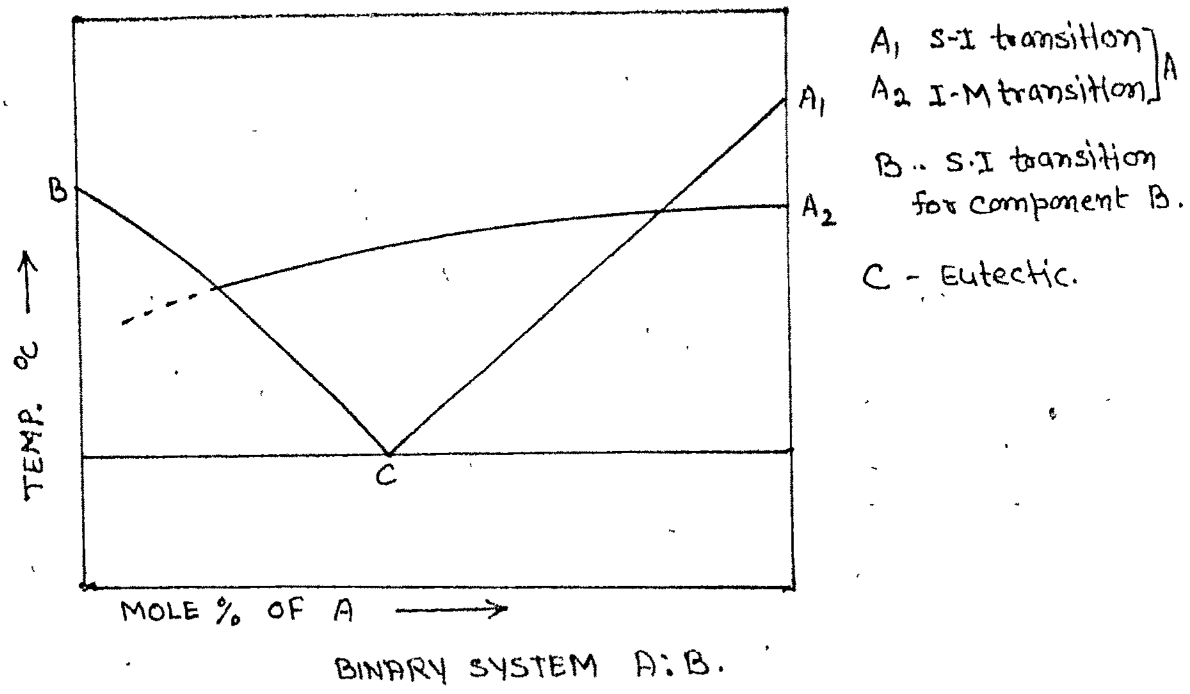
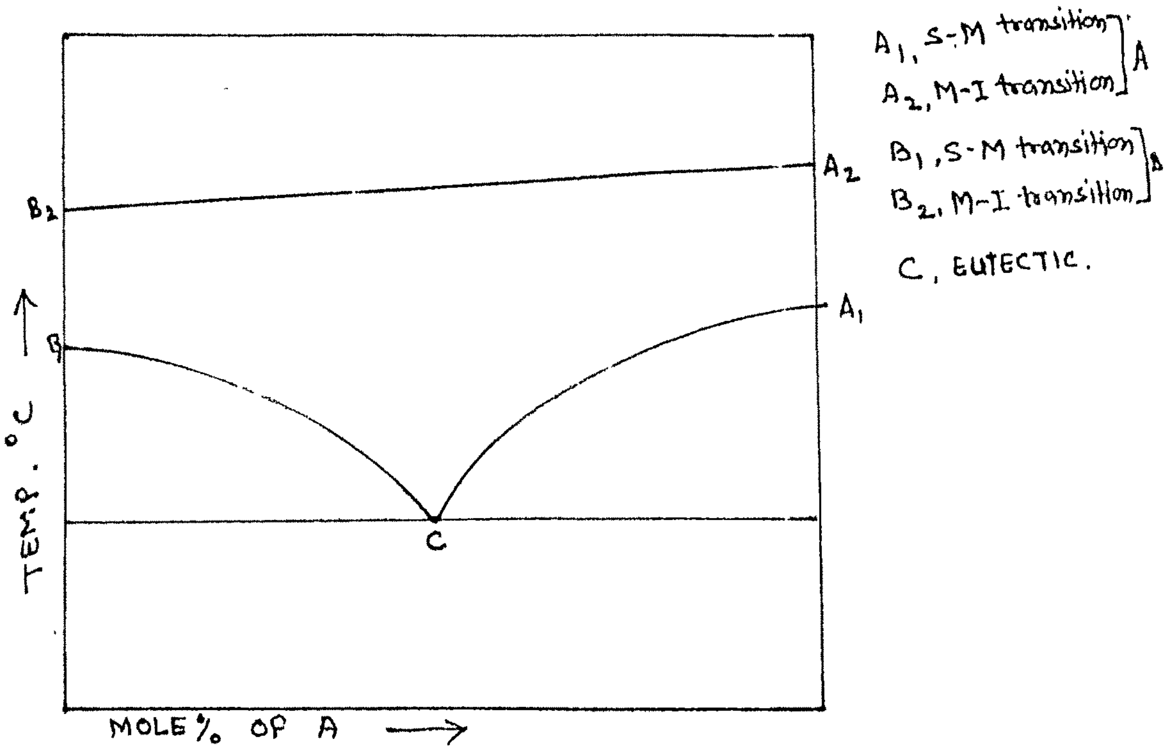
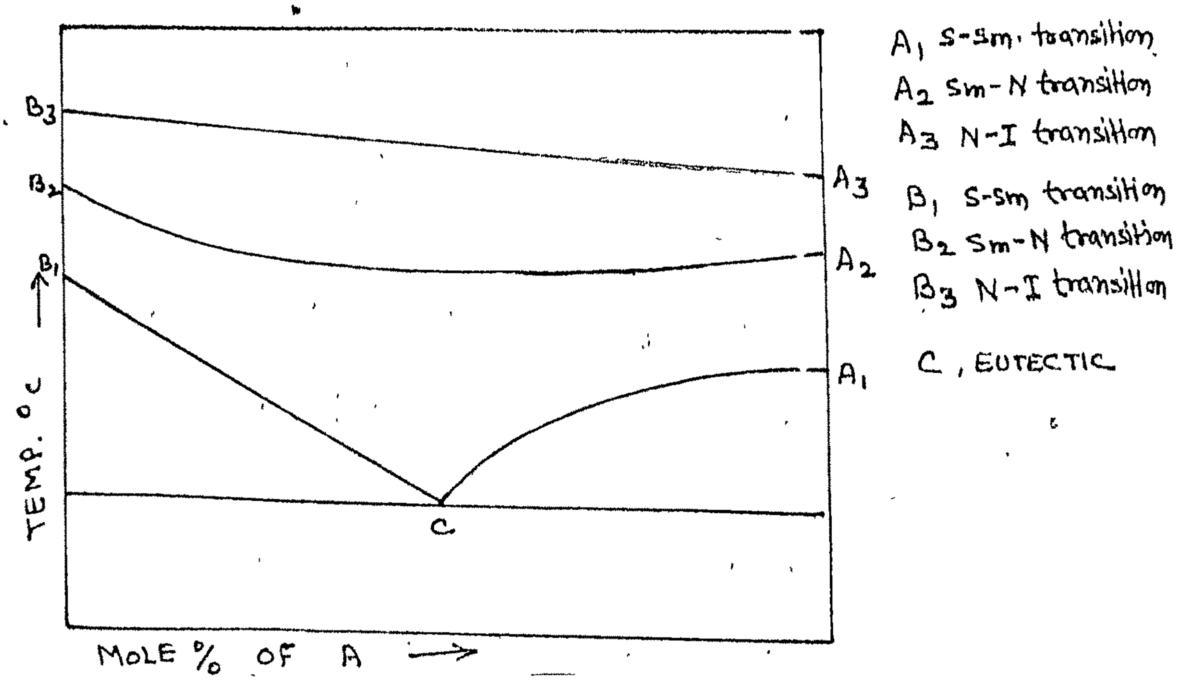


Fig 47D.



BINARY MIXTURE A:B.

FIG-47E.



BINARY MIXTURE A:B.

FIG-47F.

Addition of a substance to another normally lowers its melting point. The depression in the melting point will be greater with increasing concentration of second substance, till the composition of the mixture reaches to the eutectic point. For a binary mixture of mesogens, when these depressions are plotted, they form two curves - (i) melting point curves which meet at the eutectic point and (ii) transition curves representing the depressions in the transition points of the mixed melts. These curves, however, do not run parallel, the lowering effect on the transition temperature will depend upon the miscibility and the alignment of molecules of both the components. The transition curve may meet the melting point curve at some point known as triple point (Fig. 47A and 47B) and the region bounded by these two curves will be the region of anisotropy. If the mesogenic component is exhibiting polymesomorphism, there will be more than one transition curve since the mixed mesophase will be more than one (Fig. 47F).

If both the components are mesogens, a continuous curve showing mesomorphic and isotropic states in equillibrium will be obtained (Fig. 47E) the slope of the transition curve will depend upon the actual transition temperatures of the pure mesogens and their structural similarities. However if one component is non-mesomorphic, the mesomorphic-isotropic curve may meet the solid-isotropic curve at some point, the point is known as triple point (Fig.47C and 47D).

In all such phase diagrams, the mesomorphic-isotropic transition curve becomes quite prominent as it indicates a number of characteristics pertaining to molecular geometry as well as other factors which are responsible for exhibiting the mesophase.

The present study incorporates binary systems in which one or both components are mesogens. Most of the present binary systems studied are having one common terminal group at right or left end whereas the other terminal group differs progressively by one and in some systems more than one $-CH_2$ unit. Two things are therefore, expected in these systems viz. (i) the depression of mixed mesomorphic-isotropic transition curve will be little, and (ii) the extent of mixed mesomorphism can find a direct reference to the $-CH_2$ unit. Binary systems from 1 to 21 listed in Table - 52 show a varied nature of mesomorphic-isotropic transition curves. The theoretical phase diagrams of the binary systems which are investigated under this study are represented in figure 47, while the actual curves may represent any conceivable shape depending upon the molecular geometry and molecular forces of components.

Molecular structure in relation to initial slopes and Group slopes

The binary systems under group C will be discussed first as these systems comprise components both of which are enantiotropic smectogens. The general pattern of the phase diagram is shown in fig. 47E. There are as usual two transition curves viz. one solid-smectic curve and another smectic-isotropic curve. The curves are not meeting together at any point even though they are not running parallel. The pattern of these curves is similar to those reported earlier (354 - 357).

In binary systems 8, 9, 10 and 11 the molecules of both the components are having similar molecular geometry as the two benzene rings are joined by the same vinyl carboxyl group. It is observed in each case, that a continuous series of mixed liquid crystals is obtained. The smectic-isotropic curve for the systems 10 and 11 are slightly curved, however, no tendency for a strong minimum is observed. But a definite, though not a strong minimum is observed in smectic-isotropic curve for the binary systems 8 and 9. This slight deviation of the smectic-isotropic curve from the ideal mesomorphic-isotropic curve which should be linear is, however, on account of varying polar nature of the alkyl chain length at terminal ends.

The solid-smectic transitions for the mixtures depress appreciably on both sides giving a well defined sharp eutectic point. The eutectic points are 51.5°, 58°, 63° and 63.5° for systems 8, 9, 10 and 11, respectively. The depressions in solid-smectic transitions are quite regular until they meet at eutectic point. The total mesomorphic range over the eutectic points is about 85° for systems 8 and 9 and about 70° for systems 10 and 11 (Table 29 - 32).

In binary systems of the Group A, one non-mesomorphic component (A) is mixed with - (i) polymesomorphic component in system (1) and (2), and (ii) monotropic mesogen in system (3). A continuous series of mixed liquid crystals like the one obtained in the case of binary systems of Group C cannot be expected to be formed on account of the disturbing effect imparted by non-mesomorphic molecules, the extent of which will depend upon the structural similarities of both the components. But, as stated earlier, both the components are having similar molecular geometry, it is the polarity of terminal substituents at right and/or left end, which is impressing upon the transition temperatures.

The minimum proportion of composition that is needed to completely disrupt the mesomorphic alignment of the mesogenic melt will in turn depend upon the polar nature of its own terminal group. The more polar terminal group will cause lesser disturbance and even large proportions of the non-mesomorphic substance may not be sufficient to cause disappearance of mixed mesophase.

The above contention is very well supported by the results of the investigated systems 1, 2 and 3.

In binary system (2), the non-mesomorphic component having $-COOC_4H_9$ group is added to a monotropic mesogen having $-COOC_5H_{11}$ group at right terminal end.

Both these groups are sufficiently polar. It can be seen that the presence of a little more 60 mole percent of non-mesomorphic component converts the monotropic nematic mesophase into enantiotropic nematic mesophase. The enantiotropic mesophase persists upto the 78 mole percent of component B, beyond which again monotropic mesophase appears which is present at as such as 91 mole percent of non-mesomorphic component. The enantiotropic nematic mesophase is exhibited over a total of 18 mole % composition.

The binary systems 1 and 3 do not show this peculiar phenomenon of showing mixed enantiotropic mesophase. In both these cases, the monotropic mesophase simply disappears at a certain composition. In all these three mixtures the component B is non-mesomorphic having sufficiently polar $-OCH_3$ and $-COOC_4H_9$ group. The component A is mesomorphic either monotropic or enantiotropic. The difference in the melting points of these components is also not much, but eutectic in case of binary mixture 3 is not in proximity of the monotropic curve, but it is quite in proximity of the monotropic curve in the case of binary mixture 1. It clearly indicates towards a probability of exhibition of enantiotropic mixed mesophase in some region near the eutectic point. Yet no enantiotropic mixed mesophase could be obtained. Had the eutectic point sank a little more than it does in binary system 1, then the probability would have been perhaps a reality.

The extrapolation of solid-mesomorphic transition curve (Fig. 22, 23 and 24) towards the non-mesomorphic end indicate the probable transition temperature of this component. This extra polated values are 62°, 73.5 and 73°0 as the latent transition temperature of non-mesomorphic component p-n-butyl (p'-methoxycinnamoyloxy) benzoate in system 1, 2 and 3, respectively. The latent transition temperature 73.0° is well in accordance with the value obtained earlier.

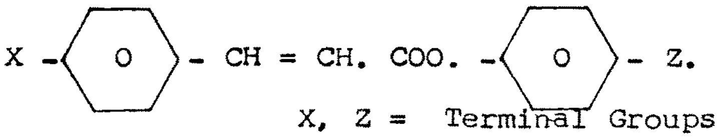
The mole percent range of exhibition of enantiotropic and monotropic mixed mesophase is given in table-53 for a comparative study.

In the category B, a polymesomorphic compound p-n-amyl (p'-ethoxycinnamoyloxy) benzoate is mixed with (a) monotropic mesogen (system 4), (b) polymesomorphic mesogen (system 5) (c) smectic mesogen (system 6 and 7). Here also, the basic molecular geometry of the components is same with the variation in

TABLE - 53

GROUP - A

General structure of the compounds undertaken for study –



X, Z = Terminal Groups.

Component A. - X = OCH_3 Z = $COOC_4H_9$

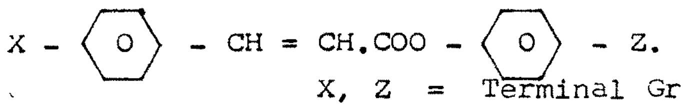
Binary System	Terminal Groups of component B.		M.P.	Mole % of component B over which enantiotropic mixed mesophase is exhibited	Mole % of component B over which monotropic mesophase is prolonged
	X	Z	(°C)		
1.	$-OC_2H_5$	$-COOC_4H_9$	92.5	35	60
2.	$-OCH_3$	$-COOC_5H_{11}$	89.0	22 - 40	60
3.	$-OC_2H_5$	$-COOC_5H_{11}$	97.5°	18	80

alkyl chain length. As molecules, differing in the magnitude of polarity are mixed, they will acquire an environment of considerably less terminal attractions. Naturally, the forces working in the direction of maintaining an end to end orientation of molecules get interrupted by the entry of such less polar molecules causing a kind of disturbance. Obviously, the molecules of the mixed melt will have less resistance to the thermal vibrations on heating and will be converted to isotropic liquid at a lower temperature causing depressions in the transition temperature. The disturbance offered by less polar molecules will be limited and increase with increasing proportion of their composition. Thus a range of mixed liquid crystal formation can be obtained. The above contention is very well supported by the results of present investigation. Table 54 shows the enantiotropic and monotropic range of mixed crystal formation. On account of similar molecular geometry in both the components, the mesomorphic-isotropic curve (fig. 25, 26, 27 and 28) follows more or less an ideal pattern of the slope yielding almost a straight line and deviating only slightly. The

TABLE - 54

GROUP - B

General structure of the compounds undertaken for study -



X, Z = Terminal Groups.

Component A. : X = - OC_2H_5, Z = $COOC_5H_{11}$.

Mesomorphic range 87.5 - 97.5

Binary system	Terminal groups of component B			Mole % of comp. over which enantiotropic mixed mesophase is exhibited	Mole % of component B over which monotropic mesophase is prolonged
	X	Z	M.P.		
4	$-OCH_3$	- $COOC_5H_{11}$	88.0	80	40
5	$-OC_3H_7$	- $COOC_5H_{11}$	87.5	20	85
6	$-OC_4H_9$	- $COOC_5H_{11}$	105.0	82	18
7	$-OC_5H_1$	- $COOC_5H_{11}$	103.0	42	96

extent of mole percent range of component B over which the mixed mesophase is exhibited could be compared with the polarity of its terminal group and a corelationship arrived at. Thus the component B in the system (6) has $-OC_4H_9$ and $-COOC_5H_{11}$ as the terminal group and the component B in the system (7) has $-OC_5H_{11}$ and $-COOC_5H_{11}$ terminal groups. The polarity of the system (7) is slightly increased by the addition of one more methylene $-CH_2$ unit. The presence of more polar $-OC_5H_{11}$ group decreases the range of mixed nematic mesophase. It can be seen that the presence of only 21 mole percent of the component B are sufficient for enantiotropic nematic to appear in system (6) while in system (7), it would need as much as 42 mole percent. However, a little less disturbance caused by system 4 can be attributed to the lower melting point of the component A.

An interesting characteristic of this category is the sudden disappearance of nematic mixed mesophase in binary systems 6 and 7. In both these systems, the component B is a smectogen having $-OC_4H_9$ and $-OC_5H_{11}$ groups respectively whereas the component A, common for both the system, is a polymesomorphic compound showing monotropic smectic and enantiotropic nematic mesophase. On account of more smectogenic character due to increased polar attractions of component B, the monotropic smectic mesophase in systems 6 and 7 remains in the monotropic region upto only 14 and 4 mole percent of component A respectively then it smoothly crosses the solid-nematic curve and shows the enantiotropic smectic mesophase. With the increasing mole percent of component A, the area of mixed nematic mesophase formation is reduced gradually. The mixed nematic mesophase disappears at 20 mole percent in system 6 and 42 mole percent of component B in system 7.

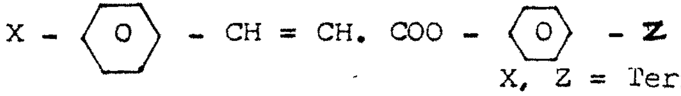
The mole percent range of enantiotropic and monotropic mixed mesophase formation is compiled in Table 55.

The Group D comprises binary mixtures, one component of which is showing polymesomorphism. The transition curves (Fig. 33 and 37) of binary systems (12) and (16), both components of these systems are polymesomorphic, are quite similar to ideal transition curve (Fig F) in this condition. The solid-mesomorphic, smectic in this case, transitions are showing a good depression. The eutectic points for systems 12 and 16 are at 60° and 68°, respectively. The upper transitions viz. smectic-nematic and nematic-isotropic transition curves are almost linear

TABLE - 55

GROUP- C

General structure of the compounds undertaken for study -



X, Z = Terminal Groups

Component (A) - X = $-OC_4H_9$, Z - $COOC_4H_9$; Mesomorphic range 73.5 - 103.5

Binary system	Terminal Groups of component B		M.P.	Mole % of component B over which maximum range of mixed meso-phase is exhibited	
				mole %	Mesomorphic range °C
8.	$-OC_5H_{11}$	$-COOC_4H_9$	100.5	51	48
9.	$-OC_4H_9$	$-COOC_5H_{11}$	105.0	58	40

Component A; x = $-OC_5H_{11}$, Z = $-COOC_5H_{11}$, Mesomorphic range. 75-103

Binary system	Terminal Groups of component B		M.P.	Mole % of component B over which maximum range of mixed meso-phase is exhibited	
				Mole %	Mesomorphic range °C
10.	$-OC_4H_9$	$-COOC_5H_{11}$	105.0	63	37.5
11.	$-OC_5H_{11}$	$-COOC_4H_9$	100.5	63.5	35

with slight deviations. These deviations are due to the difference in the polar nature of components of these systems.

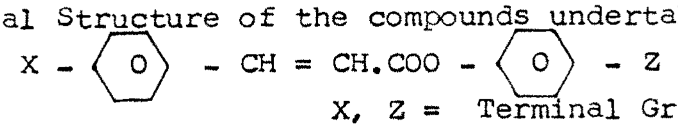
The transition curves (fig. 34, 35 and 38) of the binary systems 13, 14 and 17 are quite similar to those obtained for system 1 and 3. As both the components of these systems show more smectogenic tendency the area of mixed smectic mesophase formation is quite large. The area of mixed nematic mesophase formation gradually diminishes. The mixed nematic mesophase ultimately disappears at 40, 52, and 60 mole percent of component B. A comparative account of mole percent of B exhibiting smectic and nematic mixed mesophase is given in Table 56.

Two binary systems 5 and 15 are quite surprising in their mixed mesophase characteristics. One component p-n-amyl (p'-n'-ethoxycinnamoyloxy) benzoate is common for both the systems. The other components are p-n-amyl (p'-n'-propoxycinnamoyloxy) benzoate and p-n-butyl (p'-n'-ethoxycinnamoyloxy) benzoate for systems 5 and 15, respectively. Both the components of system 5 and 15 are almost identical in molecular geometry and forces, only the terminal alkyl chain at right or left end is longer by one methlene unit.

TABLE - 56

GROUP (D)

General Structure of the compounds undertaken for study



X, Z = Terminal Groups

COMPONENT A - X = $-OC_2H_5$, Z = $-COOC_4H_9$

mesomorphic range - 76, 85, 92.5

BINARY SYSTEM	TERMINAL GROUPS OF COMPONENT B X	Z	M.P. (°C)	MOLE % OF COMPONENT B OVER WHICH MONOTROPIC MESOPHASE IS EXHIBITED
12	$- OC_3H_7$	$- COOC_4H_9$	84	10
13	$- OC_4H_9$	$- COOC_4H_9$	103	-
14	$- OC_5H_{11}$	$- COOC_4H_9$	101	48
15	$- OC_2H_5$	$- COOC_5H_{11}$	98	03

COMPONENT A: X - OC_3H_7 Z = $COOC_5H_{11}$

mesomorphic range 75 - 87

BINARY SYSTEM	TERMINAL GROUPS OF COMPONENT B X	Z	M.P.	Mole % of Component B over which monotropic mesophase is exhibited
16	$-OC_3H_7$	$-COOC_4H_9$	84	-
17	$-OC_4H_9$	$-COOC_5H_{11}$	105	40

The more polar propoxy group at left terminal end in system (5) retains its enantiotropic nature right upto the 96 mole percent of the component B. The eutectic point is thus naturally eliminated giving a round oval to solid-smectic transition curve. Smectic - nematic and nematic - isotropic transition curves behave ideally as the transition curves are quite linear.

Addition of one more methylene unit at right terminal end also affects the eutectic point in a similar manner in binary mixture 15. Here too, the well defined eutectic is eliminated to a round minimum.

Another set of binary systems 18, 19, 20 and 21 also provides interesting study. The system 18 consists of one non-mesomorphic component and other a nematogen. The core geometry is similar for both the components though the length of the alkyl chain at left terminal is different. The component A and B are having $-OCH_3$ and $-OC_3H_9$ groups, respectively. Both the groups are sufficiently polar, though the polarity of $-OC_3H_9$ group is comparatively more than that of $-OCH_3$. By this contention, the effect of overall polarity is supposed to enhance the range of mixed mesophase formation in a good measure but this is not so. As the melting points of both the components are having a difference of almost 28°. This more difference in the melting point normally eliminates the area of mixed mesophase formation. It is evident from the system 18 where the addition of a comparatively low melting component A to high melting component B brings about regular and quick depressions in the mesomorphic - isotropic transition curve of component B, limiting the mixed mesomorphic area to only 30 mole percent of component B.

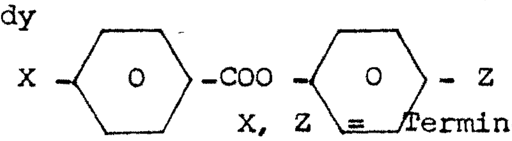
Similar observations in binary system 19 support the above contention. In this system, the difference between the melting points of two components is 12°, comparatively lessthan that of components of system 18. The depression in the mesomorphic - isotropic curve is also not as pronounced as in system 18. The curve runs almost linear, though the range of mixed mesophase formation is not quite large, the solid-mesomorphic curve shows a well defined eutectic at 103°C.

In binary system 20, one component is monotropic nematogen while the other is monotropic smectogen showing enantiotropic nematic mesophase. The monotropic smectic mesophase is retained upto 22 mole percent of component A but does not emerge as enantiotropic due to lack of resistance to the thmermal break-down processes and lateral attractions of such magnitude as to show the smectic mesophase, but on supercooling, the crystallizing tendency of mixed melt being low and the thermal agitation being absent, the smectic orientation persists. At 16 mole percentof component B, the monotropic nematic mesophase emerges as enantiotropic, as the more terminal attractions provided by much polar $-OC_4H_9$ groupof component B. After attaining enantiotropy, the nematic - isotropic transition curve follows almost linear path.

The system 21 is also a very simple case. Both the components of this muxture are smectogens, component A is showing monotropic smectic mesophase while other component is enantiotropic. As both the components are smectogenic in character, a large area of mixed mesophase formation is expected. That in reality it is so not that surprising as in fact a good

TABLE - 57

General Structure of the compounds undertaken for the study



X, Z = Terminal Groups

Binary system	Terminal groups of Component A		Terminal groups of component B		M.P		Mole % of comp B over which monotropic mesophase is exhibited	Mole % of comp B over which maximum range of enantiotropic mesophase is exhibited	
	X	Z	X	Z	A	B		Mole %	Range
18	$-OC_3H_7$	$-COC_2H_5$	$-OCH_3$	$-COC_3H_7$	115.5	99	70	-	-
19	$-OC_2H_5$	$-COC_2H_5$	$-OC_3H_7$	$-COC_2H_5$	126	116	18	78	10
20	$-OC_2H_5$	$-COC_2H_5$	$-OC_4H_9$	$-COC_2H_5$	126	125	45	70	28
21	$-OC_4H_9$	$-COC_3H_7$	$-OC_5H_{11}$	$-COC_3H_7$	100	100	32	80	25

range of mixed enantiotropic range of smectic mesophase is obtained. The smectic mesophase range of enantiotropic component is 17°, from this range, the mixed system at its optimum at 52 mole percent concentration of monotropic component A gives a smectic enantiotropic range of about 40°. The mesomorphic - isotropic transition curve shows an almost ideal curve of linearity. The solid-mesomorphic transition curve shows a well defined eutectic at 60°.

A comparative account of mole percent range of systems 18, 19, 20 and 21 over which the enantiotropic and monotropic mesophase are exhibited is given in Table 57.

INITIAL SLOPE AND GROUP SLOPE

The additive effect of the terminal groups on mesomorphic characteristic of a mesogen in its mixture with a non-mesomorphic component was first discussed by Dave and Dewar (358) and then Dave and Lohar (359) fixing two terminal groups one each from both the components, thereby finding a difference value of the initial slope of the nematic-isotropic transition curve, which turned out to be a constant for a given series. Later, a similar attempt made by Dave and

Lohar (360) with different compounds yielded results which were at great variance with those obtained earlier in terms of 'initial slope' and 'group slope' or 'additive effect'. Some other efforts (361, 362) to corelate the slope value with the terminal group also could not provide any general or regular value. In this investigation, the study of present systems could not discern any regular pattern, though the range of mixed mesophase formation are quite good in most of the systems studied. But as the mixed nematic-isotropic and/or smectic-isotropic transition curves do not show any appreciable depression, the initial consideration is ruled out.

3. SUMMARY

(a) New Homologous Series of Mesogens

Certain salient features of the "Results and Discussion" can be presented here as prominent gains of the present investigation.

1. Most of the new compounds, synthesized are mesomorphic and exhibit mesomorphic properties over a wide range of temperature.
2. The homologous series 1, 2, 3 and 4 are ester series viz. n-butyl, n-amyl, n-hexyl and n-heptyl p-(p'-n'-alkoxycinnamoyloxy) benzoates, these are having low transition temperatures as compared to their corresponding acids - a characteristic attributed to the ester mesogens in general.
3. Molecules of mesogens belonging to the newly synthesized homologous series 1, 2, 3 and 4 are long and polar with usual breadth and other facts that endow the molecules with sufficient polarizability. All these series are thus well ~~set for relatively high transitions.~~

4. The series 1, 2, 3 and 4 are not high melting series, but medium melting series with certain characteristics of low melting series.

5. The homologous series 1, 2, 3 and 4 are predominently smectogenic series. The nematic property is exhibited by ethoxy and propoxy homologues of series 1 and 2, whereas only one member viz -ethoxy member of series 3 and 4 exhibited nematic properties.

6. The methoxy homologue of series 1 is non-mesomorphic whereas the methoxy homologues of series 2, 3 and 4 exhibit monotropic mesomorphism. Monotropic smectic mesophases are also exhibited by propoxy members of series 3 and 4.

7. Polymesomorphism is shown by ethoxy and propoxy homologues of series 1 and 2 while only second member of series 3 and 4 exhibited polymesomorphism.

8. The smectic-isotropic transition curves show the odd even-effect which is a rare phenomenon as far as smectic property is concerned. The two smectic-isotropic transition curves, one for

odd and other for even members, run almost parallel to each other and do not seem to merge together in the homologous series 1, 2 and 3, but in series 4 these curves are merging together at the seventh member.

9. The molecules of series 1, 2, 3 and 4 are characterised by the n-butyl, n-amyl, n-hexyl and n-heptyl groups at right terminal end respectively. With proportionate increased length, and with increased polarity due to addition of methylene unit, the series 1, 2, 3 and 4 are expected to be more smectogenic.

10. The series 1, 2, 3 and 4 are indeed more smectogenic in character, thus, the maximum smectic mesophase length at twelth member of series 1, 2, 3 and 4 is about 52, 52, 48 and 54 respectively. It is also observed that as the alkyl chain length increases at the left end, the smectic mesophase length increases upto twelveth homologue then it decreases upto the last member studied.

11. The homologous series 5, P-(p'-n-alkoxybenzoloxy) benzoic acid, is a high melting series, the molecules undergo dimer formation through hydrogen bending which is a weaker force. Yet, the highly polar acidic group should be responsible for relatively very high transitions.

12. As first eight homologues of series 5 decompose, any regularity of the upper transition curves for these members is difficult to generalise.

13. All members of series 5 show mesomorphism over a wide range of temperatures.

14. The smectic mesophase makes its appearance in series 5 at the eigth homologue. The smectic mesophase length then increases at the cost of nematic mesophase.

15. The nematic - isotropic transitions of members not decomposing show a descending trend, a characteristic of high melting series.

16. The smectic-isotropic transitions show an ascending tendency as the series is ascended, thus reducing the nematic mesophase length

considerably.

17. The homologous series 6 and 7 are endowed with greater length and aromaticity as their molecules have three benzene rings. The added central bridge which is azomethine alongwith a third benzene ring are the major factors in enhancing the polarizability of the molecules of these series. Naturally, the series 6 and 7 are high melting series.

18. All the homologues of series 6 and 7 exhibit mesomorphism, and the range of mesomorphism is quite wide.

19. However, first four homologues of series 6 decompose at high temperatures before they can achieve a smooth transition to isotropic liquid. None of the members of series 7 show decomposition but the mesomorphic state passes through a smooth transition to isotropic liquid.

20. The nematic-isotropic transitions show the odd-even effect, both odd and even curves show a steep descending tendency as the series is ascended. Though first four members of series 6 undergo

decomposition, the odd-even effect is still noticeable.

21. Polymesomorphism is exhibited by sixth, seventh and eigth homologues of series 6 whereas fifth, sixth, seventh, eigth and tenth homologues of series 7 exhibit polymesomorphism.

22. The smetic mesophase makes its appearance at fifth member in series 7, but smectic-nematic transitions do not indicate any odd-even effect.

It is evident therefore that with some similarities and differences in their molecular geometry, the molecular forces affect the mesomorphic properties to a great extent. Some factors such as polar nature, polarizability, alkyl chain length, breadth of the molecule, length to breadth ratio and the ratio of terminal to lateral attractions work in combination and affect the mesomorphic range considerably. The effect of terminal substitution and the nature of terminal substituent plays an important role in deciding the range and type of mesophase.

With addition of an unit comprising one benzene ring and a central azomethine bridge, the mesomorphic range is greatly increased as clearly displayed by homologous series 6 and 7.

All these newly synthesized and investigated series offer a good study of molecular factors affecting the mesophase and thermal stabilities, extent of polymeso-morphism, appearance or disappearance of monotropic mesophase and comparative understanding of terminal substitution.

(b) Mixed Mesophase

Twenty one binary systems have been studied in this investigation. Both components of these systems are mostly homologues of the same homologous series and are therefore identical in their molecular structure in almost all the aspects. Mainly, the difference is in the higher or lower homologue of the same series. Some of the more important features can be presented as follows -

1. The binary systems under investigation exhibit mixed mesomorphism in keeping with the molecular

characteristics of the component molecules.

2. The mesomorphic-isotropic transition curves of most of the binary systems under groups B, C and D show just a slight deviation from the ideal linear behaviour.

3. The sinking of transition points is prominent in binary systems where the component molecules are with sufficiently polar terminal substituent.

4. In Group A, where one non-mesomorphic component is mixed with another mesomorphic components, the deviations from the ideal lenear pattern of transition curve are very prominent. Still any regularity in terms of "Group Slope Value" could not be observed. But their extrapolation for obtaining values of latent transition temperature is reasonably reliable.

5. The most significant result is observed in binary system no.2 of Group A, where the monotropic nematic mesophase passes into enantiotropic nematic mesophase very smoothly. When none of the component was exhibiting enantio-

tropic mesophase in their pure form.

6. In group B, one monotropic smectogen but enantiotropic nematogen is mixed with other mesomorphic components. In these systems 4, 6 and 7, very wide ranges of mixed mesophase formation in enantiotropy are observed. However, the regular pattern of the depression of the type reported in literature (357 -362) is not observed and therefore the possibility of reaching a corelation between the magnitude of polarity of terminal substituent and group slope value is ruled out.

7. The group C of the binary systems studied comprises binary mixtures where both the components are smectogens. All the four binary systems under this group present a wide range of mixed smectic mesophase. The mixed smectic-isotropic curves follow almost ideal patterns.

8. In the binary systems of Group D, one component is a polymesomorphic mesogen. In systems 13 and 14 where other component is a smectogen, the ranges of mixed smectic mesophase formation are

very wide. The mixed nematic mesophase too is exhibited over a limited range of temperature and concentration. In system 16, the transition curves follow the ideal pattern.

9. The last Group E, comprising four binary mixtures is very typical. Though all the four mixtures offer an interesting study, the mixture no. 18 is very interesting as it clearly indicates the effect of melting point of non-mesomorphic component over the mixed mesophase formation.

10. The systems 5 and 12 consist of a monotropic component. Very interesting, it is observed that 'rounded minima' keeping a smooth continuity of the transition curves reaching the monotropic transitions at one side and connecting the emantiotropic transition of the pure mesogen at other side. In system 15 also enantiotropic polymesomorphism is emerged over a wide range of concentration without a clear entectic and leaving a very little range of monotropic smectic meso- ~~tre~~ phase on the monotropic smectogen's side in the phase diagram.

In general, it can be said that the mixed mesomorphism is exhibited over a wide range of temperature and concentration. Sharp transitions and boundries between mixed nematic and mixed smectic mesophases in polymesomorphic regions enable understanding of delicate combination of molecular forces in relation to the concentration of the components. Non-emergence of enantiotropic mesophase in some systems having monotropic components indicates that monotropic mesophase will not be lifted up to the enantiotropic range until the other component has strong lateral attractions condusive to the formation of smectic mesophase. In some binary systems, the transition curves separating the phases run parallel without any appreciable depression present a contrast and confirm the view (362) that very identical components with nearly the same transitions fail to give rise to a mixed mesomorphism that could differ from those of individual components. Several other binary mixtures offer the possibility of presenting a mesomorphic mix at ambient temperature in the presence of a suitable third component.

The study besides shedding better light on the subject matter has provided considerable knowledge for potential applications and opened up more facets for further exploration. It is in this light that the investigation is turned out to be fruitful.