RESULTS

AND

DISCUSSION

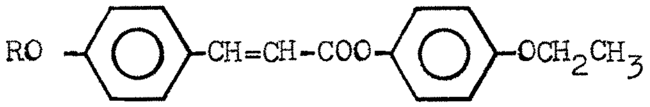
RESULTS AND DISCUSSION

4.a. New Homologous series

The following nine new homologous series, comprising totally one hundred and eight compounds, have been synthesized which are broadly classified into three main categories and their characteristics are discussed in subsequent sections of this chapter.

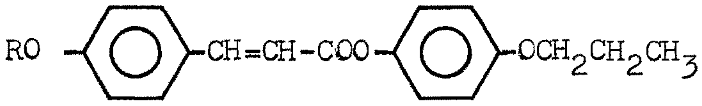
Type A

1.



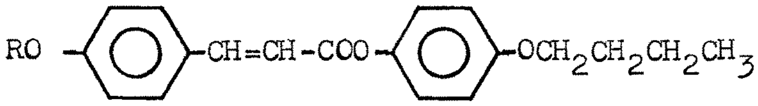
p-Ethoxyphenyl-p'-n-alkoxycinnamates

2.



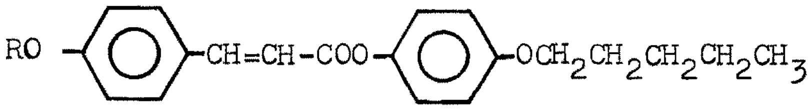
p-n-Propoxyphenyl-p'-n-alkoxycinnamates

3.



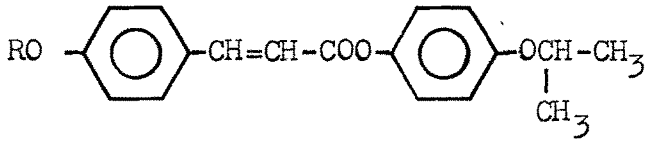
p-n-Butoxyphenyl-p'-n-alkoxycinnamates

4.

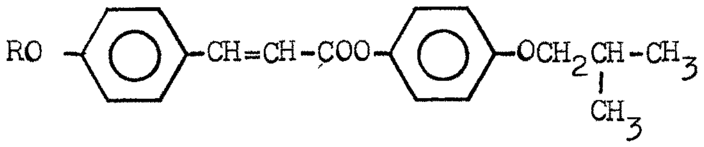


p-n-Amyloxyphenyl-p'-n-alkoxycinnamates

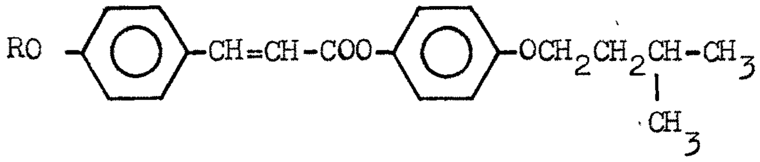
Type B

5.


p-iso-Propoxyphenyl-p'-n-alkoxycinnamates

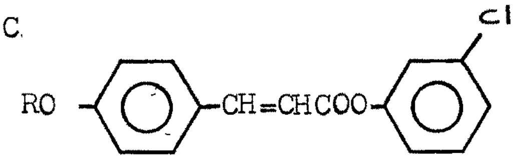
6.


p-iso-Butoxyphenyl-p'-n-alkoxycinnamates

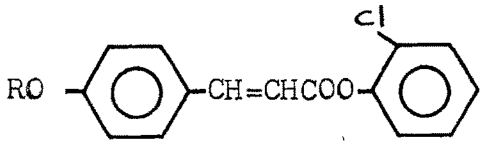
7.


p-iso-Amyloxyphenyl-p'-n-alkoxycinnamates

Type C

8.


m-Chlorophenyl-p'-n-alkoxycinnamates

9.


O-Chlorophenyl-p'-n-alkoxycinnamates

Where R stands for alkyl group from C_1 to C_8, C_{10}, C_{12}, C_{14} and C_{16}. These homologous series have certain similarities besides specific differences in the molecular geometry and positions of substituents which give rise to variations in the characteristics that command attention and interest in view of the probability of shedding more light on the prevalent considerations and ideas. The last two homologous series which though quite low melting, fail to exhibit mesomorphism even in monotropic conditions. Rest of the homologous series are high melting series and exhibit rich mesomorphism. The homologous series A-1 to A-4 vary from each other in their right terminal substituents whose alkyl chain length increases progressively by one methylene unit. From B-5 to B-7 series, the right terminal alkyl chain receives an iso-branching, while all the other features remain the same as those of A-1 to A-4 series. The series C-8 and C-9 differ in the position of chloro group which is in the meta position in C-8 series while it is in the ortho position in C-9 series. The common features in all the nine homologous series are two benzene rings, central linkage, -CH=CH-COO-, and the left terminal substituents. The only difference is in the right terminal group in series A-1 to A-4 and B-5 to B-6 and in the position of chloro group in series C-8 and C-9.

4.b. Individual Characteristics

Series A-1 p-Ethoxyphenyl-p'-n-alkoxycinnamates

The entire homologous series p-ethoxyphenyl-p'-n-alkoxycinnamates is mesomorphic in character as is the case with the similar series, A-0 p-methoxyphenyl-p'-n-alkoxycinnamates (465a) (Table 39). The series in general has the characteristics of a high melting series (466). The transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig.6) (Table 5).

The solid-mesomorphic (K-M) transition curve has overall falling tendency upto the decyloxy homologue with sharp rise and fall near the ethoxy and octyloxy homologues. From the decyloxy homologue onwards, there is an alternate rise and levelling off upto the last member studied in this investigation; though the overall rise is very small compared to the overall fall from the methoxy homologue to the decyloxy homologue. The rising tendency of the K-M transition curve for the last three homologues and the falling tendency of the nematic-isotropic (N-I) transition curve reduces the mesomorphic range.

The nematic-isotropic (N-I) transition points fall on two descending curves exhibiting odd-even effect as is the case in series A-O(Fig.34), one for the even members is the upper curve and another for the odd members is the lower one. Both odd and even curves exhibit quite steep falling tendency as the series is ascended - a tendency characteristic of high melting homologous series (466). The curve for the odd number of homologues forms a curvature - the fall from the propoxy to the pentyloxy homologue being sharp and thus both the N-I curves don't merge.

Polymesomorphism begins from the heptyloxy homologue though in the monotropic condition, with the advent of the smectic phase at lower temperature and persists upto the last, hexadecyloxy, homologue. As regards to the series A-O, polymesomorphism begins at the octyloxy homologue in monotropic

Table 39

A-O p-Methoxyphenyl-p'-n-alkoxycinnamates (465a)

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	117	141.5
Ethyl	-	125	145.5
Propyl	-	91.5	130
Butyl	-	95	130.5
Pentyl	-	89	125.5
Hexyl	-	83	122
Heptyl	-	91	120.5
Octyl	(72.5)	78.5	119
Decyl	78	83	114.5
Dodecyl	77	86	107.5
Tetradecyl	80.5	91.5	105.5
Hexadecyl	75.5	-	97
Octadecyl	81	-	106

Value in the parenthesis indicates monotropy

SERIES A-0

p-METHOXYPHENYL-p'-n-ALKOXY CINNAMATES

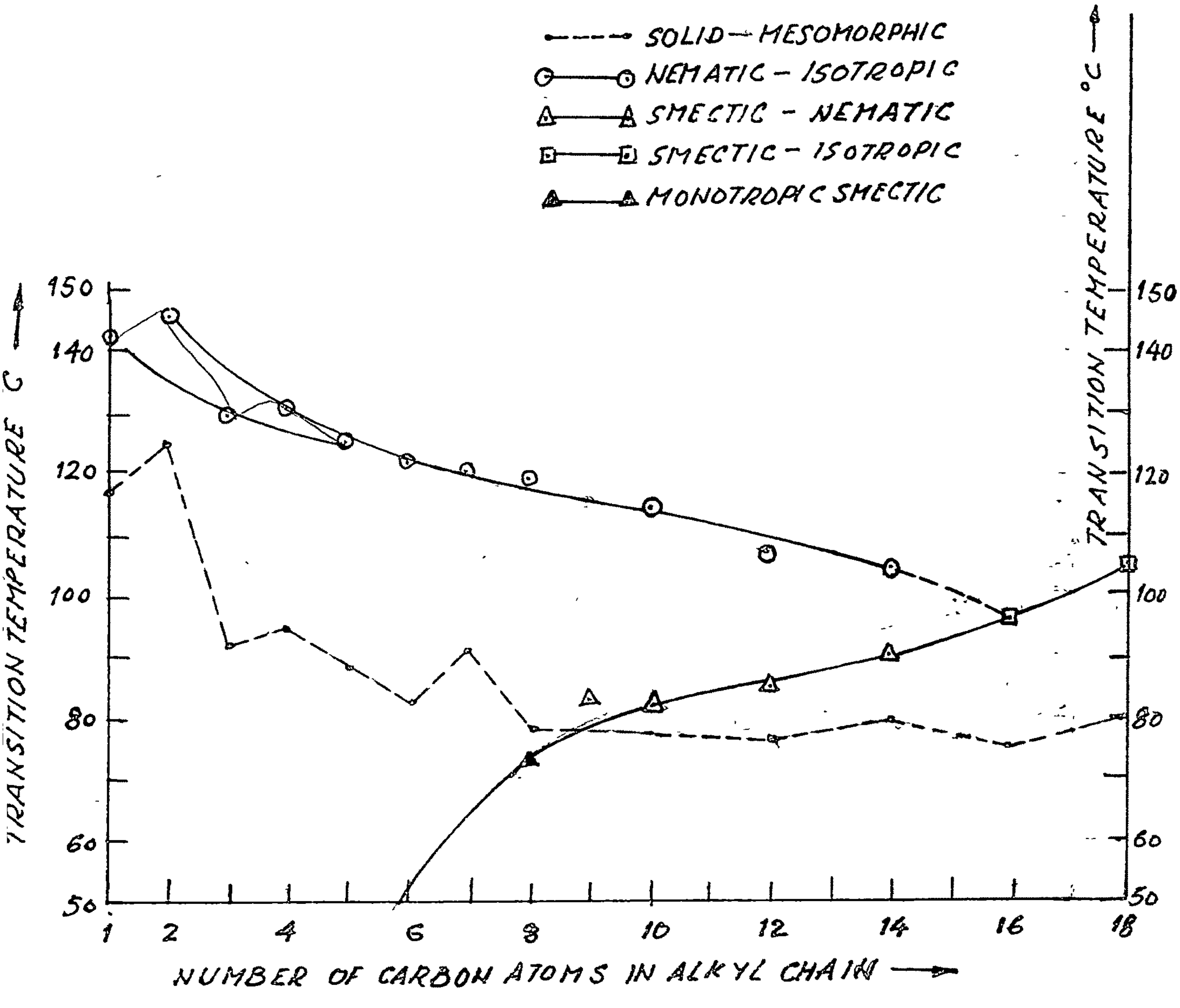


FIG.34

condition and persists upto the tetradecyloxy homologue. The smectic-nematic (S-N) transition curve rises sharply from the heptyloxy homologue to the decyloxy homologue; followed by nearly levelling off upto the hexadecyloxy homologue. The steep rise of the S-N curve almost matches the steep fall of the N-I curve. As a consequence, the smectic phase broadens up at the cost of the nematic phase. While initially only nematic mesophase is exhibited upto the hexyloxy homologue, once polymesomorphism begins both, smectic and nematic, mesophases exist upto the last homologue.

The texture of the nematic phase in the case of the first six homologues of this series is threaded-nematic, however, with the appearance of the smectic mesophase beginning from the seventh homologue, the threaded texture of the nematic phase is replaced by the homeotropic texture. It seems that the uniformally aligned nematic orientation in the single phase region receives a 90° transformation rendering its optic axis normal to the surface as a result of which the homeotropic texture prevails in the polymesomorphic region. This observation can find a parallel [illegible] in the various texture descriptions given by Demus and Sackmann (467). It has been pointed out (467-468) that such pseudo-isotropic texture of the nematic is often obtained in cases where the smectic phase is of A type. The texture of smectic mesophase, as observed under the polarizing microscope, is focal conic fan shape of A type in the case of the homologues of this series which only confirms the above observation.

Series A-2 p-n-Propoxyphenyl-p'-n-alkoxycinnamates

Mesomorphism in the series, p-n-propoxyphenyl-p'-n-alkoxycinnamates begins from the first homologue though in the monotropic condition as monotropic nematic. The series has the characteristics of a high melting series. The various transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig. 7) (Table 7).

The solid-mesomorphic (K-M) transition curve falls sharply upto the heptyloxy homologue, with equal fall and rise of about 2-3° near the ethoxy homologue. The curve rises and falls alternately from the heptyloxy homologue to the dodecyloxy homologue followed by only a marginal rise of about 3° for the last three homologues. The rising trend of the K-M curve for the last three homologues and the descending nature of the N-I curve narrows down the mesomorphic range; the maximum mesomorphic range of 37.5° is seen at the decyloxy homologue.

The methoxy and propoxy homologues show mesomorphism in the monotropic condition as monotoropic nematic. The well known odd-even effect is exhibited upto the hexyloxy homologue by the two distinct N-I curves. The N-I transition curve for the even number of carbon atoms in the alkyl chain shows descending tendency. The curve for the odd number of carbon atoms in the alkyl chain is at a lower level and forms an arc upto the pentyloxy homologue and discontinues thereafter.

Thus both the N-I curves don't merge. This is the same phenomena observed in the series A-1. The N-I transition curve for the even number of carbon atoms in the alkyl group shows continuity with S-I curve for the last two homologues.

With the advent of the additional smectic phase at lower temperature, polymesomorphism begins from the heptyloxy homologue in the monotropic condition and persists upto the dodecyloxy homologue. The S-N transition curve rises sharply between the heptyloxy and octyloxy homologue and then shows levelling off tendency upto the dodecyloxy homologue, almost parallel to the abscissa. The smectic-isotropic transition curve (S-I) for the last two members is in continuity with the N-I transition curve for the even members. Against the beginning of the polymesomorphism at the octyloxy homologue in series A-0, in series A-1 and A-2 it starts at the heptyloxy homologue.

Pure nematogens of this series yield a threaded texture characteristic of the nematic mesophase; however, during the polymesomorphic region, the nematic phase shows homeotropic texture. Because of the homeotropic nature of the smectic phase in the case of the heptyloxy, octyloxy and decyloxy homologues, texture characterisation under the polarising microscope was not possible, but the dodecyloxy, tetradecyloxy and hexadecyloxy homologues exhibited focal conic fan shaped texture of smectic A type.

Extrapolation in a smooth manner of the S-N transition curve inclusive of the monotropic transition to the left indicates the transition temperatures for the smectic phase for the hexyloxy and pentyloxy homologues at 82°C and 71°C respectively. At these temperatures both the homologues may exhibit a smectic phase in monotropic condition. However, even very careful observation does not lead to the realization of this property because of the high tendency to crystallise, hence this indication only points to a latent smectic transition.

Series A-3 p-n-Butoxyphenyl-p'-n-alkoxycinnamates

All the homologues of the series, p-n-butoxyphenyl-p'-n-alkoxycinnamates are mesomorphic in nature. The descending nature of the N-I transition curves characterises the series as a high melting series. The various transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig. 8) (Table 9).

The rise from the methoxy homologue upto the propoxy homologue and the fall from the butyloxy homologue upto the decyloxy homologue, in K-M transition curve are very steep, with the levelling off-nearly parallel to the abscissa from the propoxy to butoxy homologue. From the decyloxy homologue onwards the rise is very gradual - the overall rise upto the hexadecyloxy homologue being of only 7°C. The overall fall in the K-M transition curve is only of 5° because of the initial sharp rise for the first three homologues. The falling tendency of the K-M transition curve from the butyloxy homologue upto the octyloxy homologue is well matched with the falling tendency of the N-I transition curve as seen from nearly the same mesomorphic range. The maximum mesomorphic range of 37° is at the first two homologues. Because of the rising nature of the K-M transition curve for the last three homologues, the mesomorphic range is reduced. The fall in K-M curve is of 16° between the first and the last homologue studied.

The two N-I transition curves display odd-even effect here also; the upper one for the even number of carbon atoms in the alkyl group shows a steep fall upto the decyloxy homologue and thereafter merges with the S-I transition curve. The lower N-I transition curve for the odd number of carbon atoms forms an arc and merges with the even curve at the pentyloxy homologue. The striking feature of the odd-even effect in this series is that both the curves merge while in the series A-1 and A-2 they don't.

Polymesomorphism begins at the octyloxy homologue with the appearance of the smectic phase in the monotropic condition and continues only upto the decyloxy homologue. The S-N transition curve is sloping at an angle of nearly 45° and appears to meet the falling N-I curve at the undecyl homologue.

The pure nematogens of this series yield a threaded texture characteristic of the nematic mesophase. The texture of the smectic mesophase as observed under the polarizing microscope is focal conic fan shaped of A type. in polymesomorphs, while the pure smectogens exhibit focal conic fan shaped texture of smectic C type.

The transition temperatures for the smectic phase, for the heptyloxy to the butoxy homologues, as indicated by the extrapolation, in a smooth manner, of the S-N transition curve, are 87.5°, 81°, 74° and 67.5°C respectively. These were not realised because of the high crystallizing tendency of these members. Hence they point to latent smectic transitions.

Series A-4 p-n-Amyloxyphenyl-p'-n-alkoxycinnamates

Mesomorphism in the series p-n-amyloxyphenyl-p'-n-alkoxycinnamates begins from the first homologue. Like the previous series, this series also has the characteristics of a high melting series. The various transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig.9) (Table 11).

The K-M transition curve rises sharply upto the butyloxy homologue followed by nearly equal fall upto the decyloxy homologue. The net fall in the K-M transition curve from the first homologue upto the dodecyloxy homologue is zero. From the decyloxy homologue upto the next, dodecyloxy, homologue the K-M transition curve levels off followed by a gradual rise of 6°C upto the hexadecyloxy homologue. There is an overall rise in the K-M transition curve of 6°C from the first to the last homologue. As we go from the series A-1 to A-3 the overall fall in the K-M transition curve reduces and in this series there is an overall rise of 6°C. The first homologue has the maximum mesomorphic range of 45° and the last homologue has the range of 22°, a fall in the mesomorphic range of the order of 23° can be due to the rise in the K-M transition curve and fall in the N-I and S-I transition curves.

The odd-even effect in the N-I transition curve is more distinct; both the N-I transition curves make curvatures with a falling tendency and meet at the decyloxy homologue. Beyond the decyloxy homologue, the N-I transition curve maintains continuity with the S-I transition curve for the last three homologues. The S-I transition curve for the dodecyloxy, tetradecyloxy and hexadecyloxy homologues falls gradually. In the series A-1 and A-2, the two N-I transition curves do not merge, whereas in the series A-3 and A-4 they do so.

Polymesomorphism begins at the heptyloxy homologue in the monotropic condition, as in the series A-1 and A-2, with the advent of the additional smectic phase at lower temperature. In the series A-3, polymesomorphism was observed from the octyloxy homologue. The S-N transition curve rises sharply between the heptyloxy and octyloxy homologue but then the rise is very marginal upto the decyloxy homologue. Beyond the decyloxy homologue, the S-N transition curve seems to meet the falling N-I curve at dodecyloxy homologue.

The texture of the nematic mesophase is threaded, however, with the onset of the polymesomorphism from the heptyloxy homologue, the threaded texture is replaced by the homeotropic texture. The heptyloxy, octyloxy and dodecyloxy homologues could not be characterised for the smectic phase texture under the polarising microscope because of the homeotropic nature whereas the decyloxy, tetradecyloxy and hexadecyloxy homologues exhibit smectic-A focal conic fan shape texture.

Series B-5 p-iso-Propoxyphenyl-p'-n-alkoxycinnamates

Except for the first two homologues, the entire series p-iso-propoxyphenyl-p'-n-alkoxycinnamates exhibits mesomorphism. Like the homologous series A-2 where the propoxy group is straight chained, this series with iso-propoxy group at the right terminal has the characteristics of a high melting series. The various transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig.10) (Table 13).

The K-M transition curve falls sharply upto the decyloxy homologue after the initial sharp rise from the methoxy to ethoxy homologue. From the decyloxy homologue to the dodecyloxy homologue, the curve rises sharply followed by a gradual fall of 2°C upto the last homologue. The overall fall in K-M transition curve throughout the homologous series is of 17°. The maximum mesomorphic range of 23°C is at the decyloxy homologue because of the sharp fall in the K-M transition curve from the octyloxy to the decyloxy homologue. The mesomorphic range throughout this series is of about 10° except for the octyloxy and decyloxy homologue, which is 17° and 23° respectively.

The first two homologues are non-mesomorphic but the next four exhibit monotropic nematic mesophase. The odd-even effect persists upto the octyloxy homologue. The N-I transition curve for the even number of carbon atoms in the alkyl chain at left terminal is at a higher level and descends as the series ascends and shows continuity with the falling S-I transition curve for the last three homologues. The N-I transition curve for the odd number of carbon atoms in the alkyl chain at left terminal, remains approximately parallel to the abscissa and appears to meet the upper N-I transition curve near the nonyloxy homologue.

Polymesomorphism begins with the appearance of the smectic phase, in addition to the nematic phase, at the octyloxy homologue and persists upto the decyloxy homologue; the S-N transition curve seems to merge the S-I transition curve at the dodecyloxy homologue. The last three homologues of the series are pure smectogens and the S-I transition curve falls smoothly in continuation with the N-I transition curve. The rise in the S-N transition and the fall in the N-I and S-I transition curves are well matched and the smectic characteristic increases at the cost of the nematic phase.

The nematic phase in this series exhibits the threaded texture while the decyloxy, dodecyloxy and hexadecyloxy homologues exhibited smectic phase as smectic A focal conic fan shape under the polarizing microscope. The decyloxy and tetradecyloxy homologues could not be characterised for smectic texture under the polarizing microscope because of the homeotropic nature.

Extrapolation of the S-N curve to the left indicates the probable temperature, 85°, 83°, 81.5°, 80°, 78°, 76° and 75° at which the heptyloxy, hexyloxy, amyloxy, butyloxy, propyloxy, ethoxy and the methoxy homologues may exhibit smectic phase in monotropic condition. However, very careful observation doesn't lead to the realization of the property, hence the indication only points to a latent smectic transition. Similarly, the N-I curve is smoothly extrapolated to the left with a view to find the indications for the probable N-I transition temperature for the ethoxy homologue which is 115°. Because of the high tendency to crystallise this was not realised and points to latent nematic transition.

Series B-6 p-iso-Butoxyphenyl-p'-n-alkoxycinnamates

Mesomorphism begins in the series, p-iso-butoxyphenyl-p'-n-alkoxycinnamates, from the butyloxy homologue in the monotropic condition as monotropic nematic, one homologue later than in the series B-5. Like all the series previously discussed, this series also has the characteristics of a high melting series. The various transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig.11) (Table 15).

The K-M transition curve has an overall falling tendency upto the dodecyloxy homologue, except at the ethoxy homologue where there is a sharp rise and fall. From the dodecyloxy homologue upto the tetradecyloxy homologue there is a small rise in the K-M transition curve followed by levelling off upto the hexadecyloxy homologue. The overall fall in the K-M curve is of the order of 36° which was 17° in the series B-5 and only 5° in the series A-3, with straight chain butoxy group at right terminal. The maximum mesomorphic range is of 14° at the dodecyloxy homologue which was 23° in the series B-5 and 37° in the series A-3. The mesomorphic range in this series is of around 10°.

The first three homologues of this series are non-mesomorphic and the next three homologues viz. the butoxy, amyloxy and hexyloxy, are mesomorphic in the monotropic condition as monotropic nematic. The striking feature of this series, B-6, in contrast to all the series discussed so far under this investigation, is the absence of alternating odd-even effect though there are two N-I curves. The monotropic N-I transition points fall on an arc like curve which falls sharply from the butyloxy to the pentyloxy homologue and shows levelling off tendency upto the hexyloxy homologue. It appears to meet the upper N-I curve at the octyloxy homologue. Though there are two N-I transition curves; one formed by the monotropic transition points and the other by the enantiotropic transition points; the alternating effect is absent here. The falling N-I transition curve, for the enantiotropic transition points, exhibits a steep fall from the heptyloxy to decyloxy homologue where it meets the S-I transition curve having very little falling tendency. The last four homologues i.e. the decyloxy; dodecyloxy; tetradecyloxy and hexadecyloxy, are pure smectogens.

The only homologue exhibiting polymesomorphism in this series is the octyloxy homologue where in addition to the nematic phase, smectic phase emerges in the monotropic condition.

Pure nematogens of this series exhibit a threaded texture characteristic of the nematic mesophase while the smectic mesophase throughout the series shows focal conic fan shape texture of smectic A type.

Series B-7 p-iso-Amyloxyphenyl-p'-n-alkoxycinnamates

The entire series viz. p-iso-amyloxyphenyl-p'-n-alkoxycinnamates exhibits mesomorphism and like all other series discussed earlier, this series also has the characteristics of a high melting series. The various transitions are plotted versus the number of carbon atoms in the alkyl chain (Fig.12)(Table 17).

The K-M transition curve has overall falling tendency, with sharp rise and fall near the ethoxy and hexyloxy homologues. Beyond the hexyloxy homologue, the K-M transition curve exhibits fall upto the last, hexadecyloxy, homologue. The overall fall in the K-M transition curve is of 43° which is the maximum amongst all the series studied in this investigation. The minimum mesomorphic range of 2° is at the first homologue and the maximum range is of 37° at the hexadecyloxy homologue. There is an alternate increase in the mesomorphic range as the series progresses.

The two alternating N-I transition curves show falling tendency as the series is ascended, the lower N-I curve for the odd number of homologues first shows a slight rise between the methoxy and propoxy homologues and then falls a little bit and meets the upper curve for even number of members at the heptyloxy homologue, whereas the upper curve shows continuity with the S-I transition curve for the later homologues. Amongst the series B-5 to B-7, only in this series B-7 alternation is exhibited distinctly.

Polymesomorphism begins at the hexyloxy homologue in the monotropic condition - two homologues prior to that in the series B-5 and B-6 and one homologue earlier to that in the series A-4, with the advent of additional smectic phase at lower temperatures and persists upto the decyloxy homologue. The rising S-N transition curve appears to meet the falling N-I and S-I curve at the dodecyloxy homologue indicating that the undecyl homologue might have shown polymesomorphism if it were studied. The last three homologues are pure smectogens. Polymesomorphism persists in this series for the maximum number of homologues amongst the B type of series.

The texture of the nematic phase in the case of the pure nematogens is threaded, however, it is homeotropic in the polymesomorphic region. The texture of the smectic mesophase, as observed under the polarizing microscope, is focal conic fan shape of A type except for the hexyloxy and octyloxy homologues which are homeotropic smectic in nature.

Extrapolation of the S-N transition curve to the left indicates the N-S transition temperatures for the pentyloxy, butoxy, propoxy, ethoxy, and methoxy homologues at 93°, 91.5°, 89.5°, 87.5° and 86° respectively. At these temperatures, these homologues may exhibit smectic phase in monotropic condition. However, despite of the very careful observations, this property was not realised because of the high tendency to crystallize. Hence, this indication only points to a latent smectic transition.

4.c. Comparative Study of the New Homologous Series - A and B type of Series:

All the nine new homologous series synthesized and studied under this investigation offer quite interesting panorama of differing characteristics and provide a system of stepwise evaluation, besides giving an impression of rich mesomorphism at the very first look at them.

The new homologous series, under this investigation, are obtained by esterification of p-alkoxycinnamic acids which is also a high melting series. On esterification of the p-alkoxycinnamic acids, table (3), the transitions are expected to be lowered considerably (469). This is the fact as observed under this investigation too.

The first four homologous series A-1, A-2, A-3 and A-4 differ only in one respect, viz. the right terminal substituent which changes successively by a common difference of one -CH_2 unit as the series advance from A-1 to A-4. The other features viz. two benzene rings, the central vinyl carboxyl, -CH=CH-COO- linkage and the varying alkoxy substituents at the left terminal are all common. The variation in mesomorphic characteristics is obviously viewed, as due to the change in number of methylene units with which these series differ.

It is already observed in the discussion of the individual homologous series, viz. A-1, A-2, A-3 and A-4, that the alternating odd-even effect in nematic-isotropic transitions is very distinct in all these series. In series A-1 and A-2, both the curves show divergency, while in the series A-3 and A-4 they merge.

It is very interesting to note the alternation effect in the K-M transitions compared in the Table 40. The difference in K-M transitions, of the corresponding homologues of the series A-1 and A-2, A-2 and A-3, and A-3 and A-4 calculated in Table 40 leads to the generalization that the series with even number of methylene units at the right terminal has higher K-M transitions whereas the series with odd number of methylene units has lower K-M transitions for the corresponding homologues.

Table 40

Solid-mesomorphic transitions of A type series

Homologue	Solid-mesomorphic transition °C						
	Series						
R' →	A-1 $-OC_2H_5$	A-2 $-OC_3H_7$	A-3 $-OC_4H_9$	A-4 $-OC_5H_{11}$	(A-1)-(A-2)	(A-2)-(A-3)	(A-3)-(A-4)
C_1	131	127	95	82	-4	-32	-13
C_2	145	125	109	91	-20	-16	-18
C_3	126	128	117	110	+ 2	-11	- 7
C_4	111	110	117	111	- 1	+ 7	- 6
C_5	97	102	111	105	+ 5	+ 9	- 6
C_6	88	98	105	97	+10	+ 7	- 8
C_7	88	94	103	95	+ 6	+ 9	- 8
C_8	99	99	100	94	0	+ 1	- 6
C_{10}	80	78.5	83	82	- 1.5	+ 4.5	- 1
C_{12}	86	85	85	82	- 1	0	- 3
C_{14}	86	86	87	84	0	+ 1	- 3
C_{16}	90	88	90	88	-2	+ 2	- 2

R' - right terminal group

(-) - decrease in transition temperature

(+) - increase in transition temperature

The same effect is also observed in the N-I and S-I transitions which alternate for the even and odd number of $-CH_2-$ units in the series A-1 to A-4 (Table 41). The corresponding homologues of the series A-1 and A-3, with even number of $-CH_2-$ units at right terminal, have higher N-I or S-I transitions whereas the series A-2 and A-4, with odd number of $-CH_2-$ units at the same position, have lower N-I or S-I transitions (Table 41).

The impact of stepwise increase in the alkyl chain length of the right terminal substituent by one $-CH_2-$ unit is also felt in the appearance of the smectic mesophase enantiotropically in the A type of series under comparison. Enantiotropic smectic mesophase makes its appearance at the tenth member in series A-1 and A-3, with $-OC_2H_5$ and $n-OC_4H_9$ groups at the right terminal whereas in series A-2 and A-4, with $n-OC_3H_7$ and $n-OC_5H_{11}$ as right terminal group, smectic phase appears at the eighth member. This clearly indicates the alternating odd-even effect in the appearance of the enantiotropic smectic mesophase in series A-1 to A-4. The smectic phase in the monotropic condition appears at the seventh homologue in all the A type of series except in series A-3 where it begins at the eighth member.

Increase in length of the right terminal alkyl chain in a stepwise manner results into proportionate increase in the overall polarizability of the molecules and decrease in breadth

Table 41

Upper Transitions (N-I or S-I) of the Series A-1 to A-4

No.of carbon atoms in left terminal	N-I or S- I Transition °C						
	Series				Difference		
	A-1	A-2	A-3	A-4	(A.1)-(A.2)	(A.2)-(A.3)	(A.3)-(A.4)
C_1	150	(126)	132	127	-24	+ 6	- 5
C_2	161	144	146	135	-17	+ 2	-11
C_3	145	(127)	137	129	-18	+10	- 8
C_4	150	137	141	135	-13	+ 4	- 6
C_5	131	124	138	127	- 7	+14	-11
C_6	140	130	133	131	-10	+ 3	- 2
C_7	136	127	127	125	- 9	0	- 2
C_8	133.5	124	123	125	- 9.5	- 1	+ 2
C_{10}	126	116	115	117	-10	- 1	+ 2
C_{12}	122	111	113	112	-11	+ 2	- 1
C_{14}	116.5	107	111	109	- 9.5	+ 4	- 2
C_{16}	113	104	111	110	- 9	+ 7	- 1

( ) Monotropic transition

(-) decrease in transition temperature

(+) increase in transition temperature molecules of the homologues increases progressively with additional $-CH_2-$ units at the right terminal alkyl chain, the nematic character receives a setback though quite small. Nevertheless, there is no mistaking about the decreasing pattern, however small, of the nematic property as the overall polarizability increases.

The overall falling tendency of the nematic-isotropic transition curves in the case of all the four series under comparison is almost comparable. This tendency thus does not much contribute to the variation seen in the nematic mesophase range of the initial homologues; naturally the variation in the solid-mesomorphic transition curves and the original difference in the nematic mesophase transitions will account for the variation in the nematic mesophase range from one series to the other, while the slope of the nematic-isotropic transition curves due to their falling tendency as the alkyl chain length of the left terminal substituents increases, remains the same.

The alternation effect, in the nematic-isotropic transitions is the striking feature in the series A-1, A-2, A-3 and A-4 (Table 41). While the odd-even effect is continued to be exhibited upto the 6th, 6th, 5th and 10th homologue in series A-1, A-2, A-3 and A-4 respectively, the extent of the difference in the alternating transition temperatures vary in a sequence from the first to the fourth series. The differing values are given in Table 44.

the number of carbon atoms in the alkyl chain increases. When alternation ceases to be effective, the usual smooth transgression into 'petering off' stage is apparently taking place by an abrupt disappearance of the odd-even effect.

It is worthwhile to take into consideration one predecessor series viz. p-methoxyphenyl-p'-n-alkoxycinnamates (A-0) (465a) (Fig. 34 and Table 39), since this series has the alkyl chain at their right terminal with less number of carbon atom, while all other molecular characteristics do not differ from those of the present series A-1, A-2, A-3 and A-4. It is observed that the series A-0, under reference, exhibits wider nematic mesomorphic range as compared to those of the series A-1, A-2, A-3 and A-4. The series A-0, at the same time, exhibits smaller smectic mesophase range. If A-0, A-1, A-2, A-3 and A-4 series are taken in sequence of their right terminal substituents $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$, $-OC_4H_9$ and $-OC_5H_{11}$, respectively, then the indication for the decreasing nematic character and increasing smectic character for the series as the alkyl chain length of the right terminal substituents increases is well discerned (Table 45).

These observations are quite in keeping with the characteristics of the molecular forces. With $-OCH_3$ and $-OC_2H_5$ as terminal groups, the molecules get endowed with sufficient polarity, a force most conducive to end-to-end

Table 45

Mesophase lengths in the A type series

No.of carbon atoms in R	Mesophase Length °C									
	Series									
	A-0		A-1		A-2		A-3		A-4	
	S	N	S	N	S	N	S	N	S	N
1	-	24.5	-	19	-	1	-	37	-	45
2	-	20.5	-	16	-	19	-	37	-	44
3	-	38.5	-	19	-	1	-	20	-	19
4	-	35.5	-	39	-	27	-	24	-	24
5	-	36.5	-	34	-	22	-	27	-	22
6	-	39	-	52	-	32	-	28	-	34
7	-	29.5	16	48	2	33	-	24	3.5	30
8	6	40.5	7	34.5	2.5	22.5	6	23	14	17
10	5	31.5	24	22	23.5	14	24.5	7.5	27	8
12	9	21.5	23	13	17	9	28	-	30	-
14	11	14	23.5	7	21	-	24	-	25	-
16	21.5	-	18	5	16	-	21	-	22	-

S - Smectic phase

N - Nematic phase

parallel orientation of the nematic type. As the number of carbon atoms assumes a value 3 or more, the increased alkyl chain length will induce greater overall polarizability and hence more conducive environment in the fluid state for maintaining a longer range of layered smectic structure, is produced and becomes more effective as the series are ascended. The mesophase lengths in the A type of the series are recorded in Table 45.

The two, odd-even, curves merge at the fifth member in the A-0 series while in the series A-1 and A-2, a clear tendency of divergence is seen as the alkyl chain length at left terminal increases. In series A-3 and A-4, the tendency of divergence is changed and both the curves meet at the fifth and the tenth member respectively. The alternate odd-even effect covers more number of homologues in the last A-4 series. One thing predominantly common for all these series is the high melting character.

The next three series i.e. B-5, B-6 and B-7 are identical in all respects, except the right terminal group which is branched in B type of series in place of straight chain in A type of series. The molecules of the homologues of these series, too, have two benzene rings, one central bridge and alkoxy group at left terminal as those of the series A-1, A-2, A-3 and A-4. Due to such 'iso' linking the breadth of the molecules is somewhat increased with a proportionate decrease in the length. These two simultaneous modifications in the geometry of the moieties result into proportionate variations in molecular forces. With one methyl group protruding in space will cause a little difficulty in close packing of the molecules, consequently the specific orientations could be disturbed or broken down with lesser intake of the energy. This would result into a proportionate lowering of the transitions. The decrease in length, too, would support this effect in lowering of the transitions.

On comparing the phase diagrams (Figs.6, 7, 8, 9 and 10, 11, 12 respectively), certain differences emerge which ought to be linked with the modified geometry of the moieties, as outlined above. The pair of series, A-2 and B-5, is taken first for a comparative assessment of the effect on their transitions due to the modified 'iso' dispositions in the right terminal alkyl chain. It is observed that the upper transition of the first mesomorphic homologue viz. third member of the B-5 series, is lower by about 28° as compared to that of the series A-2. This pattern of decrease in the upper transitions for the entire homologous series B-5 is retained without any exception. Even the last homologue of this series i.e. hexadecyloxy homologue, is having the S-I transition lower by 15° than that of the series A-2 (Table 46).

Similarly, the solid-mesomorphic transitions, in an overall manner, of this series B-5 are lower (Table 47) than those of the series A-2. Both K-M and N-I or S-I transitions are lower by about 1° to 28°, when the right terminal alkyl chain acquires 'iso' disposition in comparison with those of the series A-2 where the alkyl chain has straight linking. The acquired breadth due to the 'iso' disposition should be the only responsible

Table 46

Upper Transitions (N-I or S-I) in A and B types of the series

No. of carbon atoms in R	Upper Transitions °C								
	Pair of Series								
	A-2	Difference	B-5	A-3	Difference	B-6	A-4	Difference	B-7
1	(126)	-	-	132	-	-	127	-13	114
2	144	-	-	146	-	-	135	- 1	134
3	(127)	-28	(99)	137	-	-	129	-12	117
4	137	-28	(109)	141	-29	(112)	135	-10	125
5	124	-26	(98)	138	-33	(105)	127	-10	117
6	130	-27	(103)	133	-28	(105)	131	-12	119
7	127	-28.5	98.5	127	-12	115	125	-10	115
8	124	-25	99	123	-14	109	125	-13	112
10	116	-20	96	115	-12	103	117	-11	106
12	111	-17	94	113	-11	102	112	- 7	105
14	107	-16	91	111	-10	101	109	- 4	105
16	104	-15	89	111	-11	100	110	- 4	106

(   ) Monotropic transition

Table 47

Solid-mesomorphic or Solid-isotropic Transitions in A and B type of Series.

No.of carbon atoms in R	Solid-mesomorphic or Solid-isotropic Transitions °C pair of series								
	A-2	Difference	B-5	A-3	Difference	B-6	A-4	Difference	B-7
1	127	-28	99	95	+33	128	82	+30	112
2	125	+20	145	109	+30	139	91	+26	117
3	128	-19	109	117	+11	128	110	+ 3	113
4	110	0	110	117	- 2	115	111	- 2	109
5	102	+1	103	111	- 2	109	105	- 4	101
6	98	+5	103	105	+ 5	110	97	+ 8	105
7	94	+2	96	103	+ 5	108	95	- 3	92
8	99	-17	82	100	0	100	94	- 5	89
10	78.5	-5.5	73	83	+9	92	82	- 6	76
12	85	-1	84	85	+3	88	82	-11	71
14	86	-3	83	87	+5	92	84	-14	70
16	88	-6	82	90	+2	92	88	-19	69

factor for this effect of lowering in the various transitions.

The beginning of polymesomorphism is also affected. While enantiotropic smectic mesophase makes its appearance at the eighth homologue in both series under comparison viz. A-2 and B-5, monotropic smectic mesophase is exhibited by the seventh homologue in A-2 series which is absent in the series B-5. Besides, the smectic-nematic transitions are also lower in B-5 series. However, it is very interesting to note that the smectic mesophase length reaches maximum and then decreases till the last homologue in both the series under comparison (Table 45 and 50). The unfailing impression is that with increased breadth of the molecules of the series B-5, the overall smectogenic character is somewhat enhanced though not that characteristically as expected.

Taking now the next pair of series viz. A-3 and B-6 for comparison, the solid-isotropic or solid-mesomorphic transitions of the 'iso' series B-6 present anomalous situation (Table 47). The solid-isotropic or solid-mesomorphic transitions of the 'iso' series B-6 are higher as compared to those of the corresponding homologues of the straight chain series A-3. We would see a little later that the three pairs viz.A-2 - B-5, A-3 - B-6 and A-4 - B-7 exhibit alternation as far as the solid-isotropic or solid-mesomorphic transitions are concerned. Except this behaviour of the 'iso' series B-6, almost all other transitions are lower in the same manner as those of the series B-5 when compared with the homologues of n-chain series (Table 46 and 47). The upper transitions of the B-6 series, viz. p-iso-butoxyphenyl-p'-n-alkoxycinnamates, are lower in the range of about 10° to 33° (Table 46).

Polymesomorphism starts at the eighth member, in both the series A-3 and B-6, with the appearance of the smectic mesophase in the monotropic condition but the polymesomorphism remains restricted to only eighth member in series B-6 whereas it continues to be exhibited upto the decyloxy homologue in the series A-3. This observation points put the decrease in nematic character of the 'iso' series B-6 as compared to the n-chain A-3 series. This can be more emphasized by the fact that in 'iso' series B-6 the first three members are non-mesomorphic and the next three exhibit monotropic nematic mesophase followed by only two homologues exhibiting enantiotropic nematic mesophase whereas the straight chain series A-3 exhibits enantiotropic nematic phase right from the first member upto the tenth member. The smectic mesophase length in the 'iso' series B-6 is reduced; the range being 0.5° to 14° (Table 50) and that in the n-chain it is 6° to 28° (Table 45). The last four members of the 'iso' series B-6 are pure smectogens whereas in the series A-3 last three members are pure smectogens. This fact once again points out the greater smectogenic nature and less nematogenic nature of the series B-6 as compared to series A-3.

Comparison of the last pair of series viz. straight chain A-4 and 'iso' series B-7, reveals the fact that the upper transitions of all the homologues of the series B-7 are lower by 1° to 13°C as compared to those of the series A-4 (Table 46). This can certainly be attributed to the right terminal alkyl chain acquiring 'iso' disposition in comparison with those of the series A-4 where the alkyl chain has a straight linking.

Similarly, the solid-mesomorphic transitions of this series B-7 are lower with the exception for the first three members where they are raised by 3° to 30°C. Our contention little earlier, that the three pairs under discussion viz. A-2 - B-5, A-3 - B-6 and A-4 - B-7, exhibit alternation in the solid-mesomorphic transitions is proved here (Table 47). While the first pair A-2 and B-5 exhibits lowering of the solid-mesomorphic transitions, the next one viz. A-3 and B-6 shows increase in the solid-mesomorphic transitions and the last pair viz. A-4 and B-7, exhibits lowering in the solid-mesomorphic transitions. The upper transitions in the B series are lower by 1° to 33° as compared to those in the A series (Table 46). The acquired breadth due to the 'iso' disposition in series B-7 should be the only responsible factor for the changes in the various transitions.

The smectic characteristics are also affected as both the monotropic as well as the enantiotropic smectic phase makes its appearance one homologue prior in the case of the broad 'iso' series B-7 as compared to that in the series A-4. Polymesomorphism is also exhibited by one member more in series B-7. Besides, the smectic-nematic transitions are also lower by about 10° in 'iso' series B-7 as compared to n-chain A-4 series. The smectic mesophase lengths are also more in the series B-7 as compared to those in the corresponding homologues of the series A-4 and that it increases continuously as the series B-7 ascends (Table 45 and 50). All these indications prove, beyond any doubt, the greater smectogenic nature of the broad 'iso' series B-7.

One particular point evolves, in the cross comparison of these seven homologous series, is that of the sequences of the change in transitions, in the case of the straight chain, first four series A-1 to A-4, the upper, nematic-isotropic, transitions show an alternating sequence of the series, but in the 'iso' linked B-5 to B-7 series, there is a rising sequence, i.e. the upper transitions in an overall manner are in the sequence of B-7 > B-6 > B-5 (Tables 41 and 48). Obviously, two sequences, one of the alternating and the other of rising, can not be compatible for a comparison. However, the fact remains that all these series are high melting series.

The B-5, B-6 and B-7 homologous series differ only in one respect i.e. the length of the right terminal alkyl chain increases with one $-CH_2-$ unit in a stepwise manner, while the 'iso' linking of the chain, too, remains a common feature. Thus, while the breadth of the molecules remains the same, the length increases as one passes from B-5 to B-7 homologous series. With increased alkyl chain length, the overall polarizability of the molecules, too, would be increased sufficiently to enhance the transitions of the homologues of the series under consideration. That, this is so, is easily seen in Figs.10, 11 and 12 (Tables 13, 15 and 17).

One interesting point that emerges on comparison of the B set of series is the alternation in the K-M transitions. The K-M transitions of the series B-6 are higher than those of the series B-5 and those in the series B-7 are lower than the corresponding values in the series B-6 (Table 49).

The smectogenic character increases as one passes from series B-5 to B-7, this can be said on two counts. Firstly, smectic mesophase makes its appearance at the eighth, eighth (in monotropic condition) and sixth homologue (in monotropic condition) in series B-5, B-6 and B-7 respectively. Secondly, the smectic mesophase length is progressively increased from series B-5 to B-7 (Table 50). In polymesomorphic region, too, the nematic characteristic decreases as the smectic characteristic increases (Table 50). It can safely be said that increase in length of the molecules leads to increase in smectogenic character since the enhanced polarizability lends stability to the layered structure.

Table 49

Solid-isotropic or solid-mesomorphic transitions in B type of series

No. of carbon atoms in R	Solid-Isotropic or Solid-mesomorphic transition °C				
	Series			Difference °C	
	B-5	B-6	B-7	(B-5)-(B-6)	(B-6)-(B-7)
1	99	128	112	+29	-16
2	145	139	117	- 6	-22
3	109	128	113	+19	-15
4	110	115	109	+ 5	- 6
5	103	109	101	+ 6	- 8
6	103	110	105	+ 7	- 5
7	96	108	92	+12	-16
8	82	100	89	+18	-11
10	73	92	76	+19	-16
12	84	88	71	+ 4	-17
14	83	92	70	+ 9	-22
16	82	92	69	+10	-23

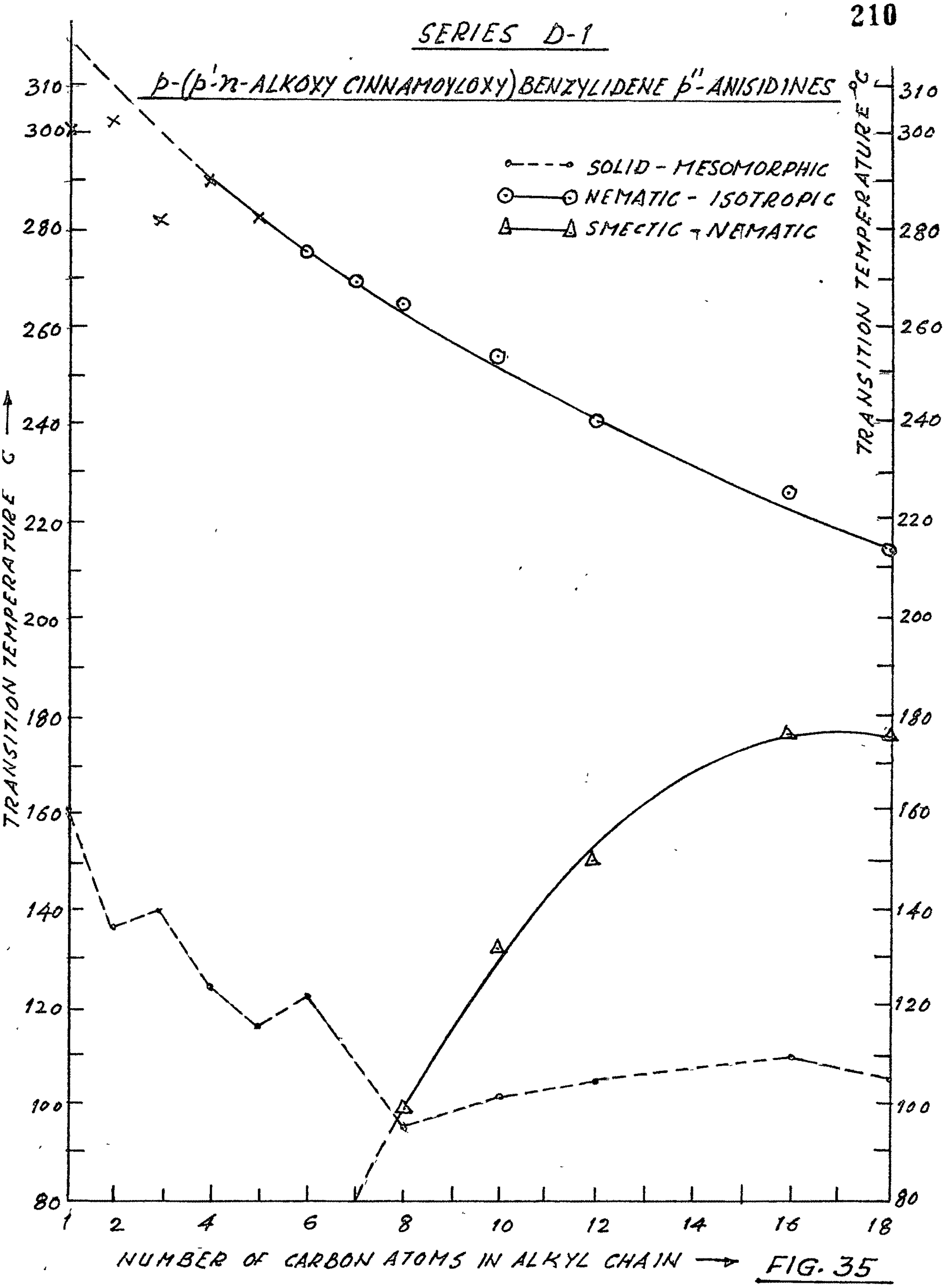
Table 50

Mesophase lengths in B type of the series

No. of carbon atoms in R	Mesophase length °C					
	Series					
	B-5		B-6		B-7	
	Smectic	Nematic	Smectic	Nematic	Smectic	Nematic
1	-	-	-	-	-	2
2	-	-	-	-	-	17
3	-	10	-	-	-	4
4	-	1	-	3	-	16
5	-	5	-	4	-	16
6	-	0	-	5	10	14
7	-	2.5	-	7	3	20
8	5	12	0.5	9	9.5	13.5
10	17	6	11	-	26	4
12	10	-	14	-	34	-
14	8	-	9	-	35	-
16	7	-	8	-	37	-

The A type of series viz. A-1, A-2, A-3 and A-4 (Fig.6, 7, 8, and 9) can find a direct comparison with the D type of series viz. D-2, D-3, D-4 and D-5 (Fig.36, 37, 38 and 39) and B type of series viz. B-5, B-6 and B-7 (Fig.10,11 and 12) with E type of series viz. E-1, E-2, and E-3 (Fig.40, 41 and 42) (Fig 43). One benzene ring and one central bridge viz. -CH=N-, azomethine, happen to be absent in the series A-1 to A-4 and B-5 to B-7. While the overall breadth of molecules in the type A and D and in the type B and E remains the same, the aromaticity and length attributable to a benzene ring as well as the polarizability and length consequent to a central bridge of the nature of azomethine will be less in the type A and B than those found in the type D and E. Thus, the length to breadth ratio in type A and B will differ from that in type D and E. The molecules of the series in type A and B will be less non-coplanar than those of the group D and E. All these factors in a combined manner affect the transitions, polymesomorphism, phase lengths and the predominance of smectogenic or nematogenic character etc. of these two pairs of sets of series under comparison.

On comparison of the series in A type with those in the D type, the following points emerge. With less length, less aromaticity, less length to breadth ratio, less polarizability, less ratio of lateral to terminal attractions and rather less non-coplanar nature while the magnitude of terminal attractions remaining almost the same due to the same polarity in both the types, the series A-1, A-2, A-3 and A-4 have their upper transitions



SERIES D-1

p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE p''-ANISIDINES

FIG. 35

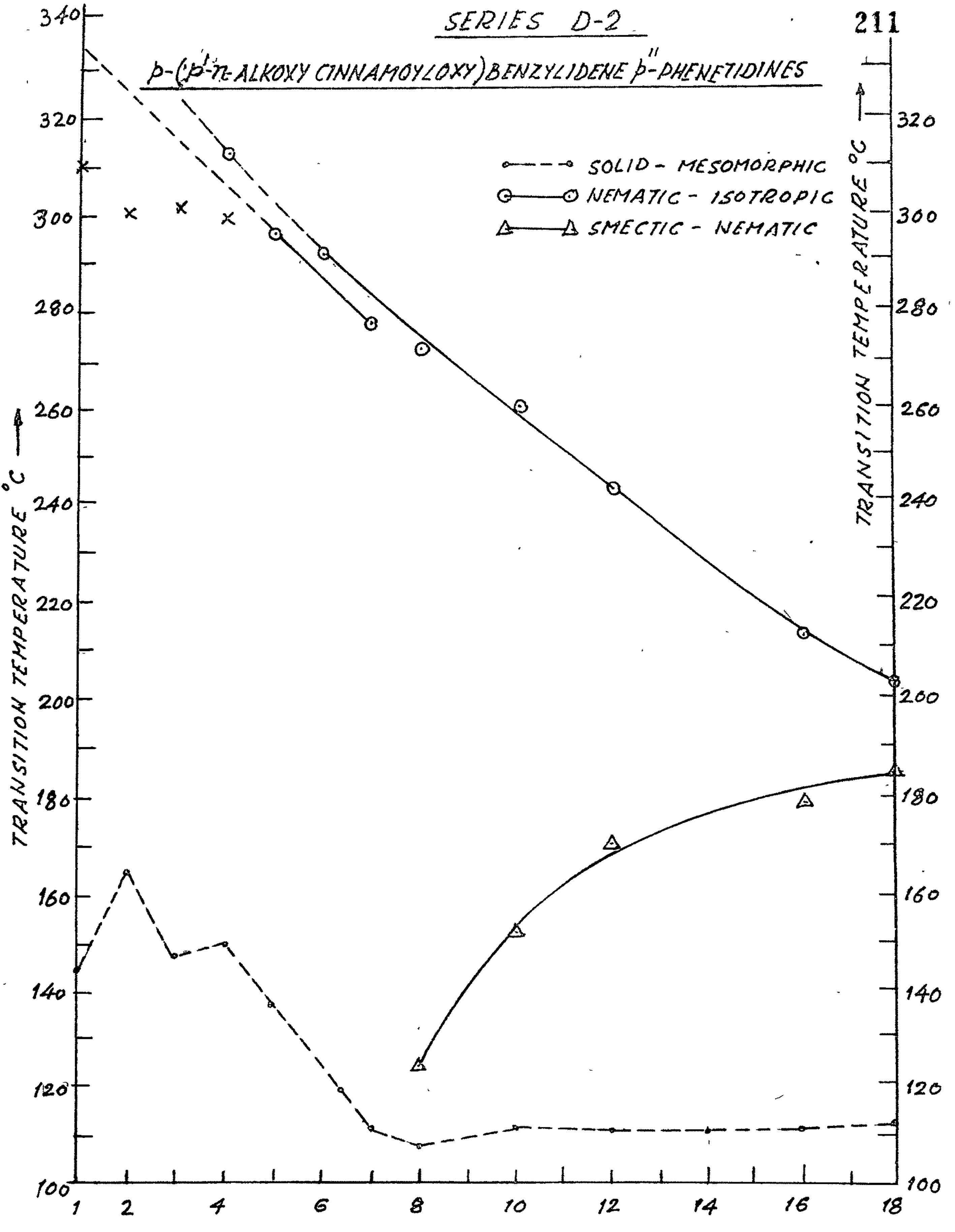

SERIES D-2
p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE p''-PHENETIDINES
SOLID - MESOMORPHIC
NEMATIC - ISOTROPIC
SMECTIC - NEMATIC
TRANSITION TEMPERATURE °C
340
320
300
280
260
240
220
200
180
160
140
120
100
1
2
4
6
8
10
12
14
16
18
NUMBER OF CARBON ATOMS IN ALKYL CHAIN

FIG. 36

SERIES D-3

p-(p′-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-p″-n-PROPOXYANILINES

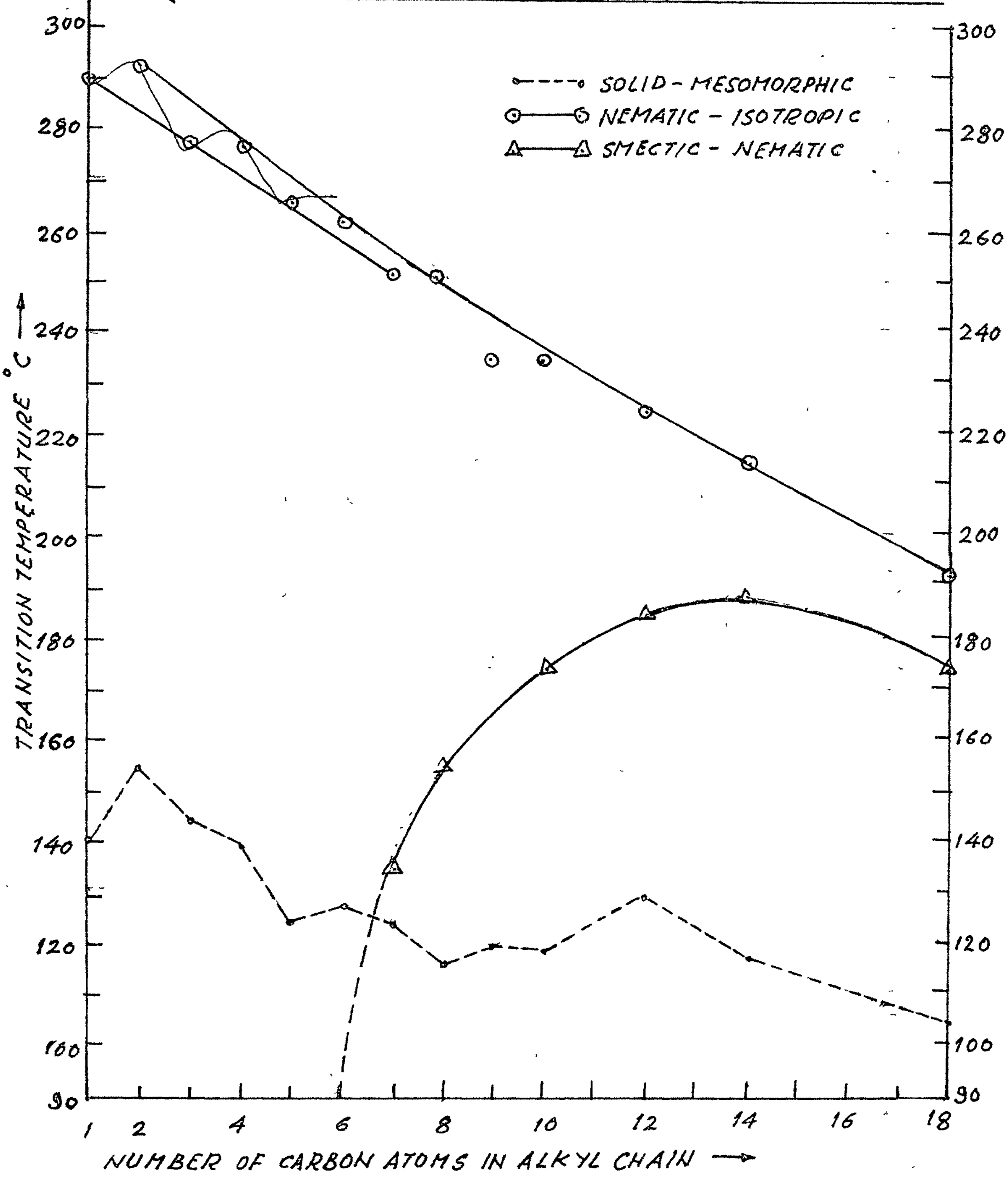


FIG. 37

SERIES· D-4

p-(p'n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-p''-n-BUTOXYANILINES

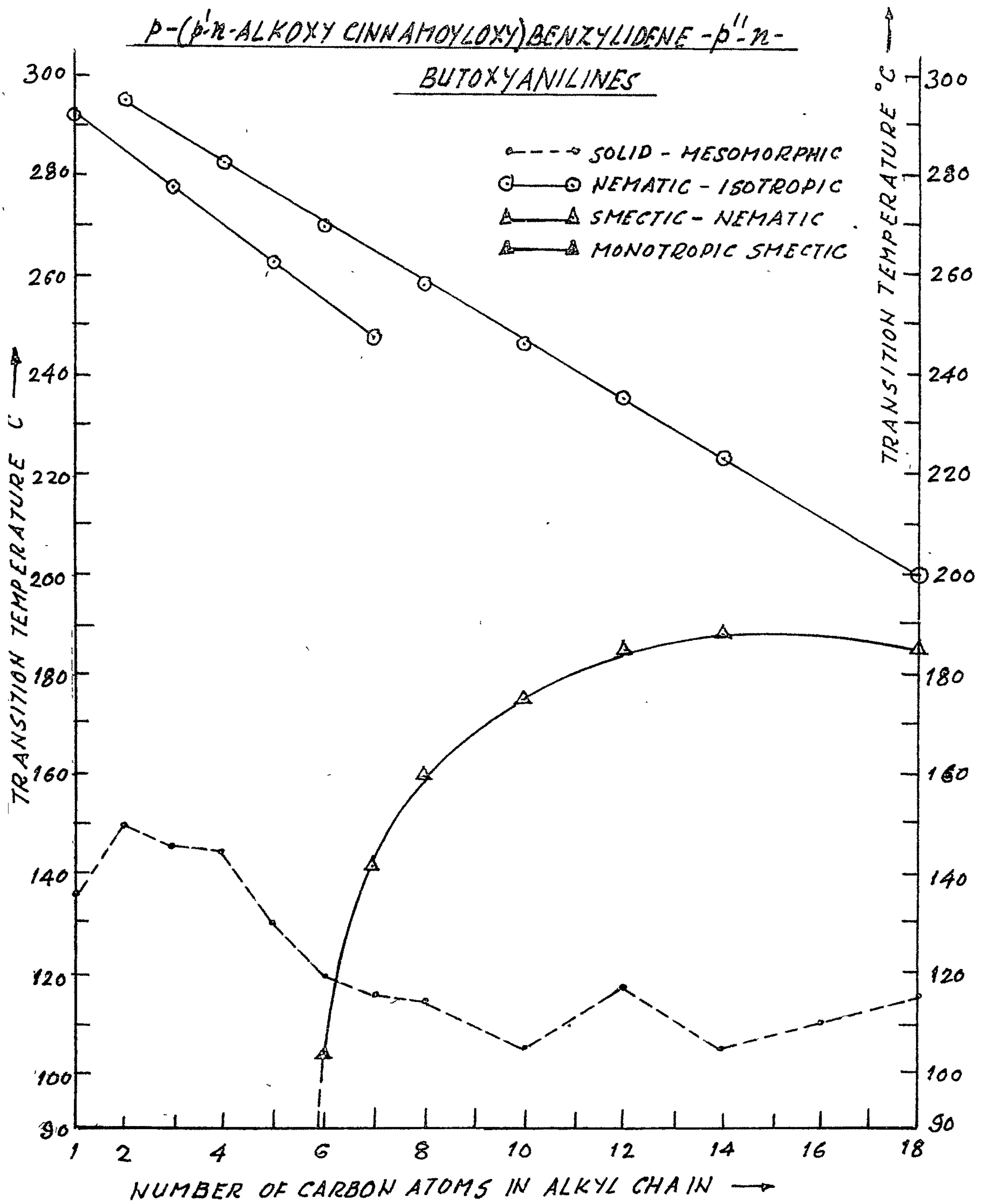


FIG. 38

SERIES D-5

p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-p''-n-AMYLOXYANILINES

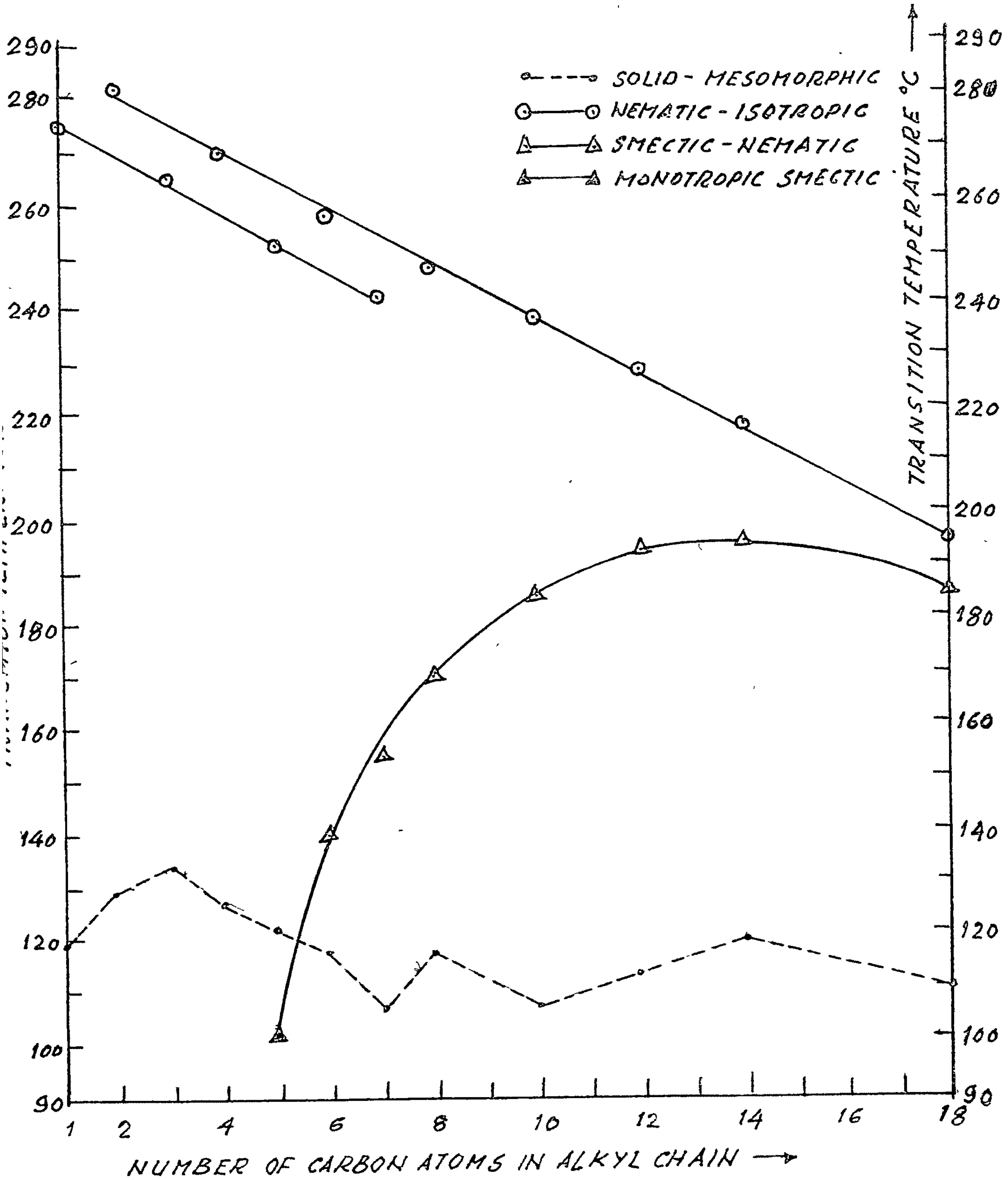


FIG. 39

SERIES E-1

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

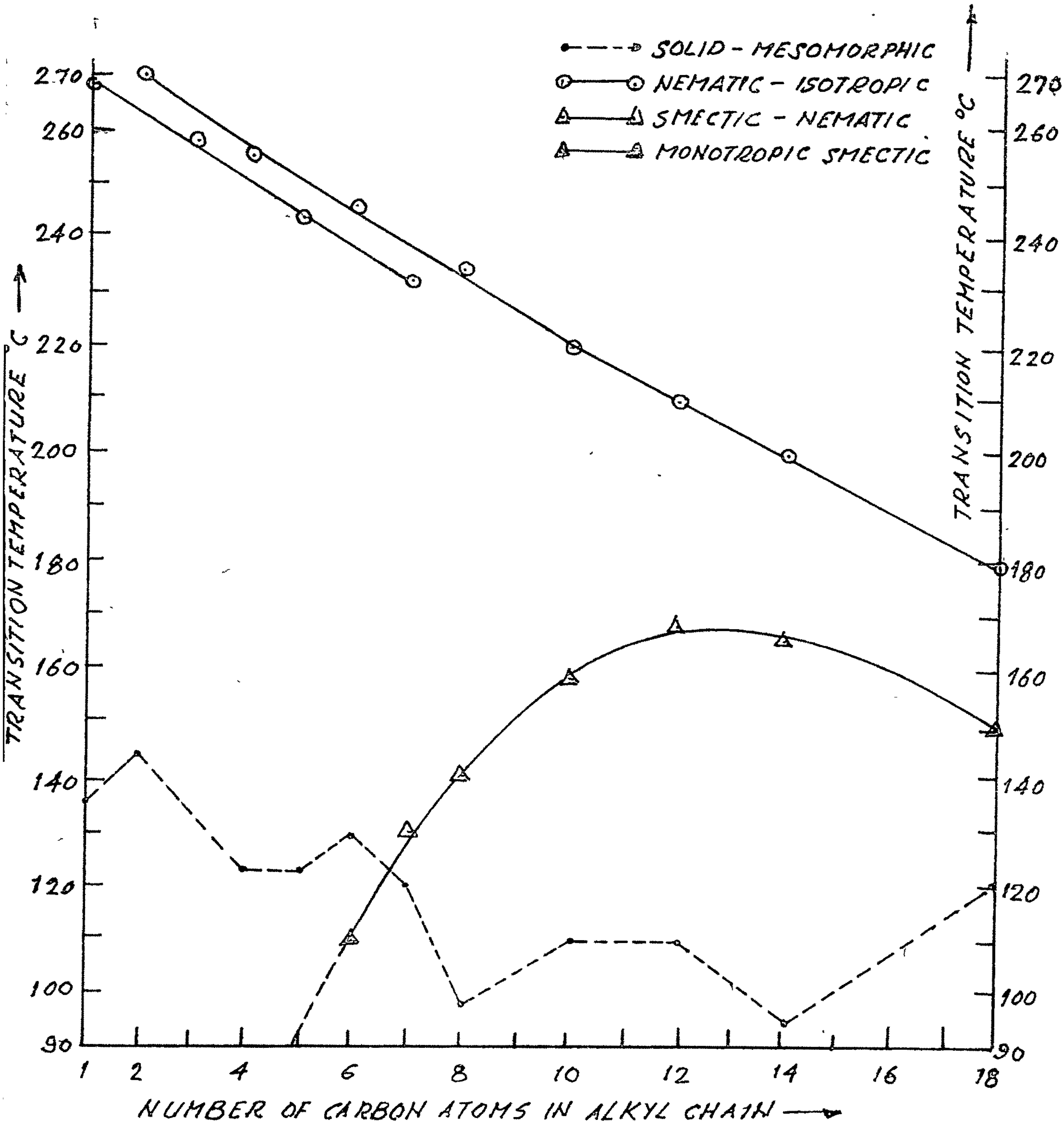


FIG. 40

SERIES E-2

p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-p''-ISOBUTOXYANILINE

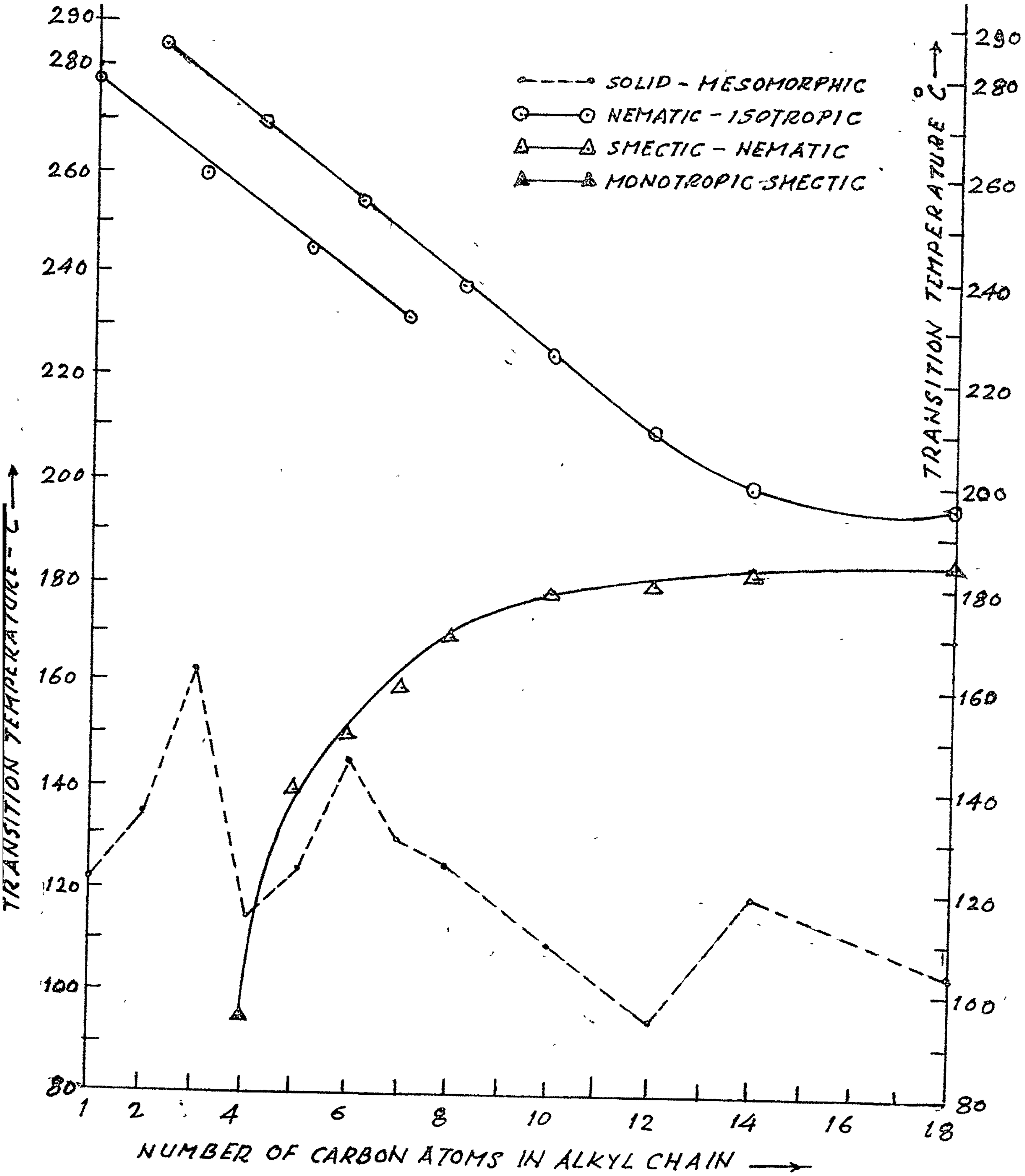


FIG. 41

SERIES E-3

p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-isoAMYLOXYANILINES

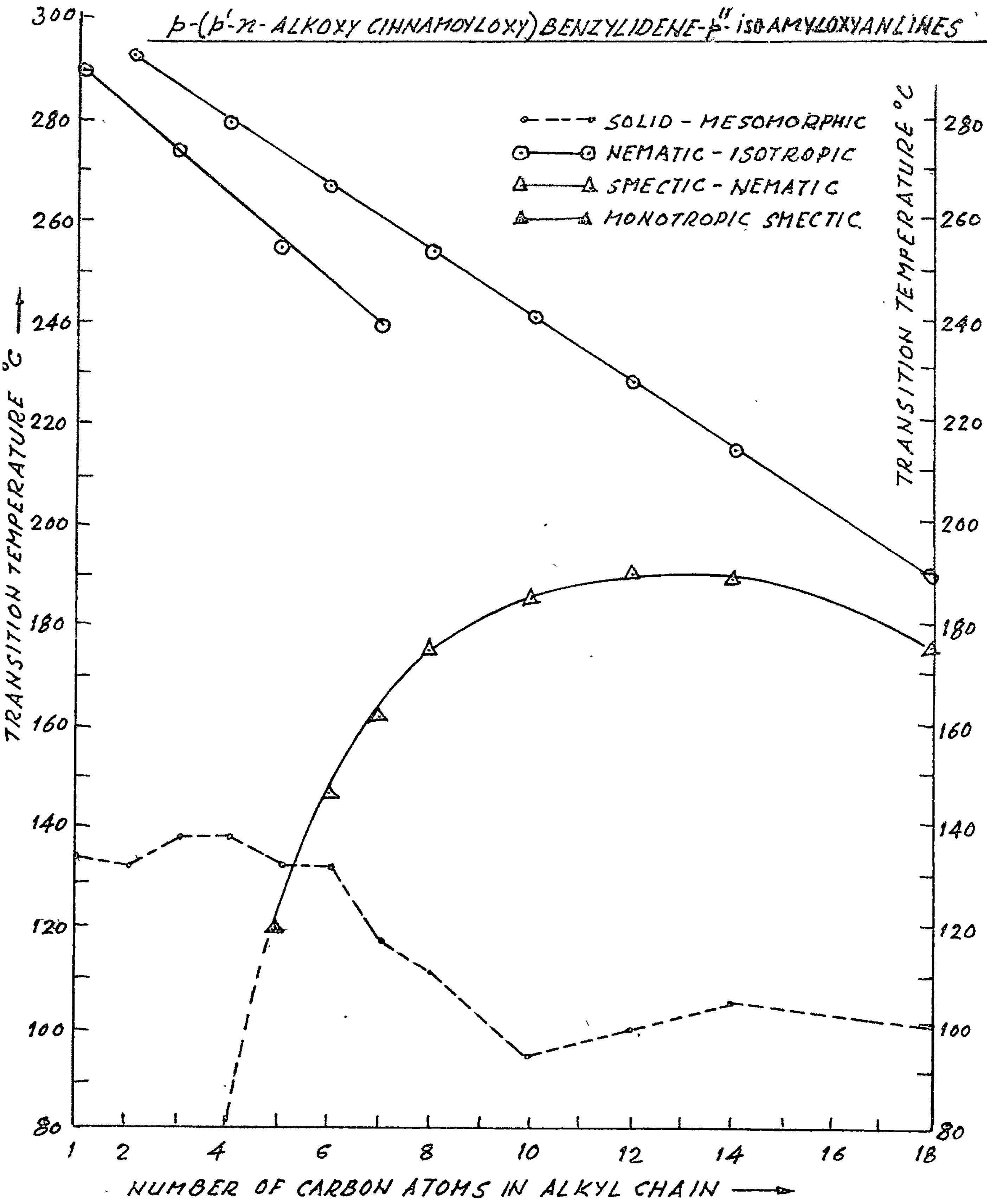


FIG. 42

reduced by 101° to 166°, 108° to 164°, 112° to 160° and 108° to 148° respectively (Table 51). The alternation effect in the N-I transitions is clearly visible in both A and D type of series (Table 51). First four members of the series D-2 decompose before passing into the isotropic phase because of the very high transition temperatures. The series A-1, with reduced length by $C_6H_5CH{=}N-$ unit, has upper transitions (N-I) lowered considerably hence doesn't show decomposition. In the subsequent D-3, D-4 and D-5 series no homologue decompose due to lowered transition temperatures.

The characteristic of high melting series, viz. the falling tendency of the N-I transition curves in both the types, A and D, is clearly seen. Polymesomorphism once sets in at the eighth, seventh, sixth and fifth member in the series D-2, D-3, D-4 and D-5 respectively, persists upto the last member, while in the series A-1 only it is exhibited upto the last homologue. In the series A-2 the last two members while in the series A-3 and A-4, last three members are pure smectogens.

The mesophase lengths in A type of the series, are much reduced than those of the corresponding D type of series (Table 52). While the maximum nematic mesophase lengths in D-2, D-3, D-4 and D-5 series are 167°, 150°, 158° and 155° at the sixth, first, first and first homologue respectively, they are only 52°, 33°, 37° and 45° in the series A-1, A-2, A-3 and A-4 at the sixth, seventh, first-second and first homologue

Table 51

Upper transitions in the A and D type of series

No. of carbon atoms in R	Upper Transitions °C											
	Pair of Series											
	D-2	A-1		D-3	A-2		D-4	A-3		D-5	A-4	
1	310D	150	[-160]	290	(126)	[-164]	292	132	[-160]	275	127	[-148]
2	301D	161	[-140]	293	144	[-149]	295	146	[-149]	282	135	[-147]
3	302D	145	[-157]	278	(127)	[-151]	278	137	[-141]	265	129	[-136]
4	300D	150	[-150]	277	137	[-140]	283	141	[-142]	270	135	[-135]
5	297	131	[-166]	266	124	[-142]	263	138	[-125]	252	127	[-125]
6	293	140	[-153]	262	130	[-132]	270	133	[-137]	258	131	[-127]
7	278.5	136	[-142.5]	252	127	[-125]	248	127	[-121]	242	125	[-117]
8	273	133.5	[-139.5]	250	124	[-126]	258	123	[-135]	248	125	[-123]
10	261	126	[-135]	235	116	[-119]	246	115	[-131]	238	117	[-121]
12	244	122	[-122]	225	111	[-114]	235	113	[-122]	228	112	[-116]
14	-	116.5	[-]	215	107	[-108]	223	111	[-112]	217	109	[-108]
16	214	113	[-101]	-	104	[-]	-	111	[-]	-	110	[-]

[ ] Difference value, ( ) Monotropic transition

D- Decomposes

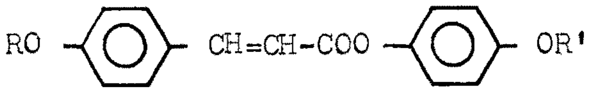
Table 52

Mesophase length in the A and D type of series

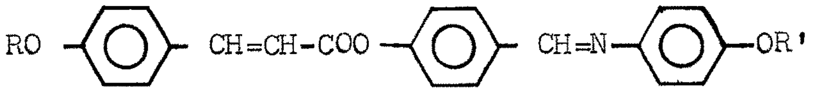
No. of carbon atoms in R	Mesophase length °C															
	Pair of series															
	D-2		A-1		D-3		A-2		D-4		A-3		D-5		A-4	
	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N
1	-	165	-	19	-	150	-	1	-	158	-	37	-	155	-	45
2	-	136	-	16	-	138	-	19	-	145	-	37	-	152	-	44
3	-	154	-	19	-	133	-	1	-	132	-	20	-	131	-	19
4	-	150	-	39	-	137	-	27	-	138	-	24	-	142	-	24
5	-	160	-	34	-	141	-	22	-	132	-	27	21	129	-	22
6	-	167	-	52	-	134	-	32	15	150	-	28	22	118	-	34
7	-	166.5	16	48	10	117	2	33	26	106	-	24	47	87	3.5	30
8	16	148	7	34.5	39	95	2.5	22.5	45	98	6	23	53	78	14	17
10	41	108	24	22	55	60	23.5	14	70	71	24.5	7.5	77	53	27	8
12	58.5	73.5	23	13	55	40	17	9	68	50	28	-	81	34	30	-
14	-	-	23.5	7	70	27	21	-	83	35	24	-	75	22	25	-
16	67.5	34.5	18	5	-	-	16	-	-	-	21	-	-	-	22	-

S - Smectic phase

N - Nematic phase



A type



D type

For A-1 and D-2 R' $=-C_2H_5$

A-2 and D-3 $= n-C_3H_7$

A-3 and D-4 $= n-C_4H_9$

A-4 and D-5 $= n-C_5H_{11}$

Table 53

Upper transitions in the B and E type of series

No.of carbon atoms in R	Upper Transitions °C								
	Pair of Series								
	E-1		B-5	E-2		B-6	E-3		B-7
1	268	[-]	-	278	[-]	-	290	[-176]	114
2	270	[-]	-	285	[-]	-	293	[-159]	134
3	258	[-159]	(99)	260	[-]	-	274	[-157]	117
4	255	[-146]	(109)	270	[-158]	(112)	280	[-155]	125
5	244	[-146]	(98)	246	[-141]	(105)	255	[-138]	117
6	245	[-142]	(103)	255	[-150]	(105)	267	[-148]	119
7	232	[-133.5]	98.5	232	[-117]	115	240	[-125]	115
8	234	[-135]	99	239	[-130]	109	254	[-142]	112
10	220	[-124]	96	225	[-122]	103	241	[-135]	106
12	210	[-116]	94	210	[-108]	102	228	[-123]	105
14	200	[-109]	91	199	[-98]	101	214	[-109]	105
16	-	[-]	89	-	[-]	100	-	[-]	106

[ ] - Difference value

( ) - Monotropic transitions

As is the case in the previous pair of series viz. A and D, this pair of series B and E, also have the characteristic of high melting series, viz. the nematic-isotropic transition curves have falling tendency. Polymesomorphism once sets in, at the sixth, fourth and fifth homologue in E-1, E-2 and E-3 respectively, persists upto the last, hexadecyloxy, homologue whereas that begins at the eighth, eighth and sixth member in the series B-5, B-6 and B-7 respectively and persists upto the tenth member in series B-5 and B-7 and in series B-6 only one member exhibits polymesomorphism.

The mesophase lengths in the B type of series are considerably reduced as compared to those in E type of series (Table 54). While the maximum mesophase lengths in the series E-1, E-2 and E-3 at the first, first and second homologue are of 133°, 157° and 160° respectively in nematic phase, they are only 17°, 14° and 37° in the series B-5, B-6 and B-7,respectively at the decyloxy, dodecyloxy and the hexadecyloxy homologue in smectic phase. The nematic character is reduced much in the B type of series. The maximum nematic mesophase lengths are of 12°, 9° and 17° in the series B-5, B-6 and B-7 respectively whereas those in the series E-1, E-2 and E-3 are 133°, 157° and 160° respectively. The maximum smectic phase lengths in the B-5, B-6 and B-7 series are of 17°, 14° and 37° respectively while those in the series E-1, E-2 and E-3 are 70°, 85° and 90° respectively.

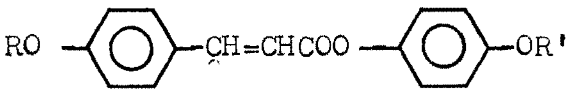
Table 54

Mesophase length in B and E type of series

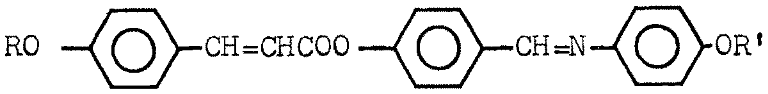
No. of carbon atoms in R	Mesophase length °C											
	Pair of series											
	E-1		B-5		E-2		B-6		E-3		B-7	
	S	N	S	N	S	N	S	N	S	N	S	N
1	-	133	-	-	-	157	-	-	-	155	-	2
2	-	126	-	-	-	150	-	-	-	160	-	17
3	-	125	-	10	-	97	-	-	-	136	-	4
4	-	132	-	1	21	155	-	3	-	142	-	16
5	-	121	-	5	16	106	-	4	13	122	-	16
6	20	115	-	0	4	105	-	5	14	120	10	14
7	10	102	-	2.5	30	72	-	7	44	78	3	20
8	42	94	5	12	44	69	0.5	9	63	79	9.5	13.5
10	48	62	17	6	68	47	11	-	90	56	26	4
12	58	42	10	-	85	30	14	-	90	38	34	-
14	70	35	8	-	62	17	9	-	84	25	35	-
16	-	-	7	-	-	-	8	-	-	-	37	-

S - Smectic phase

N - Nematic phase



B type



E type

For B-5 and E-1 R' = iso-C_3H_7

B-6 and E-2 = iso-C_4H_9

B-7 and E-3 = iso-C_5H_{11}

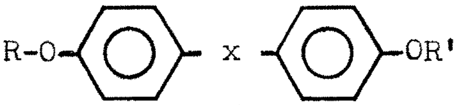
The maximum mesophase lengths in the E type of series are in the nematic phase while those in the B type of series are in the smectic phase though both the mesophase lengths in the B type of series are reduced much.

It may be concluded here that one benzene ring and one central bridge viz. -CH=N-, azomethine, are less in the A and B type of series, while the overall breadth of the molecules in the A-D and B-E pairs of series remains more or less the same. Thus the aromaticity and length attributable to a benzene ring as well as the polarizability and length consequent to a central bridge viz. azomethine, are also reduced along with length to breadth ratio which in turn reduce the transitions, mesophase lengths and polymesomorphism and increases the smectogenic character in A and B type of series.

The effect of linkage groups on the clearing points have been evaluated by comparing p,p'-dialkoxy-trans-stilbenes with similar compounds where the terminal groups are the same (470). For a sample survey, the first homologues of the series A-1, A-2, A-3, A-4 and the second member of the series A-1 are compared with the identical p,p'-dialkoxy-trans-stilbenes. As shown in Table 55, the clearing points of the compounds, prepared under this investigation, are lower and the monotropic nematic phase, in stilbenes, is transformed into enantiotropic nematic with the replacement of the -CH=CH- central linkage by -CH=CHCOO-. The central linkage -CH=CH- will be planar, and the relative lower transitions for the compounds with -CH=CH-COO- central linkage are due to nonplanar nature of the molecules.

Table 55

Comparison of transitions in stilbene and p-alkoxyphenyl-p'-n-alkoxycinnamates



Terminal substituents		Transitions °C				Difference °C	
		X= -CH=CH-COO-		X= -CH=CH-			
R	R'	N	I	N	I	N	I
$-CH_3$	$-C_2H_5$	131	150	(179)*	197*	48	47
$-CH_3$	$-C_3H_7$	(126)	127	(161)*	177*	35	50
$-CH_3$	$-C_4H_9$	95	132	(162)*	169*	67	37
$-CH_3$	$-C_5H_{11}$	82	127	(154)*	162*	72	35
$-C_2H_5$	$-C_2H_5$	145	161	(189)*	209*	44	48

N - Solid-nematic transition

I - Nematic-isotropic transition

( ) - Monotropic transition

* - (470)

The variations in the transitions and phase lengths of the heptyloxy and decyloxy homologues in A, B, D and E type of series are recorded in Table 56, and an attempt is made to rationalize these results. The difference between the pairs of D, A and E, B is that of the $-C_6H_4-CH=N-$ unit only. The change in transitions and phase lengths for nematic and smectic phases are recorded and a ratio of the depression in the transitions to the decrease in mesophase lengths due to elimination of the $-C_6H_4 - CH=N-$ unit is calculated. It is noted that the effect of the elimination of the $-C_6H_4-CH=N-$ unit is the most in the pair D-5, A-4 and the least in the pair D-2, A-1 as far as the nematic phase is concerned. The effect of elimination of this unit increases from the pair A-1 - D-2 to the pair A-4, D-5. In the case of the smectic mesophase the order is exactly the reverse; the effect of the elimination of the unit, in discussion, is the most in the first pair D-2, A-1 and it reduces from the pair D-2, A-1 to the pair D-5, A-4. In other words, the first pair D-2, A-1, with $-OC_2H_5$ group at the right terminal, is more conducive to the nematic mesophase whereas the last pair D-5, A-4, with $-OC_5H_{11}$ at the right terminal, is more conducive to the smectic mesophase.

The pattern in the variations in the transitions and the phase lengths as far as the pair E and B is concerned, is identical with the pair D and A. From the pair E-1, B-5 to E-3, B-7, the ratio of the depression in the transitions to the decrease in phase lengths, d/I, increases as far as the nematic phase is concerned and decreases as far as the smectic mesophase is concerned.

Table 56

Effect of the -CH=N- Unit

Pair of series	No. of carbon atoms (alkyl chain R) C_7		Ratio d/I	No.of carbon atoms (alkyl chain R) C_{10}		Ratio d/I
(Right terminal group R')	Transition °C N-I d	Phase length °C I		Transition °C S-N d	Phase length °C I	
D-2(OC_2H_5)	278.5	166.5		153	41	
A-1(OC_2H_5)	136	48		104	24	
Depression	142.5(d)	118.5(I)	1.20	49(d)	17(I)	2.88
D-3(OC_3H_7)	252	117		175	55	
A-2(OC_3H_7)	127	33		102	23.5	
Depression	125(d)	84(I)	1.49	73(d)	31.5(I)	2.32
D-4(OC_4H_9)	248	106		175	70	
A-3(OC_4H_9)	127	24		107.5	24.5	
Depression	121(d)	82(I)	1.48	67.5(d)	45.5(I)	1.48
D-5(OC_5H_{11})	242	87		185	77	
A-4(OC_5H_{11})	125	30		109	27	
Depression	117(d)	57(I)	2.05	76 (d)	50(I)	1.52
E-1(iso-OC_3H_7)	232	102		158	48	
B-5(iso-OC_3H_7)	98.5	2.5		90	17	
Depression	133.5(d)	99.5(I)	1.34	68(d)	31(I)	2.19
E-2(iso-OC_4H_9)	232	72		178	68	
B-6(iso-OC_4H_9)	115	7		-	-	
Depression	117(d)	65(I)	1.8	Pure smectogen		
E-3(iso-OC_5H_{11})	240	78		185	90	
B-7(iso-OC_5H_{11})	115	20		102	26	
Depression	125(d)	58(I)	2.16	83(d)	64(I)	1.30

In other words, the pair E-3, B-7 is more conducive to smectic mesophase and the pair E-1, B-5 is more conducive to the nematic mesophase.

It was of great interest to compare the present series with those where the central linkages are different from the vinyl carboxyl, -CH=CH-COO-, e.g. -CH=CH-, $-\underset{\overset{\downarrow}{O}}{N}=N-$, -N=N-, -CH=N-, etc. But the transitions of the homologous series with the above linkages are not available with us hence few compounds with the -CH=CH- linkage, have been compared in the early discussion (Table 55). Transitions of few more compounds with the carboxyl group, -COO- as the central linkage are recorded in Table 57 for comparison.

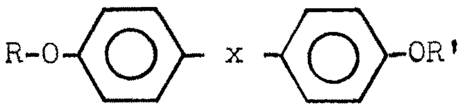
The two benzene rings and the two alkoxy groups at the terminals are the common features of these two groups of the compounds under comparison in Table 57; the only difference is in the central linkage viz. vinyl carboxyl, -CH=CH-COO-, is the central linkage of the newly synthesized series and the carboxyl -COO- is the central linkage of the compounds from the literature available.

The various transitions like the upper transitions, solid-mesomorphic, smectic-nematic and the mesophase lengths of the smectic and nematic phase are all higher in the newly synthesized series with -CH=CH-COO- as the central linkage.

The length of the newly synthesized series is more by -CH=CH- unit because of the central linkage -CH=CH-COO-.

Table 57

Comparison of the transitions of the compounds



Terminal substituents		Transitions °C						Difference °C		
		x = -CH=CH-COO-			x = -COO-					
R	R'	Smectic	Nematic	Isotropic	Smectic	Nematic	Isotropic	Smectic	Nematic	Isotropic
$-CH_3$	$-C_2H_5$	-	131	150	-	(93.8)	96(1)	-	37.2	54
$-CH_3$	$-C_3H_7$	-	(126)	127	-	(88)	106(1)	-	38	21
$-CH_3$	$-C_4H_9$	-	95	132	-	73.5	82(1)	-	21.5	50
$-CH_3$	$-C_5H_{11}$	-	82	127	-	68	73.2(1)	-	14	53.8
$-C_2H_5$	$-C_2H_5$	-	145	161	-	118	119.5(1)	-	27	41.5
$-C_2H_5$	$-C_3H_7$	-	125	144	-	(100)	114.5(1)	-	25	29.5
$-C_2H_5$	$-C_4H_9$	-	109	146	-	94	104.8(1)	-	15	41.2
$-C_2H_5$	$-C_5H_{11}$	-	91	135	-	(94)	102 (1)	-	3	33
$-C_6H_{13}$	$-C_4H_9$	-	105	133	-	66	89.5(2)	-	39	43.5
$-C_7H_{15}$	$-C_5H_{11}$	(91.5)	95	125	(50)	59	82 (2)	41.5	36	43
$-C_8H_{17}$	$-C_2H_5$	(92)	99	133.5	-	77.5	92.5(2)	-	21.5	41
$-C_8H_{17}$	$-C_3H_7$	99	101.5	124	(59)	69	81 (2)	40	32.5	43
$-C_8H_{17}$	$-C_4H_9$	(94)	100	123	S_C(59), S_A(60)	65	89 (2)	34	35	34
$-C_8H_{17}$	$-C_5H_{11}$	94	108	125	S_C58, S_A 63	65	85 (2)	31-36	43	40
$-C_{10}H_{21}$	$-C_5H_{11}$	82	109	117	S_B(46), S_C64, S_A68	80	85 (2)	14-18	29	32
$-C_{12}H_{25}$	C_5H_{11}	82	-	112	S_B(53.5), S_C 63, S_A 66	-	84.5(2)	16-19	-	27.5

(1) - (472), (2) - (471)

( ) - monotropic transition

Enhanced length and added double bond help in increasing the overall polarizability and lateral forces of the molecules, hence all the transitions of the newly synthesized series are higher than those of the corresponding compounds with -COO- as central linkage.

4.d. Thermal Stabilities:

In absence of a real quantitative procedure that can speak for the mesomorphic behaviourism in unmistaking terms, thermal stabilities have provided the approximate pivotal contrivance to weigh, on a relative basis, the mesomorphic property in terms of the molecular forces and as a consequence to attribute the characteristics to definite structural aspects of the molecules.

Homologous series reported in literature and having structural similarities which can be linked in a reasonable manner with those of the homologous series newly synthesized and studied in the present investigation have been taken into consideration. In Table (58) are given thermal stabilities of twenty five homologous series inclusive of the seven forming the subject matter of this dissertation; for a ready reference, their molecular geometry, too, is presented in Fig.43.

The homologous series A-0, A-1, A-2, A-3 and A-4 (in all five) should be viewed together in a sequence, as the central bridge, two benzene rings and the left terminal alkoxy groups are the common features of these series. The alkyl chain of the

Table 58

Thermal Stabilities

Series	A-0	A-1	A-2	A-3	A-4	D-1	D-2	D-3	D-4	D-5
Nematic-isotropic transition °C	132.5 C_1-C_6	146.2 C_1-C_6	131.6 C_1-C_6	137.8 C_1-C_6	130.7 C_1-C_6	289.3d C_1-C_6	300.5d C_1-C_6	277.7 C_1-C_6	280.2 C_1-C_6	267 C_1-C_6
Smectic-nematic or smectic-isotropic transition °C	89.4 C_{10}-C_{16}	107.6 C_{10}-C_{16}	103.8 C_{10}-C_{16}	110.6 C_{10}-C_{16}	110 C_{10}-C_{16}	152.7 C_{10}-C_{16}	167.7 C_{10}-C_{16}	182.7 C_{10}-C_{14}	182.7 C_{10}-C_{14}	191.3 C_{10}-C_{14}
Commencement of smectic phase	C_{10} (C_8)	C_{10} (C_7-C_8)	C_8 (C_7)	C_{10} (C_8)	C_8 (C_7)	C_8	C_8	C_7	C_7 (C_6)	C_6 (C_5)

(   )-Monotropic transition

d - decomposes

Table 58 (contd)

Series	F-1	F-2	F-3	M-2	M-3	M-4
Nematic-isotropic transitions °C	135.7	165.7	143.2	138.0	115.2	117.8
	C_3-C_5	C_3-C_5	C_3-C_5	C_3-C_5	C_3-C_5	C_3-C_5
Smectic-nematic or smectic-isotropic transitions °C	141	156.2	148	133.7	119.8	116.7
	C_{10}-C_{16}	C_{10}-C_{16}	C_{10}-C_{16}	C_{10}-C_{16}	C_{10}-C_{16}	C_{10}-C_{16}
Commencement of smectic phase	C_5 (C_4)	C_4	C_4 (C_3)	C_4	C_4 (C_2-C_3)	C_4 (C_2-C_3)

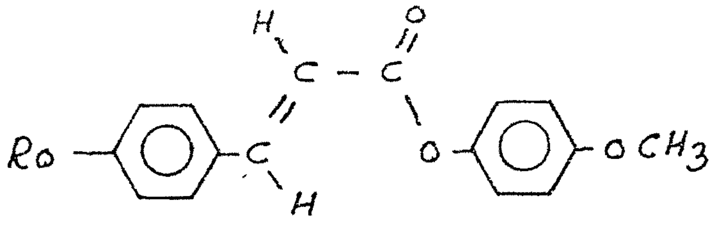
( ) - Monotropic transition

Table 58 (contd)

Series	B-5	B-6	B-7	E-1	E-2	E-3	M-5	M-6	M-7
Nematic-isotropic transitions °C	(103.3)	(107.3)	120.3	248	257	267.3	-	111.8	(51)
	C_4-C_6	C_4-C_6	C_4-C_6	C_4-C_6	C_4-C_6	C_4-C_6		C_4-C_6	C_1
Smectic-nematic or smectic-isotropic transitions °C	91.7	102	104	163.7	180	188	91.3	106.3	99.5
	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}	C_{10}-C_{14}
Commencement of smectic phase	C_8	C_{10}	C_7	C_7	C_5	C_6	C_8	C_4	C_3
		(C_8)	(C_6)	(C_6)	(C_4)	(C_5)	(C_4-C_7)	(C_2-C_3)	(C_1-C_2)

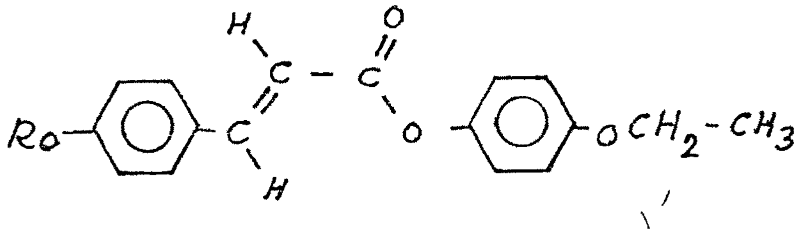
( ) Monotropic transition

A-0 →



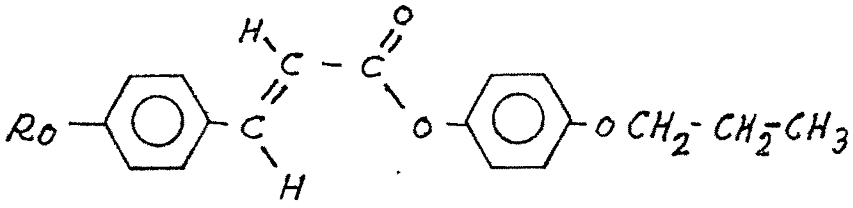
p-METHOXYPHENYL p'-n-ALKOXY CINNAMATES (465a)

A-1 →



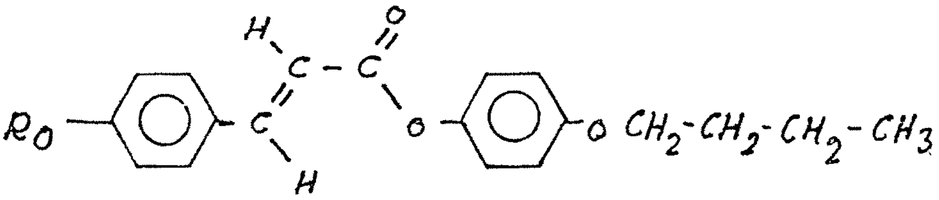
p-ETHOXYPHENYL-p'-n-ALKOXY CINNAMATES (465b)

A-2 →



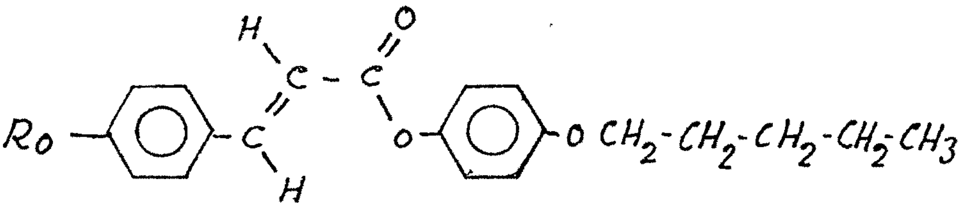
p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES (465c)

A-3 →



p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

A-4 →

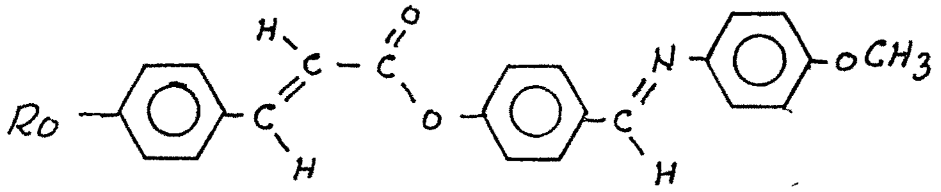


p-n-AMYLOXYPHENYL-p'-n-ALKOXY CINNAMATES

THERMAL STABILITIES: MOLECULAR STRUCTURE OF THE HOMOLOGOUS SERIES

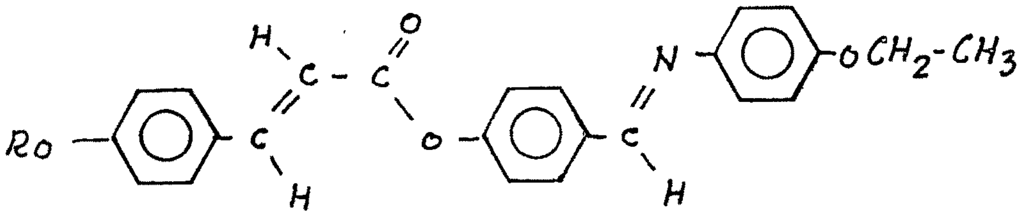
FIG. 43

D-1 →



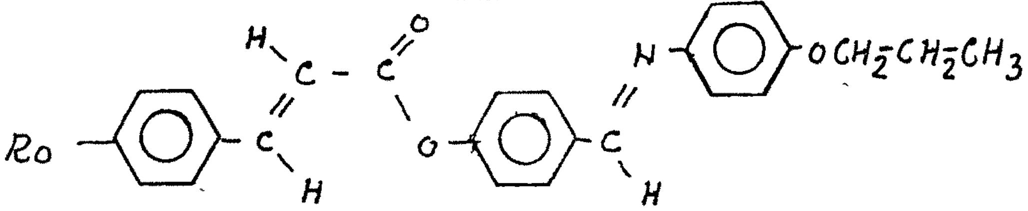
p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-ANISIDINES (473)

D-2 →



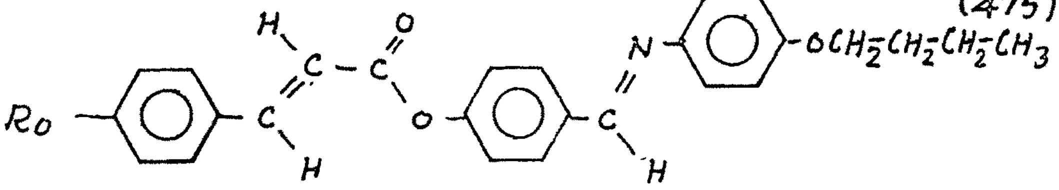
p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-PHENETIDINES (474)

D-3 →



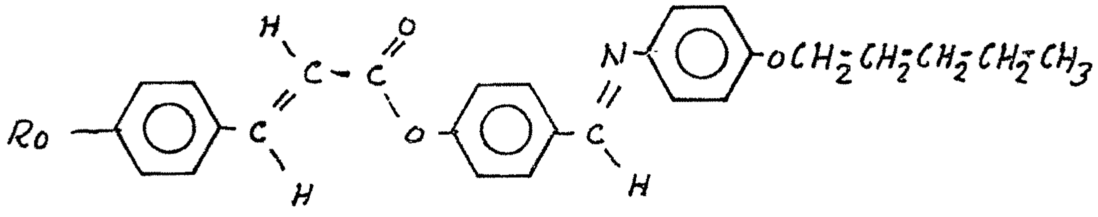
p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-n-PROPOXYANILINES (475)

D-4 →



p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-n-BUTOXYANILINES. (475)

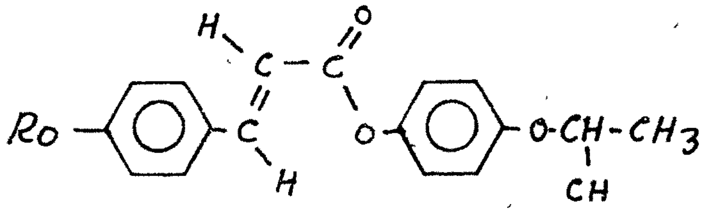
D-5 →



p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-n-AMYLOXYANILINES. (475)

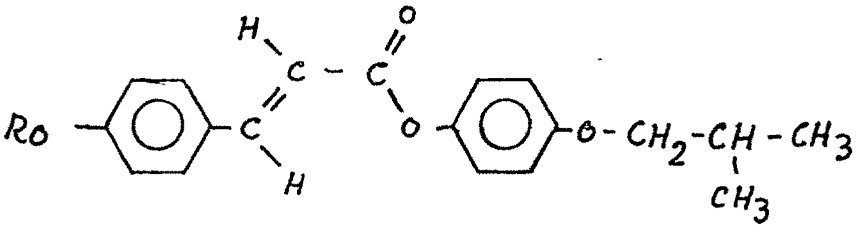
FIG. 43 (CONTINUED)

B-5 →



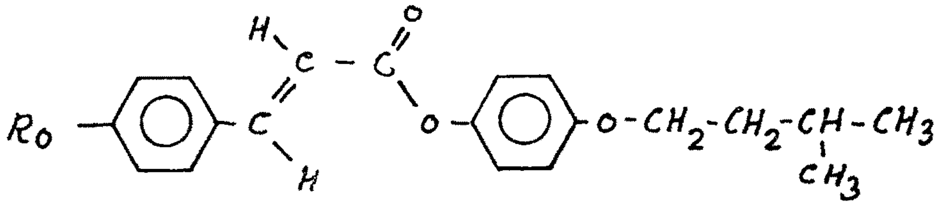
p-iso-PROPOXY PHENYL-p'-n-ALKOXY CINNAMATES.

B-6 →



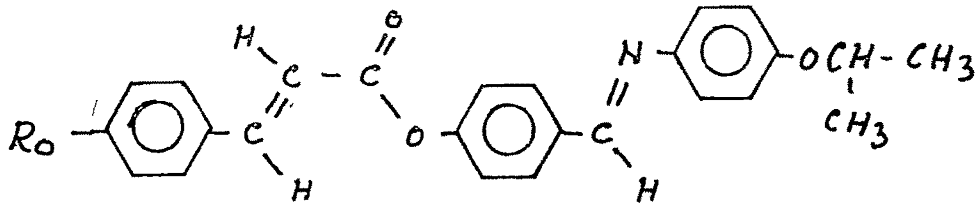
p-iso-BUTOXY PHENYL-p'-n-ALKOXY CINNAMATES

B-7 →



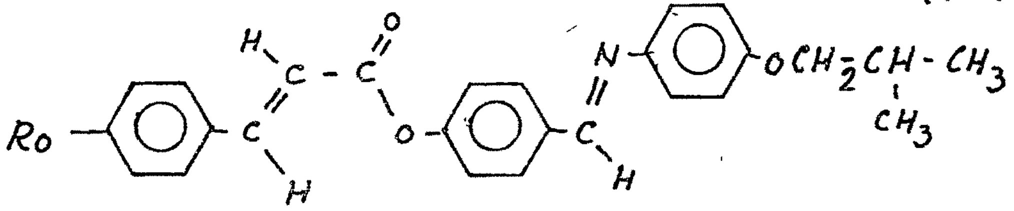
p-iso-AMYLOXY PHENYL-p'-n-ALKOXY CINNAMATES.

E-1 →



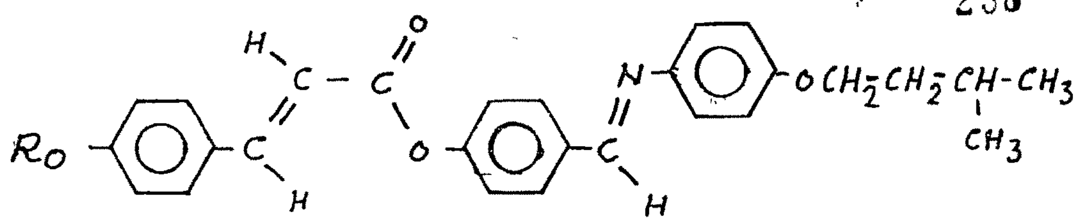
p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-iso-PROPOXYANILINES.
(475)

E-2 →

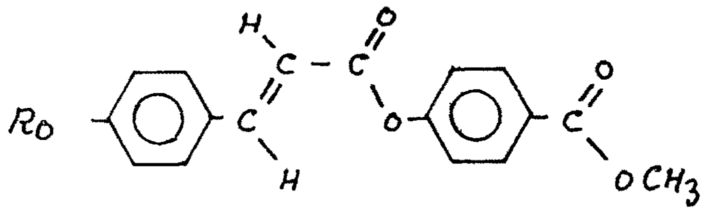


p-(p'-n-ALKOXY CINNAMOYLOXY) BENZYLIDENE-p''-iso-BUTOXYANILINES
(475)

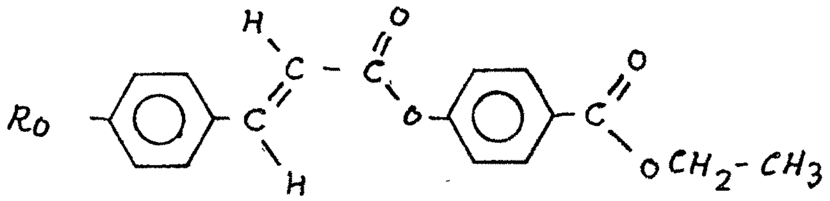
FIG. 43 (CONTINUED)

E-3 →


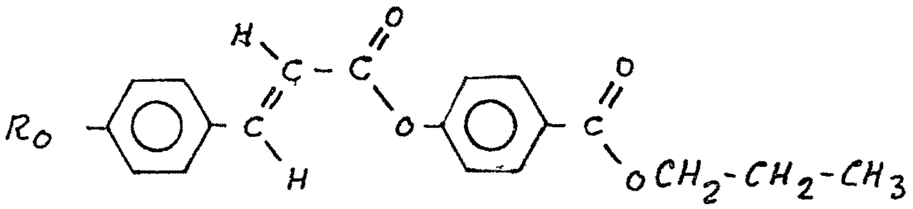
p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-p''-isoAMYLOXYANILINES (475)

M-2 →


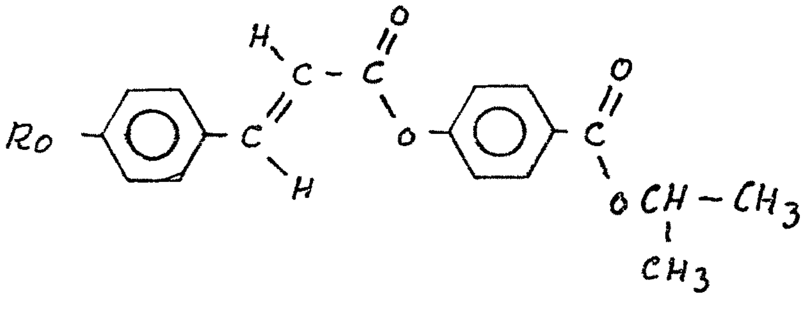
METHYL p-(p'-n-ALKOXY CINNAMOYLOXY)BENZOATES (477)

M-3 →


ETHYL p-(p'-n-ALKOXY CINNAMOYLOXY)BENZOATES (478)

M-4 →


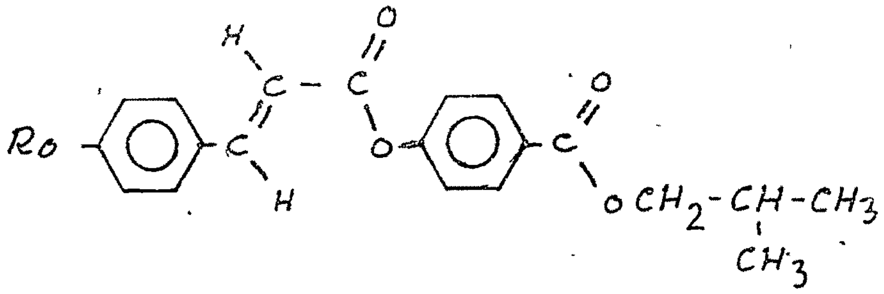
n-PROPYL-p-(p'-n-ALKOXY CINNAMOYLOXY)BENZOATES (476)

M-5 →


iso-PROPYL-p-(p'-n-ALKOXY CINNAMOYLOXY)BENZOATES (479)

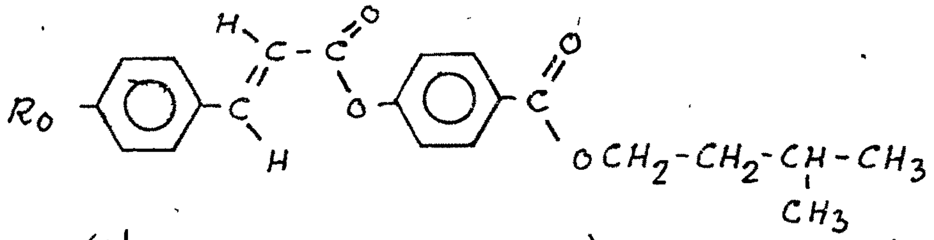
FIG. 43 (CONTINUED)

M-6 →



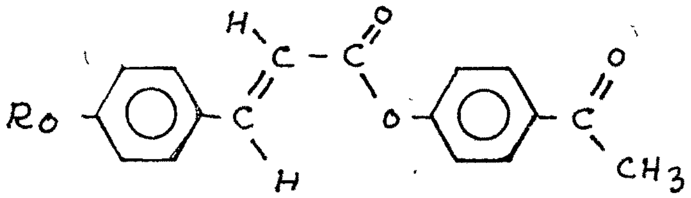
iSO-BUTYL-p-(p'-n-ALKOXY CINNAMOYLOXY) BENZOATES (479)

M-7 →



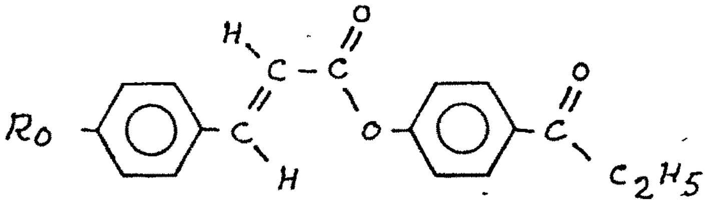
iSO-AMYL-p-(p'-n-ALKOXY CINNAMOYLOXY) BENZOATES (479)

F-1 →



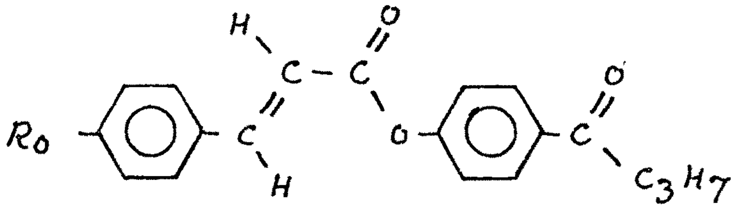
p-(p'-n-ALKOXY CINNAMOYLOXY) ACETOPHENONES (480)

F-2 →



p-(p'-n-ALKOXY CINNAMOYLOXY) PROPIOPHENONES (481)

F-3 →



p-(p'-n-ALKOXY CINNAMOYLOXY) BUTYROPHENONE (482)

FIG. 43 (CONTINUED)

right terminal substituents of these series has a changing sequence from methoxy to amyloxy through ethoxy, propoxy and butoxy groups. At each stage one $-CH_2-$ unit is added. Variations in thermal stabilities would thus find a correlation with $-CH_2-$ unit in a progressive manner.

Nematic-isotropic thermal stabilities of these five series are not quite high. The highest one is for the A-1 series, viz. p-ethoxyphenyl-p'-n-alkoxycinnamates which is 146.2° (Table 58). It is observed that as the $-CH_2-$ units are added at the right terminal alkyl chain i.e. as the number of carbon atoms in the alkyl chain increases, the nematic-isotropic thermal stability decreases, though in an alternation. With increasing polarizability of the molecules, the nematic-isotropic stability would be decreasing since not polarizability as the singularly exclusive factor, but the end-to-end adhesions have more than any other factor to contribute to the nematic orientation. Highly polar end groups will cause greater end to end adhesions; the $-OC_2H_5$ group of the A-1 series under reference is highly polar which gives rise to high end to end adhesions. Any further addition of $-CH_2-$ units will not be enhancing polarity of the molecules, but the overall polarizability of the molecules will be greatly affected giving rise to large variation in molecular forces. The homologous series p-methoxyphenyl-p'-n-alkoxycinnamates (A-0) has methoxy group at the right terminal which is of lesser value in terms of polarity of the molecules than that of the series A-1, since it has an ethoxy group at the corresponding location. Therefore, the end-to-end adhesion forces of the molecules of the series A-0 will be less as compared to those of the A-1 series. Hence, it is not surprising to find the nematic-isotropic thermal stability of the A-0 series lower by 13.7° being 132.5° versus 146.2° of the A-1 series.

The alternation of the nematic-isotropic stabilities of the five series, viz. A-0, A-1, A-2, A-3 and A-4 is the striking feature; this is in keeping with the normal behaviour of the homologous series where the terminal substituents' alkyl chains are with increasing length (256).

Next three newly synthesized series, under comparison, are B-5, B-6 and B-7 whose nematic-isotropic thermal stabilities are lower than the corresponding series A-2, A-3 and A-4. The possible explanation is in the increased breadth of the molecules due to 'iso-linking' of the alkyl chain at the right terminal. The increasing tendency of the nematic-isotropic thermal stabilities is very well observed while the alternating pattern disappears as the number of carbon atoms at the right terminal alkyl chain of the molecules of these three series increases. The difference in the extent of increase is given in Table 59.

The difference in the nematic-isotropic thermal stabilities of the corresponding 'strain-chain' and 'iso-linked'

Table 59

Extent of increase in Nematic thermal stability

Homologous series	Thermal stability °C	Difference °C
B-5	(103.3)	4
B-6	(107.3)	
B-7	120.3	13

( ) Monotropic transition

(alkyl chains at right terminals) homologous series presents another interesting feature. The difference values are given in Table 60.

The nematic-isotropic thermal stabilities of the 'iso-linked' series are less than the corresponding 'straight chain' series. The maximum difference is in the pair A-3 and B-6 and the minimum difference is in the pair A-4 and B-7 (Table 60).

Table 60

Difference values

(Nematic-Isotropic Thermal Stabilities of straight-chain and iso-linked series)

Homologous series	Nematic-Isotropic Thermal stabilities °C		
	Alkyl chain at right terminal		
	C_3 (series)	C_4 (series)	C_5 (series)
Straight-chained	131.6 (A-2)	137.8 (A-3)	130.7 (A-4)
iso-linked	103.3 (B-5)	107.3 (B-6)	120.3 (B-7)
Difference	28.3	30.5	10.4

Molecules of the pairs of series A-1 and B-5, A-2 and B-6 and A-3 and B-7 have equal length but the breadth of the molecules of series B-5, B-6 and B-7 is proportionately (one $-CH_3$ branch) more as compared to those of the molecules of the A series. By taking into consideration the nematic-isotropic thermal stabilities of these pairs of the molecules, the effect due to the breadth variation alone can be adjudged the values are given in Table 61.

It is easy to conclude from the values in Table 61 that the effect of breadth in lowering the nematic-isotropic thermal stability is quite appreciable, but with increasing length as one passes from serial Nos. 1 to 3 (Table 61), the effect of breadth becomes appreciably less operative. It means that the increasing length nullifies the impact of breadth more than what

Table 61

Difference values

(Nematic-Isotropic Thermal Stabilities of the pairs)

Sr. No.	Homologous pairs	Thermal stabilities °C	Difference °C
1	A-1	146.2	42.9
	B-5	103.3	
2	A-2	131.6	24.3
	B-6	107.3	
3	A-3	137.8	17.5
	B-7	120.3	

breadth can originally damage the nematic thermal stability. It may be that after a certain length of the alkyl chain, say after C_5, the breadth effect may become nil or non-operative. From this observation, it is proper to state that the mesomorphic property has greater reliance on the length of a linear molecule and that the breadth of a molecule can have only moderating type of impact.

Comparison of the A-type of series with the corresponding D type of the series reveals very interesting results. Structurally both the types of the series are identical viz. two benzene rings, both the terminal alkoxy groups and a central -CH=CH-COO- linkage, are all common in both of them; the only difference is the absence of the third benzene ring and central linkage, -CH=N-, in the A type of series. That is, the A type of series is less by $-C_6H_4-CH=N-$ unit as compared to the D type of series leading to lowering of the nematic-isotropic transitions. In the series D-1 and D-2, nematic-isotropic transitions could not be determined accurately as the homologues decompose before passing into the isotropic phase whereas in the A-0 and A-1 series there is no decomposition and the nematic-isotropic transitions are also lower by about 155°C.

Table (62) shows the difference in the nematic-isotropic transitions between the corresponding A and D type of the series. As the pair of series progresses from D-1, A-0 to D-5, A-4 i.e. from methyl to pentyl group at the right terminal, the difference in the nematic-isotropic transitions of the pairs decreases gradually. This difference can be attributed to the absence of the $-C_6H_4-CH{=}N-$ unit in the A type of the series.

Table 62

Difference in the nematic-isotropic transitions of the A and D type of series

No.of carbon atoms at right terminal alkoxy group	Pair of series	Nematic-Isotropic transitions °C	Difference °C
1	D-1	289.3 d	156.8
	A-0	132.5	
2	D-2	300.5 d	154.3
	A-1	146.2	
3	D-3	277.7	146.1
	A-2	131.6	
4	D-4	280.2	142.4
	A-3	137.8	
5	D-5	267	136.3
	A-4	130.7	

The next cluster of the series under comparison is the B and E types of the series. In this pair of the series, the alkyl group at the right terminal has the iso-linking, the only difference between the B and E type of the series again, is the absence of the -C_6H_4-CH=N- unit in B type like in the previous cluster of series discussed. Here also, because of the absence of the -C_6H_4-CH=N- unit in B type of the series the nematic-isotropic transitions are less than those in E type of series (Table 63).

Table 63

Difference in nematic-isotropic transitions of E and B type of series

No.of carbon atoms at right terminal iso-alkoxy group	Pair of series	Nematic-Isotropic transitions °C	Difference °C
3	E-1	248	144.7
	B-5	103.3	
4	E-2	257	149.7
	B-6	107.3	
5	E-3	267.3	147.0
	B-7	120.3	

This pair of series, B and E, exhibits alternate rise and fall so far as the difference in the nematic-isotropic transitions is concerned.

Another comparable cluster of series, with iso-linking at the right terminal, is M-5 to M-7. The series from B-5 to B-7 are less in length by -$\overset{O}{\overset{\|}{C}}$- unit as the right terminal groups in B type of series are iso $-OC_3H_7$, iso $-OC_4H_9$ and iso $-OC_5H_{11}$ whereas those in series M-5 to M-7 are iso-$COOC_3H_7$, iso-$COOC_4H_9$ and iso-$COOC_5H_{11}$. Both the types of the series have iso linking and hence the molecules are separated apart and increase in the breadth of the molecules reduces the N-I transitions. The N-I transitions of the series B-5 to B-7 and M-5 to M-7 are the lowest amongst the series under comparison. The overall polarizability of the molecules as well as the ratio of lateral to terminal attractions for the series M-5 to M-7 speak for their low nematic thermal stability as compared to the series B-5 to B-7. It is also known that the $-C_6H_4-COOR$ linkage is having dipole moment acting across the long molecular axis leading to more smectogenic characteristic and less nematogenic character. This is evident from the absence of the nematic phase in the series M-5 and only the first member exhibiting the nematic phase in series M-7. The overall N-I thermal stabilities of the B type of series are higher than those of the M-5 to M-7 series due to higher terminal attractions in the former.

The series M-2, M-3 and M-4, with $-COOCH_3$, $-COOC_2H_5$ and $-COOC_3H_7$ at the right terminal, can be compared with the series A-0, A-1 and A-2, with $-OCH_3$, $-OC_2H_5$ and $-OC_3H_7$ at the corresponding place. Because of the stronger polarity of $-OCH_3$, $-OC_2H_5$ and $-OC_3H_7$ groups leading to stronger end to end attractions the nematic-isotropic transitions should be higher in A type of the series. Moreover, in M-2 to M-4 series the right terminal groups i.e. $-COOCH_3$, $-COOC_2H_5$ and $-COOC_3H_7$ are longer which enhance the polarizability and reduce the nematic stability. The nematic stability is higher by 31° and 19.8° in the series A-1 and A-2 as compared to the corresponding series M-3 and M-4. But it is surprising to see that the nematic stability in the series A-0, with $-OCH_3$ group is lower by 5.5° than the corresponding series M-2. The series M-2 to M-4 are also known for the dipole moment acting across the long molecular axis leading to increase in the lateral attractions.

The next series under comparison are the F-1, F-2 and F-3 with $-COCH_3$, $-COC_2H_5$ and $-COC_3H_7$ groups at the right terminal. The F- type of the series have longer right terminal groups leading to higher polarizability and more length to breadth ratio. The higher nematic thermal stability of the F-1, F-2 and F-3 series is attributed to the increase in polarizability and length to breadth ratio.

All these series have similarities in molecular geometry and differ from each other in 'one' manner only. Thus, a comparative picture is quite convincing, though a generalization may be difficult to evolve. The different nematic 'orders' are as follows:

A-0, A-1, A-2, A-3 and A-4 series :

$-OC_2H_5 > -OC_4H_9 > -OCH_3 > -OC_3H_7 > -OC_5H_{11}$

B-5, B-6 and B-7 series:

iso $-OC_3H_7 <$ iso-$OC_4H_9 <$ iso-OC_5H_{11}.

The homologous series A-0, A-1, A-2, A-3 and A-4 have a sequence of alternate increasing smectic-nematic or smectic-isotropic thermal stabilities as the alkyl chain length increases at the right terminal. The values for the series A-0, A-2 and A-4, with $-OCH_3$, $-OC_3H_7$ and $-OC_5H_{11}$ at the right terminal, are 89.4°, 103.8° and 110° and for the series A-1 and A-3, with $-OC_2H_5$ and $-OC_4H_9$ are 107.6° and 110.6° respectively. With all segments of the molecules of these series being common, the increase in alkyl chain length by additions of $-CH_2-$ units at the right terminal of the molecules will account for increase in polarizability and subsequent enhancement in smectic thermal stability. High polarizability will work in the direction of increasing the smectic thermal stability. From the values given in Table 64 it can be seen that the increase in smectic thermal stability per $-CH_2-$ unit gets reduced and after certain increase in length at the right terminal, say after C_5 carbon numbers, the polarizability may

Table 64

Increase in smectic thermal stability in A type of series

Homologous series	A-0	A-2	A-4	A-1	A-3
No.of carbon atoms at the right terminal	1	3	5	2	4
Smectic thermal stability °C	89.4	103.8	110	107.6	110.6
Difference °C	14.4	6.2		3.0	
Increase per $-CH_2-$ group	7.2	3.1		1.5	

not be much effective to increase the smectic thermal stability. The smectic thermal stability order as emerging from the study of these five series is :

$$-OC_4H_9 > -OC_5H_{11} > -OC_2H_5 > -OC_3H_7 > -OCH_3$$

The 'iso' linked series B-5, B-6 and B-7 show smectic thermal stability in the increasing order, as the number of carbon atoms in the right terminal alkyl chain is increased. The B-5 series, viz. p-iso-propoxyphenyl-p'-n-alkoxycinnamates, has 'iso' linking at the right terminal which makes the molecules broader by branched $-CH_3$ linking and shortens the length by one $-CH_2-$ unit. Increase in breadth of the molecules with simultaneous decrease in their length, decreases the smectic thermal stability by about 12.1°, when the smectic thermal stabilities of the A-2 and B-5 series are compared since both these series are identical in all respects except the 'iso' linking at the right terminal alkyl chain in the case of B-5 series. The difference between A-3 and B-6 series is 8.6° and between A-4 and B-7 series is 6°. The increase in smectic thermal stability is due to lengthening of the molecules progressively by one $-CH_2-$ unit from B-5 to B-7 series and the lower transitions are due to the increased breadth of the molecules of these series due to 'iso' linking as compared to series in A type (Table 65).

Molecules of the pairs of the series A-1 and B-5, A-2 and B-6, and A-3 and B-7 have the same length, but the breadth

Table 65

Difference values

(Smectic-Isotropic or smectic-nematic thermal stabilities of straight chained and iso-linked series)

Homologous series	Smectic-Isotropic Thermal Stabilities °C					
	Alkyl chain at right terminal					
	C_3	(Series)	C_4	(Series)	C_5	(Series)
Straight-chained	103.8	(A-2)	110.6	(A-3)	110	(A-4)
iso-linked	91.7	(B-5)	102	(B-6)	104	(B-7)
Difference	12.1		8.6		6.0	

of the molecules of B-5, B-6 and B-7 series is proportionately (one $-CH_3$ branch) increased as compared to those of the molecules of the A series. By taking into consideration the smectic-isotropic or smectic-nematic thermal stabilities of these pairs of the molecules, the effect due to the breadth variation alone can be adjudged, the values are given in Table (66).

It is easy to conclude from the values in Table 66 that the effect of breadth in lowering smectic thermal stability is significant, but with increasing length as one passes from serial No.1 to 3, the effect of breadth appreciably decreases. It means that the increasing length nullifies the impact of breadth more than what breadth can originally damage the smectic thermal stability; we may say that after a certain length of the alkyl chain, say after C_5, the breadth effect may become nil or non-operative. It is proper to state that the mesomorphic property has greater reliance on the length of a linear molecule and that the breadth of a molecule can have only moderating type of impact.

Table 66

Difference values

(Smectic-nematic or smectic-isotropic thermal stabilities of the pairs)

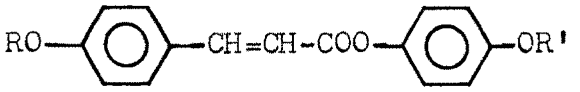
Sr. No.	Homologous pairs	Thermal stabilities °C	Difference °C
1	A-1	107.6	15.9
	B-5	91.7	
2	A-2	103.8	1.8
	B-6	102	
3	A-3	110.6	6.6
	B-7	104.0	

The next comparable pairs of series are A and D, and B and E (Table 67). The A and B types of series are less in length by $-C_6H_4-CH=N-$ unit, and also less in aromaticity by one benzene ring. The reduced aromaticity, length of the molecule and length to breadth ratio lower the smectic thermal stability in A and B type of the series. The difference values increase in an alternate manner in the pair A and D while in the

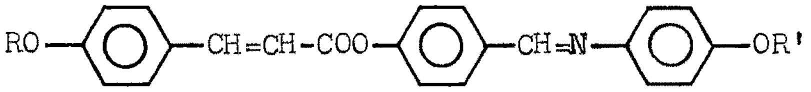
Table 67

The effect of $-C_6H_4CH{=}N-$ unit on smectic-nematic or smectic-isotropic transitions.

Right terminal R' group	Pair of series	Smectic-Nematic or Smectic-isotropic transitions °C	Difference °C
$-OCH_3$	A-0	89.4	63.3
	D-1	152.7	
$-OC_2H_5$	A-1	107.6	60.1
	D-2	167.7	
$-OC_3H_7$	A-2	103.8	78.9
	D-3	182.7	
$-OC_4H_9$	A-3	110.6	72.1
	D-4	182.7	
$-OC_5H_{11}$	A-4	110	81.3
	D-5	191.3	
iso $-OC_3H_7$	B-5	91.7	72.0
	E-1	163.7	
iso $-OC_4H_9$	B-6	102.	78.0
	E-2	180	
iso $-OC_5H_{11}$	B-7	104.0	84.0
	E-3	188	



A and B type



D and E type

pair B and E the sequence is of increasing order.

Another comparable clusters of series, with iso-linking at the right terminal, are M-5, M-6 and M-7 series and B-5, B-6 and B-7 series. The right terminal groups in the series B-5 to B-7 are iso $-OC_3H_7$, iso $-OC_4H_9$ and iso-OC_5H_{11} and in the series M-5 to M-7 they are iso-$COOC_3H_7$, iso-$COOC_4H_9$, and iso-$COOC_5H_{11}$ respectively. The homologous series M-5 and M-6 have higher S-N or S-I thermal stability than the series B-5 and B-6 due to more overall polarizability of the molecules as well as higher ratio of lateral to terminal attractions. The molecules in series M-5 to M-7 have dipole moment across the long molecular axis and exhibit more smectogenic characteristics (489). However, the lower S-N stability of the series M-7 than B-7 is rather surprising. Both these types of series are lowest in the smectic thermal stability, but the series in the M type have more smectogenic characteristics as seen from the commencement of the smectic phase. The smectic phase commences from the eighth, eighth and sixth homologue in the series B-5 to B-7 whereas from the fourth, second and first homologue in the M-5 to M-7 series.

Comparison of the series M-2, M-3 and M-4 having $-COOCH_3$, $-COOC_2H_5$ and $-COOC_3H_7$ groups at the right terminal, with the corresponding series A-0, A-1 and A-2, having $-OCH_3$, $-OC_2H_5$ and $-OC_3H_7$ groups at the same position, reveal that the smectic stability of the M-2, M-3 and M-4 series is higher by 44.3°, 12.2° and 12.9°. This is attributable to the ester groups, $-COOCH_3$, $-COOC_2H_5$ and $-COOC_3H_7$, having dipole moment acting across the long molecular axis (489) leading to more lateral to terminal attractions stabilizing the layer structure of the smectic phase.

The next series in the decreasing order of the smectic thermal stability are the F and A types. The right terminal groups in the F-series are $-COCH_3$, $-COC_2H_5$ and $-COC_3H_7$ whereas those in the A type are $-OCH_3$, $-OC_2H_5$ and $-OC_3H_7$. Obviously, the groups in the F type are longer and have more polarizability enhancing the smectic thermal stability as compared to those in the A type of series. The difference in the smectic thermal stability of the corresponding F-1 and A-0, F-2 and A-1, and F-3 and A-2 is 51.6°, 48.6° and 44.2°. The ratio of lateral to terminal attractions is also more in F type of series than in A type.

The smectogenic nature of the homologous series is normally judged on the basis of the commencement of smectic mesophase in the homologous series. An early commencement is an indication of greater smectogenic nature. Smectogenic order for the series studied in the present investigation may be suggested as follows:

<u>A series</u>:

$-OC_4H_9 > -OC_5H_{11} > -OC_2H_5 > -OC_3H_7 > -OCH_3$

B series :

iso-OC_5H_{11} > iso-OC_4H_9 > iso-OC_3H_7

4.e. New Homologous series - C type :

This type consists of two homologous series viz.

C-8 m-chlorophenyl-p'-n-alkoxycinnamates and

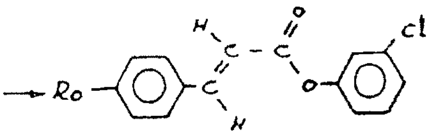
C-9 o-chlorophenyl-p'-n-alkoxycinnamates.

These two series though quite low melting (Tables 19 and 21), fail to exhibit mesomorphism even in monotropic conditions inspite of the perfect primary geometry being conducive to the formation of liquid crystals, but may provide a very significant link in the understanding of the phenomenon. In this respect, these non-mesomorphic series attain greater relevance and importance. Some of these could be 'improved' upon in their structural facets which may be instrumental in turning them to become liquid crystals. Non-mesomorphs of this investigation have acquired the significance of shedding better light for the proper 'designing' of molecular facets in absence of which the liquid crystalline order in the fluid state may not be obtained. Plots of the melting points versus the number of carbon atoms in the alkyl chain are given in Fig. 13 and 14.

The series C-8 and C-9 have chloro group in the meta and ortho positions respectively. As it is very well known that chloro group as a lateral substituent decreases the transition temperatures (465a), in the series C-8 and C-9 also the melting points of the homologues are less as compared to the homologous series C-10 where chloro is at the para position (465a). The lateral substituent increases the breadth of the molecule and as the present series comprise of only two phenyl rings, it seems that length to breadth ratio is not conducive to the mesomorphic properties. In series C-10 where the chloro substituent is in para position, the series behaves like a normal nematogenic series with moderately stable mesophases. If one more benzene ring along with central linkage, viz. -CH=N-, is introduced with chloro in meta position (series C-12), the system exhibits mesogenic properties as the length to breadth ratio is just enough to induce mesomorphism. Similarly, by introducing $-C_6H_4CH=N-$ unit and keeping chloro substituents at meta and para positions (C-13) system behaves like normal mesomorphic system. The series C-11, with $-C_6H_4-CH=N-$ unit and chloro at the para position also exhibits rich mesomorphism.

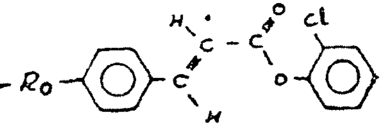
It may be concluded from this data and discussion that with a lateral substituent in a molecule, the molecular geometry should be such that the length to breadth ratio is favourable to mesogenic character. To observe monotropic mesophases, homologues must exhibit appreciable super-cooling tendencies which is also absent in the present two series.

C-8



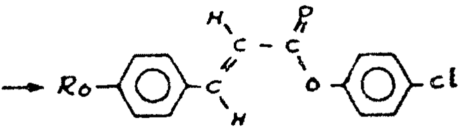
m-CHLOROPHENYL-p'-n-ALKOXY CINNAMATES

C-9



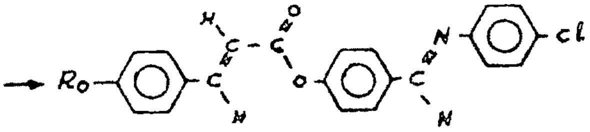
O-CHLOROPHENYL-p'-n-ALKOXY CINNAMATES

C-10



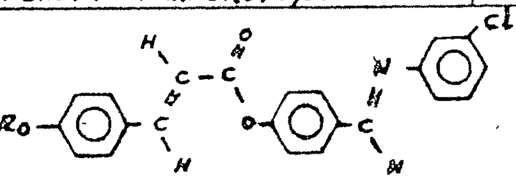
p-CHLOROPHENYL-p'-n-ALKOXY CINNAMATES (465a)

C-11



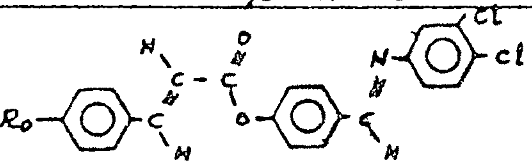
p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-p''-CHLOROANILINES (465b)

C-12



p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-m''-CHLOROANILINES (465a)

C-13



p-(p'-n-ALKOXY CINNAMOYLOXY)BENZYLIDENE-m''-p''-DICHLOROANILINES (465a)

THERMAL STABILITIES: MOLECULAR STRUCTURE OF THE HOMOLOGOUS SERIES. FIG. 44

Legand for DSC curves

The number given to the curves indicate number of carbon atoms in the n-alkyl group of the compound. The name of series is mentioned at the bottom of each figure.

4.f. Calorimetric study :

While the DTA apparatus of the Applied Chemistry Department where this investigation was carried out, is out of order for several years by now, through the generous help of my employer, Indian Petrochemicals Corporation Limited, three of the new homologous series synthesized during this investigation were subjected to DSC study.

Very sharp peaks for solid-mesomorphic (Solid-nematic, Solid-smectic), smectic-nematic, nematic-isotropic, smectic-isotropic etc. transitions are obtained (Fig. 15 to 17). As the cooling system was not working, the monotropic transitions could not be confirmed in the DSC study. Most of these transitions within the limits of the experimental errors, conform with those obtained by optical microscopy, except in the series A-1, where the difference is because of the instrumental error. A comparative statement of these transitions is given in Tables 68 to 70.

The following formula is utilised for calculating ΔH and ΔS :

$$\Delta H \ (\text{K cal mol}^{-1}) = \frac{A}{m} (60 \times B \times E \times \Delta qs) \times \text{Mol.wt.} \times 10^{-3}$$

$$\Delta S \ (\text{cal/mole/}^{\circ}\text{K}) = \frac{\Delta H}{T}$$

Table 68

Comparative statement of temperatures (Microscope and DSC method)

A-1 p-Ethoxyphenyl-p'-n-alkoxycinnamates

Homologues	$K_1 \longrightarrow K_2$ °C		$K \longrightarrow S$ °C		$K \longrightarrow N$ or $S \longrightarrow N$ °C		$N \longrightarrow Iso$ or $S \longrightarrow Iso$ °C	
No.of carbon atoms in n-alkyl chain	Micro-scope	DSC	Microscope	DSC	Microscope	DSC	Microscope	DSC
C_1	-	-	-	-	131	125	150	142
C_2	-	-	-	-	145	138	161	150
C_3	-	70	-	-	126	125	145	145
C_4	-	-	-	-	111	103	150	136
C_5	-	62,73	-	-	97	95	131	123
C_6	-	-	-	-	88	87	140	129
C_7	-	-	(72)	-	88	85	136	126
C_8	-	-	(92)	-	99	94	133.5	125
C_{10}	-	-	80	75	104	98	126	118
C_{12}	-	-	86	78	109	102	122	114
C_{14}	-	68	86	82	109.5	100	116.5	106
C_{16}	-	70	90	85	108	102	113	105

K - Solid, S- Smectic, N- Nematic, Iso-Isotropic

Table 69

Comparative Statement of temperatures (Microscope and DSC method)

A-2 p-n-Propoxyphenyl-p'-n-alkoxycinnamates

Homologues	$K_1 \longrightarrow K_2$ °C		$K \longrightarrow S$ °C		$K \longrightarrow N$ or $S \longrightarrow N$ °C		$N \longrightarrow Iso$ or $S \longrightarrow Iso$ °C	
No. of carbon atoms in n-alkyl chain	Microscope	DSC	Microscope	DSC	Microscope	DSC	Microscope	DSC
C_1	-	-	-	-	(126)	-	127	127
C_2	-	120	-	-	125	124	144	144
C_3	-	86	-	-	(127)	-	128	126
C_4	-	-	-	-	110	112	137	137
C_5	-	-	-	-	102	102	124	124
C_6	-	85	-	-	98	97	130	126
C_{10}	-	—	78.5	81	102	104	116	119
C_{16}	-	80	88	88	-	-	104	104

K- Solid, S- Smectic, N- Nematic Iso-Isotropic

Table 70

Comparative statement of temperature (Microscope and DSC method)

A-3 p-n-Butoxyphenyl-p'-n-alkoxycinnamates

Homologues	$K_1 \longrightarrow K_2$ °C		$K \longrightarrow S$ °C		$K \longrightarrow N$ or $S \longrightarrow N$ °C		$N \longrightarrow Iso$ or $S \longrightarrow Iso$ °C	
No.of carbon atoms in n-alkyl chain	Microscope	DSC	Microscope	DSC	Microscope	DSC	Microscope	DSC
C_1	-	94	-	-	95	98	132	134
C_2	-	-	-	-	109	110	146	146
C_3	-	-	-	-	117	117	137	138
C_4	-	-	-	-	117	117	141	142
C_5	-	102	-	-	111	111	138	138
C_6	-	-	-	-	105	105	133	133
C_7	-	-	-	-	103	103	127	126
C_8	-	84	(94)	-	100	96	123	120
C_{12}	-	-	85,-	85,110	-	-	113	113

K- Solid, S-Smectic N- Nematic Iso-Isotropic

Where ΔH = Enthalpy of fusion (Kcal/mole)

A = Area under the curve (Sq.in.)

m = Mass of the sample (mg)

B = Time base (Min/in.)

E = Cell calibration coefficient at the temperature of the experiment

Δqs = Y-axis range

T = Transition temperature (°K)

ΔS = Entropy (Cal/mole/°K)

As for example, for the decyloxy homologue of the series A-2 viz. p-n-propoxyphenyl-p'-n-alkoxycinnamates, the data are as follows:

Table 71

DSC data for p-n-propoxyphenyl-p'-n-decyloxycinnamate

Phase	Peak area sq.in.	Temp.°C	Δ H Kcal/mole	Δ S Cal/mole/°K
Smectic	0.5919	81	5.15	14.55
Nematic	0.0116	104	0.10	0.27
Isotropic	0.026	119	0.22	0.57

Where E = 1.00; B= 1.00, Δ qs = 1.00 and m = 3.02.

As per these values, Δ H and Δ S for this homologue are calculated as follows:

Smectic phase

$$\Delta H \text{ (Kcal/mole)} = \frac{A}{m} (60 \times B \times E \times \Delta qs) \times \text{mol.wt} \times 10^{-3}$$

$$= \frac{0.5919}{3.02} (60x1x1x1)x438 \times 10^{-3}$$

$$= 5.150$$

$$\Delta S \ (\text{cal mole}^{-1} \ {}^\circ K^{-1}) = \frac{\Delta H}{T} \times 10^3$$

$$= \frac{5.150x10^3}{354} = 14.55$$

Nematic phase

$$\Delta H \ (\text{Kcal/mole}^{-1}) = \frac{A}{m} (60 \times B \times E \times \Delta qs) x \text{ mol.wt. } x10^{-3}$$

$$= \frac{0.0116}{3.02} (60 \times 1 \times 1 \times 1) \times 438 \times 10^{-3}$$

$$= 0.10$$

$$\Delta S \ (\text{Cal mole}^{-1} \ {}^\circ K^{-1}) = \frac{\Delta H}{T} \times 10^3$$

$$= \frac{0.101}{377} \times 10^3 = 0.27$$

Isotropic phase

$$\Delta H \ (\text{Kcal mole}^{-1}) = \frac{A}{m} (60 \times B \times E \times \Delta qs) \times \text{Mol.wt.} x \ 10^{-3}$$

$$= \frac{0.260}{3,02} (60 \times 1 \times 1 \times 1)x \ 438 \times 10^{-3}$$

$$= 0.22$$

$$\Delta S \ (\text{Cal mole}^{-1} \ {}^\circ K^{-1}) = \frac{\Delta H}{T} \times 10^3$$

$$= \frac{0.226x10^3}{392} = 0.57$$

The values of ΔH and ΔS along with other data are recorded in Tables 72 to 74.

The results are quite interesting. It is observed that when the homologues exhibit mesomorphism, the ΔH value for the

Table 72

Series A-1 p-Ethoxyphenyl-p'-n-alkoxycinnamates

No. of carbon atoms in n-alkyl chain 1	Phase 2	Peak Area (Sq.in) 3	Temperature °C 4	Cell coefficient (E) 5	Time Base (B) 6	Sensitivity (Δqs) 7	Weight of compound (m) mgm 8	Mol. wt. 9	Enthalpy of fusion ΔH Kcal mole^{-1} 10	Entropy ΔS cal mole^{-1} °K^{-1} 11	Total ΔS cal mole^{-1} °K^{-1} 12
C_1	Nematic	0.7518	125	1	1	2	5.00	298	5.38	13.51	13.92
	Isotropic	0.0239	142	1	1	2	5.00	298	0.17	0.41	
C_2	Nematic	1.557	138	1	1	2	9.00	312	6.48	15.76	16.37
	Isotropic	0.062	150	1	1	2	9.00	312	0.26	0.61	
C_3	Solid	0.02418	70	1	1	1	2.65	326	0.18	0.52	15.65
	Nematic	0.7852	125	1	1	1	2.65	326	5.80	14.56	
	Isotropic	0.03224	145	1	1	1	2.65	326	0.24	0.57	
C_4	Nematic	1.1577	103	1	1	2	7.00	340	6.75	17.95	18.83
	Isotropic	0.062	136	1	1	2	7.00	340	0.36	0.88	
C_5	Solid-1	0.0093	62	1	1	2	4.40	354	0.089	0.26	18.30
	Solid-2	0.0302	73	1	1	2	4.40	354	0.29	0.84	
	Nematic	0.6268	95	1	1	2	4.40	354	6.05	16.44	
	Isotropic	0.031	123	1	1	2	4.40	354	0.30	0.76	
C_6	Nematic	0.9247	87	1	1	2	5.00	368	8.17	22.69	23.38
	Isotropic	0.0316	129	1	1	2	5.00	368	0.28	0.69	
C_7	Nematic	1.0033	85	1	1	2	5.00	382	9.20	25.69	26.29
	Isotropic	0.0260	126	1	1	2	5.00	382	0.24	0.60	
C_8	Nematic	0.9095	94	1	1	2	7.00	396	6.17	16.82	17.52
	Isotropic	0.0409	125	1	1	2	7.00	396	0.28	0.70	

Table 72 (contd)

Series A-1

1	2	3	4	5	6	7	8	9	10	11	12
C_{10}	Smectic	0.6408	75	1	1	2	5.00	424	6.52	18.74	20.02
	Nematic	0.0136	98	1	1	2	5.00	424	0.14	0.37	
	Isotropic	0.0349	118	1	1	2	5.00	424	0.36	0.91	
C_{12}	Smectic	0.5121	78	1	1	2	5.00	452	5.56	15.83	17.68
	Nematic	0.022	102	1	1	2	5.00	452	0.24	0.63	
	Isotropic	0.0434	114	1	1	2	5.00	452	0.47	1.22	
C_{14}	Solid	0.0279	68	1	1	2	4.80	480	0.33	0.98	25.47
	Smectic	0.6291	82	1	1	2	4.80	480	7.55	21.27	
	Nematic	0.0476	100	1	1	2	4.80	480	0.57	1.53	
	Isotropic	0.0535	106	1	1	2	4.80	480	0.64	1.69	
C_{16}	Solid	0.0239	70	1	1	2	7.00	508	0.20	0.61	25.11
	Smectic	0.8866	85	1	1	2	7.00	508	7.72	21.27	
	Nematic	0.0790	102	1	1	2	7.00	508	0.69	1.84	
	Isotropic	0.0604	105	1	1	2	7.00	508	0.53	1.39	

Table 73

Series A-2 p-n-Propoxyphenyl-p'-n-alkoxycinnamates

No.of carbon atoms in n-alkyl chain 1	Phase 2	Peak area (Sq.in.) 3	Temp-erat-ure °C 4	Cell coeff-icient (E) 5	Time Base (B) 6	Sensi-tivity (Δ qs) 7	Weight of compo-und (m) mgm 8	Mol. wt. 9	Enthalpy of fusion Δ H Kcal mole^{-1} 10	Entropy Δ S Cal mole^{-1} °K^{-1} 11	Total Δ S Cal mole^{-1} °K^{-1} 12
C_1	Isotropic	0.7037	127	1	1	1	3.08	312	4.33	10.83	10.83
C_2	Solid	0.0801	120	1	1	1	3.06	326	0.51	1.30	8.79
	Nematic	0.4484	124	1	1	1	3.06	326	2.87	7.22	
	Isotropic	0.0174	144	1	1	1	3.06	326	0.11	0.27	
C_3	Solid	-	86	1	1	1	3.44	340	-	-	9.35
	Isotropic	0.6293	126	1	1	1	3.44	340	3.73	9.35	
C_4	Nematic	0.4836	112	1	1	1	3.30	354	3.11	8.08	8.40
	Isotropic	0.0204	137	1	1	1	3.30	354	0.13	0.32	
C_5	Nematic	0.9002	102	1	1	1	3.17	368	6.27	16.72	17.11
	Isotropic	0.0223	124	1	1	1	3.17	368	0.16	0.39	
C_6	Solid	0.1569	85	1	1	1	2.99	382	1.20	3.38	20.20
	Nematic	0.7896	97	1	1	1	2.99	382	6.05	16.36	
	Isotropic	0.0242	126	1	1	1	2.99	382	0.19	0.46	
C_{10}	Smectic	0.5919	81	1	1	1	3.02	438	5.15	14.55	15.39
	Nematic	0.0116	104	1	1	1	3.02	438	0.10	0.27	
	Isotropic	0.0260	119	1	1	1	3.02	438	0.22	0.57	
C_{16}	Solid	0.0546	80	1	1	1	3.31	522	0.52	1.46	18.74
	Smectic	0.5524	88	1	1	1	3.31	522	5.23	14.48	
	Isotropic	0.1116	104	1	1	1	3.31	522	1.06	2.80	

Table 74

Series A-3 p-n-Butoxyphenyl-p'-n-alkoxycinnamates

No. of carbon atoms in n-alkyl chain 1	Phase 2	Peak area (sq. in.) 3	Temperature °C 4	Cell coefficient (E) 5	Time Base (B) 6	Sensitivity Δqs 7	Weight of compound (m) mgm 8	Mol. wt. 9	Enthalpy of fusion ΔH Kcal $mole^{-1}$ 10	Entropy ΔS Cal $mole^{-1}$ $°K^{-1}$ 11	Total ΔS Cal $mole^{-1}$ $°K^{-1}$ 12
C_1	Solid	-	94	1	1	1	3.26	326	-	-	
	Nematic	1.1121	98	1	1	1	3.26	326	6.672	18.13	18.59
	Isotropic	0.031	134	1	1	1	3.26	326	0.19	0.46	
C_2	Nematic	0.9108	110	1	1	1	3.35	340	5.55	14.48	14.97
	Isotropic	0.0335	146	1	1	1	3.35	340	0.20	0.49	
C_3	Nematic	0.8959	117	1	1	1	3.49	354	5.45	13.98	14.46
	Isotropic	0.0321	138	1	1	1	3.49	354	0.20	0.48	
C_4	Nematic	0.7986	117	1	1	1	2.86	368	6.17	15.81	16.28
	Isotropic	0.0251	142	1	1	1	2.86	368	0.19	0.47	
C_5	Solid	-	102	1	1	1	2.83	382	-	-	
	Nematic	0.7789	111	1	1	1	2.83	382	6.31	16.43	16.87
	Isotropic	0.0223	138	1	1	1	2.83	382	0.18	0.44	
C_6	Nematic	0.4389	105	1	1	1	3.06	396	3.41	9.02	9.42
	Isotropic	0.0209	133	1	1	1	3.06	396	0.16	0.40	

Table 74 (contd)

Series A-3

1	2	3	4	5	6	7	8	9	10	11	12
C_7	Nematic	0.5675	103	1	1	1	2.97	410	4.70	12.50	12.79
	Isotropic	0.0139	126	1	1	1	2.97	410	0.12	0.29	
C_8	Solid	0.0853	84	1	1	1	3.4	424	0.64	1.79	10.46
	Nematic	0.3976	96	1	1	1	3.4	424	2.97	8.06	
	Isotropic	0.0322	120	1	1	1	3.4	424	0.24	0.61	
C_{12}	Smectic C	0.5245	85	1	1	1	2.99	480	5.05	14.11	16.88
	Smectic II	0.0639	110	1	1	1	2.99	480	0.615	1.61	
	Isotropic	0.0465	113	1	1	1	2.99	480	0.447	1.16	

isotropic change is the lowest and that in the polymesomorphic situations, the values for nematic transitions are as a rule lower than those for the smectic transitions. Most of the present series subjected to the DSC study are nematogenic or predominantly nematogenic. With regard to the Δ H values of smectic and nematic transitions for all these series, the observation is that the Δ H value increases as the number of carbon atoms increases in the alkyl chain.

Series A-1 p-Ethoxyphenyl-p'-n-alkoxycinnamates:

The point of interest in this series is the solid-solid transitions for the third, fifth, fourteenth and sixteenth homologues as shown in the DSC graph (Fig. 15). The fifth homologue exhibits two solid-solid transitions and the sixth and seventh homologues give indications of solid-solid transitions but the peaks are not resolved sufficient enough for calculation. The solid-solid transitions have been shown in the various figures by cross. Lack of adequate facility for the study of x-ray patterns made any further study in this regard impossible otherwise the solid transitions could have provided better understanding regarding mesomorphic characteristics since a pre-history of the solid state of a mesogen could be sufficiently important for variations in mesomorphic characteristics.

In the plots of Δ H versus number of carbon atoms in the alkyl chain Fig. 45, the enthalpy for the solid-mesomorphic

ENTHALPY CHANGES (ΔH) OF HOMOLOGOUS SERIES A-1

p-ETHOXY PHENYL-p'-n-ALKOXY CINNAMATES

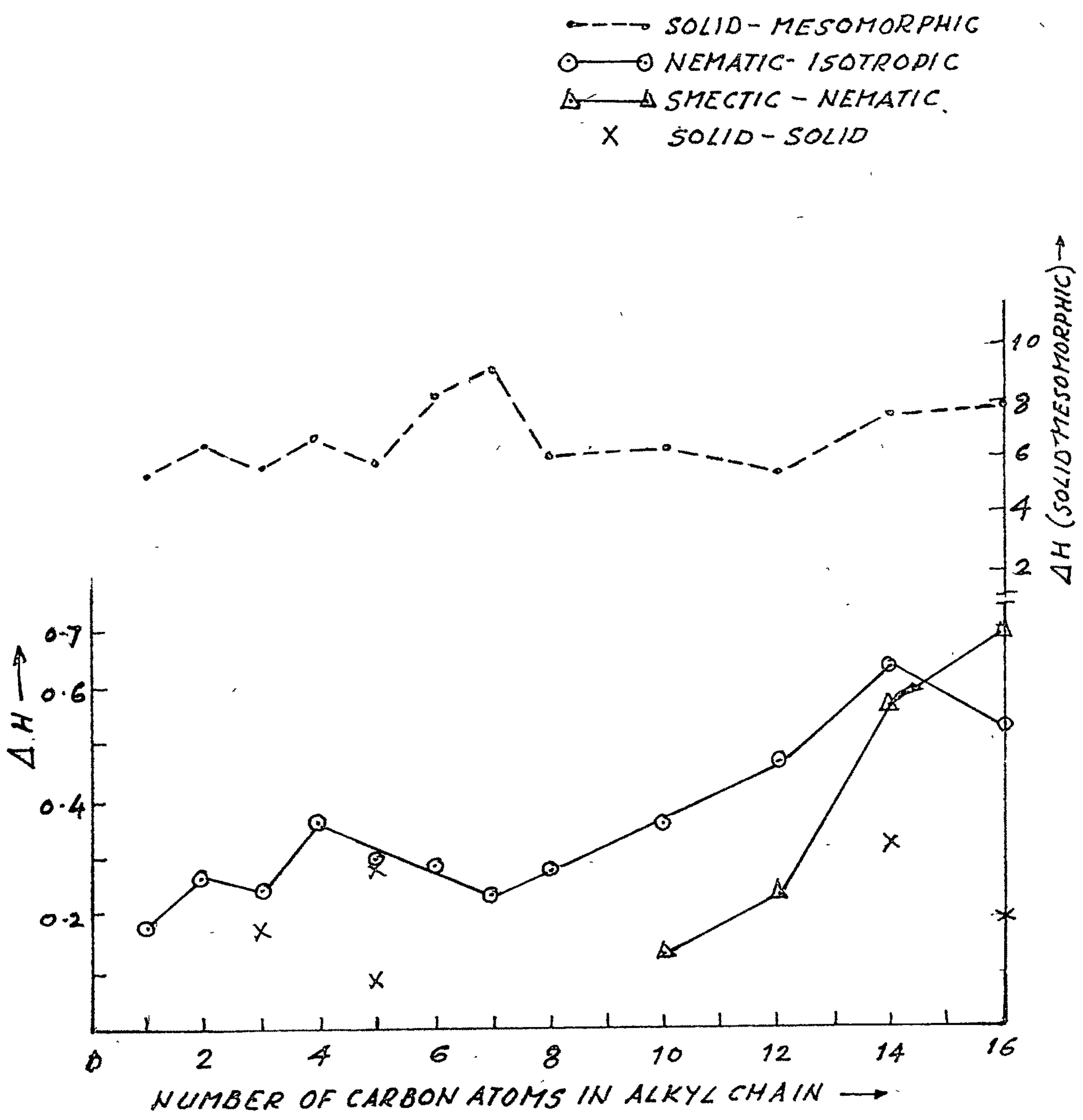


FIG. 45

ENTROPY CHANGES (ΔS) OF HOMOLOGOUS SERIES A-1

p-ETHOXY PHENYL-p'-n-ALKOXY CINNAMATES

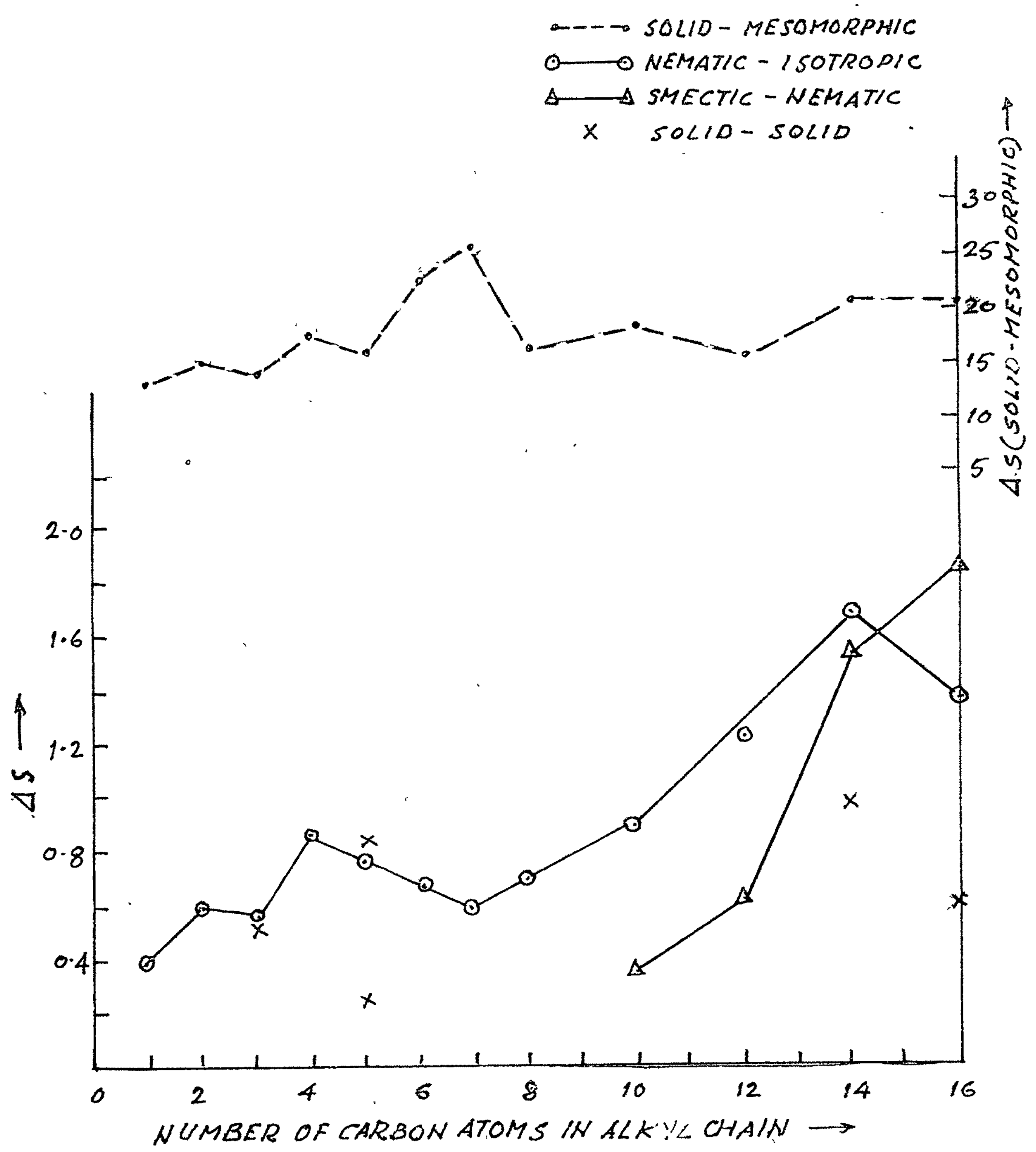


FIG. 46

SERIES A-2

p-n-PROPOXY-p'-n-ALKOXY CINNAMATES

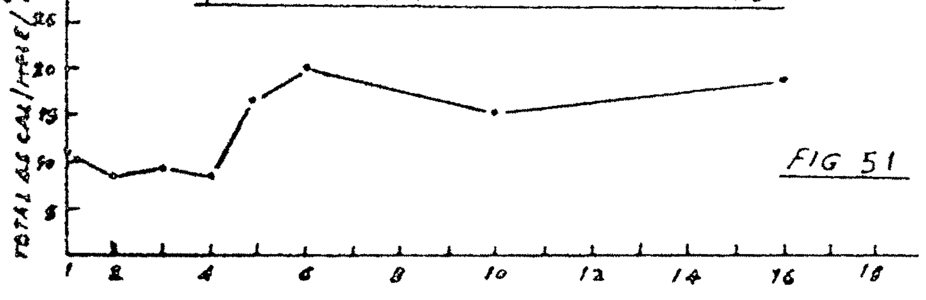


FIG 51

SERIES A-1

p-ETHOXYPHENYL p'-n-ALKOXY CINNAMATES

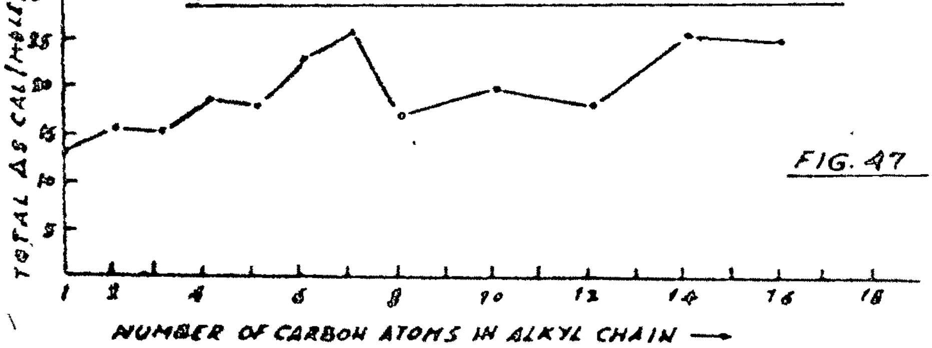


FIG. 47

SERIES A-3

p-n-BUTOXYPHENYL p'-n-ALKOXY CINNAMATES

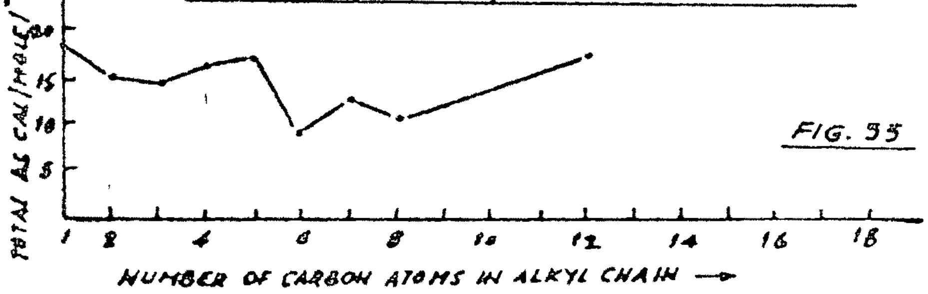


FIG. 35

SERIES A-1

p-ETHOXYPHENYL-p'-n-ALKOXY CINNAMATES (DSC METHOD)

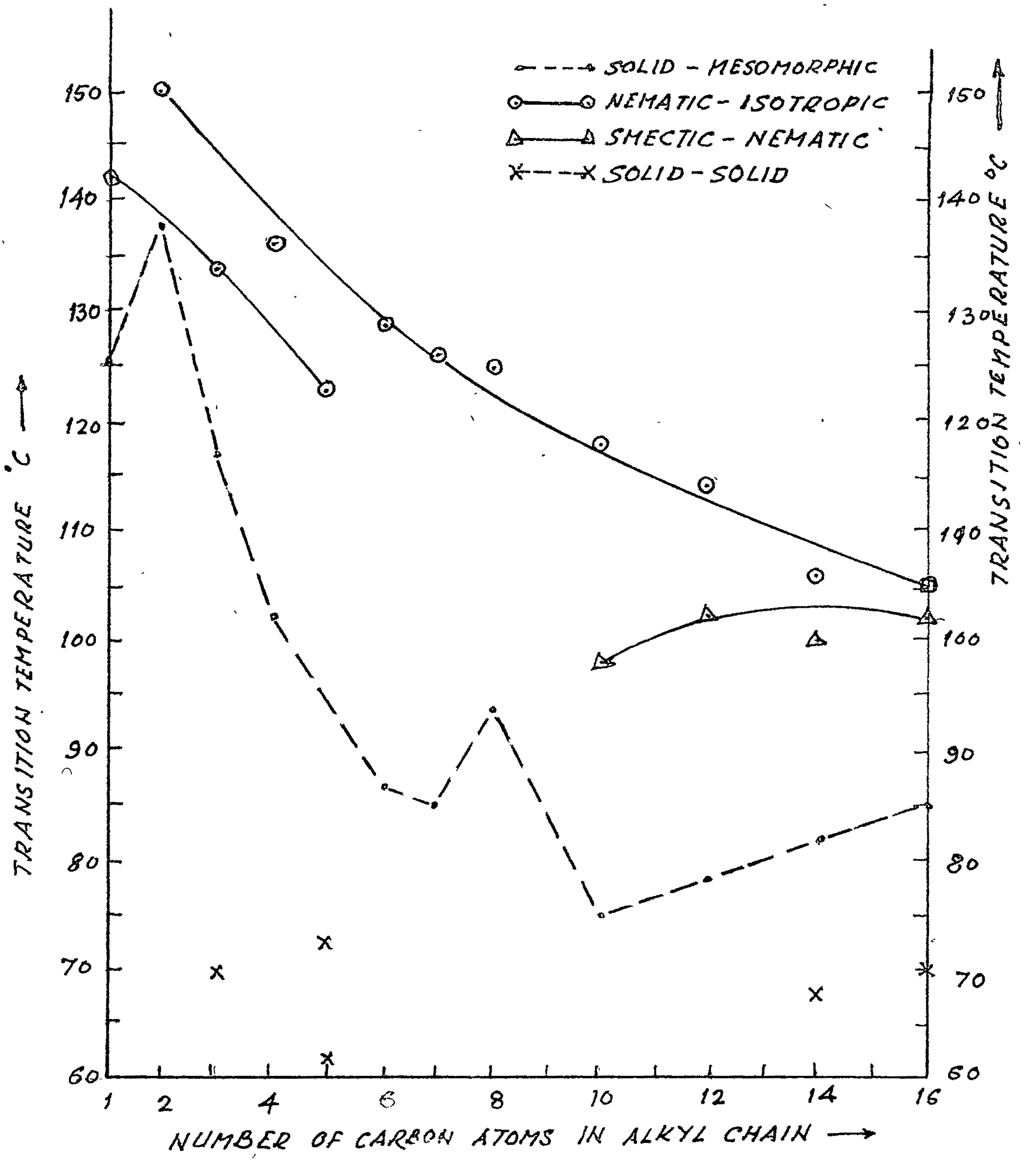


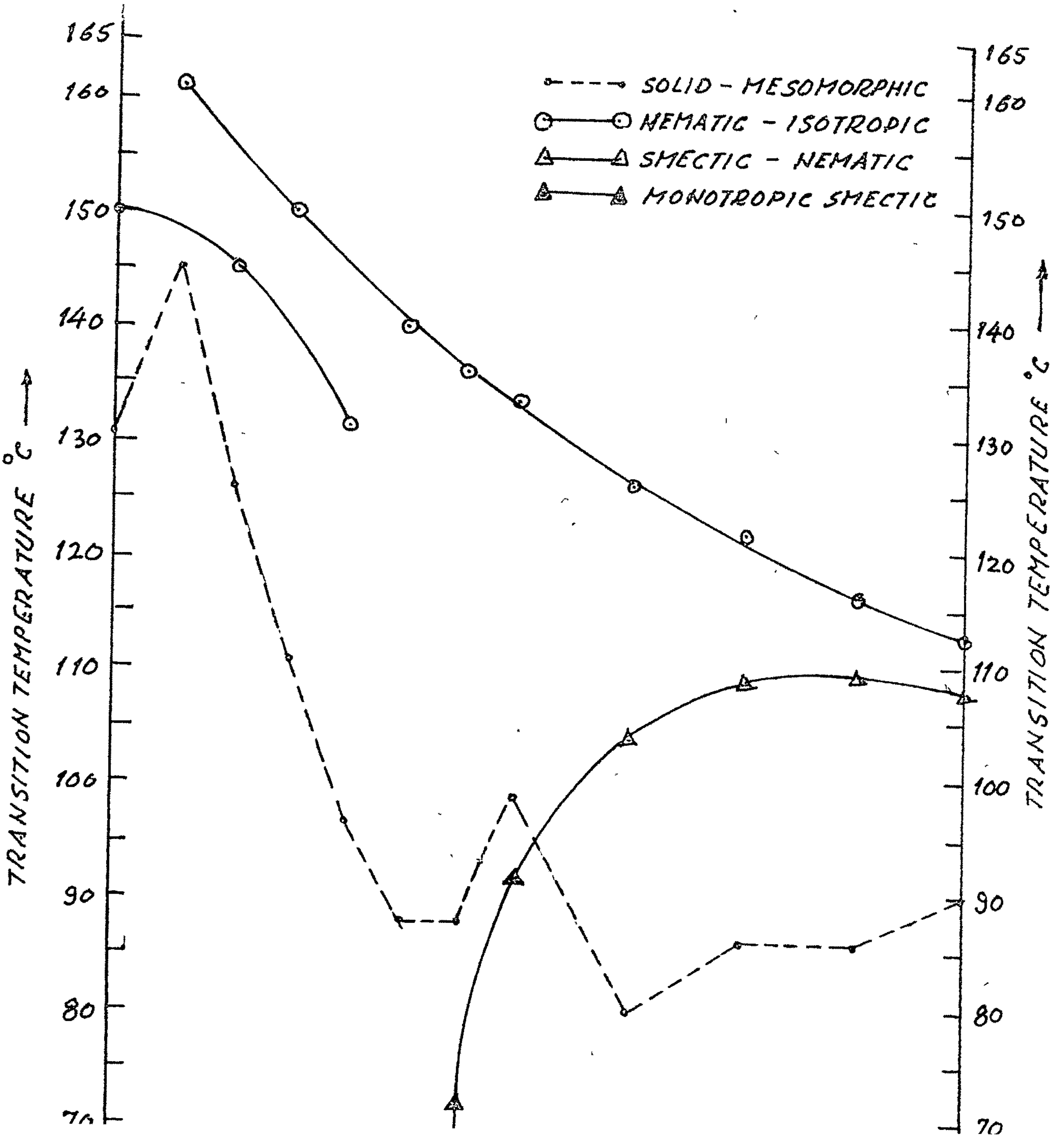
FIG.48

transitions increases alternately. The enthalpy for the N-I transitions show alternation upto the fifth member and after showing fall upto the seventh member it increases gradually. The enthalpy for the S-N transitions shows steep rise. The same pattern is observed in the entropy changes also (Fig. 46). The plot of total Δ S i.e. the summed up

---

SERIES A-1

p-ETHOXYPHENYL-p'-n-ALKOXY CINNAMATES



ENTHALPY CHANGES (ΔH) OF HOMOLOGOUS SERIES A-2

p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

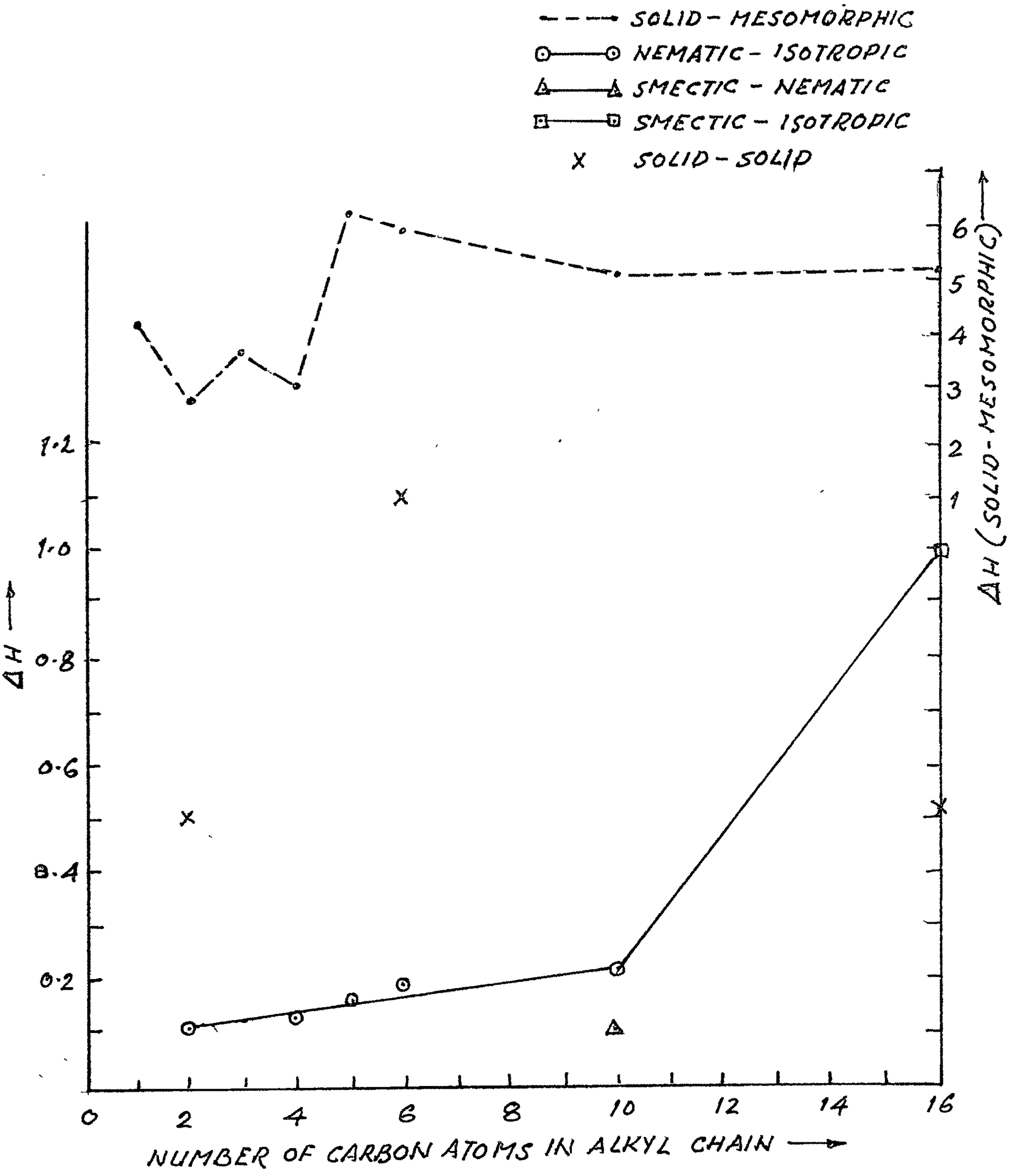


FIG. 49

ENTROPY CHANGES (ΔS) OF HOMOLOGOUS SERIES A-2

p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

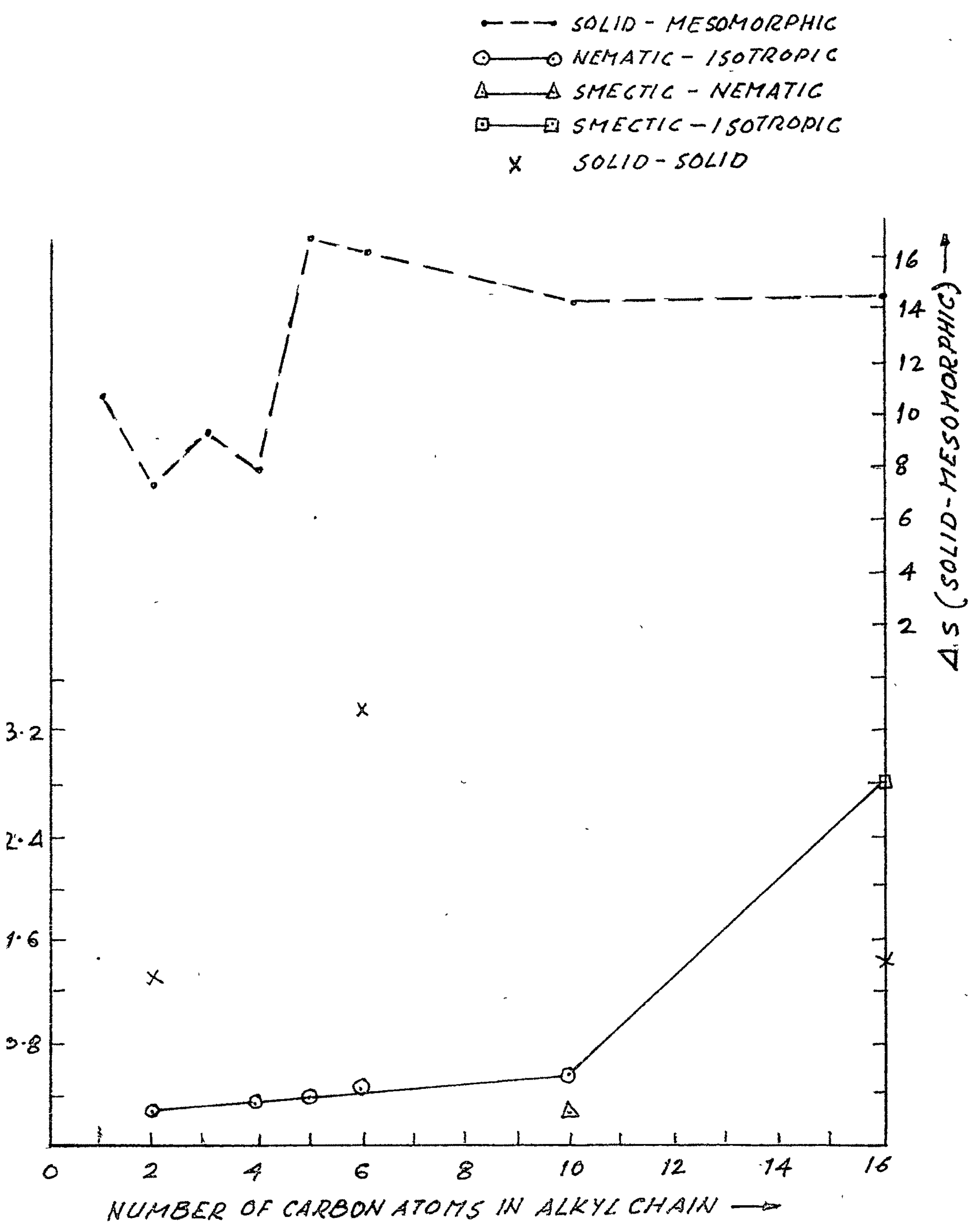


FIG. 50

SERIES A-2

p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

(DSC METHOD)

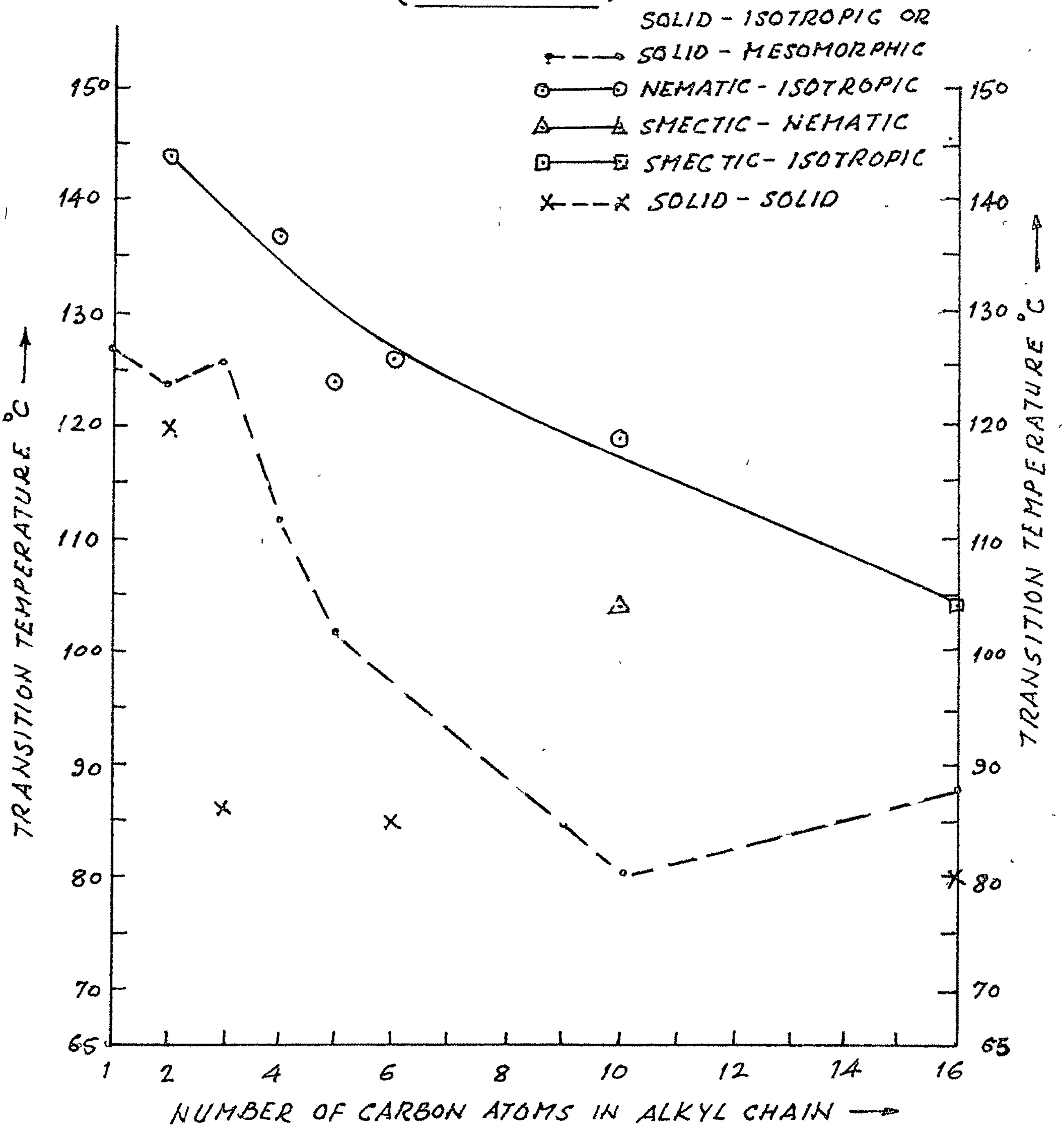


FIG. 52

SERIES A-2

p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

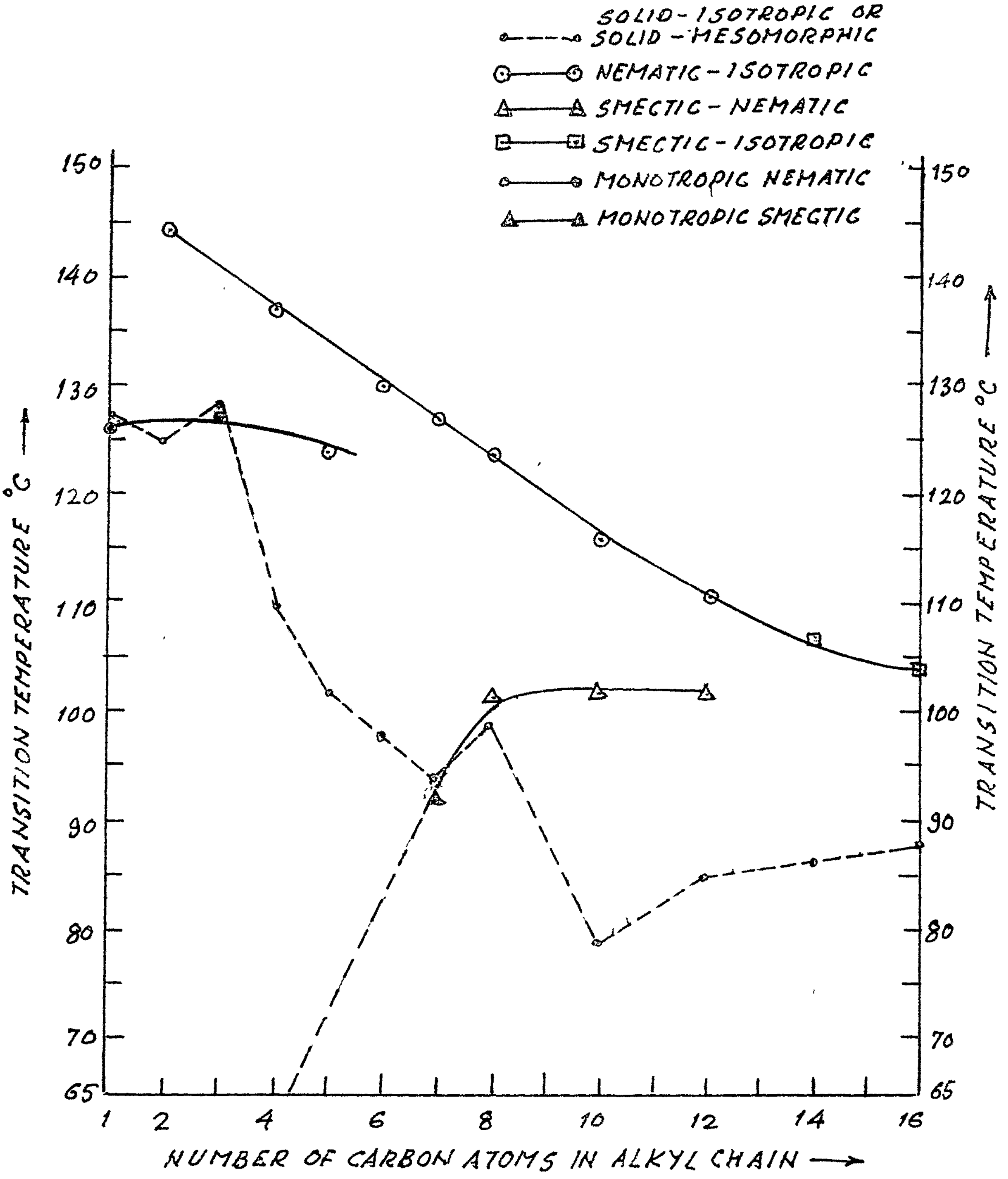


FIG. 7

transition also alternate upto the sixth member followed by a fall and levelling off. Entropy changes also exhibit the similar pattern Fig. 50. The plot of total Δ S versus the number of carbon atoms in the alkoxy chain also exhibits alternate increase throughout (Fig.51). The seventh, eighth twelfth and fourteenth members were not subjected to DSC study hence the transitions for these members are missing.

The plots of transition temperatures obtained by DSC method and under polarizing microscope versus the number of carbon atoms in the alkyl chain (Fig.7 and 52) are identical except the monotropic transitions as well as the transitions for the members not subjected to the DSC study are missing.

Series A-3 p-n-Butoxyphenyl-p'-n-alkoxycinnamates

The solid-solid transitions are again indicated clearly by the DSC graph (Fig.17) for the first, fifth and eighth members. As the peaks for the first and fifth members are not resolved sufficiently, the enthalpy values are not calculated separately. This homologous series is more interesting since besides solid-solid transitions, the two smectic phases, i.e. smectic C and smectic II are clearly indicated by the DSC measurements whereas only one smectic phase was observed under polarizing microscope despite of careful observation. The change in texture from S_C to S_{II} is hardly observable except that the fluidity between the two phases differed markedly.

ENTHALPY CHANGES (ΔH) OF HOMOLOGOUS SERIES A-3

p-n-BUTOXY PHENYL-p'-n-ALKOXY CINNAMATES

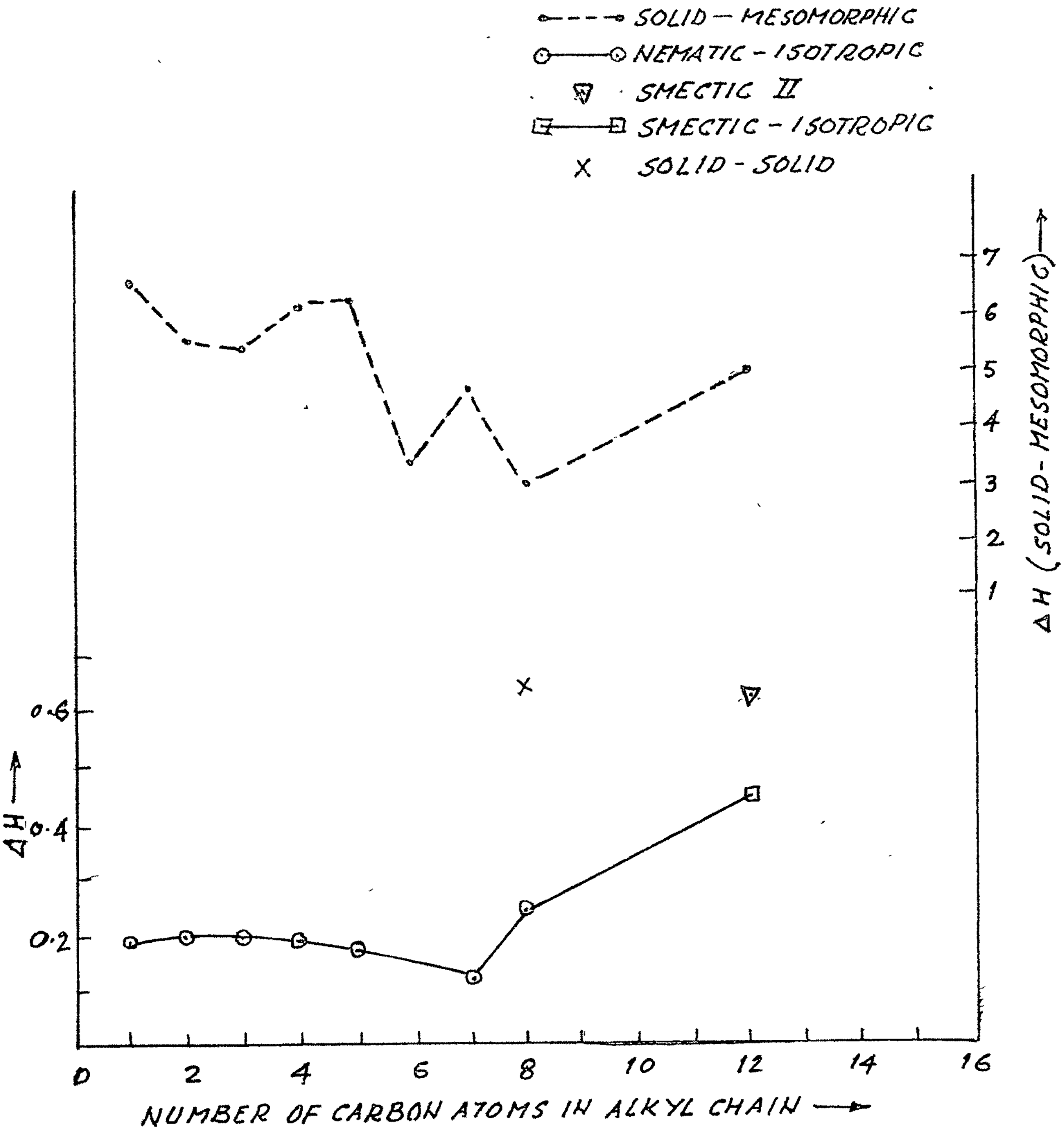


FIG. 53

ENTROPY CHANGES (Δ S) OF HOMOLOGOUS SERIES A-3

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

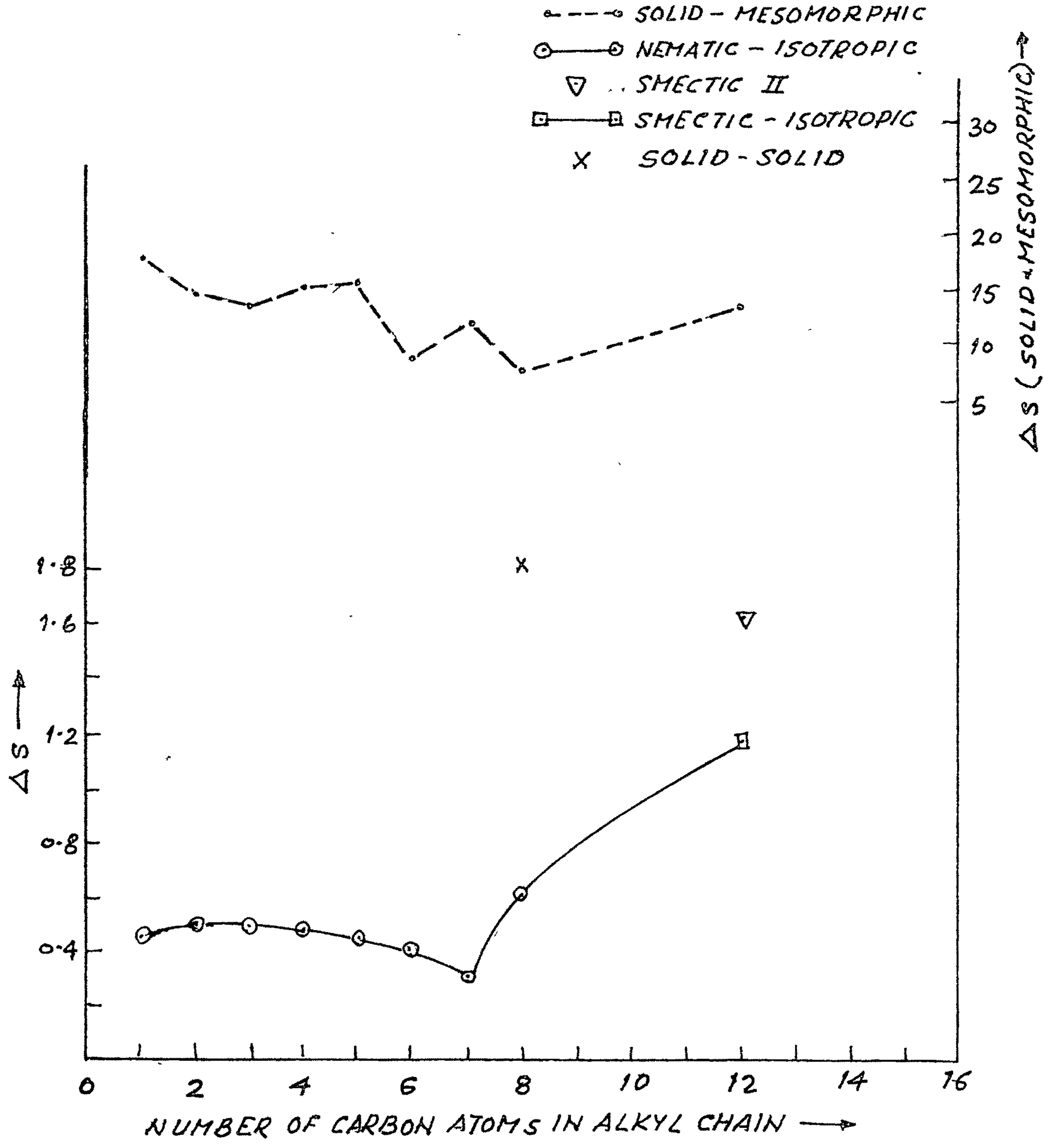


FIG. 54

SERIES A-3

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

(DSC METHOD)

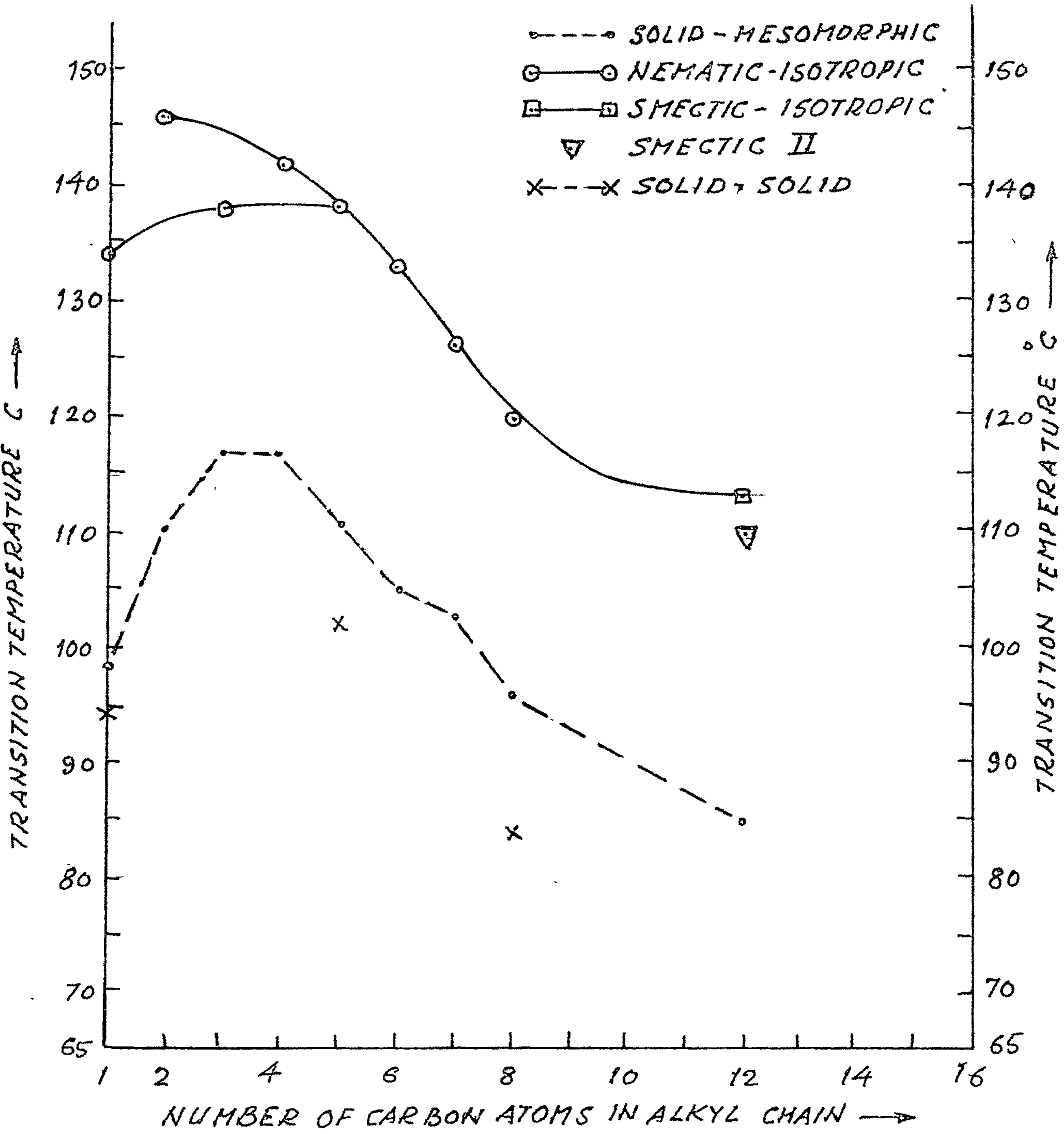


FIG. 56

SERIES A-3

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

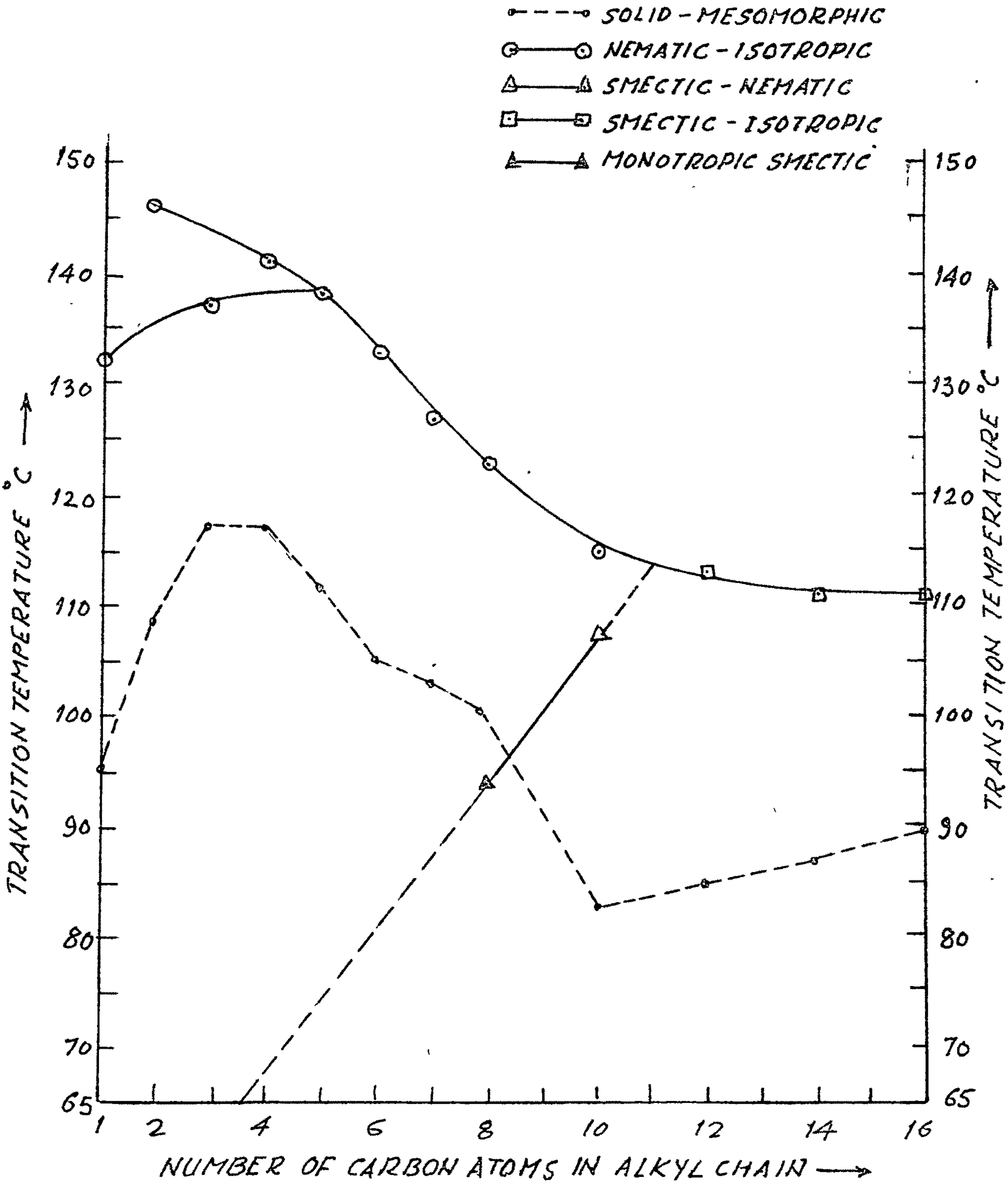


FIG. 8

There is a good enthalpy change for this transition but no appreciable change in the texture. Further characterization of the S_{II} phase by contact method was made difficult by the small phase length. The S_C to S_{II} transition is indicated in the various graphs by $\bigtriangledown$.

In the plot of Δ H versus the number of carbon atoms in the alkyl chain (Fig. 53), the enthalpy for the N-I transitions decreases upto the seventh member followed by a considerable rise upto the last member. Δ H for the solid-mesomorphic transitions shows an overall falling tendency. Similar pattern is also observed in the entropy changes (Fig.54). The plot of total Δ S versus the number of carbon atoms in the alkyl chain exhibits peculiar pattern (Fig.55).

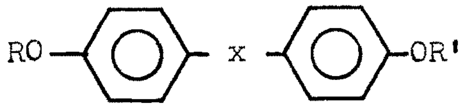
In general, the plot of the total energy Δ S versus the number of carbon atoms (Figs. 47, 51, 55) exhibits an overall rising tendency in alternation as the chain length increases though the last series shows a falling tendency with alternation in the latter half of the series (Fig.55). These observations are in agreement with those reported in literature (484-488).

Enthalpy values of the structurally similar compounds (Table 75) reveal that the values for the newly synthesized homologues are comparable.

As known from other homologous series reported in literature, the melting enthalpies increase in these series

Table 75

Comparison of Enthalpy



ΔH (Kcal/mole) For x=-CH=CH-COO-		R	R'	X	ΔH (Kcal/mole)	
K-N	N-I				K-N	N-I
6.17	0.28	C_8H_{17}	C_2H_5	-COO-	8.36(1)	0.33(1)
3.41	0.16	C_6H_{13}	C_4H_9	-COO-	8.36(1)	0.32(1)
6.67	0.19	CH_3	C_4H_9	-CH=CH-	9.48(2)	0.18(2)

(1) - (471), (2)-(470)

also, with increase in chain length. The enthalpies of various transitions also fall in the range of the reported values. The clearing enthalpies and enthalpies of the nematic phases show alternating increasing trend with increase in alkyl chain length. In general the enthalpies of transitions within the liquid crystalline state show an increasing trend with growing alkyl chain.

It may be said that calorimetry is a valuable help to detect polymesomorphism and can yield some clues to phase classifications. But an exact classification on the basis of calorimetry alone is not possible.

4.g. Mixed Mesomorphic Systems:

It has been thought that study of some binary systems, comprising certain homologues of the presently investigated homologous series, may turn out quite interesting. Of course while selecting the homologues as components, the only aspect that was predominant was the extent of lowering of the mixed transitions and obtaining a range as low as 25°-50°. While this objective is not well fulfilled, the mixed study nevertheless has presented very interesting panorama with possibilities for further investigations. Binary systems comprising components none, one or both of which are liquid crystals have been studied in this investigation and the results are quite interesting.

The binary systems studied by optical microscopy are given in Table 76 with their transitions mentioned against the components.

The selection of the components is made to account for one single variation for a group of binary systems, so that the results could be well attributed to the single varying factor. System No.1 and 2 belong to the series p-ethoxyphenyl-p'-n-alkoxycinnamates, series A-1, No.3 and 4 belong to the series p-n-propoxyphenyl-p'-n-alkoxycinnamates, series A-2, while system No.5 to 11 belong to p-iso-propoxyphenyl-p'-n-alkoxycinnamates, series B-5.

Table 76

Binary Systems

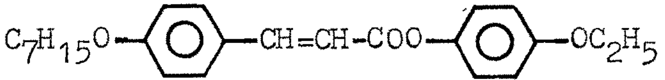
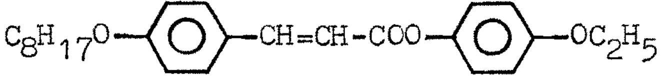
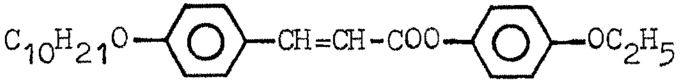
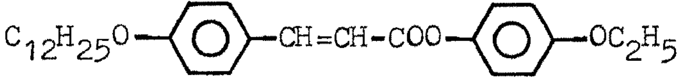
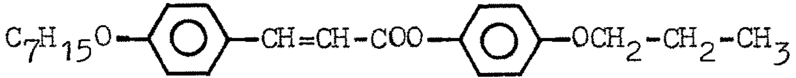
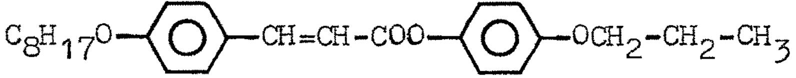
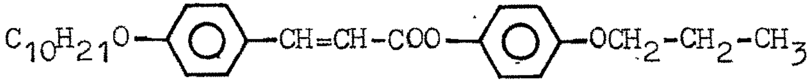
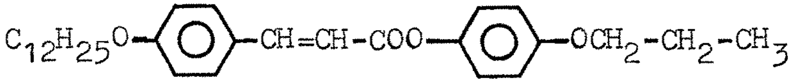
System No.	Compounds	Molecular Geometry	Transitions °C			Fig. No.
			Smectic	Nematic	Isotropic	
1	2	3	4	5	6	7
1	(A)		(72)	88	136	18
	(B)		(92)	99	133.5	
2	(A)		80	104	126	19
	(B)		86	109	122	
3	(A)		(92)	94	127	20
	(B)		99	101.5	124	
4	(A)		78.5	102	116	21
	(B)		85	102	111	

Table 76 (contd)

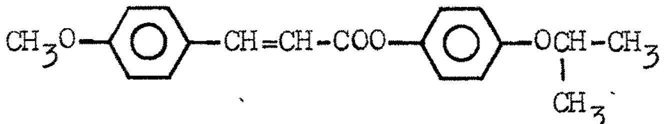
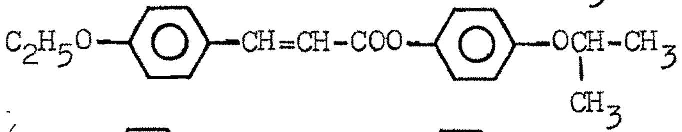
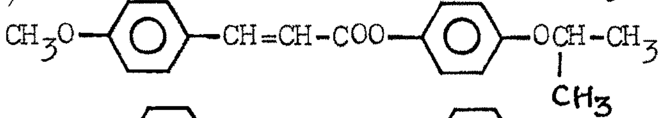
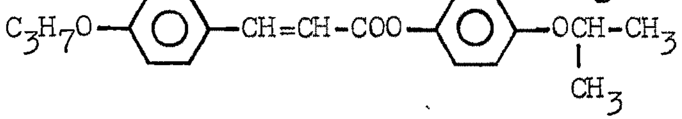
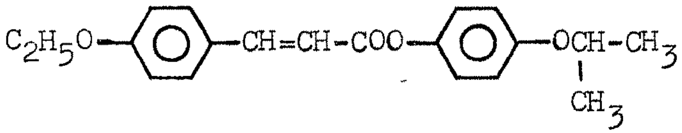
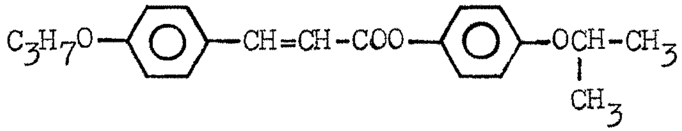
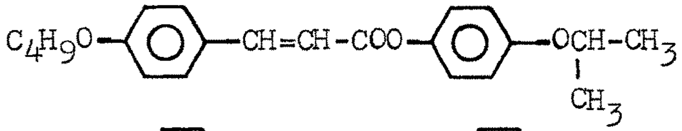
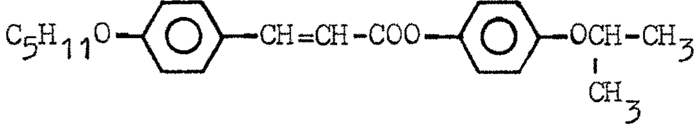
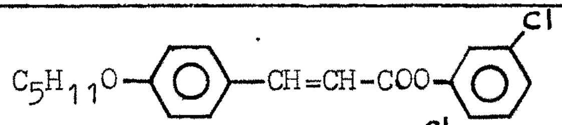
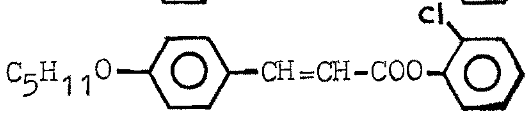
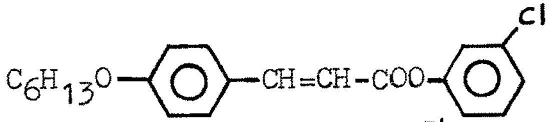
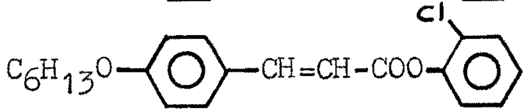
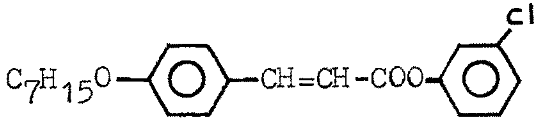
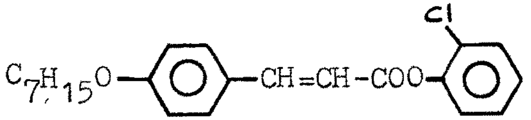
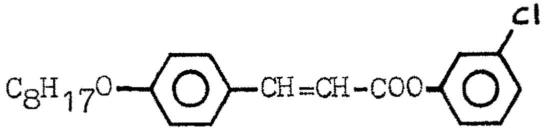
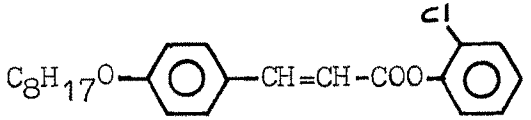
1	2	3	4	5	6	7
5	(A)		-	-	99	22
	(B)		-	-	145	
6	(A)		-	-	99	23
	(B)		-	(99)	109	
7	(A)		-	-	145	24
	(B)		-	(99)	109	
8	(A)		-	(109)	110	25
	(B)		-	(98)	103	

Table 76 (contd)

1	2	3	4	5	6	7
13	(A)		-	-	82	30
	(B)		-	-	65	
14	(A)		-	-	73	31
	(B)		-	-	72	
15	(A)		-	-	54	32
	(B)		-	-	61	
16	(A)		-	-	56	33
	(B)		-	-	60	

The two components of the binary system No.1 (Fig.18) are p-ethoxyphenyl-p'-n-heptyloxycinnamate (A) and p-ethoxyphenyl-p'-n-octyloxycinnamate (B). Both components have the same molecular geometry inclusive of the same alkoxy group at the right terminal, but differ in length due to one more methylene unit in the alkyl chain at left terminal of the component B. Since the molecules of both species are almost identical in molecular structure, almost perfect compatibility in packing of the molecules in the oriented state is ensured, which is quite conducive to enhancing the mesomorphic property in the mixed condition. Both components are polymesomorphs with smectic phase in monotropic conditions and their upper transitions differ by only 2.5°, consequently the mixed nematic-isotropic transition curve nearly follows the ideal linearity criterion. This would suggest that the molecular forces responsible for exhibition of nematic mesophase do not alter much in the mixed condition-neither the forces conducive to the mesophase are enhanced nor decreased.

The component B has octyloxy group at the left terminal whereas component A has heptyloxy group at the same position, this means the molecular length of component B is more by one methylene $-CH_2-$ unit leading to more polarizability of the molecule. The increase in mole % of the more polarizable component increases the mixed S-N transition as seen from the rising nature of the curve. The forces conducive to smectogens are enhanced leading to increase in the smectic thermal stability.

But smectic mesophase length is not increased much, it shows rise and fall, because of the nature of the solid-mesomorphic transition curve. With increase in the proportion of B, the mixed S-N transition curve rises gradually from left to right side of the phase diagram. During this rise, at about 40 mole % B the curve crosses into enantiotropic region, and travers through this region till mole % of B reaches the value of about 67, when the curve again enters the monotropic region. This crossing of the mixed S-N transition curve from monotropic region to enantiotropic region and again into the monotropic region results into increase and decrease in the smectic mesophase range. The smectic mesophase length above eutectic is of 9° versus 16° and 7° in the component A and B respectively. The molecular forces have certainly increased the resistance of the smectic mesophase to the thermal agitation but because of the mixed K-M transition curve the mesophase length has not increased much.

The packing of the molecules in solid state has certainly yielded to the thermal agitation as seen from the fall in the K-M transitions upto the eutectic at 75° with about 58 mole % of B. This shows a fall in K-M transition from 88° at the left side to 75° i.e. a fall of 13°. As the proportion of B increases beyond 58 mole %, the mixed K-M transition curve registers a sharp rise.

The system exhibits wide nematic range while the smectic mesophase length is of less than 10°. The molecular forces have not enhanced the mesophase length as it varies between 64° and 41.5°, the former is the mesophase length of the component A and the later that of component B. Table 23 reveals that when the nematic mesophase length increases, the smectic mesophase length decreases and vice versa. It may be said that with 55 ± 15 mole % of either of the components, the binary system exhibits smectic mesophase in enantiotropy. The mixed nematic phase length is in the range of 40-55° and mixed smectic phase length in the range of 5-10°. The maximum mixed nematic phase length is of 55° versus 48° and 34.5° in the components A and B respectively. The maximum mixed smectic mesophase length is of 12° and over the eutectic it is of 9° versus 16° and 7° in the components A and B respectively

The binary system No.2 (Fig. 19) comprises of two polymesomorphs viz. p-ethoxyphenyl-p'-n-decyloxycinnamate (A) and p-ethoxyphenyl-p'-n-dodecyloxycinnamate (B). The molecular geometry of the two components is identical except that at the left terminal in component A there is decyloxy group whereas in B it is dodecyloxy group. The molecules of component B are longer by two methylene units, as the right terminal group, ethoxy, is the same in both the components. The variations in the various transitions can be attributed to longer length of the component B as otherwise both the components are identical.

The nematic-isotropic and smectic-nematic transitions of the two components differ by 4° and 5° respectively. The mixed N-I transitions on the left side of the phase diagram show little convex elevation followed by more or less ideal behaviour.

In contrast to this, the mixed smectic-nematic transition curve shows gradual rise from left to right side of the phase diagram. This indicates that the longer and more polarizable component B predominates over the component A. It reduces the forces conducive to the nematic mesophase and enhances the smectic mesophase. The combined effect of this is the gradual decrease in the nematic mesophase length and increase in the smectic mesophase length. The nematic phase length decreases from 22° (nematic phase length of the component A) to 13° (mesophase length of the component B) with only marginal rise of 1° at about 9 mole % of B. The mixed N-I transitions yield to thermal agitation while the mixed S-N transitions resist it and the increased polarisability increases the thermal stability.

The packing of the molecules in the solid state yields to the thermal agitation as the mole % of dodecyloxy homologue is progressively increased till it reaches eutectic composition of 46.5 mole % of B at 63°C. With further increase in the proportion of the component B the mixed K-M transitions show sharp rise. This depression in the mixed K-M transitions increases the smectic mesophase length gradually from 24° at the left to 43.5° over the eutectic composition while that of the component B is 23°. Both pure components have smectic phase length of 23° (B) and 24° (A), while the system has the mesophase length more than these. The more polarizable molecule of the component B predominates in the system and increases the smectic phase length and decreases the nematic phase length. The overall mesophase length of the system is also more, maximum at the eutectic is 62°. It may be said that the forces conducive to mesophase are enhanced in the system. The interesting part of this binary system is that the lowest temperature, at which the system would be in the mesomorphic orientation, is 63°, which is the lowest in the binary systems studied under this investigation. A third component of suitable structure and characteristics could bring down the temperature range still further.

The extent of sinking of the mixed melting points may be assessed by taking a difference of the higher solid-mesomorphic transition of the two components and the eutectic temperature, which are given in Table 77. A glance at the difference value in the Table 77 conveys that the extent of mixed K-M transitions' depression or sinking is greater in the system 2 as compared to system No.1. In other words, the resistance offered by the mixed packing of the molecules in the solid state of the system No.2 is less than that offered by those of the previous system. Since the binary system No.2 has the components one of which is longer than the other by two methylene units ($-CH_2-$) at the left terminal, the greater resistance to the thermal agitation offered by it is perhaps due to the type of packing of the mixed molecules.

The molecules of the system No.3 and 4 are geometrically identical with those of No.1 and 2 respectively, as the left

Table 77

Solid-Mesomorphic Transition (K-M) and the Eutectic Temperature

System	K-M transition (the higher of the two) °C	Eutectic temperature °C	Difference i.e extent of sinking
1	92	75	17
2	86	63	23

terminals of components in system No.1 and 3 are the heptyloxy and octyloxy groups whereas those in the system No.2 and 4 are the decyloxy and dodecyloxy groups. The only difference between the two pairs of systems, viz. No.1 and 2, and 3 and 4, is at the right terminal. Ethoxy group is at the right terminal in pair of system No.1 and 2 while n-propoxy group is at the same position in the pair of system No.3 and 4. So the two components in the binary system No.3 are p-n-propoxyphenyl p'-n-heptyloxycinnamate (A) and p-n-propoxyphenyl-p'-n-octyloxycinnamate (B)(Fig.20).

The mixed nematic-isotropic transition curve deviates a little from the ideal linearity behaviour, the difference between the two upper transitions being of 3° only. This would suggest that the molecular forces responsible for exhibition of nematic mesophase do not alter much in the mixed condition. Taking into consideration the monotropic smectic mesophase property of component A viz. p-n-propoxyphenyl-p'-n-heptyloxycinnamate on par with the other liquid crystallinity of nematic nature, the total mesophase length of the components A and B of this system are 35° and 25° respectively. The component A of the system No.3 has more pronounced nematic character in a relative sense and this is not disturbed much. Therefore, the mixed nematic-isotropic transition curve deviates a little from the ideal linearity behaviour.and shows a small downward trend. The molecular forces responsible for the smectogenic property enhance as the mole % of the longer, octyloxy, homologue increases. The mixed smectic-nematic transitions show a rising trend and the more predominant smectogen B transforms monotropic character of component A into enantiotropy at about 10 mole % of component B. The increase in the mixed thermal stability of the smectic mesophase reduces the mixed nematic characteristics.

The solid-mesomorphic transitions of the mixture sink wonderfully giving rise to two eutectics quite unusually. The depressions in the mixed solid-mesomorphic transitions on the right and left sides of the phase diagram are of 15° (B") and 7.5° (A") and between the two eutectics, the proportionate slope of the transition curve is maintained. In otherwords, under the mixed condition the packing of the molecules in the solid state is one such that easily yields to thermal agitation as compared to that of the individual components which offer greater resistance. The mixed smectic mesophase ranges at the two eutectic compositions A" and B" are of 10.5° and 17° respectively, which are more by 8.5° and 14.5° respectively than those of the individual components. The mixed nematic mesophase is reduced at the middle region of the phase diagram due to the rising tendency of the mixed S-N curve and falling nature, though little, of the mixed N-I curve. Thus, in the mixed condition, the molecular forces of this system are more conducive to smectic mesophase. Existence of two eutectic compositions would indicate formation of molecular complex AB. The mesophase lengths over the eutectic points A" and B" are of 39.5° and 41° versus 35° and 25° for the components A and B respectively.

The phase diagrams of the system No.1 and No.3 are comparable as the components have identical geometry. Both the systems show increase in smectogenic property and decrease in nematogenic nature. The mixed N-I transitions show a decrease though marginal and mixed S-N transitions show a rise. It is the arrangement of the molecules in solid state that yields to thermal agitation and shows good depressions, the system No.1 having one and No.2 having two eutectics.

The system No.4 (Fig.21) belongs to the same series viz. A-2 and the two components are p-n-propoxyphenyl-p'-n-decyloxycinnamate (A) and p-n-propoxyphenyl-p'-n-dodecyloxycinnamate (B). Both components have the same molecular geometry inclusive of the same alkoxy group at the right terminal, but differ in length due to two more methylene units in the alkyl chain at the left terminal of the component B. Both the components exhibit polymesomorphism with more smectic phase length and comparatively less nematic phase length. The mixed nematic-isotropic transition curve is a straight line sloping downward marginally whereas the mixed smectic-nematic transition curve follows the ideal linearity behaviour, the difference between the two upper transitions being of 5° only and there is no difference between the two smectic-nematic transitions of the individual components. The nematic mesophase length decreases gradually with increase in the mole % of B which may be attributed to its more length by two $-CH_2-$ units and in turn more polarizability. The mixed smectic mesophase length increases from left to the right side of the phase diagram and reaches maximum value of 36° at the eutectic point. The increase in the smectic mesophase length can be attributed to the decrease in the mixed solid-mesomorphic (K-M) transitions.

The molecular forces responsible for exhibition of the nematic phase are reduced as indicated by the decrease in mixed N-I transition temperature while the forces conducive to the smectic phase are not altered as observed from the mixed S-N transition curve which is nearly parallel to the abscissa.

The mixed K-M transitions are depressed and reaches eutectic at 66°. With increase in alkyl chain length at the left terminal by two methylene units, the depression in the mixed K-M transitions is more. The packing of the molecules in the solid state yields to thermal agitation as seen from the depression of 12.5° from 78.5° in the component A at left side of the phase diagram. In all, the addition of the dodecyloxy homologue to decyloxy homologue does not alter the mixed S-N transitions, the mixed N-I transitions yield to the thermal agitation marginally while the mixed solid-smectic transitions does not resist the thermal agitation much. The net effect of this is decrease in the nematic mesophase and increase in smectic mesophase. The nematic phase length in components A and B is of 14° and 9° respectively while over the eutectic it is of 12°, whereas the smectic phase length of 23.5° and 17° in components A and B respectively becomes 36° over the eutectic. In turn, the mixed mesophase length is more than that of the pure components. The forces conducive to smectic phase predominate in the system. Taking system No.3 and 4 for comparison, the extent of sinking of the mixed K-M transitions may be assessed by taking difference of the higher K-M transition of the two components and the eutectic temperature (Table 78). The difference values in the Table 78 conveys that the extent of mixed solid-mesomorphic transitions' depression is greater in the system No.4 as in system No.2. The resistance offered by the mixed packing of the molecules in the solid state of the system No.4 is less than that offered by the system No.3. Similar depressions are also observed in the pair of system No.1 and 2. The phase diagrams of the pair of system No.2 and 4 are once again similar

Table 78

Solid-Mesomorphic (K-M) Transition and the Eutectic Temperature : System No. 3 and 4

System No.	K-M-Transition (the higher of the two) °C	Eutectic temperature °C	Difference i.e. extent of sinking
3	99	86.5	12.5
3	99	84	15
4	85	66	19

as is the case in pair of system 1 and 3. The components in this pair have decyloxy and dodecyloxy groups, at left terminal while the right terminal groups are ethoxy and propoxy in system No.2 and 4 respectively. Increase in length of the corresponding homologues in system No.4 reduces nematic characteristic and increases smectogenic one. The same phenomenon is observed in the system No. 2. In both the systems it is the mixed solid-mesomorphic transitions which yield much to thermal agitation.

The system No.5 to 11 have the components from the series B-5 having iso-propoxy group at the right terminal. The system No.5 (Fig.22) has components viz. p-iso-propoxyphenyl-p'-methoxycinnamate (A) and p-iso-propoxyphenyl-p'-ethoxycinnamate (B), both of which are non-mesomorphic with melting points 99° and 145° respectively.

The component B is longer by one methylene unit, than the component A. The $-OCH_3$ and $-OC_2H_5$ groups are more polar and both the groups together in the binary system of A and B induce enough terminal attractions for exhibiting the nematogenic characteristics. The addition of more polar molecule B to the less polar A molecule induces nematic property at only about 10 mole % of B and the mixed nematic isotropic transitions show rising tendency. Both the mixed K-M and N-I transition curves show rising tendency upto 90 mole % of B on the right side of the phase diagram. Between 90 mole % of B and pure component B, the system looses its mesomorphic property. The left and the right side of the phase diagram (Fig.22) indicate that the system must contain minimum of about 10 mole % of either of the component A or B to induce liquid crystalline property.

The addition of the ethoxy homologue to the methoxy homologue enhances the molecular forces in the system leading to increase in the mixed N-I transition. The mixed N-I transitions not only resist the thermal agitation, but the resistance increases. Even the packing of the molecules in the solid state becomes stronger and the resistance to the thermal agitation increases progressively as the mole % of B increases.

This system No.5 is particularly more interesting as it is a multi-eutectic system not only in the mixed K-M transitions, but also in the mixed N-I transitions. The mixed K-M transition curve exhibits as many as five eutectic points out of which only one is on depression, the rest are in the increasing order of temperature. The mixed N-I transition curve shows three eutectics, all of them in the increasing order of temperature. The nematic mesophase length is of 1° at about 10 mole % of B and reaches maximum of 16° at the 29 mole % of B. The molecular forces conducive to nematic characteristics are well enhanced here leading to producing nematic mesophase from non-mesogens. The rise in the transitions gives convexity to the transition curves.

Extrapolation of the mixed N-I transition curve to the left side of the phase diagram indicates the N-I transition temperature for the component A at 87.5° and on the right side of the diagram at 142° for the component B. These were not realised because of the high tendency to crystallise and may be taken as the latent N-I transition temperature.

The components A and B of the system No.6 (Fig.23) have methoxy and propoxy groups at the left terminal with the right terminal group being iso-propoxy, the same as in the system No.5. The non-mesomorphic component A is common in the system No.5 and 6, thus the difference in the length of the components in the system No.5 is of one methylene unit and in the system No.6 is of two methylene units. The component B is nematogenic in the monotropic condition.

Addition of more polarizable nematogen (B) to non-mesomorphic component (A) fails to exhibit mesomorphism even in monotropic condition till mole % of B reaches the value of about 9 where enantiotropic nematic mesophase is exhibited. The mixed N-I transition curve decreases upto 88° from 97° where mole % of B is 38. Further increase in the proportion of B increases the mixed N-I transition temperatures gradually and during this process at about 72 mole % of B the curve enters the monotropic region. The system is predominantly nematogenic and the molecular forces conducive to nematogens are enhanced to the extent that with only 9 mole % of B enantiotropic nematic phase is exhibited against non-mesomorphic nature of component A and component B being nematogen in monotropic condition. The mixed N-I transition curve has two eutectics at 19 and 38 mole % of B with the corresponding temperatures 91° and 88° respectively.

The molecular packing of the system in solid state yields to thermal agitation resulting in the fall of mixed K-M transitions upto 72° from 99° at the left side of the phase diagram where the mole % of B is 41.5. Beyond this eutectic A" as the proportion of the component B increases progressively, the mixed K-M transitions rise to the right side of the phase diagram showing one more eutectic B" in the process. The nematic mesophase above the eutectic A" is 16.5° which is the maximum in the system. The molecular forces of the system increase the mesophase but fail to induce smectogenic character.

Like the system No.5, this system also has a multi-eutectic phase diagram. The mixed solid-nematic transition curve has two eutectics, one each while descending and ascending. The mixed nematic-isotropic transition curve also has two eutectics, both while the curve descends. The right side of the diagram indicates that the shorter non-mesogen molecule could reduce the mixed K-M transitions more than the mixed N-I transitions in monotropy and this leads to transforming monotropic nematic to enantiotropic nematic phase. While the left side of the phase diagram indicates that the non-mesomorphic component A needs about 9 mole % of mesomorphic (in monotropy) component B to change its non-mesogenic characteristics into enantiotropic mesomorphism directly. In system No.5, the mixed transitions had the thermal stability increased remarkably while in the system No.6, the variation in mixed N-I transitions is marginal but the mixed K-M transitions fall and rise.

The system No.7 (Fig.24) consists of the non-mesomorphic component viz. p-iso-propoxyphenyl-p'-ethoxycinnamate (A) and mesomorphic component viz. p-iso-propoxyphenyl-p'-n-propoxy cinnamate (B). The component A is the B component in the system No.5 and component B is common between this system and system No.6.

The addition of the mesomorphic (in monotropy) component B to the non-mesomorphic component A decreases the melting points quite sharply till the second eutectic A" at 86 mole % of B, the first eutectic B" being at 34 mole % of B. Further increase in proportion of B increases the mixed melting points. The packing of the molecules in the solid state is such that yields to thermal agitation reducing melting point from 145° at left side of phase diagram to 107° at the second eutectic A".

Mesomorphism in monotropy is first exhibited at 29 mole % of B against 10 mole % of the other component in the system No.5 and 6 and it is at this point that the nematic phase length is maximum of 24°, as further increase in the proportion of B decreases the mesophase length. The mixed N-I transition temperatures decrease after appearance of nematic phase and has one eutectic in the process at 64 mole % of B. Extrapolation of the mixed N-I transition temperatures in monotropy to the left side of the phase diagram indicates the temperature 107° for the component A where it should exhibit nematic mesophase. This is much below the melting point 145° and due to its crystallizing tendency, this was not realized, hence it points to the latent N-I transition temperature. The melting points show decrease of 14.5° and 38° at the first(B") and second eutectic(A") of 34 mole % and 86 mole % of B respectively.

In this system No.7, it seems that the molecular forces are not much enhanced with the result that the monotropy is not transformed into enantiotropy. The molecular length of B is more by one methylene unit, but in the system of p-iso-propoxyphenyl-p'-n-propoxycinnamate (B) with p-iso-propoxyphenyl-p'-methoxycinnamate (A) (System No.6), where the component B is longer by two -CH_2- units, the molecular forces are enhanced so much that with 9 mole % of the component B the system exhibits mesomorphism in enantiotropy and persists for quite a long range.

The two components of the binary system No.8 (Fig.25) are p-iso-propoxyphenyl-p'-n-butoxycinnamate (A) and p-iso-propoxyphenyl-p'-n-amyloxycinnamate (B). Both have identical molecular geometry inclusive of the same iso-propoxy group at the right terminal. The left terminal groups are butoxy in (A) and amyloxy in (B) which gives more length to the later by -CH_2- unit. Both the components are nematogens in monotropy and their mixed N-I transition temperatures and melting points differ by 11° and 7° respectively.

Though both the components are nematogens in monotropy, their system fails to convert monotropy into enantiotropy. The mixed melting points and N-I transitions are close, the difference is of about 1°C, and both descend together maintaining the difference of 1°C till the proportion of B reaches a value of 72.5 mole %, registering a fall of about 8°C. Beyond this, as the mole % of B increases the melting points rise giving convexity to the curve while the monotropic mixed N-I transitions continue to fall. There are two eutectics at 35 mole % and 72.5 mole % of the component B in both, the mixed N-I and mixed melting point, curves.

The molecular forces in the system are not altered much as monotropy of the pure components continues to be exhibited without getting transformed into enantiotropy and fall in the mixed N-I transitions is also not much. Even the packing of the molecules in the solid state yields to thermal agitation to the same extent as the mixed N-I transitions upto the eutectic A''. Thereafter, as the proportion of the component B increases more than 72.5 mole %, the resistance by the packing of the system increases and melting points rise marginally. The molecular forces of the system are not conducive to nematic phase as the mesophase length varies between 1° and 5°, the former being of the component A and the latter of component B.

The system No.9 (Fig.26) has two components viz.p-iso-propoxyphenyl-p'-n-hexyloxycinnamate (A) and p-iso-propoxyphenyl-p'-n-heptyloxycinnamate (B), both are nematogens, the former in monotropy. The molecular geometry of both the components is identical except that the molecular length of the component (B) is more by one methylene unit.

The monotropy nature of the component A transforms into enantiotropy with about 4 mole % of the component B and persists upto the right side of the phase diagram. This indicates that the more polarizable component B predominates in the system and the molecular forces conducive to nematogens are enhanced transforming monotropy into enantiotropy. The molecular orientations in the mesophase yield to thermal agitation easily with the result the mixed N-I transition curve descends from left to right side of the phase diagram giving convex shape to the curve with three eutectic points. The more polarizable component B fails to increase the mesophase length and the thermal stability of the mixed N-I transitions. The eutectic points in the mixed N-I transition curve are at 103°, 99° and 97° at the corresponding mole % 20, 64.5 and 97.5 of the component B. The nematic mesophase length is of 2 to 3° versus 0° and 2.5° in the components A and B respectively.

The packing of the molecules in the solid state also yields to the thermal agitation more or less to the same extent as the mixed N-I transitions. The mixed K-M curve also contains three eutectics and descends in the same fashion as mixed N-I transition curve maintaining the mesophase length of 2 to 3°. The eutectic points in the mixed K-M transition curve are at 100°, 95.5° and 96° at the corresponding 20, 65 and 95 mole % of the component B.

Though the longer heptyloxy homologue predominates in the system neither the phase length nor the thermal stability of the mixed N-I transitions is increased.

The system No.10 (Fig.27) consists of two components viz.p-iso-propoxyphenyl-p'-n-heptyloxycinnamate (A) which is a nematogen and p-iso-propoxyphenyl-p'-n-octyloxycinnamate (B) which exhibits polymesomorphism. The molecular geometry of both the components is once again identical in this system except that the molecular length of the component B, having octyloxy group at the left terminal group, is longer by one methylene group.

The upper transitions of the two components differ by only 0.5° with the result that the mixed N-I transition curve deviates little from the ideal linearity behaviour. On the left side of the phase diagram, the mixed N-I transition curve shows small concave depression. This suggests that the molecular forces responsible for exhibition of nematic mesophase do not alter much in the mixed condition.

The component B though, has more length and polarizability, fails to induce smectogenic property in the system till its mole % reaches the value 39, when the system exhibits smectic mesophase in monotropic condition. When the mole % of the component B reaches the value of about 50, the mixed smectic-nematic transition curve crosses into the enantiotropic region. The rise in the mixed S-N transition curve is of only 5° from 82° at 39 mole % of B. The maximum mixed nematic mesophase length is of 16° at 49 and 79 mole % of component B.

The mixed solid-mesomorphic transitions fall sharply as the proportion of the component B increases till it reaches the eutectic composition registering an overall fall of 22° from the left side of the phase diagram. Beyond the eutectic point, at 88 mole % of B, as the proportion of B increases, the mixed K-M transitions also rise sharply reducing the length of smectic mesophase. Over the eutectic, the smectic mesophase length is of 11.5° which is the maximum and nematic mesophase length is of 15°. Thus, the mesophase length of 26.5° is the maximum one at the eutectic composition.

Polymesomorphism in the system begins at 39 mole % of B and at about 50 mole % of B it exhibits smectic mesophase, enantiotropically.

Extrapolation of the mixed S-N transition curve to the left side of the phase diagram indicates temperature 81° where it will exhibit smectic mesophase in monotropy. Due to high crystallizing tendency of the mesophase, this was not realised. The phase diagram of the series B-5 (Fig.10) suggests 82.5° as the latent S-N transition which is quite comparable. These two values can be viewed as in fine agreement, thereby, lending credibility to the concept of extrapolation method for determining the latent transition temperatures (490).

The last system from the series B-5, viz. system No.11 (Fig.28), consists of a polymesomorph, p-iso-propoxyphenyl-p'-n-decyloxycinnamate (A) and a pure smectogen, p-iso-propoxyphenyl-p'-n-dodecyloxycinnamate (B). The molecular geometry of the two is identical except the length of the component B which is more by two methylene units.

The upper transitions of the two components differ by 2° only and the mixed N-I and S-N transition curves follow identical pattern. The mixed nematic-isotropic transition curve shows continuity with the mixed smectic-isotropic transition curve beyond 90 mole % of B. The system exhibits polymesomorphism upto 90 mole % of B.

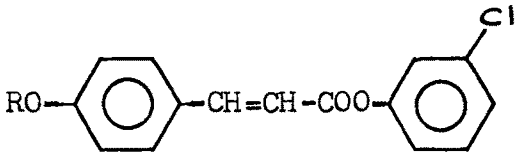
The mixed solid-mesomorphic transition curve shows a drop upto 4.5 mole % of component B followed by rise upto 10 mole % of B. The mixed K-M transition curve again exhibits a drop upto 73° with 36.5 mole % of B, with further increase in the proportion of B, the mixed K-M transition curve rises gradually. The mesophase lengths at the eutectics A" and B" are of 23° and 19° with 4.54 and 36.5 mole % of B. The smectic mesophase length varies between 10° and 20°. With more or less similar changes in the three transition curves, the nematic mesophase length decreases from 6° to 1.5°, while the smectic mesophase length is more than that of pure smectogen. The maximum phase length of 23° is at the eutectic point A".

The system No.12 to 16 (Fig.29 to 33) are from the two non-mesomorphic series C-8 and C-9. The object of studying the mixtures of these non-mesomorphic compounds was to see if mesomorphism is induced by both non-mesomorphs as in the

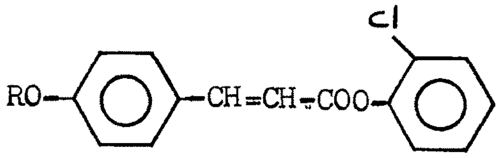
Table 79

Depression In Melting Points (System No.12 to 16)

System No.	Components		Melting point (Higher of the two)	Eutectic Temperature	Difference (Depression)
	A (R=)	B (R=)	°C	°C	°C
12	C_4H_9	C_4H_9	61	41.5	19.5
13	C_5H_{11}	C_5H_{11}	82	63	19
14	C_6H_{13}	C_6H_{13}	73	56.5	16.5
15	C_7H_{15}	C_7H_{15}	61	45	16
16	C_8H_{17}	C_8H_{17}	60	39.5	20.5



(A) Series C-8



(B) Series C-9

system No.5 at low temperatures. The eutectic temperature as low as 39.5° is attained by the depression of 20.5° which is maximum as presented in Table 79. The depressions in the systems No.12 to 16 are in the range of 15° to 20°.

The low melting points of the components of these systems under investigation are attributed to the lateral substituent. Chloro group which push apart the molecules and weaken the molecular packing. The packing of the molecules in solid state of systems seems to be such that yields to thermal agitation easily and passes into isotropy before exhibiting mesomorphism, though, eutectic as low as 39.5° is obtained.