RESULTS AND DISCUSSION

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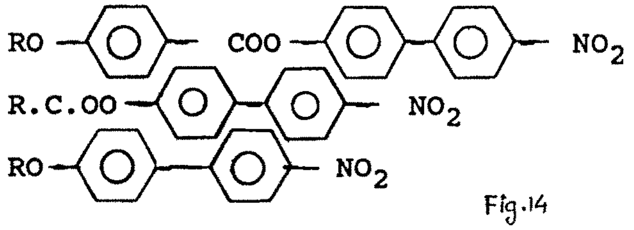
MESOGENIC BIPHENYL DERIVATIVES

RESULTS AND DISCUSSION

1. Mesogenic Biphenyl Derivatives :

Number of homologous series (302, 303) with biphenyl moiety are reported in the literature. Most of these series have terminal cyano group in the moiety. Low melting mesogenic cyano biphenyl compounds gave impetus for applications. Gray (302) has mentioned that terminal nitro group normally imparts yellow colour hence they did not persue it further. However, terminal nitro group has provided some interesting new mesogens. The effect of terminal nitro group on the commencement of smectic mesophase is quite interesting. It was thought quite interesting to synthesize and study the mesogenic property of biphenyl derivatives having terminal nitro group. With this in view, three homologous series are synthesized as indicated in fig. - 14

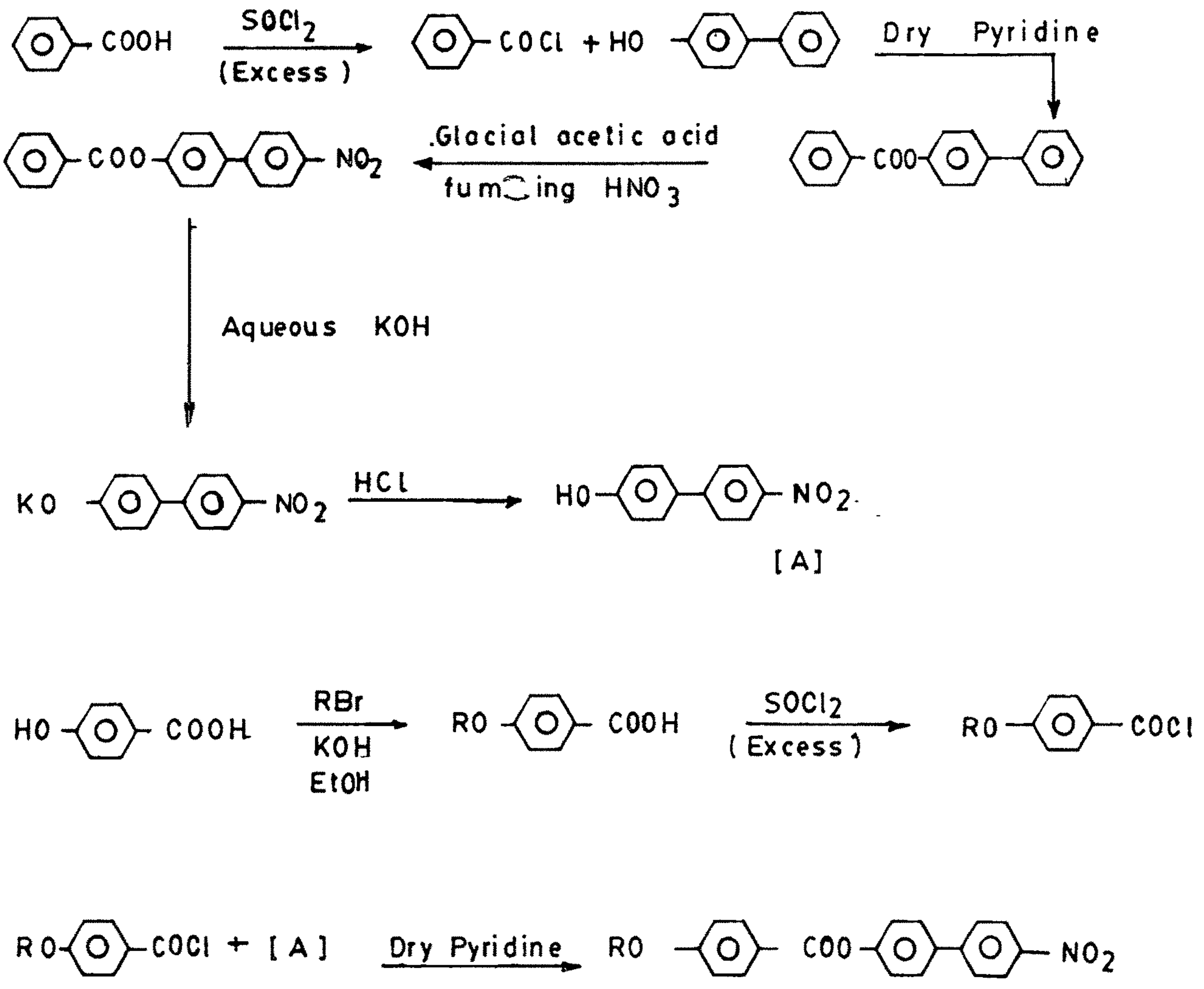


Series - I
Series - II
Series - III

Fig.14

Series - I 4(4-n-Alkoxybenzoyloxy)-4'- nitrobiphenyl.

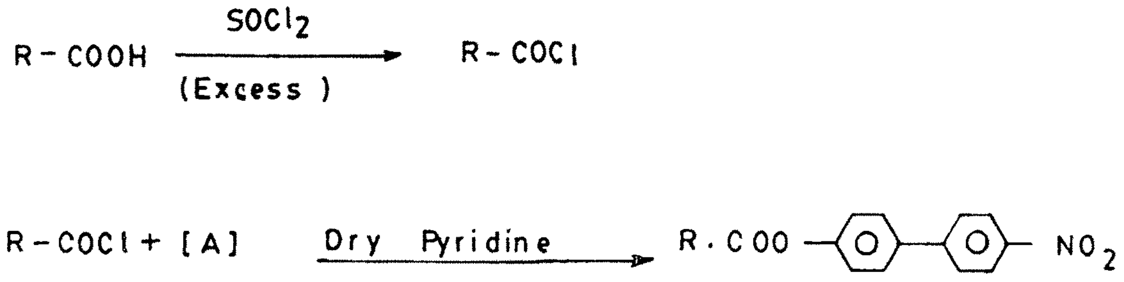
Thirteen compounds have been synthesized and their mesogenic properties were evaluated. The route of synthesis for this homologous series is given in fig. (15.a). The transition temperatures are recorded in table - 3.



R = $C_n H_{2n+1}$, n = 1 to 8, 10, 12, 14, 16 & 18.

SYNTHETIC ROUTE TO SERIES - I

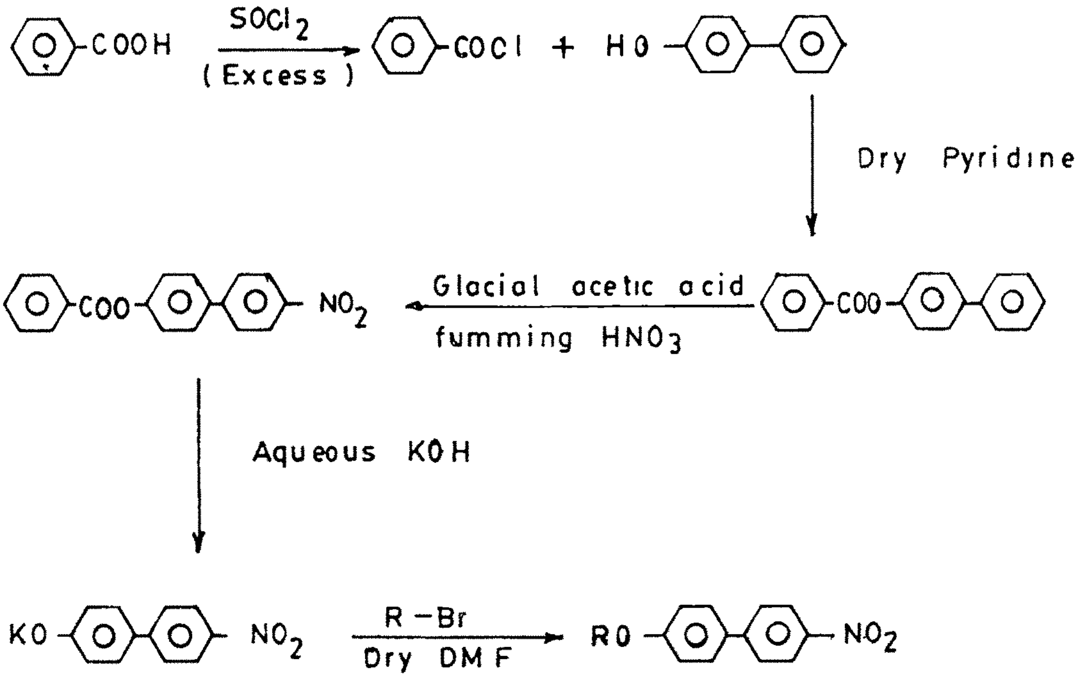
FIG :- 15.a



$R = C_nH_{2n+1}$, n = 6 to 11, 13 & 15.

SYNTHETIC ROUTE TO SERIES II

FIG:-15 b



R = C_nH_{2n+1} , n = 4 to 8 10, 12, 14, 16 & 18

SYNTHETIC ROUTE TO SERIES III

FIG -15.C

The methoxy to n-propoxy derivatives exhibit nematic mesophase. Smectic mesophase appears from n-butoxy derivative as monotropic phase. n-Butoxy to n-octyloxy derivatives exhibit smetic and nematic phases. n-Decyloxy to n-octadecyloxy derivatives exhibit only smectic phases.

Series - II 4(n-Alkanoyloxy)-4'-nitrobiphenyl

Seven members of the series are synthesized. The route of the synthesis for this series is shown in fig. 15.b and transition tempratures are recorded in table - 6. In this series only higher homologues are synthesized as mesophase commences from heptyl derivative (octanoate) as monotropic nematic phase. Nematic phase remains monotropic throughout the series i.e. upto nonyl derivative. Smectic phase commences from nonyl derivative as monotropic phase. n-Undecyl derivative to n-pentadecyl derivatives exhibit enantiotropic smectic phases.

Series - III 4 -n-Alkoxy-4'-nitrobiphenyl

Gray (302) and Gray et al (303) have reported pentyloxy to octyloxy derivatives. It was planned to compare mesogenic properties of terminally substituted nitrobiphenyl derivatives. The whole series was synthesized so as to compare mesogenic properties with series - I and II, eventhough some members were reported in the literature (302, 303). The route of synthesis for this series is given in fig. 15.c and transition temperatures are recoreded in table - 9.

n-Heptyloxy to n-hexadecyloxy derivatives exhibit mesomorphism. Gray et al (303) have reported monotropic nematic mesophase for n-pentyloxy and n-hexyloxy derivatives. In the present study monotropic nematic phases could not be observed even with the repeated observations under microscope. In both the casescrystallization starts before the monotropic transitions reported by Gray et al (303) are reached. This explains the absence of monotropic phases in n-pentyloxy and n-hexyloxy derivatives. The 50:50 mixture of n-pentyloxy and n-hexyloxy derivatives do not exhibit any mesophase. Normally one would expect atleast stable monotropic phase in mixtures of two potential mesogens. Gray (302) has reported enantiotropic nematic phase for the n-octyloxy derivative whereas in the present study this phase could not be observed. There is even 10°C higher isotropic temperature comapared to the reported compound. Except those three cases the mesogenic properties are compareable, with the reported one.

1.1 Common features of series I, II & III :

All the three homologous series exhibit mesomorphism. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain does not exhibit prominent odd-even effect for nematic - isotropic transition temperatures (fig. 16.a). Odd-even effect is observed only up to second member of the series. Though smectic phase is

4 (4''- n-ALKOXYBENZOYLOXY) 4'- NITROBIPHENYL

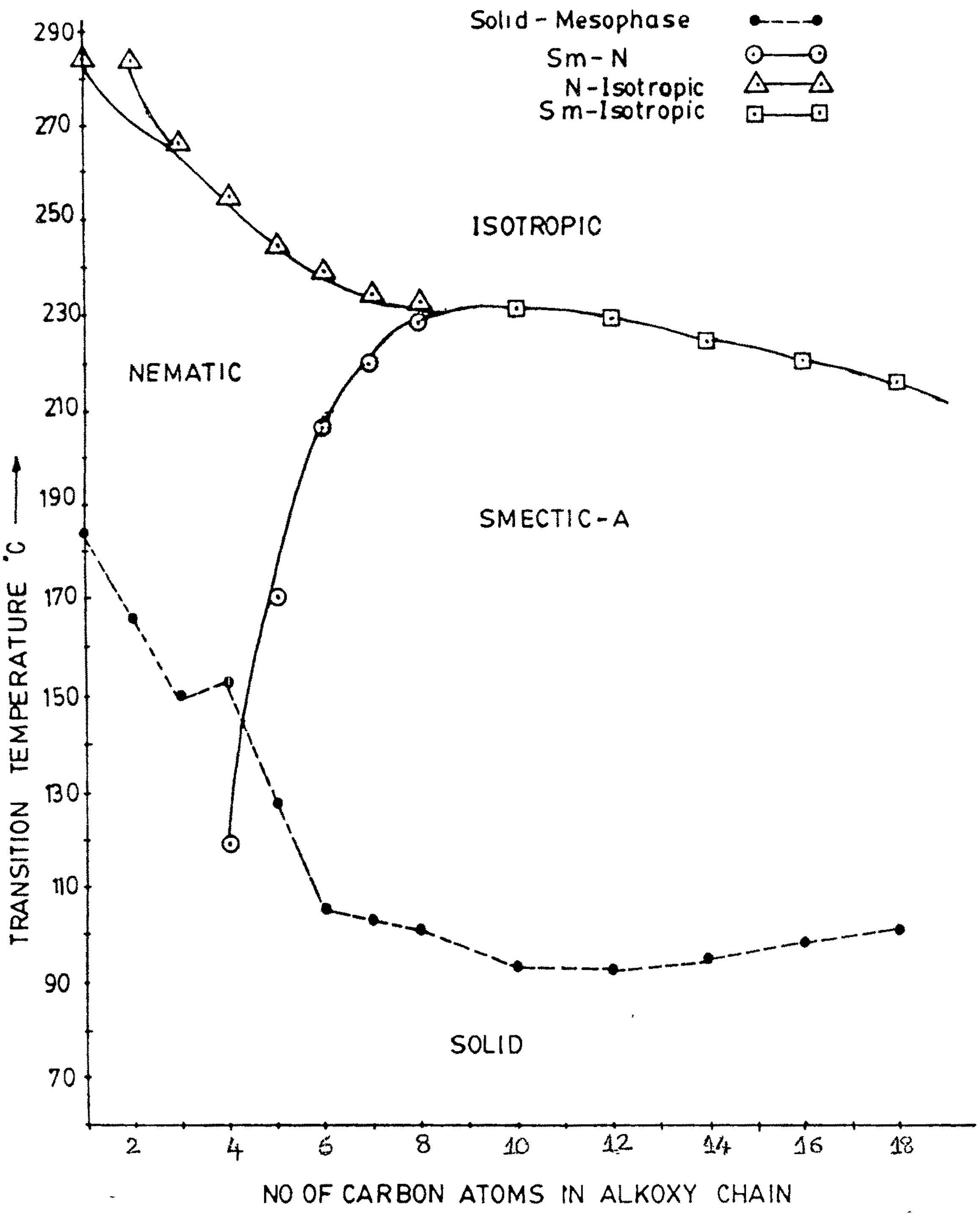


FIG.:- 16.a

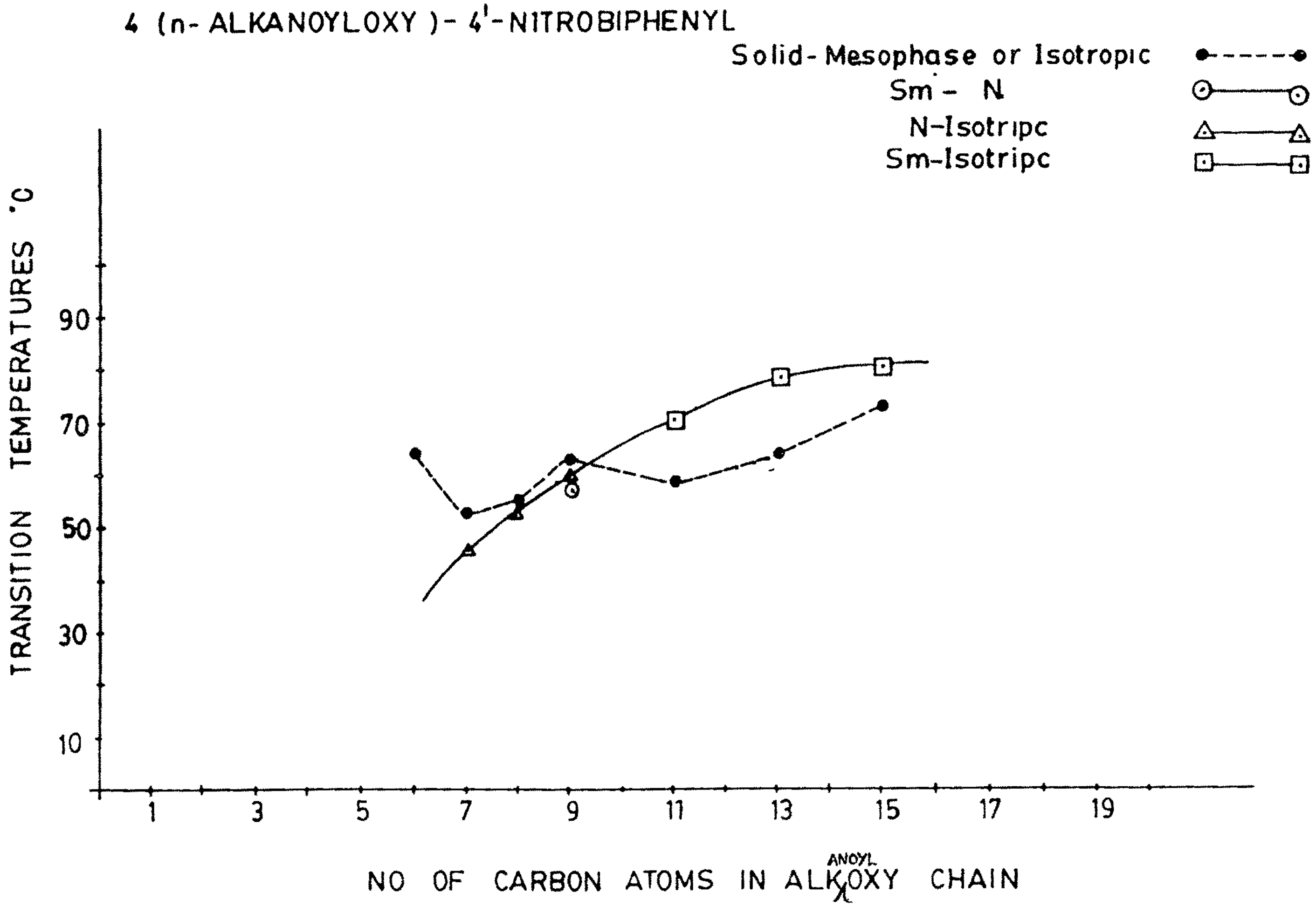

4 (n- ALKANOYLOXY)- 4'-NITROBIPHENYL
Solid- Mesophase or Isotropic
Sm - N
N-Isotripc
Sm-Isotripc
TRANSITION TEMPERATURES °C
90
70
50
30
10
1
3
5
7
9
11
13
15
17
19
NO OF CARBON ATOMS IN ALKANOYLOXY CHAIN

FIG ·16·b

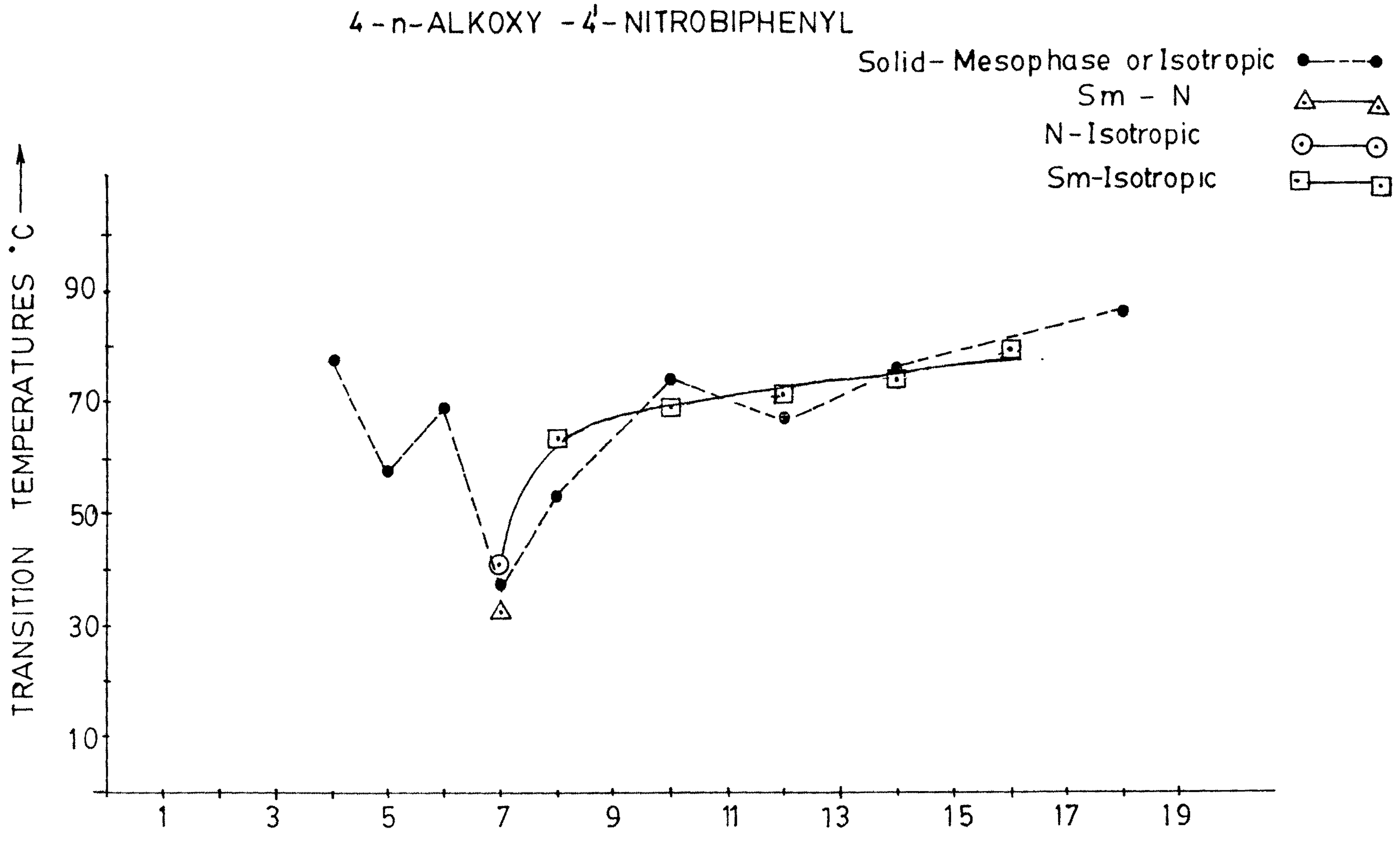

4-n-ALKOXY-4'-NITROBIPHENYL
Solid-Mesophase or Isotropic ●----●
Sm - N △—△
N-Isotropic ⊙—⊙
Sm-Isotropic ⊡—⊡
TRANSITION TEMPERATURES °C
90
70
50
30
10
1
3
5
7
9
11
13
15
17
19
NO OF CARBON ATOMS IN ALKOXY CHAIN

FIG : 16.C

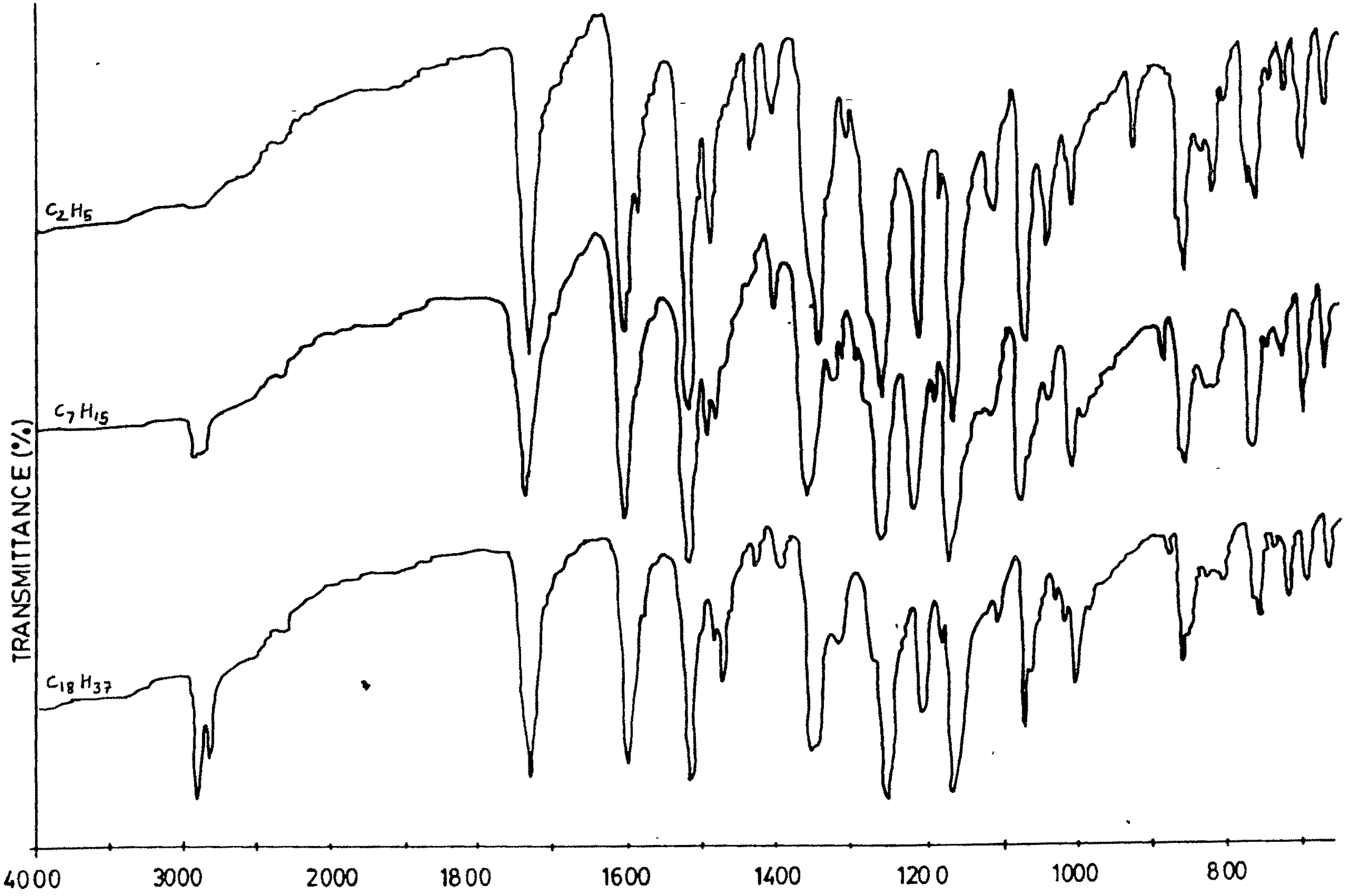


Fig: 17.a: IR Spectra of Mesogens of Series - I

Fig: 17a

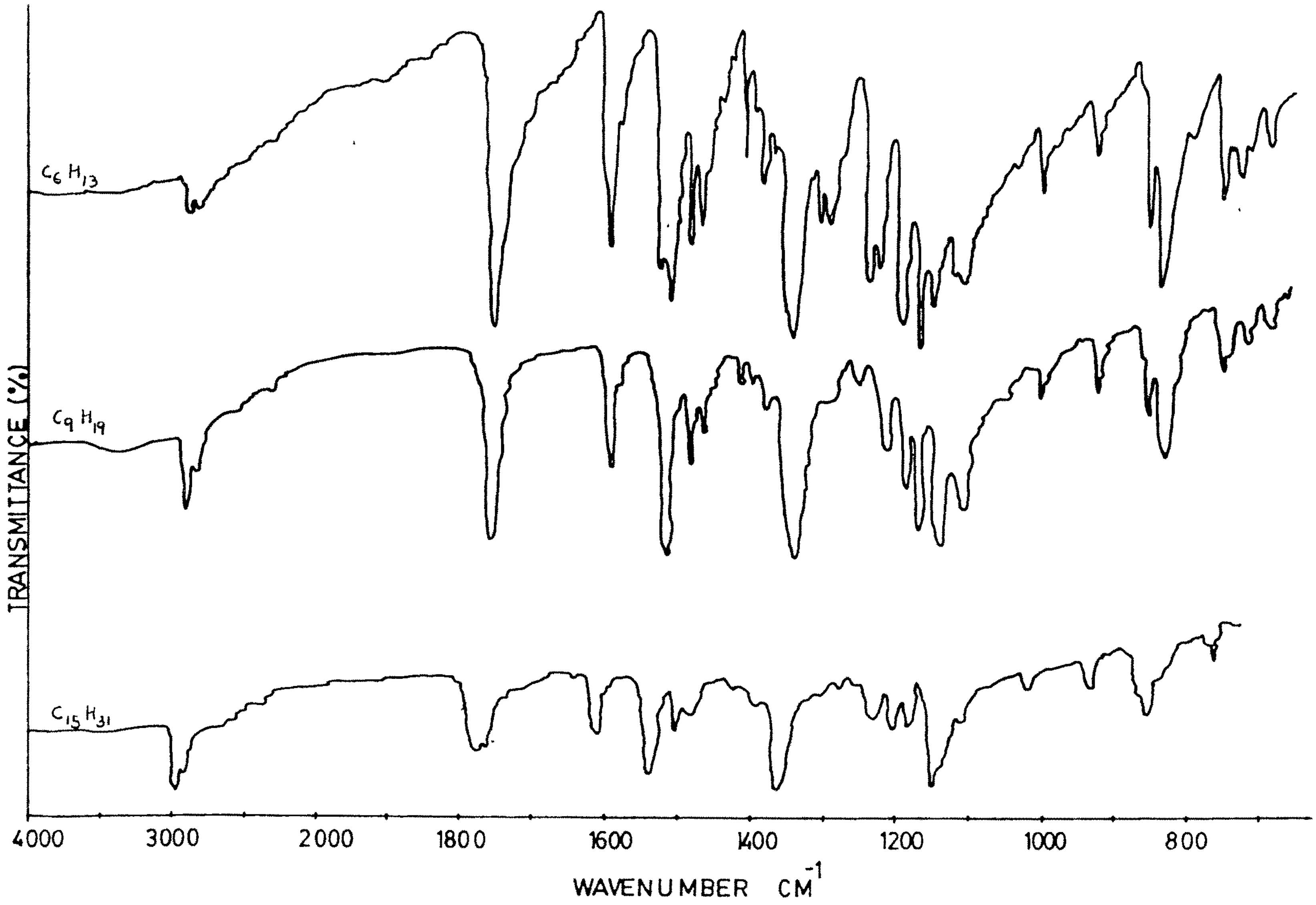


Fig:17·b IR Spectra of Mesogens of Series - II

Fig:17b

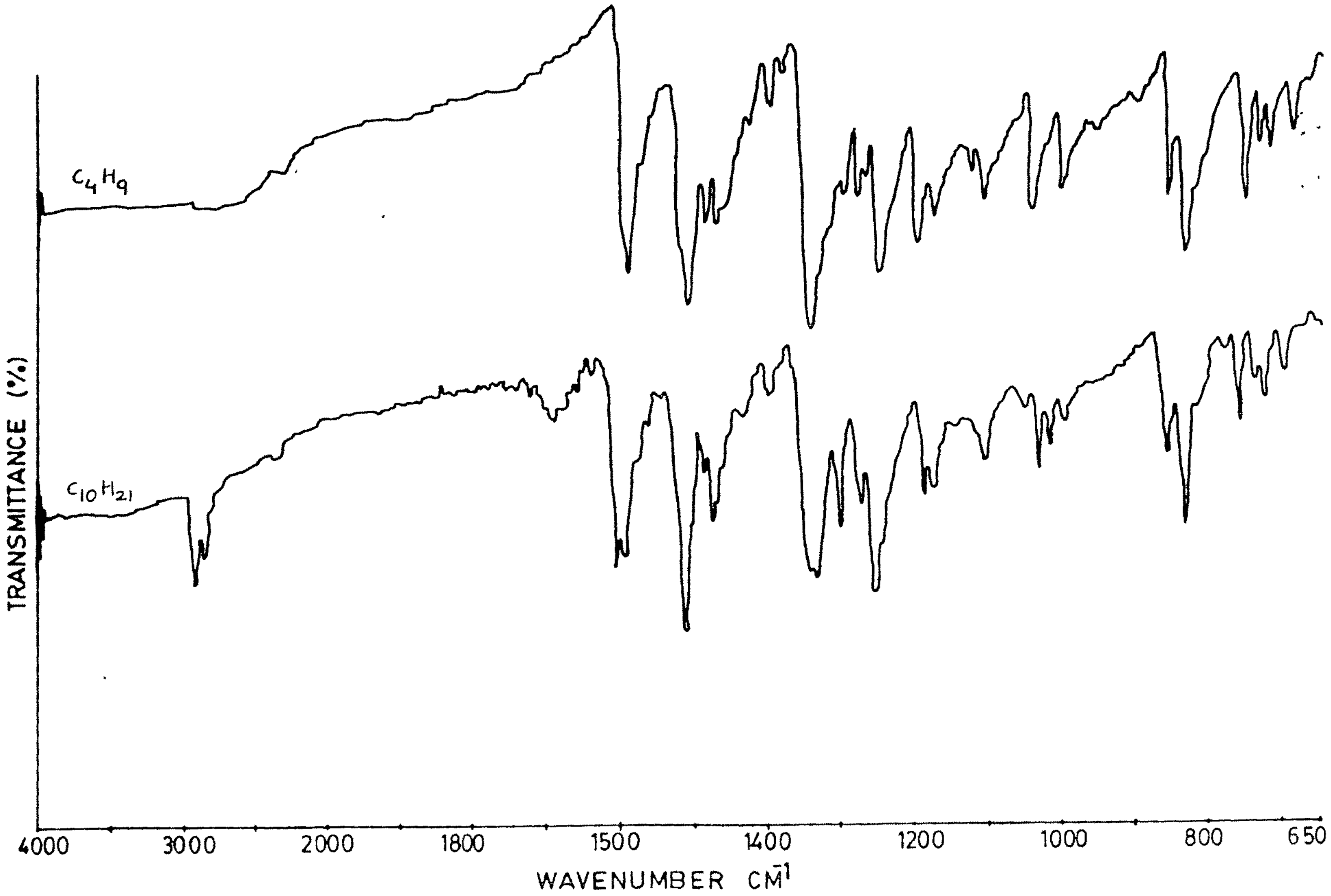


Fig. 17.C: IR spectra of Mesogens of Series-III

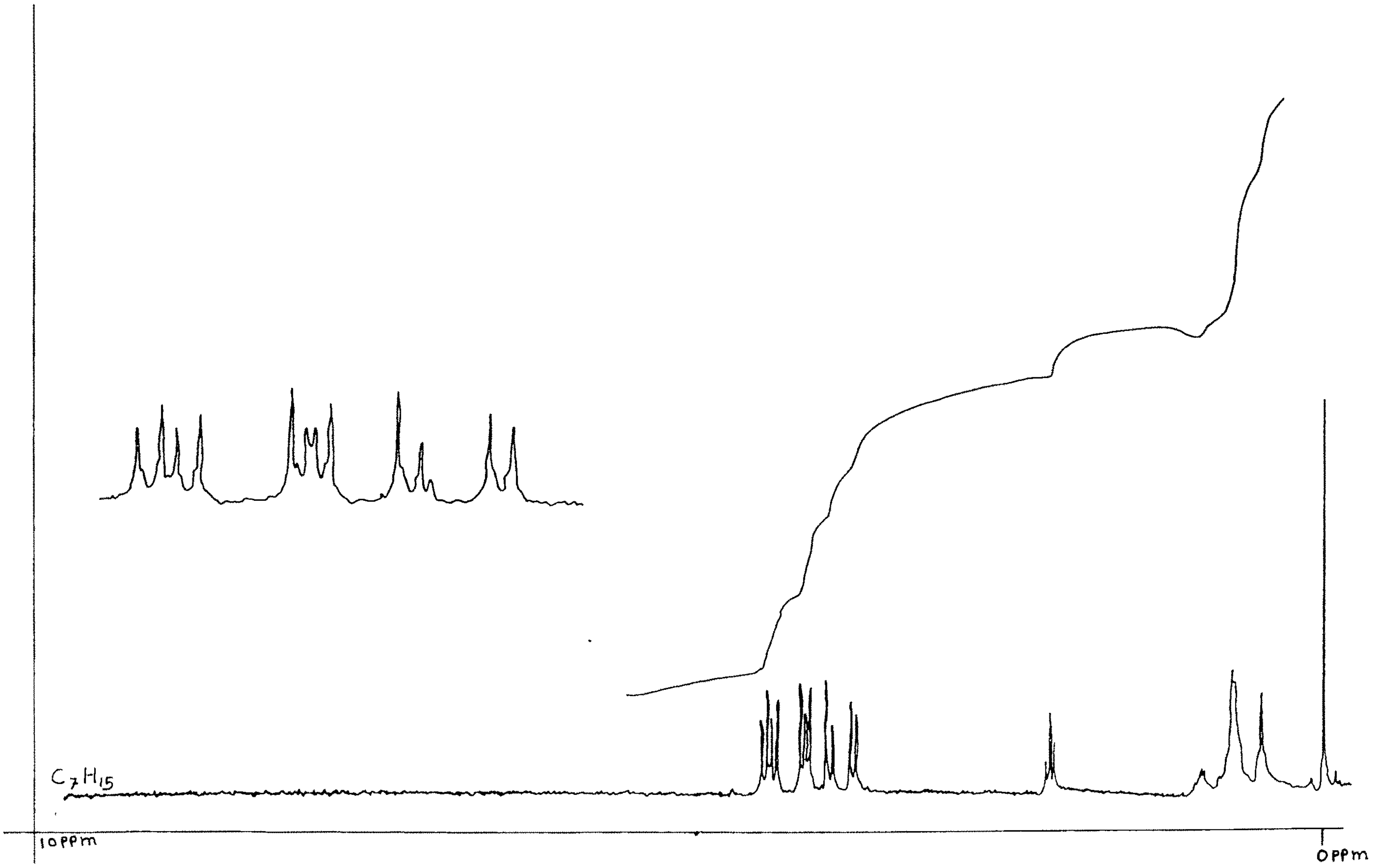


FIG · 18 a

NMR Spectra of Mesogen of Series- I

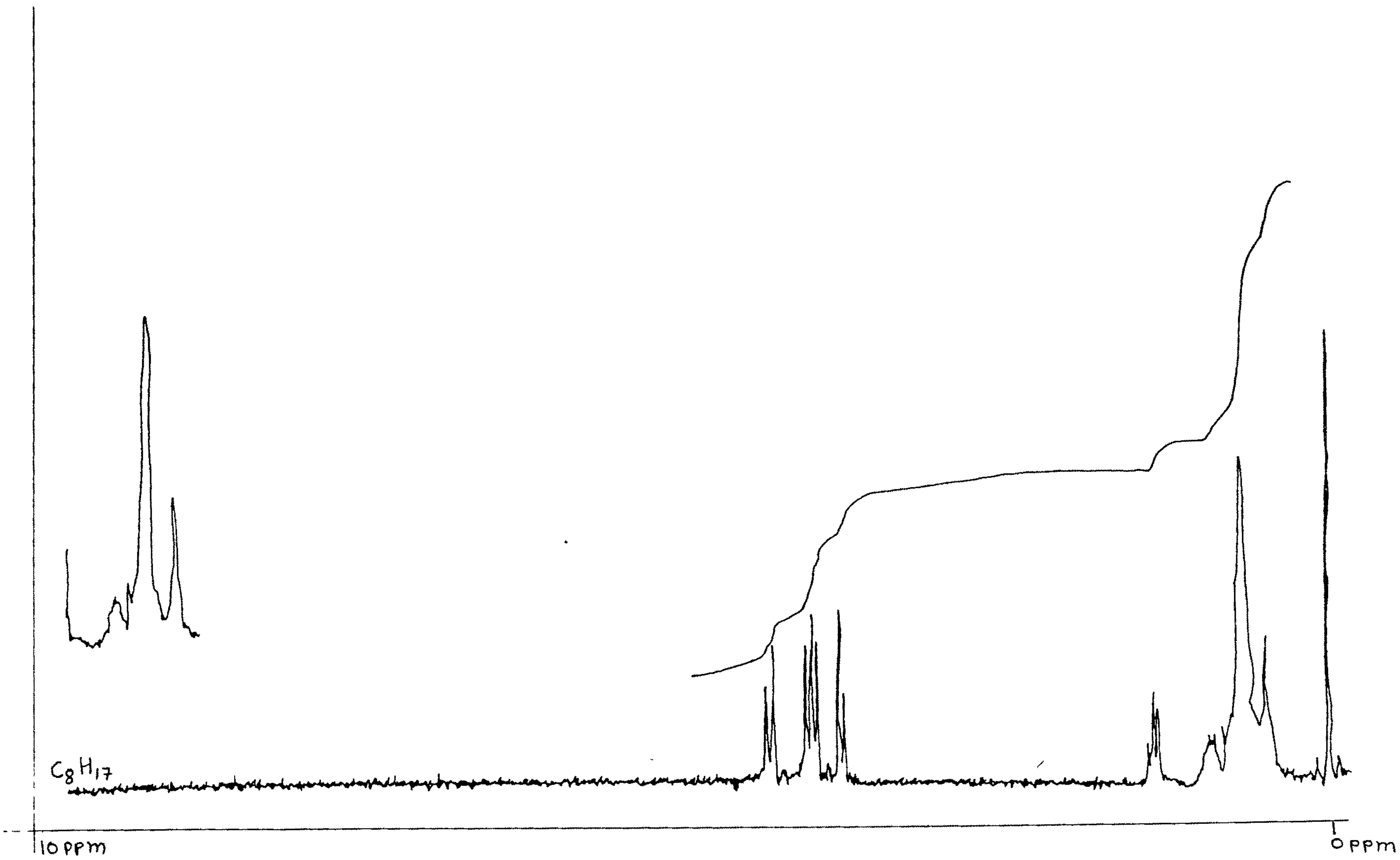


FIG - 18·b

NMR Spectra of Mesogen of Series-II

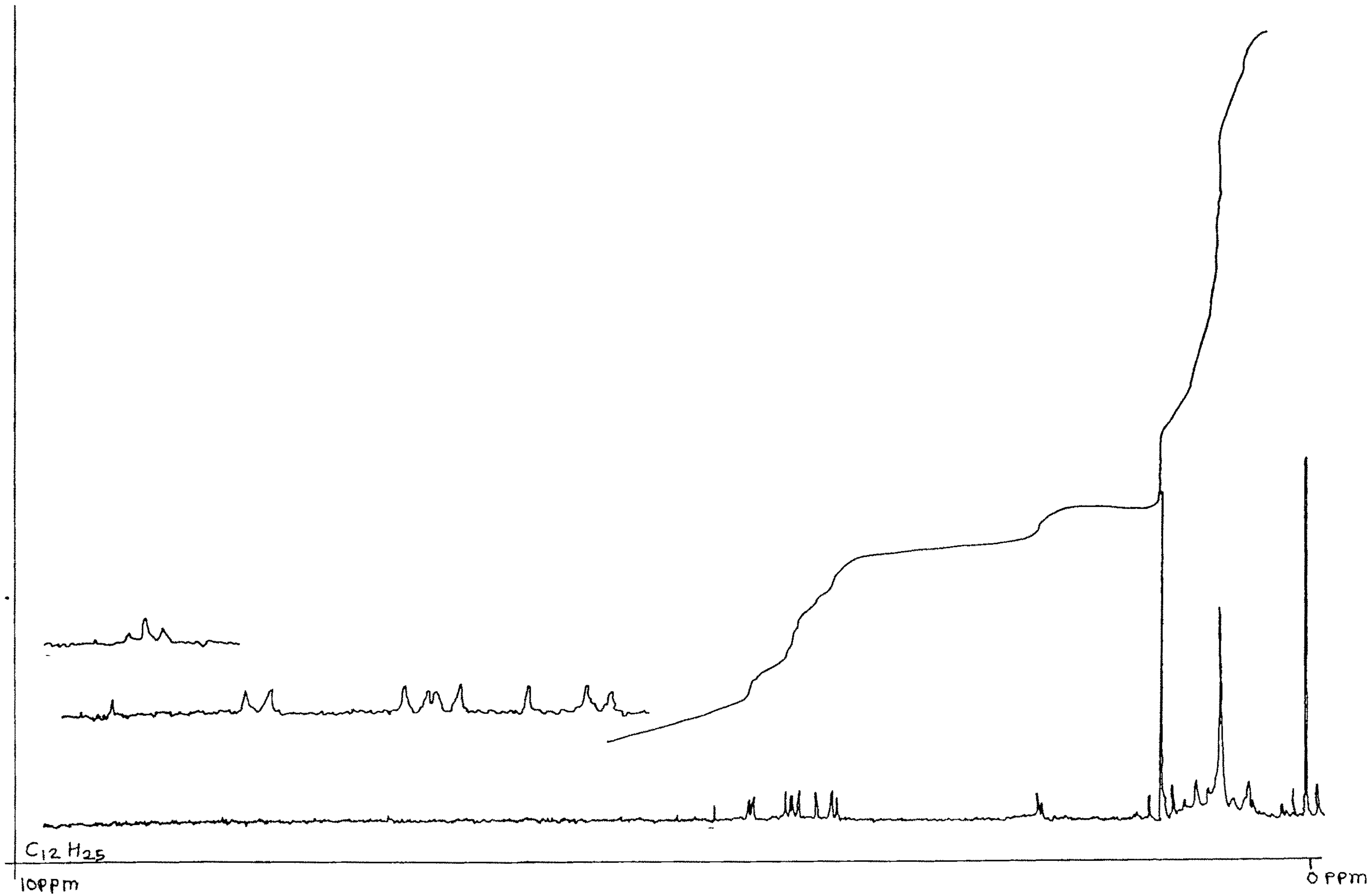
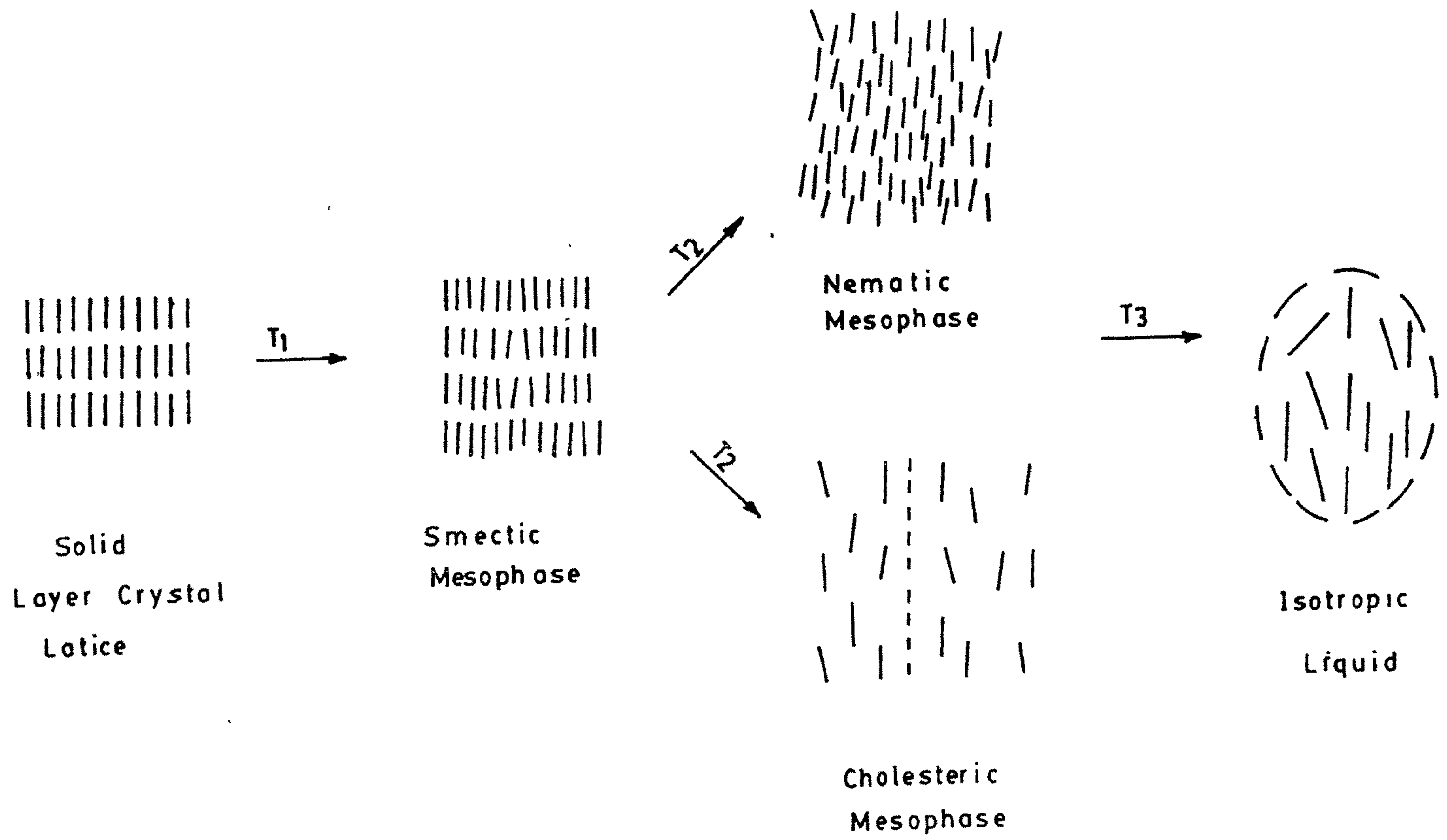


FIG 18·C

NMR Spectra of Mesogen of Series -III


Solid
Layer Crystal
Latice
T1
Smectic
Mesophase
T2
Nematic
Mesophase
T2
Cholesteric
Mesophase
T3
Isotropic
Liquid

FIG·19

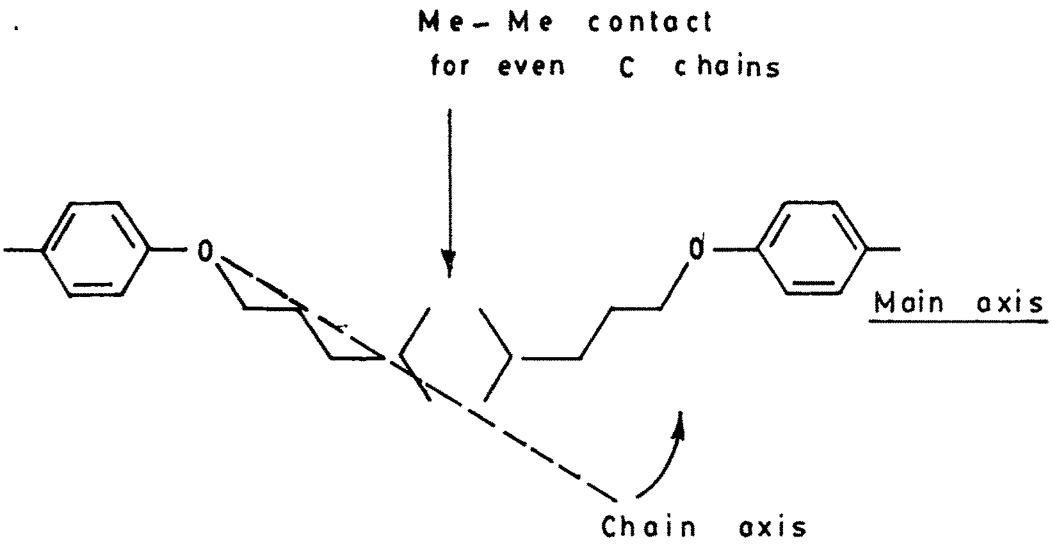


FIG.- 20

observed from the fourth member of the series - I, the smectic - nematic transition temperatures do not exhibit odd-even effect. Reference to fig. 16.a indicates that the smectic - nematic transition temperature curve rises steeply. Naturally it will be difficult to observe odd - even effect if there is small variations in these transition temperatures.

The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits smooth rising curve in the case of series II and series III. (fig. 16.b, 16.c). In the case of series II and III, the mesophases commence very late in the series hence odd - even effect can not be observed for nematic - isotropic, smectic - nematic or smectic - isotropic transition temperature curves. The odd - even effect normally peters out from hexyloxy or heptyloxy derivatives (327).

The molecules, forming liquid crystals, generally possess the basic skeleton of relatively rigid aromatic or alicyclic rings with alkoxy or alkyl chains attached to one or both the ends. Within the isotropic or nematic phases, different regions of each molecule are continuously in contact with parts of neighbouring molecules. The energy of the system depends on different conformations of molecules, London - Vander Walls dispersive forces between the neighbouring molecules and on steric repulsions between different molecules (328). For the mesogenic homologous series, Gray (329, 330) has successfully used the concepts of molecular arrangement and complex molecular interactions with lateral and terminal attractions between neighbouring molecules. These ordering forces, which are strongly dependent on molecular separations, have to compete with disordering thermal fluctuations.

Due to the presence of balancing lateral and terminal cohesions and long lath-like molecules, mesogenic compounds melt in stages. They pass through one or more ordered intermediate stages before changing to isotropic liquid phase. The molecular layer structure of the smectic phase occurs in temperature regions where lateral attractions dominate, while the parallel molecular arrangement of nematic phase occurs in a temperature interval with predominant terminal attractions. Thus at the crystal - smectic transition, the primary terminal cohesions of the molecules are overcome and at the smectic - nematic or smectic - cholesteric change, the strong lateral attractions are overcome, and a nematic or cholesteric mesophase is formed. The molecules, either in the nematic or in the cholesteric mesophase are maintained by the residual lateral and terminal chesions. On further heating all the Vander Walls forces are again broken down and the molecules pass into randomly arranged isotropic liquid state. These changes can be represented schematically as shown in the fig. 19.

In a mesomorphic homologous series, usually the mesomorphic - isotropic transition temperatures change in a regular manner. The increment of each methylene unit brings about regular changes in the transition temperatures of the series. Gray (218) explained this behaviour by taking into consideration the chain length of terminal alkyl or alkoxy group. As the alkoxy or alkyl chain is lengthened, the separation of the aromatic centres, which are highly polarizable and have permanent dipolar substituents, is increased, consequently there should be a decrease in the strength (218) of the terminal intermolecular cohesions. However, Gray (218) and Maier and Baumgartner (331) have suggested that the addition of each methylene unit simultaneously increases the overall polarizability of the molecules and the lateral intermolecular attractions. The lower homologues are purely nematic, i.e. for the short chainlength compounds, the separation of the aromatic nuclei is at a minimum and the terminal cohesions are strongest. As we ascend the series, smectic phase commences from the middle members of the series, because as the alkyl chain - length increases, the lateral cohesive forces are also increased and the molecules align themselves in the layered structure before passing to nematic phase. Hence, with increase in the alkyl chainlength, the smectogenic character should predominate at the expense of nematic mesophase. Therefore in a homologous series, at a certain chain - length of alkyl group, no nematic mesophase would be observed and system would exhibit pure smectic phase. At this stage, smetic mesophase will directly pass into isotropic liquid stage, presumably because the terminal intermolecular attaractions are inadequate to maintain the parallel molecular orientation, required for the normal nematogenic homologous series.

A number of other homologous series, however, do not behave exactly as discussed above. In the cholesteric homologous series, the earlier members with shorter alkyl chains exhibit pure cholesteric mesophase, while the higher homologues exhibit both the smectic and cholesteric meshophases. In lower homologues, the terminal cohesive forces are relatively strong, with the increase in alkyl chain - length, the lateral cohesive forces increase and the molecules can align themselves in parallel layered arrangement, before cholesteric mesophase commences at higher temperatures. The cholesteric systems differ from normal nematogenic series in one aspect, i.e. the last members of nematogenic series exhibit purely smectic mesophases, while those of cholesterogenic series exhibit smectic mesophases along with the cholesteric phase. This may be attributed, possibly to the broad and flat cholesterol moiety.

In the case of series 4-n-alkoxybenzylideneaminofluorenones and 4-n-alkoxybenzylideaminobiphenyls, having substitution in 2 or 3 positions (332) and 2-methyl-1, 4-phenylene bis (4'-n-alkoxybenzoates), (244) the last members of the series do not exhibit pure smectic mesophases. In all the above mentioned series, the steric effect increases the thickness of the molecules. This should make it more difficult for the molecules to pack economically side by side in a parallel alignment and should result in a weakening of the lateral intermolecular cohesions. Thus even at the octadecyloxy derivative the smectic - nematic curve does not merge with the nematic - isotropic curve. Dave et al (333 - 335) have studied a number of naphthylidene Schiff bases and have evaluated the effect of broad naphthalene nucleus. They have reported that in all these series, even the last member is not purely smectic, but exhibits polymesomorphism. This can be attributed to the increase in breadth which reduces lateral cohesive forces and to exhibit pure smectic mesophase, the lateral cohesive forces should be much higher than the terminal forces. In such systems, even in the last member, the molecules are so arranged that on heating, the molecular layers slide over one another and do not get disrupted to the disorderd isotropic stage, but pass to the nematic mesophase. A nematic phase is thus obtained from the smectic mesophase, on further heating the disruption is complete to give the isotropic liquid. However, there are also a number of homologous series, exhibiting pure nematic mesophase upto the last member of the series, without the commencement of the smectic phase (218, 336 - 338). All these series contain a lateral substituent, which increases the breadth of the molecules to such an extent that the economical packing of the molecules is not achieved to give a smectic mesophase.

The alternations of nematic - isotropic transitions (odd - even effect) have been discussed by different workers. Gray (329) has tried to explain such behaviour for nematic - isotropic transitions in terms of the conformation of the alkyl chain. He has considered the Zig-Zag conformation for the chain, as evidenced from the X-ray studies of crystalline state of some liquid crystalline compounds.

The increase in chain-length will have the following effects and the nematic-isotropic transition temperatures will be determined by those effects which predominate : -

(i) The longer molecules will be rotated less readily out of the ordered state.
(ii) The overall polarizability increases with each added methylene unit.
(iii) The frequency with which readily polarizable aromatic parts of the molecules lie next to one another in the fluid nematic melt will decrease i.e., the residual lateral attractions will tend to decrease.
(iv) Each methylene unit forces apart polarizable centres in the molecules and decreases the residual terminal attractions.

Effects (i) and (ii) would increase the nematic - isotropic transition temperatures and (iii) and (iv) would decrease the nematic - isotropic temperatures. Thus rising transition lines are obtained where the effects (i) and (ii) predominate and vice versa. Keeping this in view, the rising mesomorphic - isotropic transition lines are found in the series whose transition temperatures are low, and the residual attractions are weak. Gray has explained the alternations of nematic isotropic transition temperatures by a diagramatic representation of the possible relative orientations of terminal methyl groups in an end-to-end packing of the molecules of n-alkyl aryl ethers, such as p-n-alkoxybenzoic acids. For short alkyl chains, if the chain extends strictly along its own axis (dotted line in fig. 20), then the terminal methyl groups present different faces to one another or to other end groups in the molecules depending on whether the chain is even or odd. The different resultant attractive forces would affect the energy of the system and account for an alternation of the transition temperatures.

With the higher homologues the alkyl chain may be forced (curved arrow in fig. 20) p.148 into line with the main axis defined by the more rigid aromatic parts. Gradually the end groups contact would become the same in nature for odd even carbon chains, and can explain the petering out of the alternation as the series is ascended.

So far, the effects of changes in terminal attractions between the molecules on the nematic - isotropic transition temperatures have been considered, but the effect of residual lateral interactions between the molecules, which would also play some role in determining the thermal stability of the nematic mesophase, has not been discussed.

Maier (339), Maier (331)* and Baumagartner* have also tried to explain the alternation effect on the basis of their study of the dipole moment and dielectric anisotropies of a nematogenic homologous series.

Maecelja's (328) theory explains the odd - even effect in isotropic - nematic transition temperatures and entropies. From the geometry of p ,p' -di-n-alkoxyazoxybenzenes, they have shown that the additon of carbon atom C_2, increase the anisotropy of the molecule and helps the ordering process, subsequent addition of atom C_3 hinders the ordering, atom C_4 helps again, and so on. As the chains become longer, their flexibility makes the effect progressively smaller until for long end chains, it becomes unnoticeable. Pines et al, (340) have measured the order parameters in a series of nematic liquid crystals p-n-alkoxy azoxybenzenes, by 13_C NMR. The oerdering exhibits an odd-even alternation along the series. They conclude that the benzene rings rotate or flip about the para axes, at a rate greater than 1 KHz for the whole series, throughout the nematic ranges.

de Jeu and Van der Veen (341) have reviewed some experimental results on the variation of the nematic - isotropic transition temperatures T_{NI} and evaluated molecular structure with the aid of expressions for T_{NI}, from molecular statistical theories.

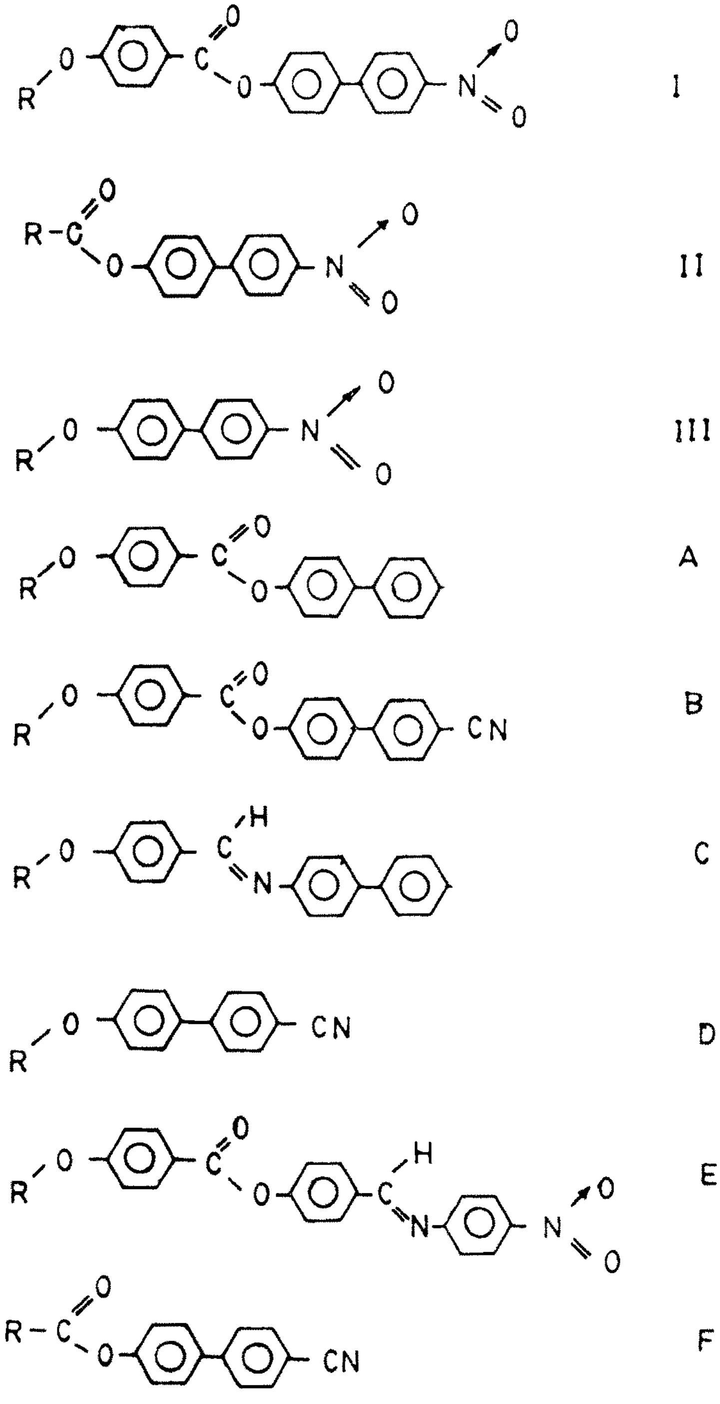


FIG.-21

There is a close relationship between mesomorphism and molecular constitution of orgainc compounds. Hence, thermal stability, a measure of mesomorphism can be correlated with the molecular constitution of the compounds.

Table 35.C summarizes the average thermal stabilities of different mesogenic homologous series synthesized i.e.

(i) 4(4"-n-Alkoxy benzoyloxy)-4-nitrobiphenyls - I

(ii) 4-n-Alkanoyl$\overset{\text{oxy}}{\wedge}$-4'-nitrobiphenyls II

(iii) 4-n-Alkoxy-4'-nitrobiphenyls III

and are compared with those of

(iv) Biphenyl 4-p-n-alkoxybenzoates - A (342)

(v) 4(4"-n-Alkoxy benzoyloxy)-4'-Cyanobiphenyls- B (343-345)

(vi) 4(4'-n-Alkoxybenzylidene)-aminobiphenyls- C (346)

(vii) 4-n-Alkoxy-4'-cyanobiphenyls - D (302)

(viii) 4(4'-n-Alkoxybenzoyloxy) benzylidene -4"-nitroanilines - E (347)

(ix) 4-n-Alk$\overset{\text{a}}{\text{o}}$noyl$\overset{\text{oxy}}{\wedge}$-4'-cyanobiphenyl - F (348)

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

Reference to table 35.c shows that the smectic and nematic thermal stabilities of series I are much higher than those

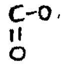
TABLE - 35. c

Average Thermal Stabilities °C

Series	I	II	III	A	B	C	D	E	F
Nematic-Isotropic C_1 - C_{10}	255 C_1-C_8	57.0 C_7-C_8	40.0 C_7	142.9	244.0	169.3	77.0 C_1-C_9	–	73.5 C_5-C_9
Smetic-Nematic or Isotropic C_{10}-C_{18}	233.8	72.35 C_9-C_{15}	77.1	115.6	218.0	152.0	81.2	230.0	67 C_8-C_9
Commencement of Smetic mesophase in the series	C_4	C_9	C_7	C_9	C_8	C_5	C_8	C_1	C_8

of seris - II and III. This is obvious because the molecules of series - I possess 4, 4'- disubstituted phenyl ring more compared to the molecules of series - II and III. Normally increase in the length of a mesogenic molecule by one phenyl ring increases the thermal stabilities of mesophases by about 100 °C (218). However, in the case of Series - I the increase in thermal stabilities is more than 160°C. This may be due to the biphenyl nucleus which enhances over all polarizability of the molecules with the incorporation of phenyl nucleus through a polar group. Series - I is also more mesogenic i.e. all the members exhibit mesomorphism compared to series - II and III. Where mesomorphism appears late in series.

Series - I and Series - A have the same molecular geometry except the terminal substituent. Molecules of Series - I have nitro terminal substituent on biphenyl nucleus where as molecules of series - A do not have a terminal substituent. It is known that a terminal polar group enhances the thermal stability of a system (218) as it increases the length and polarizability of the molecules. This is evident from the comparisom of mesogenic thermal stability of series - I and A (Tasble - 35.c). The difference between the thermal stabilities of series - I and A is of the order of 110°C. This shows very potential effect of a terminal nitro group on the mesomorphic properties of homologous series. The molecules of series - I and Series - B differ in terminal groups at one end only (Fig. 21). Molecules of series - I have terminal nitrogroup where as molecules of series - B have cyano group at that end. The reference to table 35.c shows that there is a very little difference between the thermal stabilities of two series. Cyano and nitro groups increases polarity of the molecules of both the series. Both are strongly polar groups. Due to this reason both the series have very little difference in their thermal stabilities. However, series - I is more smectogenic compared to series - B. The smectic phase commences much early in the case of series - I and nematic phase is eliminated from the decyloxy member of the series. This might be due to the favourable adjustment of molecules in smectic layers having terminal nitro group. Gray (349) has explained the effect of terminal nitro group on mesomorhpism in detail. The nitro group provides favourable packing of the molecules in the layers which enhances the smectogenic tendencies in the molecules of series - I. Series - B exhibits re-entrant phenomena. Re-entrant nematic phases are absent in the case of series - I. It is reported that - CN group is more conducive to re-entrant phenomena compared to - NO_2 group (77, 78, 89).

Molecules of series - I and series - A have the same molecular geometry except the terminal nitro group. In the case of series - C, the molecules differe in central group and in terminal nitro substituent. molecules of series - I have terminal nitro group where as molecules of series A and C do not have terminal substituent at that end. Molecules of series - C have - CH=N - as the central linkage whereas molecules of series - I have an ester -  $\underset{\overset{\|}{O}}{C}-O$ central linkage. It is known that a terminal polar group enhances mesogenic thermal stability of the system as it increases the length and polarizability of the molecules. This is reflected in the thermal stability behaviour of series - I (Table - 35.c). The smectic and nematic thermal stabilities of series - I is much higher compared to those of series - A and C. This shows very potential effect of a terminal nitro group on the mesomorphic properties of a homologous series.

Reference to fig. 21 shows that molecules of series - I and E differ in central linkages as well as in mode of phenyl nucleus. Molecules of series - I have an ester linkage and biphenyl nucleus where as molecules of series - E possess an ester and an azomethine linkage. Totally both the series have three phenylene units - though series - I has two directly linked i.e. a biphenyl nucleus. Incorporation of ester and azomethine linkages increases the acoplanarity of the system (244, 350). To re~~s~~duce the steric interaction one of the phenyl ring goes little out of plane compared to another phenyl ring. Naturally series - E will be more acoplanar due to the presence of two central linkages. Over and above that a biphenyl nucleus in series I will impart higher polarizability compared to two phenyl rings joned by a linking group (218). This indicates that in both the series the factors favorable to smectic mesophase prevails. However, forces which are non-conducive to smectogenic tendencies are also present in both the series. The reuslts indicate that deterrent forces are less pronounced and over all length and polarizability of the molecules give rich meosmorphism in both the series.

The smetogenic tendencies of series - E is more pronounced. The comparison of smectic thermal stability of C_4 - C_{18} members of series I and E indicates that the smetic thermal stability of series - E are greater by 38°C compared to those of series - I. It will be difficult to explain this behaviour of series - E. A qualitative explanation can be forwarded based on trans - conformation of series - E which will help closer packing of the molecules. The length and polarizability of an azomethine linkage also will induce smectogenic tendencies. These factors explain the pronounced smectogenic tendency of series - E.

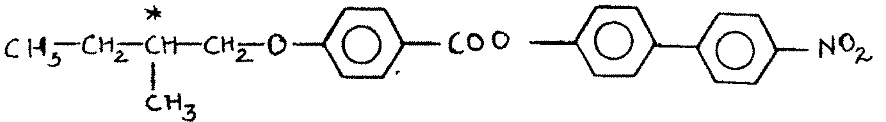
The molecules of series II and F, differ in their terminal substituent. Molecules of series - II have a - NO_2 substituent at one end whereas molecules of series F possess - CN substituent at that end (fig. 21). The reference to table 35.c indicates that the smectic and nematic thermal stabilities of series F are higher than those of series II. Comparision of the C_9 homologue of both the series indicate that the smectic thermal stability of series F is also higher compared to that of series - II. Comparision was limited to C_9 members as higher homologues of series F are not reported. This is exactly opposite trend compared to the one observed in the case of series - I and

series - B. This is quite interesting. Simple Biphenyl molecules having 4, 4'-disubstitution will have more pronounced effect of the terminal groups. It seems that -NO_2 group will not have fullest breadth increasing effect in the case of series I but it will impart breadth to the molecules of series F as indicated in figure (21). Even the molecular models also indicate similar behaviour. Naturally increase in the breadth will have deterrent effect on the stability of both the phases. This explains the mesogenic behaviour of series - II.
The molecules of series - III and series - D also have the difference in terminal groups. In this case also (table 35.c) the smectic and nematic thermal stability of series - D are higher than those of series III. The explanation given above can be extended to series - III. The increase in the breadth of the molecules of series - III compared to series - D would be responsible in decreasing the thermal stabilities of series III (fig. 21).

The comparision of series I, II and III has provided very interesting observations.

Thermal stabilities of series - I are higher than the cyano (CN) analogue of series - I. In the case of series II and III a reverse trend is observed.

A chiral derivative of series I was prepared having following structure.



(*MBBNB)

The homeotropic tendency of lower temperature smectic phase makes it difficult to characterise it by observing the texture of the phase. However, focal - cones are observed between 167 - 205°c in the homeotropic region. This indicates that it may be a smectic A phase. The higher temperature smectic phase appears with stripes - a very distinct texture is observed. The smectic phase is similar in texture reported by Goodby et al (351). They have designated such a phase as chiral smectic A. The higher temperature phase is a chiral nematic exhibiting classical texture of cholesteric phase.

The comparision of mesogenic behaviour of chiral mesogen *MBBNB with the n-butoxy analogue of series - I (ABNB) will be quite interesting. *MBBNB can be considered as the 2 - methyl analogue of n - butoxy homologue.

*MBBNB

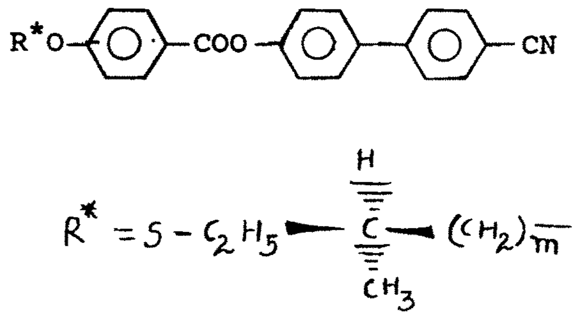
$$K \xrightarrow{167\,^{\circ}c} S_A \xrightarrow{205\,^{\circ}c} S_{mx} \xrightarrow{215\,^{\circ}c} \overset{*}{N} \xrightarrow{225\,^{\circ}c} Iso$$

ABNB

$$\begin{tikzcd}
K \arrow[rr, "153\,^{\circ}c"] & & N \arrow[dl, "119\,^{\circ}c"] \arrow[r, "255\,^{\circ}c"] & Iso \\
& S \arrow[ul, "107\,^{\circ}c"] & &
\end{tikzcd}$$

The above comparision shows that chiral analogue exhibits two smectic phases along with a cholesteric phase. The butoxy analogue exhibits a monotropic smectic and a nematic phase. The smectic thermal stability of butoxy analogue is much lower compared to the chiral analogue but nematic thermal stabilities of butoxy analogue is higher than the cholesteric mesophase of *MBBNB.

Normally branching on the alkoxy chain affects smectic, nematic and even the cholesteric phase. The deterrent effect is more on smectic phase compared to nematic / cholesteric phase. Whereas in the present system the effect is exactly opposite. Comparision of such other homologues with their chiral analogue (352) (fig. 22.a,b) will be quite interesting.



$R^* = S - C_2H_5 - \overset{H}{\underset{CH_3}{C}} - (CH_2)_m$

FIG. 22.a

Linear	n	m	K	Sc^*	$N_r e$	S_A	N^*	I
	6	3	74	-	99	178	231	
	7	4	66	-	-	202	223	
	8	5	72	(42)	0	214	220	

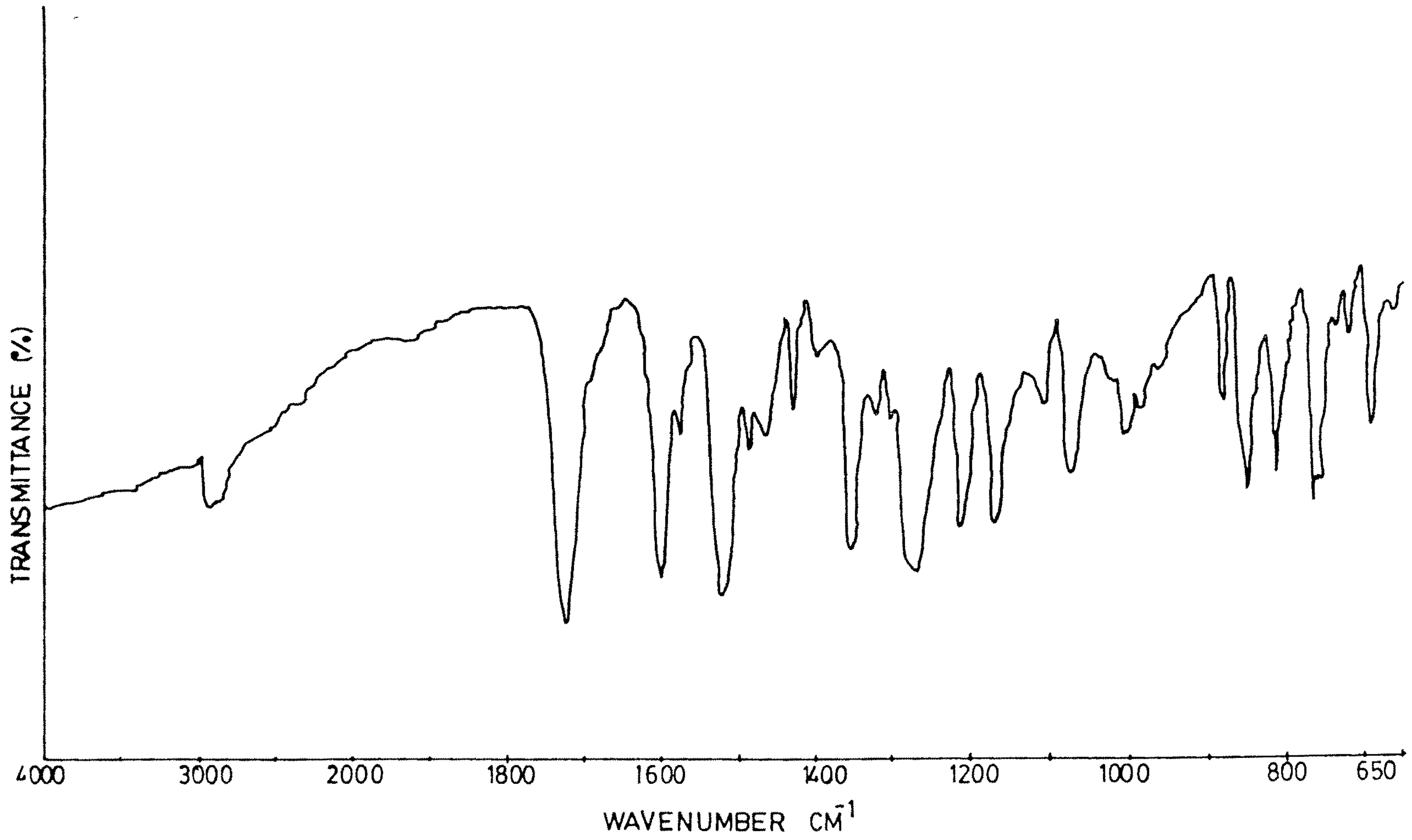
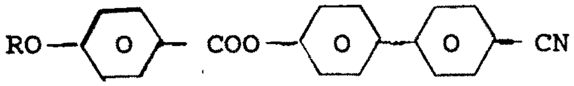


Fig: 23

IR Spectra of *MBBNB



R = C_nH_{2n+1}

Fig: 22.b (343 - 345)

n	k	Nre	SA	N	I
6	. 103	-	-	. 246	
7	. 89	-	-	. 246	
8	. 97	120	. 201	. 240	

The comparison reveals similar behaviour as observed in the present study. This indicates that the chiral centre should not be considered as simple branching. Two protuding groups on the chiral carbon imparts the twist to the molecules which not only help in inducing smectic phases but also imparts them higher thermal stabilities. A molecular model with packing in a smectic phase will give a clear picture. It seems this geometry at chiral carbon when arranges in the cholesteric layers affects the cholesteric phase adversely. This explains that `screw axis' of the chiral molecules play an important role in affecting mesophase thermal stabilities.

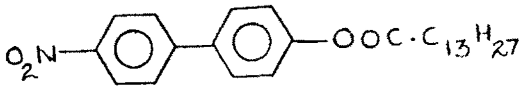
1.2 Mesogenic Binary Systems :

None of the mesogens of homologous series I, II and III exhibit mesophase below room temperature. Binary systems where both the components are mesogens may exhibit solid-mesomorphic transitions at room temperature or they may exhibit phases even around 0°C. With this in view to initiate the study in this direction three binary systems were selected for the study.

Three binary systems comprised of following components were studied.

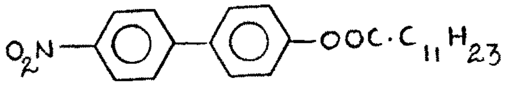
Sys~~a~~tem : A

Component : a



$$K \xrightarrow{64.7\,^{\circ}C} S \xrightarrow{78.6\,^{\circ}C} Iso$$

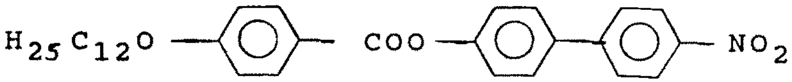
Component : b



$$K \xrightarrow{58.8\,^{\circ}C} S \xrightarrow{71.1\,^{\circ}C} Iso$$

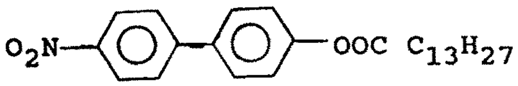
System : B

Component : a



$$K \xrightarrow{93\,^{\circ}C} S \xrightarrow{229\,^{\circ}C} Iso$$

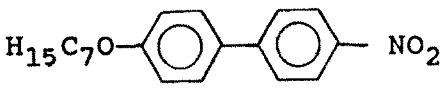
Component : b



$$K \xrightarrow{64.7^\circ C} S \xrightarrow{78.6^\circ C} Iso$$

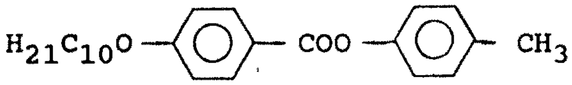
System : C

Component : a



$$\begin{tikzcd} K \arrow[r, "37.0^\circ C"] & N \arrow[r, "40.0^\circ C"] \arrow[dl, dash, "32.4^\circ C"] & Iso \\ S \arrow[u] & & \end{tikzcd}$$

Component : b



(318)

$$\begin{tikzcd} K \arrow[r, "56.0"] & N \arrow[r, "60.5^\circ C"] \arrow[dl, "51.0^\circ C"] & Iso \\ S \arrow[u] & & \end{tikzcd}$$

Binary system - A (fig. 24) exhibits rounded minimum for solid - mesomorphic transition temperatures there by increasing the mesophase range and decreasing solid mesogenic temperatures by about 25°c compared to individual components.

System - B exhibits biphasic regions (fig. 25) where smectic and isotropic phases co-exist.

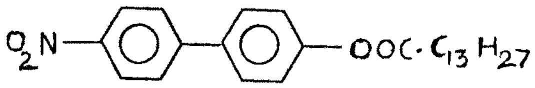
System-C exhibits maxima for mesogenic - isotropic

Table : 35.d

Binary systems

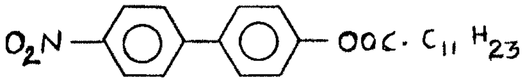
System : A

Component : a



$K \xrightarrow{64.7^{\circ}C} S \xrightarrow{78.6^{\circ}C} Iso.$

Component : b



$K \xrightarrow{58.8^{\circ}C} S \xrightarrow{71.1^{\circ}C} Iso.$

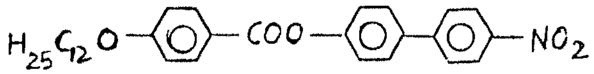
Mole % of a	Transition Temperatures °C Smectic	 Isotropic
10.30	57	73
19.53	52	74
29.12	47	75
38.76	44	75
49.16	47	75
59.89	49	76
70.55	54	78
80.53	61	78
89.00	63	79

Table : 35.e

Binary System

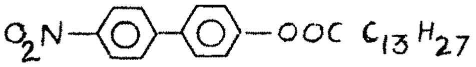
System : B

Component : a



$K \xrightarrow{93^{\circ}C} S \xrightarrow{229^{\circ}C} Iso.$

Component : b



$K \xrightarrow{64.7^{\circ}} S \xrightarrow{78.6^{\circ}C} Iso.$

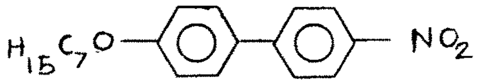
Mole % of a.	Transition Temperatures °C Smectic	S_m + Iso	Isotropic
9.02	64	90	102
17.86	63	98	117
25.95	58	110	134
35.40	56	120	146
46.18	57	135	166
56.16	69	147	174
66.87	76	162	186
75.35	80	176	202
87.76	88	186	211

Table : 35·f

Binary System

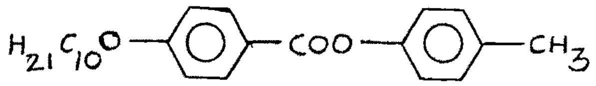
System : C

Component : a



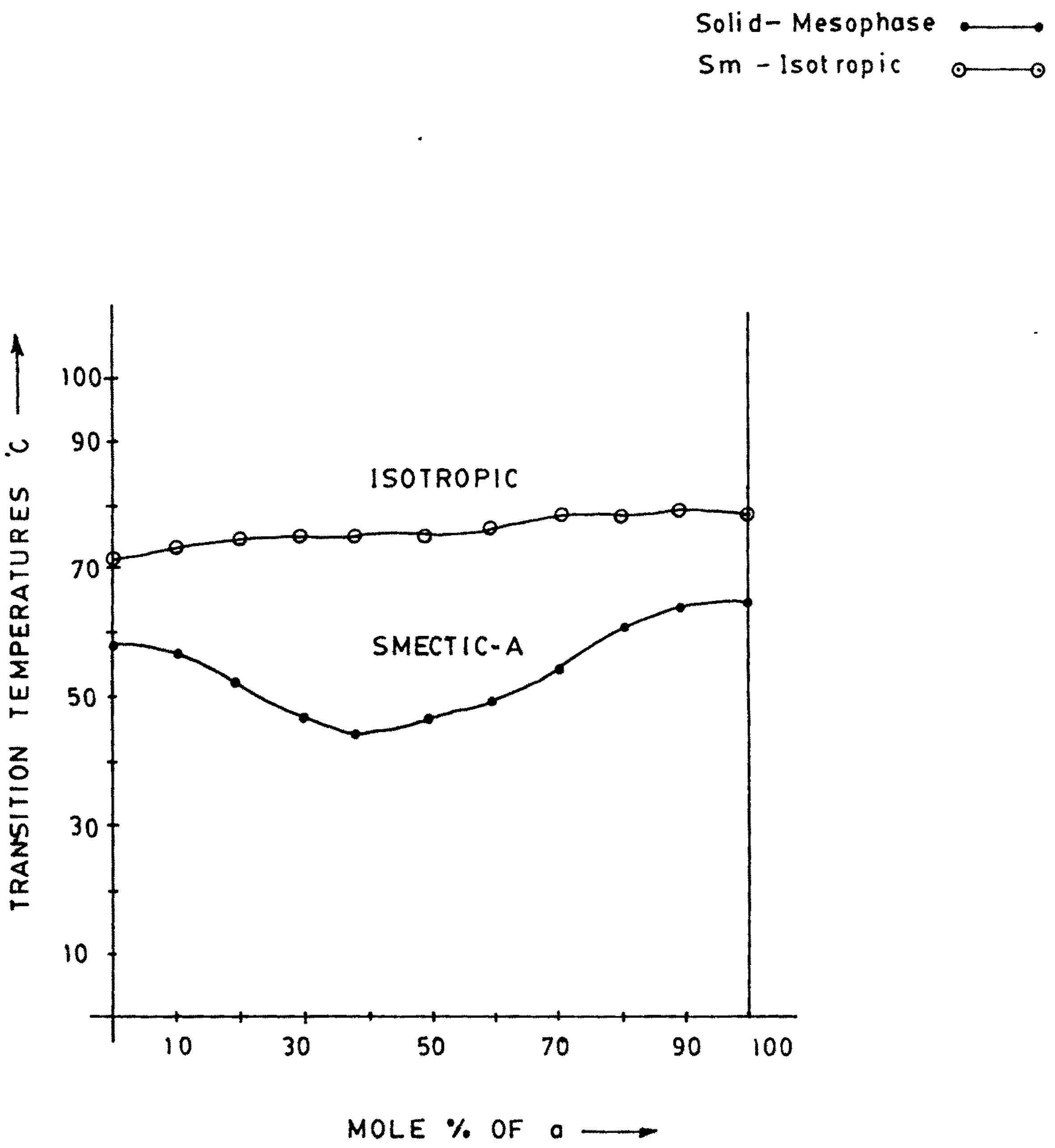
$$\begin{tikzcd}
K \arrow[r, "37.0°C"] & N \arrow[r, "40.0°C"] \arrow[dl, "32.4°C"] & Iso \\
S \arrow[u] & &
\end{tikzcd}$$

Component : b



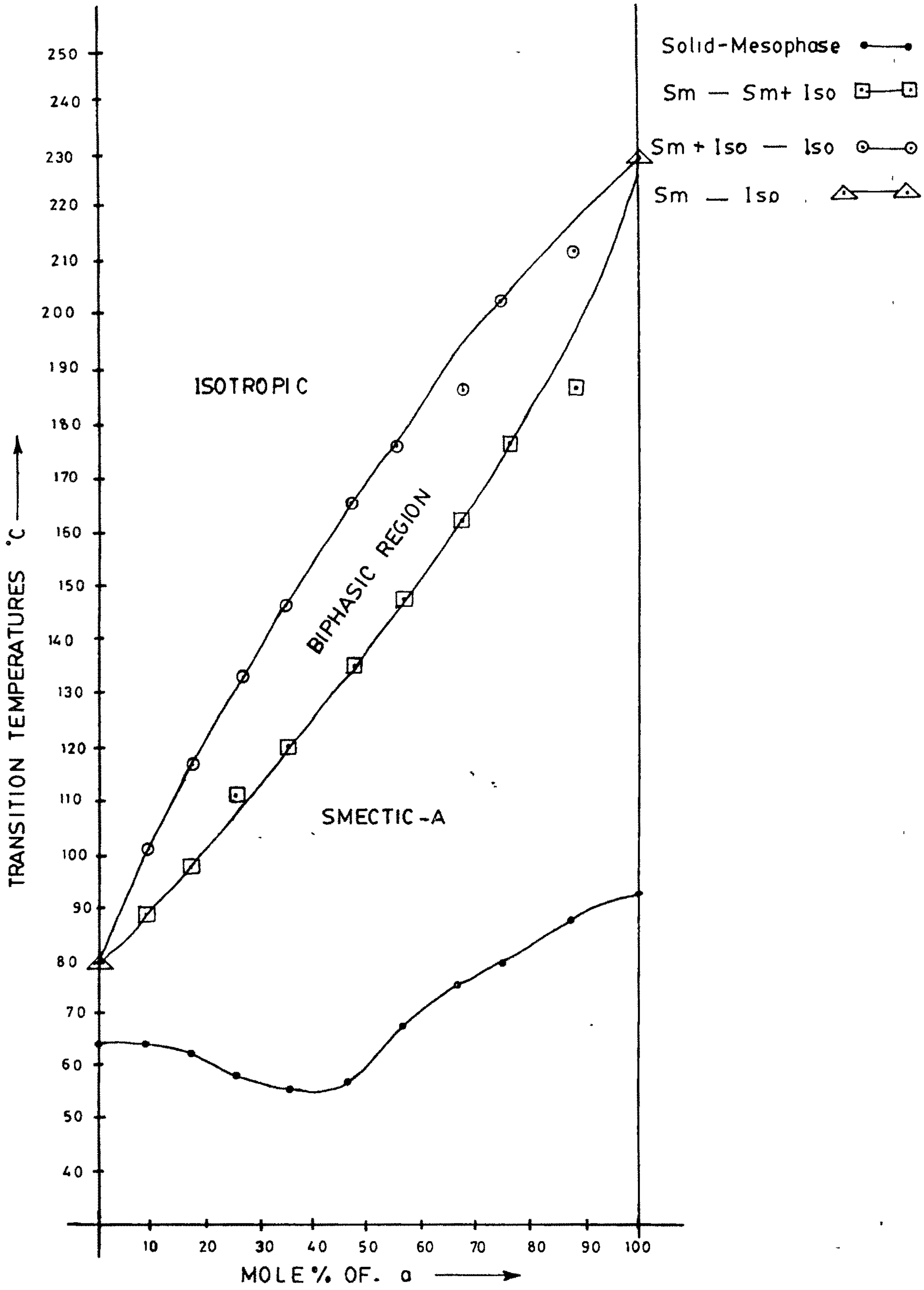
$$\begin{tikzcd}
K \arrow[r, "56.0°C"] & N \arrow[r, "60.5°C"] \arrow[dl, "51.0°C"] & Iso. \\
S \arrow[u] & &
\end{tikzcd}$$

Mole % Of a	Transition Temperatures °C Smectic	Nematic	N+Iso	S+Iso	Isotropic
12.82	53	62	64	-	65
22.27	47	-	-	65	75
32.19	45	-	-	70	77
44.87	Mixture remains smectic on quenching even at 0°C	-	-	72	77
54.72		-	-	72	78
59.25		-	-	71	77
73.31		-	-	62	70
81.44		-	-	56	64
92.52	37	42.5	45	-	47



SYSTEM - A

FIG.:- 24



SYSTEM: B

FIG:- 25

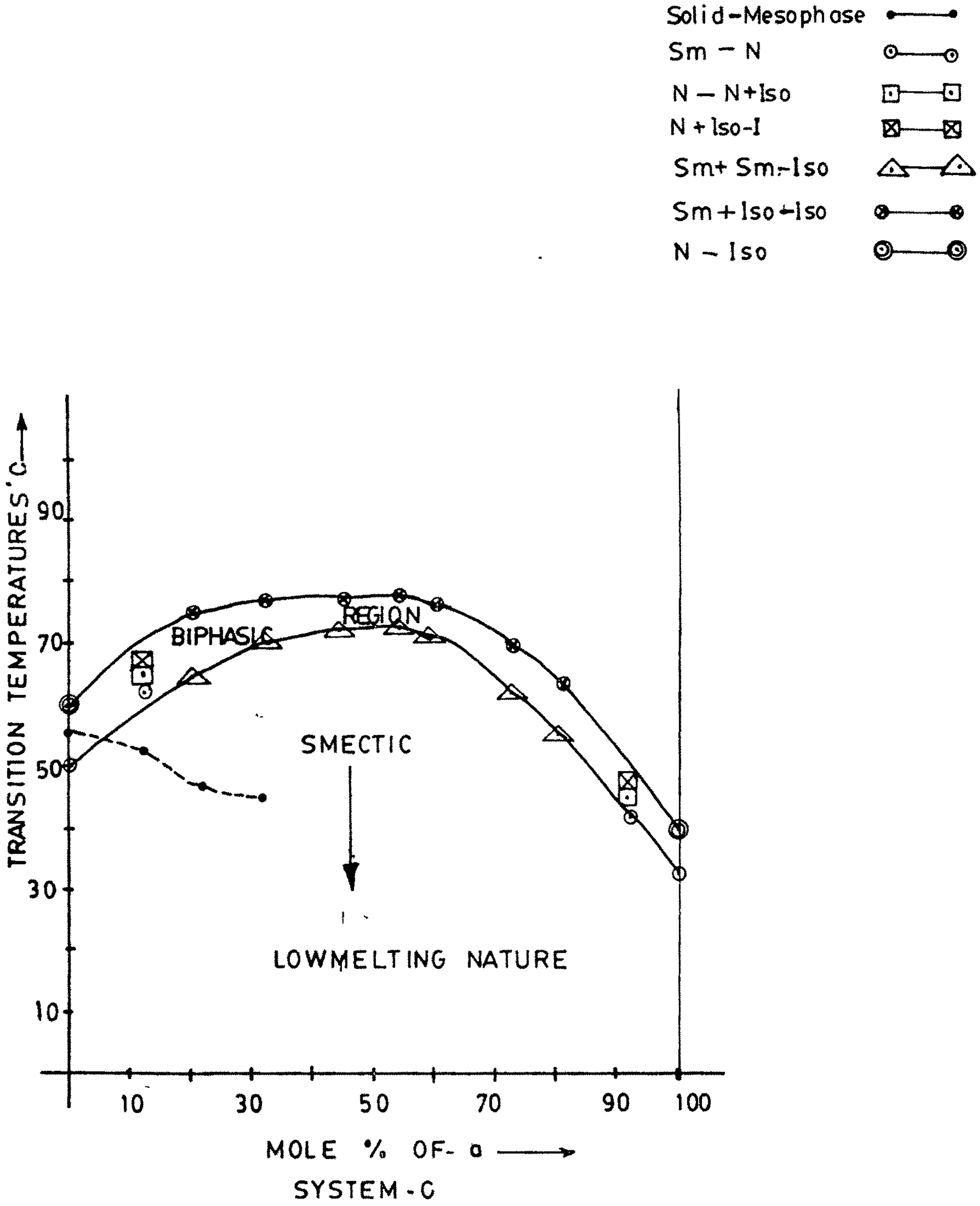

Solid-Mesophase
Sm – N
N – N+Iso
N + Iso-I
Sm+ Sm-Iso
Sm+Iso+Iso
N – Iso
TRANSITION TEMPERATURES °C
90
70
50
30
10
10
30
50
70
90
100
BIPHASIC REGION
SMECTIC
LOWMELTING NATURE
MOLE % OF- a
SYSTEM - C

FIG.-26

transition temperatures. The smectic phase becomes enantiotropic and nematic phase is eliminated from the system. Small area of biphasic region (sm + isotropic) is observed in most of the binary compostions (fig. 26). The enhanced smectic phases and elimination of nematic phase in such systems, where one of the component has strongly polar terminal group, has been observed by many researchers (198, 199) and our group (196, 197, 204, 205). Different explainations are offered including charge transfer complexes. The mixtures of system-C remained mesogenic below 0°C. These mixtures exihibit smectic A phases below room temperature. To envisage applications further study will be carried out regarding the stability of mesophase in terms of time factor at room temperature.

2

CHOLESTERYL DERIVATIVES

2.0 : Cholesteryl Derivatives :

2.1 Series :IV : Dicholesteryl carbonates with flexible and rigid spacers :

Griffin et al, (353) Jin Jung IL et al (354) and Vora et al (355) have reported mesogenic twin dimers and have evaluated the role of flexible spacers and mesogenic moiety including the central linkages on the onset and stability of mesophases. Flexible spacers normally favours nematic phases compared to biphenyl terminal groups. Schiff bases and esters exhibit higher nematic thermal stabilities. They have tried to explain the mesogenic behaviour on conformational aspects of central flexible linkages. They may adopt a fully extended trans conformation or a gauch conformation depending upon the nature of flexible spacers. The pronounced odd-even effect is observed by Griffin et al (353) and Jin Jung - IL et al (354). Cholesteryl carbonates and thiocarbonates are known to exhibit mesomorphism (305, 363). It was thought interesting to design mesogen with terminal cholesterol moiety and central flexible and rigid spacers. With this in view, thirteen dicholesteryl carbonates were synthesized by condensing one mole of dihydroxy and aminohydroxy compound with two moles of cholesteryl choloroformate as described in the experimental section.

The route for the synthesis of all the compounds is given in fig. 27. The transition temperatures are reported in table 12.b. The graph of transition temperatures is plotted against no. of (CH_2 - CH_2 - O) units in central

$$2ClCOOC_{27}H_{45} + HO-X-OH \xrightarrow[\text{Dry Pyridine}]{\text{Dry Benzene}} H_{45}C_{27}OOCO-X-OCOOC_{27}H_{45}$$

For: X→See table : 12 . a

SYNTHETIC ROUTE TO SERIES IV

FIG.:- 27

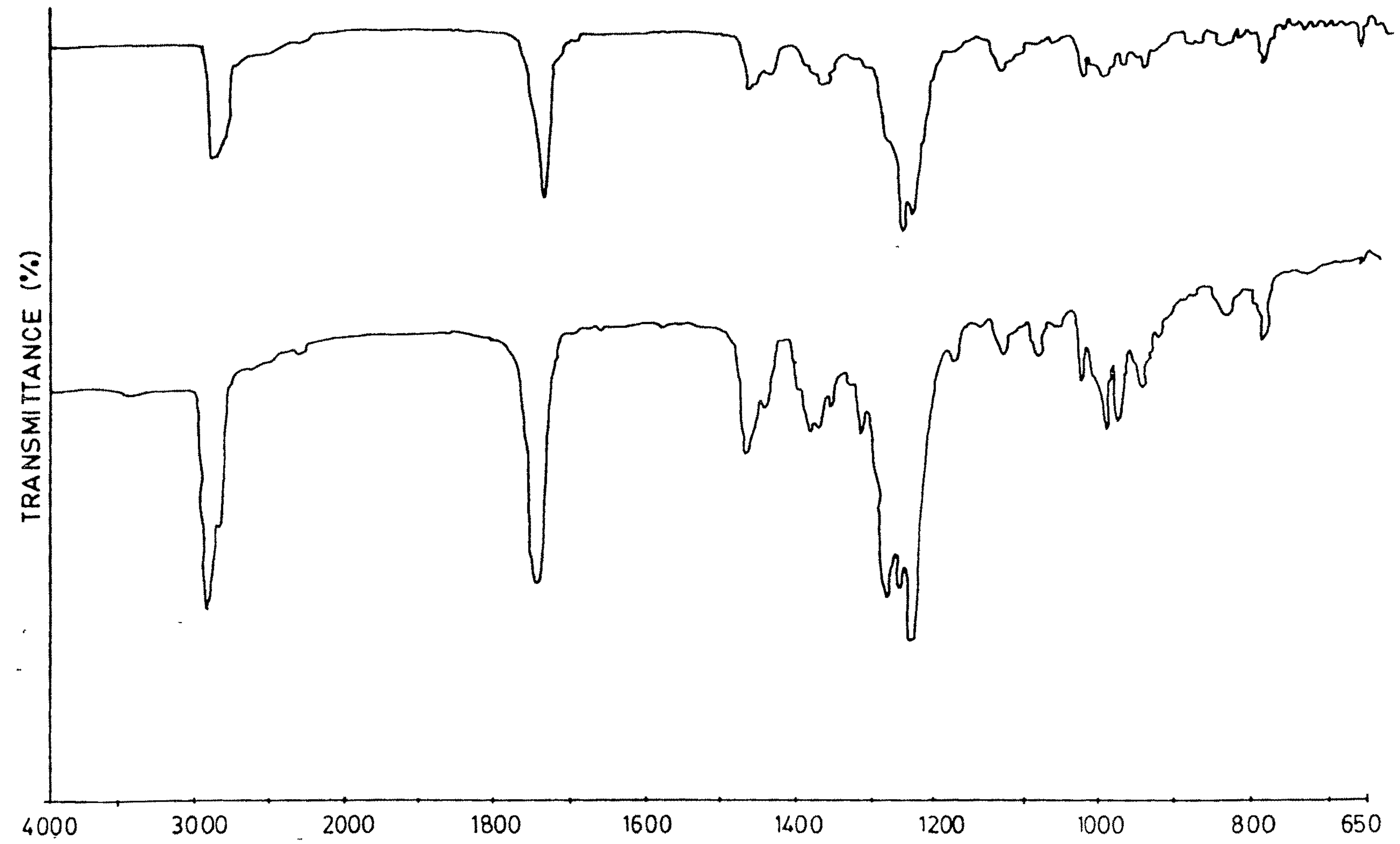


Fig: 28.a

IR Spectra of CC-1 & CC-5

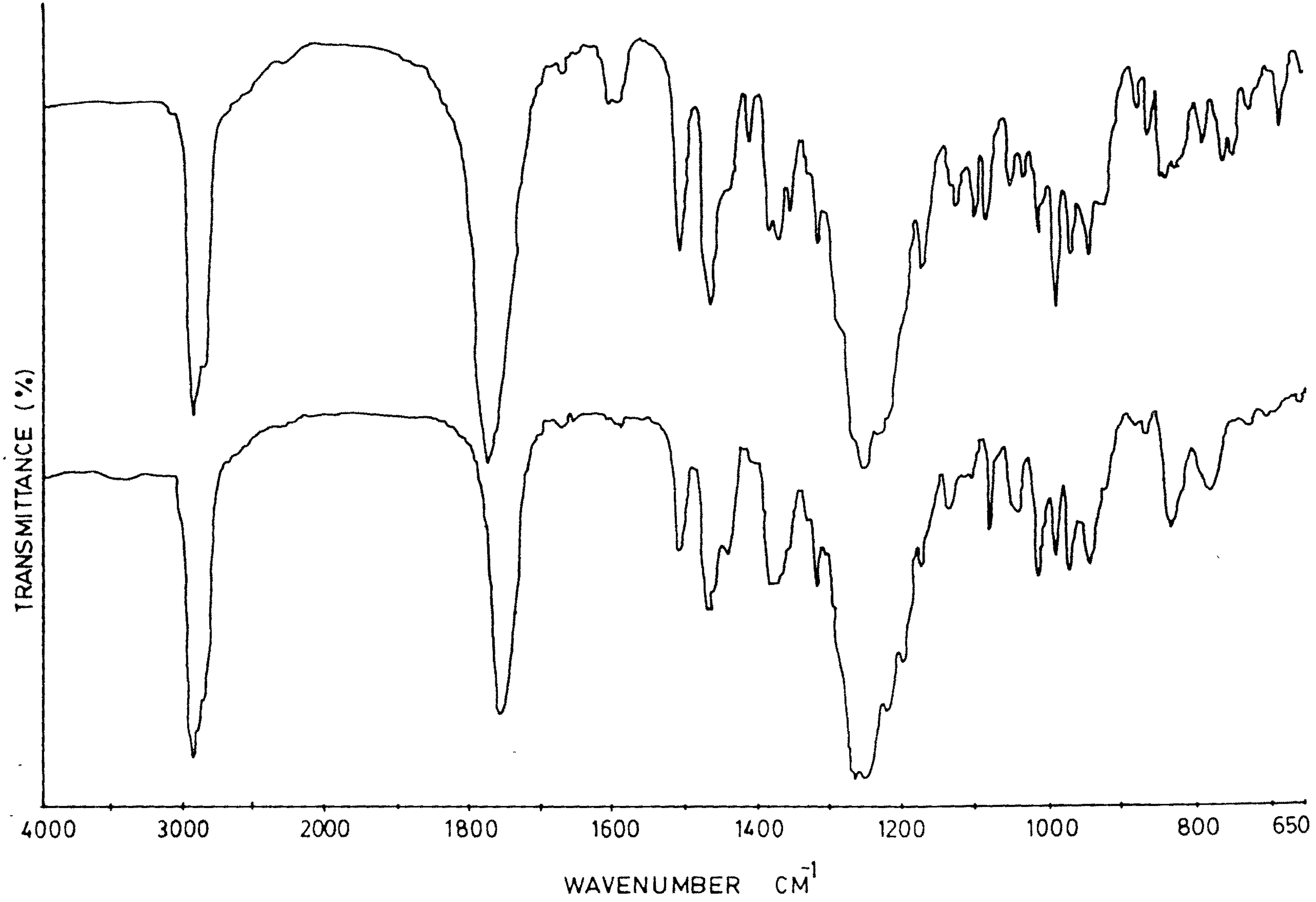


Fig:28·b

IR Spectra of CC-10 & CC-12

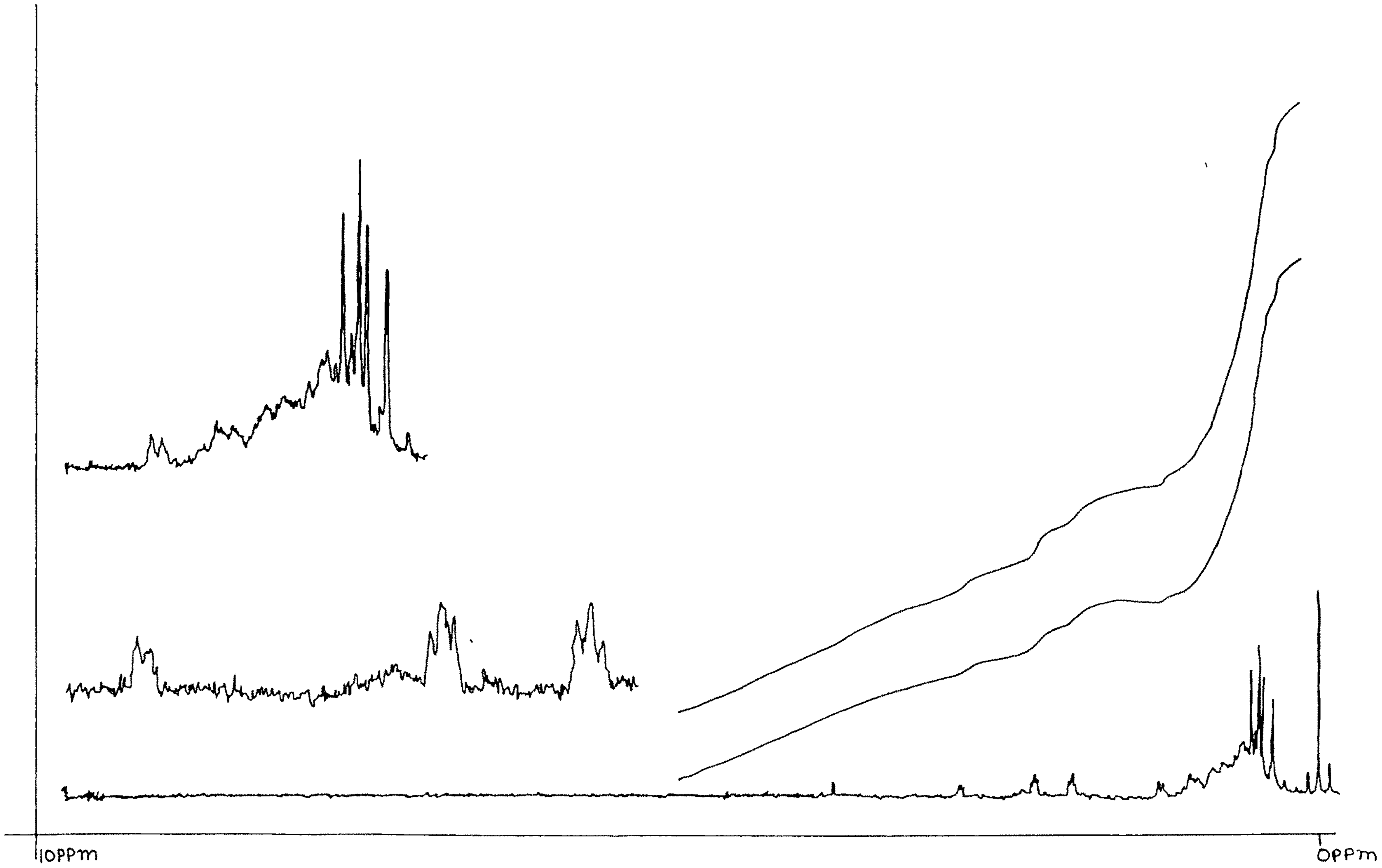
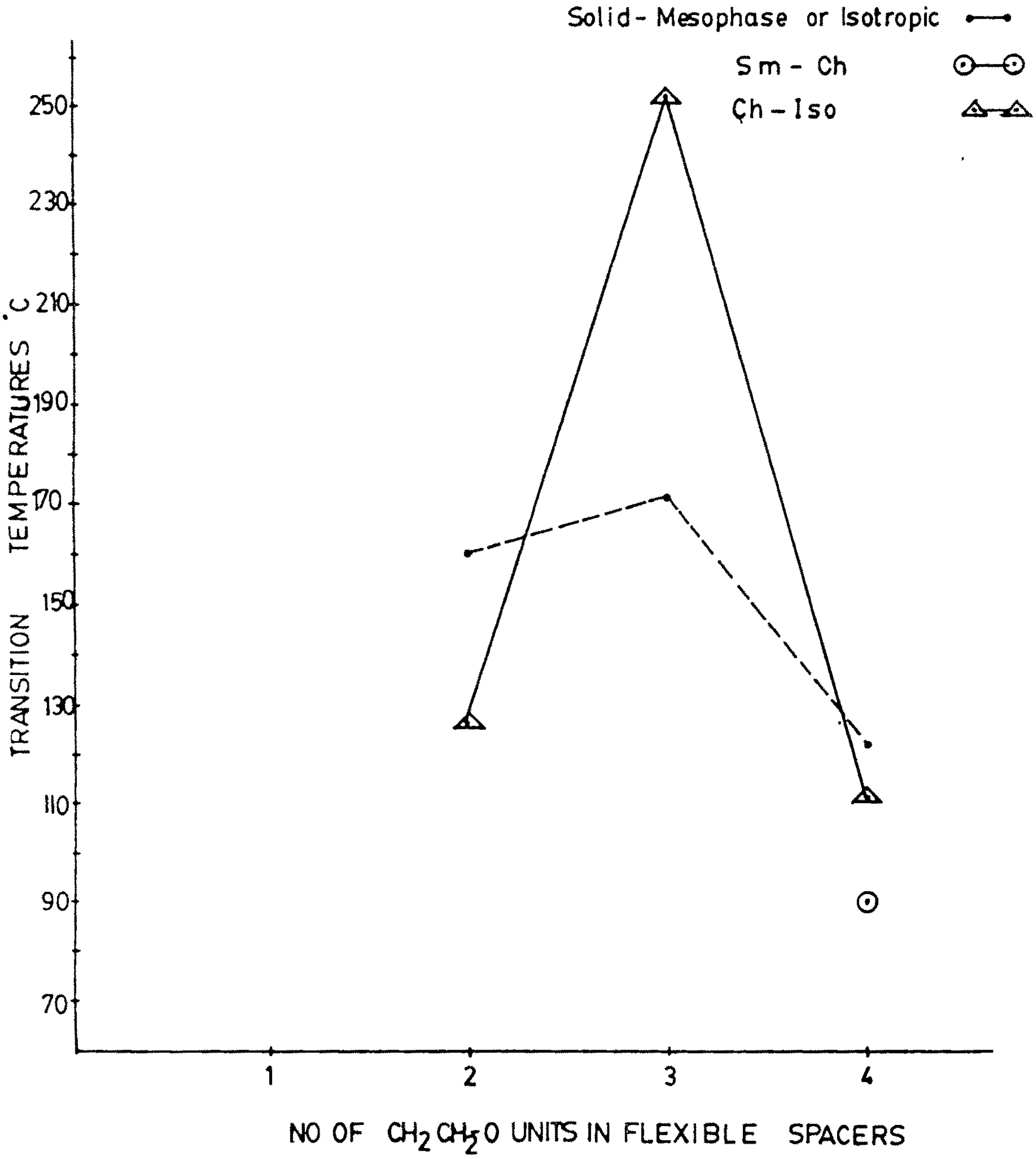


FIG :- 29

NMR Spectra of CC-1

DICHOLESTERYL CARBONATES WITH FLEXIBLE & RIGID SPACERS:



FIG· 30

linkage fig (30).

Reference to table - 12.b shows that except for two, all the compounds exhibit mesomorphism. All the mesogenic compounds exhibit cholesteric phase with one exception. Compound no.3 exhibits smectic phase along with choloesteric phase.

Compound No. 1 to 3 are having the diffenerence of $-CH_2$ $-CH_2$ -O flexible spacer increasing from 2 to 4. The reference to table - 12.b indicates that cholesteric phase is monotropic in nature in compound No 1 and No 3 with lower thermal stabilities where as compound No. 2 exhibits enantiotropic cholesteric phase of higher thermal stability. The system has highly flexible central linkage. The change in mesogenic behaviour of compounds No. 1 to 3 can easily be attributed to classical odd-even effect observed in number of homologous series. Compounds No. 1 and 3 have seven and thirteen (odd) spacers whereas compound No. 2 has ten spacers. The results indicate that odd-even effect is quite marked, comparable to the results of Gray et al (302, 353, 354) and others.

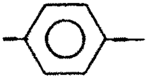
Compound No. 3 exhibits monotropic smectic phase which is absent in other homologues. This can be attributed to the increased length of spacers.

The mesogenic behaviour of compounds No. 4 to 7 is quite interesting. The flexible spacer with α-mehtyl group also exhibits cholesteric phases of comparable thermal stabilities. The geometry of flexible spacers must be getting adjusted in such a way to avoid steric interaction which can only be highlighted by NMR and X-ray study of these compounds.

All these compounds have very high super-cooling tendency. Cholesteric phase persists up to room temperature in some mesogens. Out of four aromatic rigid spacer carbonates (No. 8 to 12), only two (No. 9 and 12) do not exhibit mesomorphism. Compounds having 1, 4 - phenylene substitution (no. 8 and 10) exhibit higher cholesteric - isotropic transition temperatures. The 1, 3 - phenylene substitution (No. 9) is not conducive to mesomorphism. These findings are in support of accepted effect of chemical constitution on mesomorphism. Compound No. 10 has a breadth increasing non-linear bisphenol moiety. Even then, it exhibits enantiotropic cholesteric phases. However, the effect of non - linearity is reflected in its lower cholesteric - isotropic transition temperatures compared to No. 8 and 11 where only one phenylene spacer is present. Non-mesomorphism of compound No. 12 can be attributed to breadth increasing effect of phthaloyl moiety. Dicholesteryl carbonate of polyethylene glycol (compound no. 13) was also synthesized. One mole of polyethylene glycol (Av. mole wt. 400) was condensed with two moles of cholesteryl chloroformate. The dicholesteryl carbonate of polyethylene glycol (400) exhibits smectic phase from room temperature to 107°C. On cooling, it gives homogeneous plane texture of smectic phase. The repeated pressing of the coverslip gives

TABLE - 36

(356 - 358)

Sr.	R	K	Ch	I
1.	-O-OC-CO-O	*(84)	(227)	253
2.	$-OOC-(CH_2)_2-COO-$	-	(208)	217
3.	$-OOC-(CH_2)_3-COO-$	-	-	195.5
4.	$-OOC-(CH_2)_4-COO-$	-	193.8	225.5
5.	$-OOC-(CH_2)_6-COO-$	-	164	183
6.	$-OOC-(CH_2)_8-COO-$	-	(175.8)	180.4
7.	-OOC--COO-	-	-	179

* Monotropic Value

homeotropic texture. The compound is highly viscous. The room temperature polymeric dicholesteryl carbonate is a good material to investigate different application aspects. It will be quite interesting to compare mesogenic properties of dicholesteryl carbonates with discholesteryl esters. The comparison of two tables 12.b and 36 indicates that dicholesteryl carbonates exhibit higher transitions and rich mesomorphism compared to compounds with similar flexible methylene spacer diesters. (e.g. table - 12.b compound No. 4, 6, 8 and table -36 compound No. 2, 4 and 7).

The mesomorphic behaviour of present series must be originating out of more flexible carbonate linkages compared to less flexible ester linkages of the reported series.

Comparision with the mesogenic properties of dicholestryl carbamates (Table - 15) indicates that carbamate linkage induces smectic phases. Whereas carbonates induces cholesteric properties.

Most of the compounds exhibit vivid colours at different temperatures in cholesteric phase. The study has provided host of new cholesteric compounds and has brought out some unusual effect of molecular structure on cholesteric behaviour of the mesogens.

2.2 :Series V : Dicholesteryl Carbamates :

Dicholesteryl esters and cholesteryl carbonates with flexible spacer are known (305, 356 - 358.) Forgoing discussion has indicated that cholesteryl carbonates and carbamates provide an interesting comparision to understand mesomorphism in cholesteric compounds.

Dicholesteryl carbamates were synthesized by condensing different diamines with cholesteryl chloroformate. Route for synthesis of dicholestryl carbamates is given in fig 31. The transition temperatures are recorded in table 15.

All the members with methylene spacer length 2 - 8 exhibit smectic mesophase. The texture appears as batonnets and changes to homeotropic texture on further cooling. Transition temperatures are plotted against number of methylene spacers (fig. 34). Marked odd-even effct is not observed in the smectic - Isotropic transition temperature curev. The solid-smectic transitions also do not exhibit marked odd-even effect. The flexibility in the central linkages is normally deterrent in aromatic systems but Gray and McDonnell (359) have reported that cyclohexane gives better mesogenic properties compared to benzene in such systems. Last member of the series exhibits monotropic smectic phase and enantiotropic cholesteric phase. This is quite unusual. Normally increase in methylene spacers enhances smectogenic tendencies. It seems that increase in flexibility might have afected the smectic phase and would

$$2\cdot ClCOOC_{27}H_{45} + H_2N-R-NH_2 \xrightarrow[\text{Dry Pyridine}]{\text{Dry Benzene}} H_{45}C_{27}OOCHN-R-NHCOOC_{27}H_{45}$$

$R = -(CH_2)_x-$, $X = 2$ to 6 , 8

=


SYNTHETIC ROUTE TO SERIES V

FIG:- 31

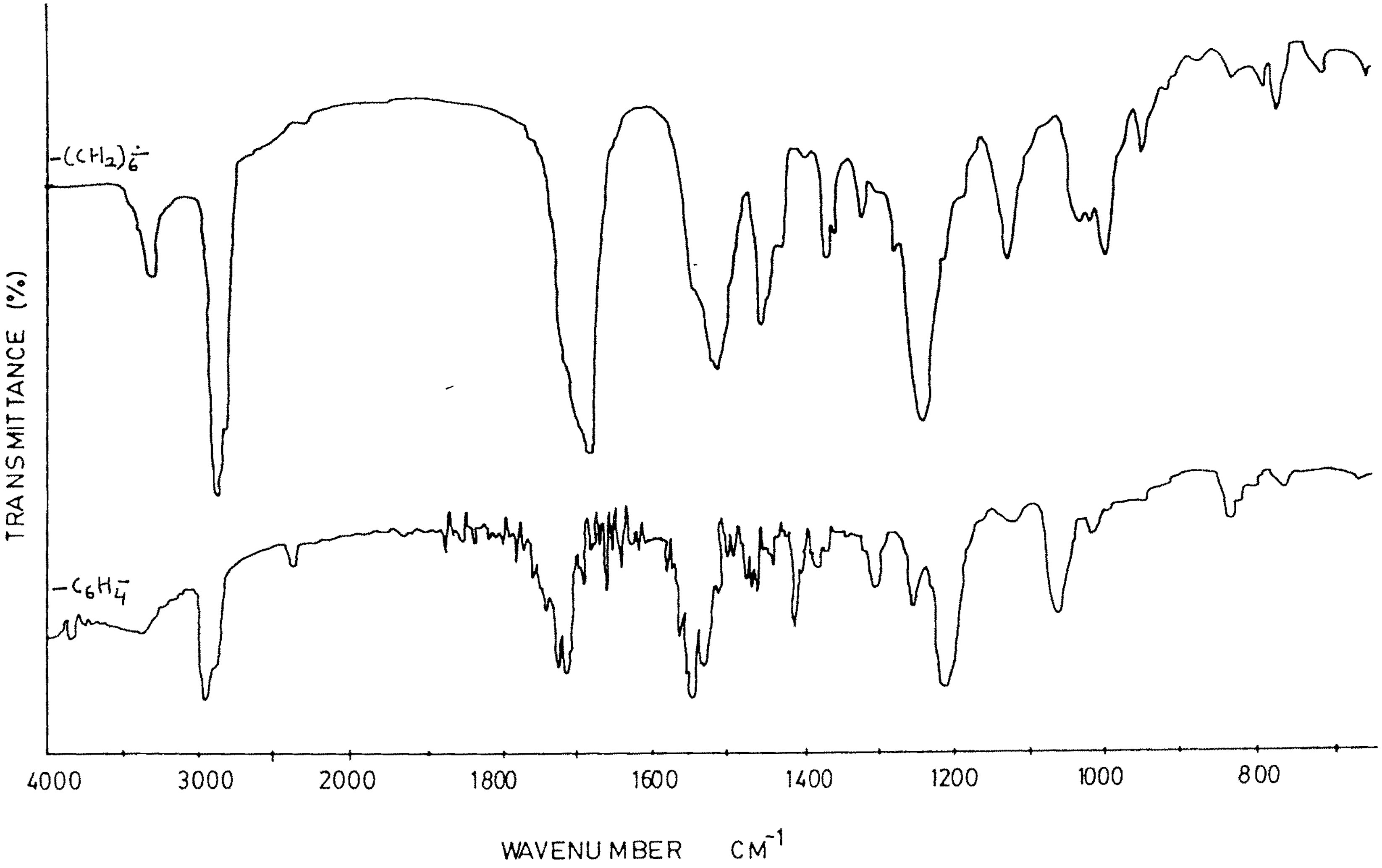


Fig - 32

IR Spectra of Mesogens of Series-V

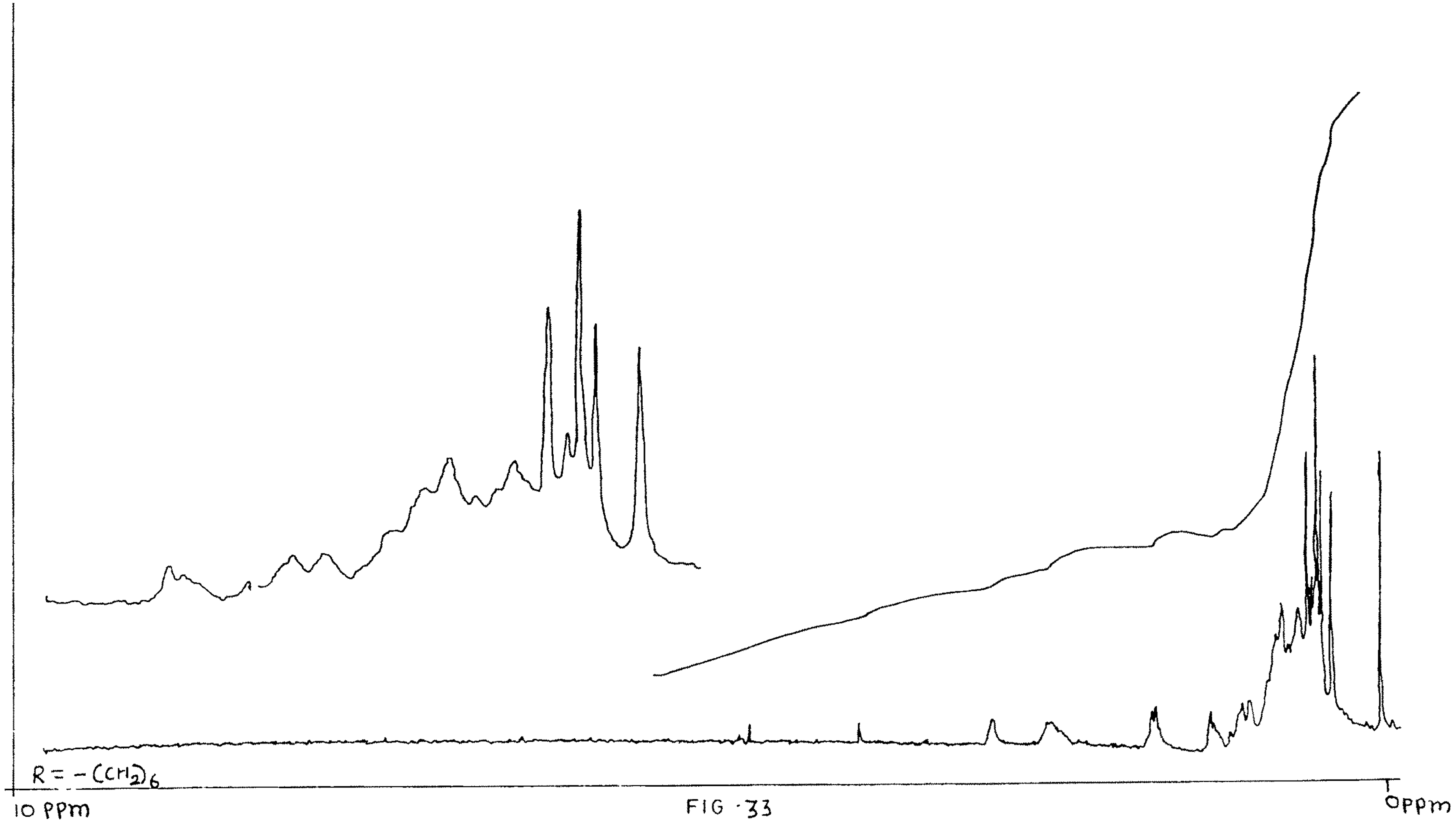


FIG ·33

NMR Spectra of Mesogen of Series-V

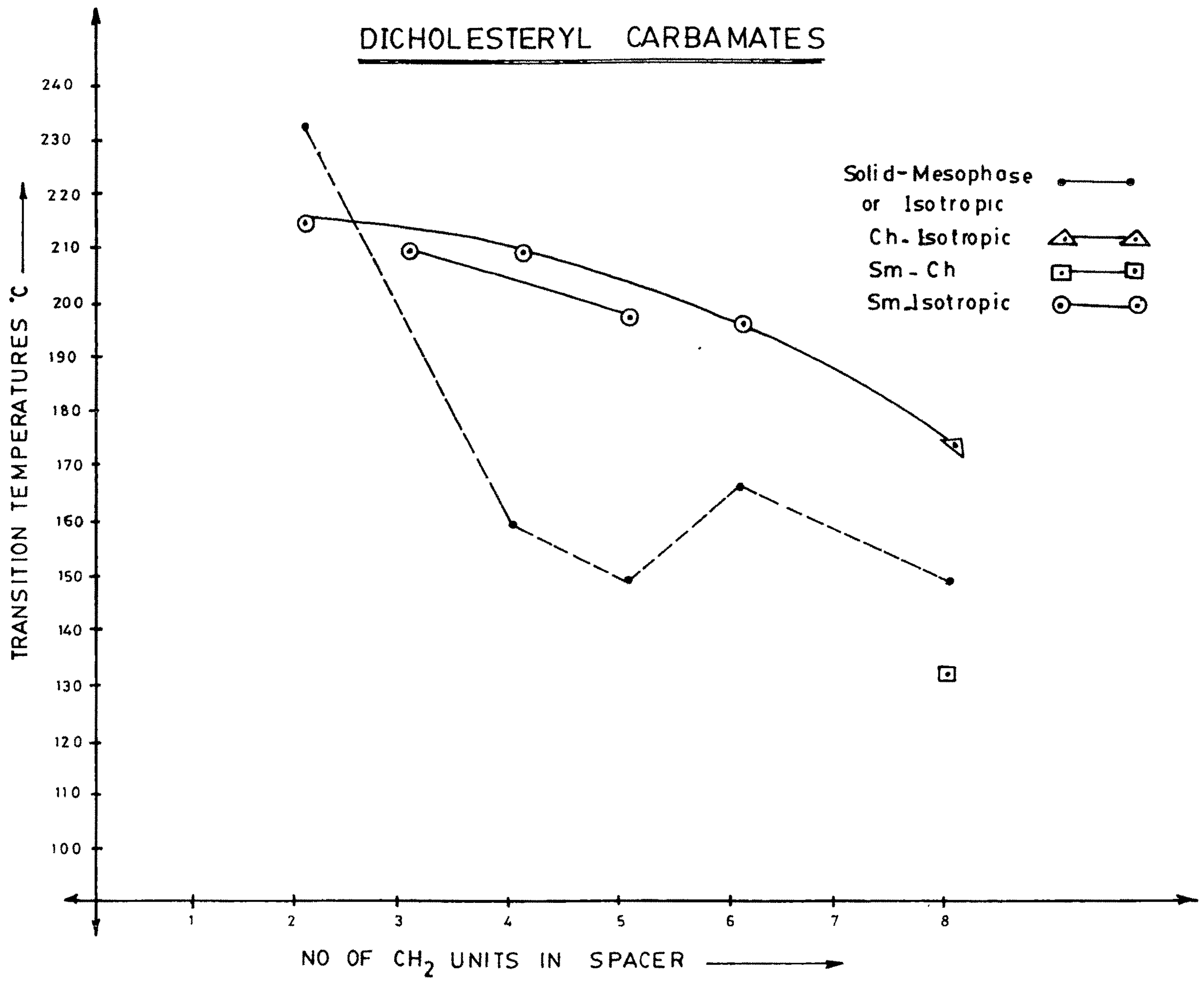

DICHOLESTERYL CARBAMATES
Solid-Mesophase or Isotropic
Ch.-Isotropic
Sm.-Ch
Sm.-Isotropic
TRANSITION TEMPERATURES °C
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
1
2
3
4
5
6
7
8
NO OF CH_2 UNITS IN SPACER

FIG.-34

have induced cholesteric phase, study of some higher homologues will be essential for understanding such behaviour. Coumpound No. 7 was synthesized by condensing two moles of cholesteryl chloroformate with one mole of p-phenylene diamine. This compound exhibits cholesteric phase of higher thermal stability.

The comparision of mesogenic properties of dicholesteryl carbamates with dicholesteryl carbonate indicates that both the series differ in exhibition of mesomorphism. Dicholesteryl carbonates exhibit predominantly cholesteric phases where s dicholesteryl carbamates exhibit smectic phases. The two carbamate linkages will enhance polarizability of the molecules which will induce smectic mesophase, Vora et al (360, 361) have explored the effect of amide linkage on mesomorphism and they have found that high polarizability of amide linkage and its linearity induces smectogenic tendencies and increases the thermal stability of nematic as well as smectic mesophase but enhancement is quite marked in smectic thermal stabilities. Smectogenic behaviour of this series is al~~e~~ready explained in detail in foregoing discussion.

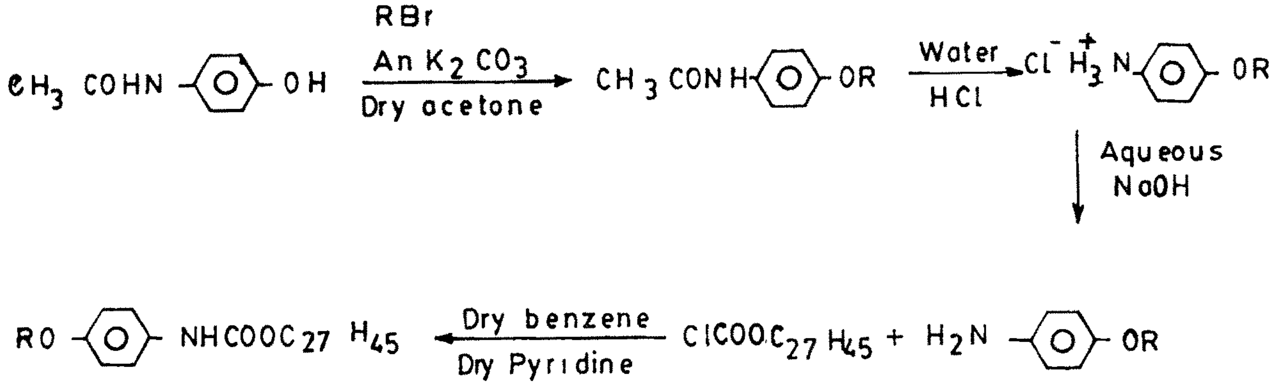
2.3 : Series VI : Cholesteryl 4-n-alkoxyphenyl Carbamates:

Gray (362) and Dave and vora (310) have reported aliphatic and aromatic esters of cholesterol. Cholesteryl carbonates and thiocarbonates are already reported in the literature (305, 363).

In the foregoing discussion the mesogenic behaviour of dicholesteryl carbonates and carbamates is discussed. Many of these cholesterogens have flexible spacers and are mesogenic twins having two terminal cholesteryl units. It was thought quite interesting if cholesteryl carbamates are synthesized with one phenyl substituent and the mesogenic properties are compared with aromatic esters. The role of carbamate linkage in supporting smectic properties will be further enchanced.

With this in view thirteen cholesteryl 4-n-alkoxyphenyl carbamates were synthesized by condensing 4-n-alkoxy anilines with cholesteryl chloroformate as shown in fig. 35.

Reference to table 18 shows that methoxy and n-propoxy derivatives exhibit monotropic smectic and enantiotropic cholesteric phases. Ethoxy derivative exhibits only cholesteric phase. The cholesteric melt crystallizes before monotropic smectic phase could commence. n-Butoxy derivative exhibits enantiotropic smectic and cholestric phases. n-Pentyloxy to n-octadecyloxy derivatives exhibit only smectic phases. The mesogenic behaviour indicates that series



R= C_nH_{2n+1} , n= 1 to 8 , 10, 12, 14, 16. & 18

SYNTHETIC ROUTE TO SERIES VI

FIG.:- 35

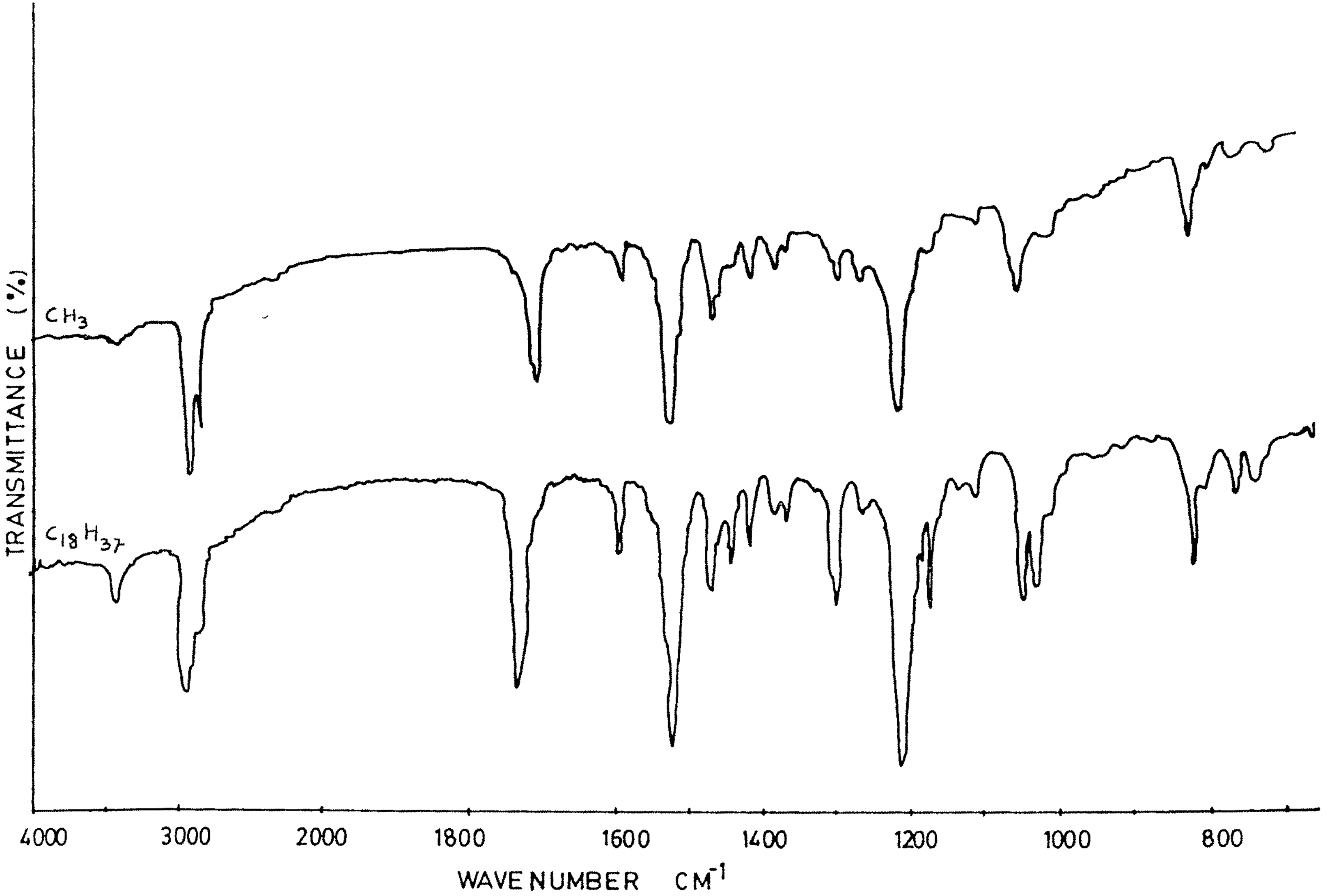


Fig: 36

IR Spectra of Mesogens of Series VI

CHOLESTERYL 4-N-ALKOXYPHENYL CARBAMATES

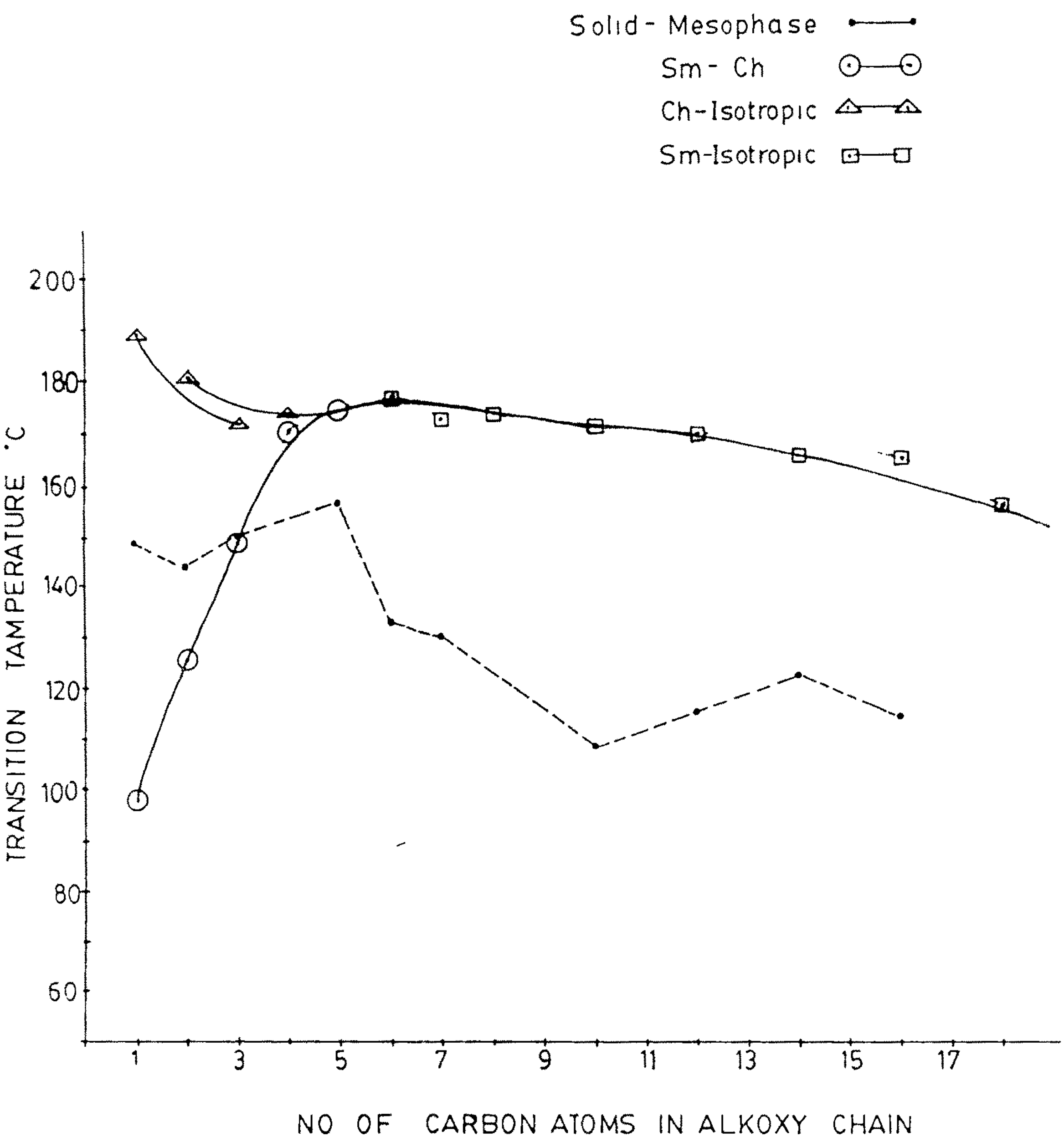
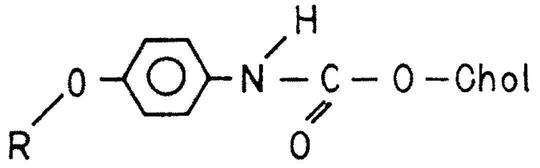
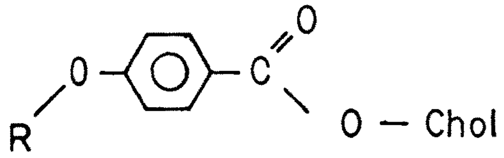


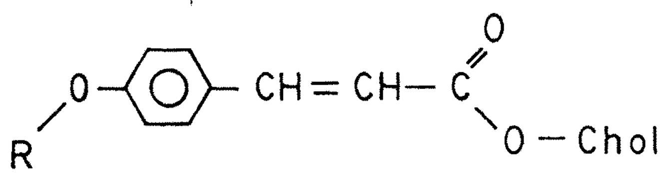
FIG ·37



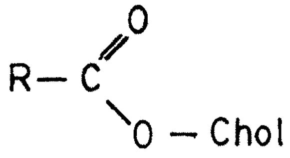
VI



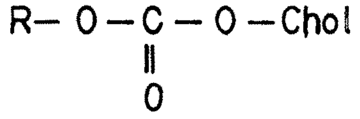
A



B



C



$R-O-\underset{\underset{O}{\|}}{C}-O-\text{Chol}$

D

Fig: 38

exhibits smectogenic tendencies.

The plot of number of carbon atoms against the transition temperatures (fig. 37) exhibits odd-even effect for cholesteric - isotropic transitions upto fourth member only. The smectic cholesteric transition temperature curve rises steeply and merges with cholesteric - isotropic transition temperature curve from n-pentyloxy derivative giving smectic isotropic transition temperature curve which exhibits falling tendency as series is ascended.

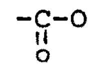
There is a close relationship between mesomorphism and molecular constitution of organic compounds. Hence the thermal stability, a measure of mesomorphism can be correlated with the molecular constitution of the compounds.

Table 37 summarises the average thermal stabilities of different mesogenic homologous series synthesized i.e.

(1) Cholesteryl 4-n-alkoxy phenyl cabamates	VI
and are compared with those of	
(2) cholesteryl 4-n-alkoxy benzoates	A (310)
(3) cholesteryl trans-4-n alkoxy cinnamates	B (364)
(4) cholesteryl n-alkanoates	C (362)
(5) cholesteryl n-alkyl carbonates	D (305)

The geometry of above homologous series is given in fig. 38.

Reference to table 37 shows that cholesteric thermal stability of series - A is higher than that of series - VI. Reference to the geometry (fig. 38) of two series indicate that they differ in central linkages. Series - A has



$-\underset{\underset{O}{\|}}{C}-O$,

TABLE - 37

Average Thermal Stasbilities ^{0}C

Series	VI	A	B	C	D
Cholestric-Isotropic C_1-C_4	178.5	233.5	286.8	110.7	103.0
Smectic-Cholesteric or Smectic-Isotropic C_7-C_{18}	167.8	170.0	174.3 C_{10}-C_{18}	77.25	48.6 C_8-C_{18}
Commencement of smectic mesophase in series	C_1	C_7	C_{10}	C_6	C_8

an ester linkage whereas series - VI has $-NH-\underset{\underset{O}{\|}}{C}-O-$ central linkage. The carbamate linkage will impart higher polarizability as well as more flexibility to series VI compared to the ester linkage. Both these factors act opposite to each other in sternthening of cholesteric phase. Higher polarizability enhances mesophase thermal stability and increased flexibility decreases mesophase thermal stability. The net effect is that carbamate linkage adversely affects the cholesteric thermal stability compared to ester linkage as observed in the present series. Though cholesteric thermal stability of series - VI and series A differ markedly,

Smectic thermal stability of both the series is almost equal (Table - 37). This is quite an interesting phenomena. This indicates that the high polarizability of carbamate linkage enhances smectic properties compared to cholesteric properties, Vora et al (360) have observed that amide central linkage is conducive to smectic and nematic phases but it enhances smectic phases much more compared to nematic phases due to linearity and high polarizability. In the similar manner carbamate linkage enhances smectic thermal stability in series - VI compared to series A.

The cholesteric thermal stability of series B is much higher compared to that of series - VI (Table 37).

The difference in two series (fig. 38) is in central linkages. Series - B has trans -CH=CH-COO- central linkage where as series - VI has $-NH-\underset{\overset{\|}{O}}{C}-O-$ carbamate linkage, trans -CH=CH-COO - linkage will enhance length and polarizability of the molecules of series - B. As discussed earlier molecules of series - VI will be more polarizable and flexible compared to series - B due to the presence of carbamate linkage. Naturally the cholesteric thermal stabilities of series - B will be higher compared to series VI as discussed above.

The smectic thermal stability of series VI and B differ a little. It has been pointed out that higher polarizability of carbamate linkage enhances smectic stability in series - VI and trans -CH=CH-COO- group will adversely affect the smectic thermal stability of series B due to its breadth increasing effect and less polarizability. The over all effects are reflected in their smectic thermal stability which differs by about 6^{o}C.

Smectic and cholesteric thermal stabilities of series - VI are much higher compared to those of series - C and series - D. This is as expected because, incorporation of a phenyl ring enhances cholesteric and smectic thermal stabilities over and above the effect of carbamate linkage.

The overall length and polarizability of series - VI predominates in the enhancement of mesophases. Gray (218) has pointed out that increase of length by one phenyl ring enhances mesophase thermal stability by 60 - 100^{o}C.

Dave et al (310, 364) prepared number of homologous cholesteric series to establish that the effect of chemical constitution on cholesteric phase is similar to nematic phase. However they could not obtain only smectic phase in the last member of the homologous series as observed in normal nematogenic homologous series. Dave et al (335, 365) surveyed typical nematogenic homologous series and pointed out that nematogenic series having broad nuclei or lateral substituent also behave like cholesteric homologous series. Last members do not exhibit only smectic phases. Dave et al (246, 247) also synthesized mesogenic naphthalene derivatives to strengthen this point. This study was taken in late sixties when it was pointed out that cholesteric phase should be considered like the smectic or as an unique phase as it exhibited focal - conic texture. Dave et al (310, 364) stressed that the effect of chemical constitution on cholesteric phase is similar to nematic phase and much different compared to the effect on smectic phase. However by early seventy the data of different physical properties indicated beyond doubt that cholesteric phase is a twisted nematic phase which vindicated Friedel's observation of 1920.

The mesogenic behaviour of series - VI is quite interesting from this view point. The smectic phase appears from the first member of the series along with the cholesteric phase, the homologues from n-pentyloxy derivative onwards exhibit only smectic phase, cholesteric phase is eliminated from the system. This indicates that breadth increasing effect of cholestrol nucleus is outweighed by the high polarizability of carbamate linkage which helps close packing of the molecules in layers favourable to smectic phase. In our earlier studies even dicholesteryl carbamates exhibited smectic phases whereas dicholesteryl carbonates exhibited predominatly cholesteric phases.

The mesogenic behaviour of series provided very interesting results by exhibiting predominantly smectic phases. Smectic phases are characterized by textures or contact method and miscibility studies.

2.4 : Series VII : Dicholesteryl Imide Esters :

Kricheldorf and Pakull (307) reported liquid crystalline polymers incorporating of N,N'-alkane -α,ω - diyl bis (Trimellitimides) fig. 39.a.

They had not studied any model compounds. In countinuation of our work of effect of two cholesteryl units with flexible and rigid spacers the imide acids (fig. 39.a) seemed to be quite interesting for use as starting material as the molecules will have flexible and rigid segments with polar keto groups.

With this in view six compounds were synthesized by varying the methylene spacers from 2 to 8. (fig. 39.b). Route of synthesis is given in Fig. 40.

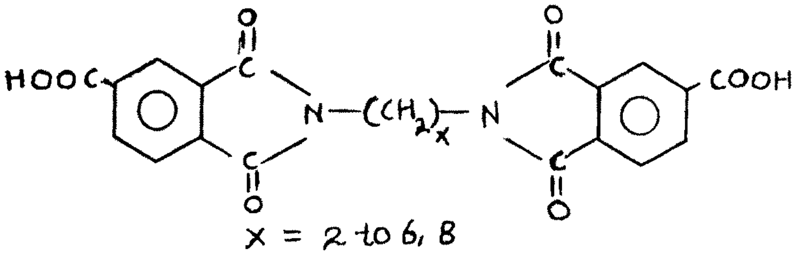
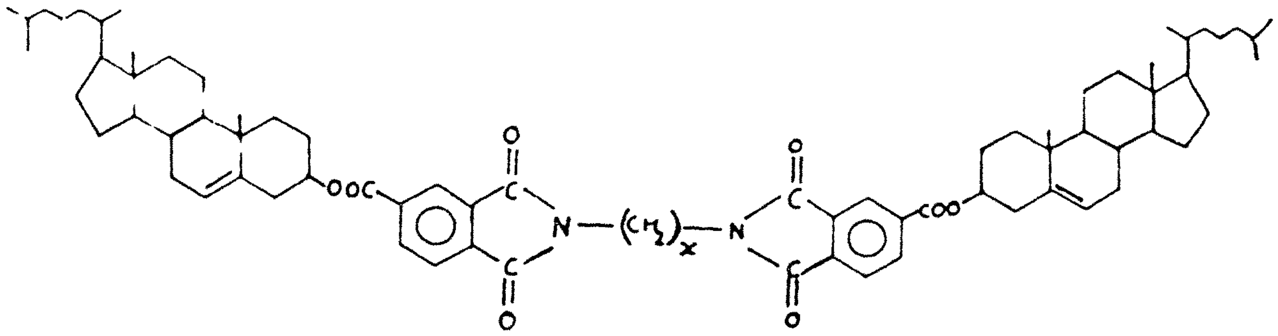


Fig: 39.a

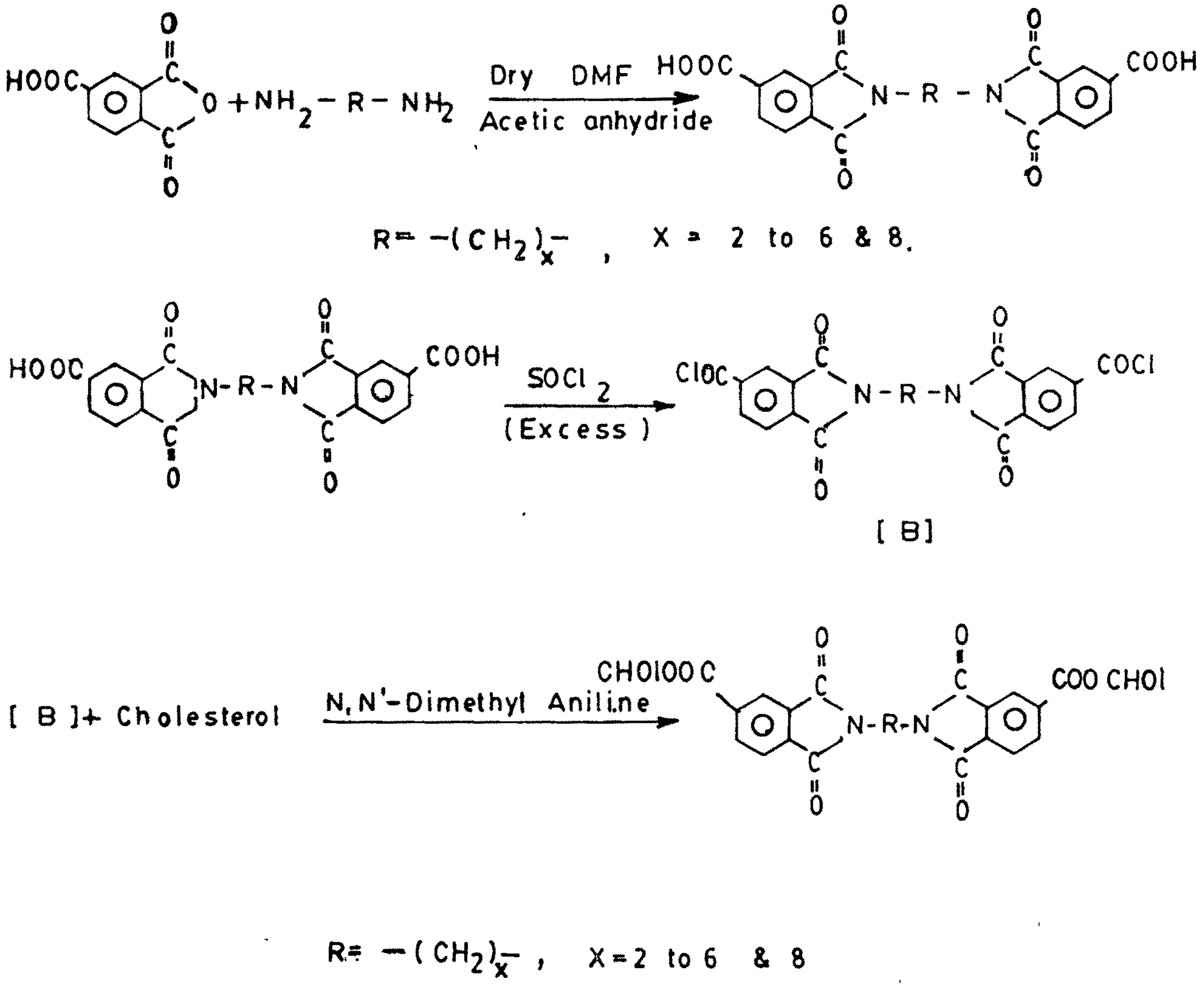
First member (Table - 21) with two methylene spacer is non-mesogenic, the other members exhibit cholesteric phases at higher temperatures. The solid - mesogenic transition temperatures are above 200^{0}C.

The graph of transition temperatures against the number of methylene spacers exhibits odd - even effect (fig. 42) for cholesteric - isotropic transition temperatures as well



X = 2 to 6, 8

Fig: 39.b



SYNTHETIC ROUTE TO SERIES VII

FIG:- 40

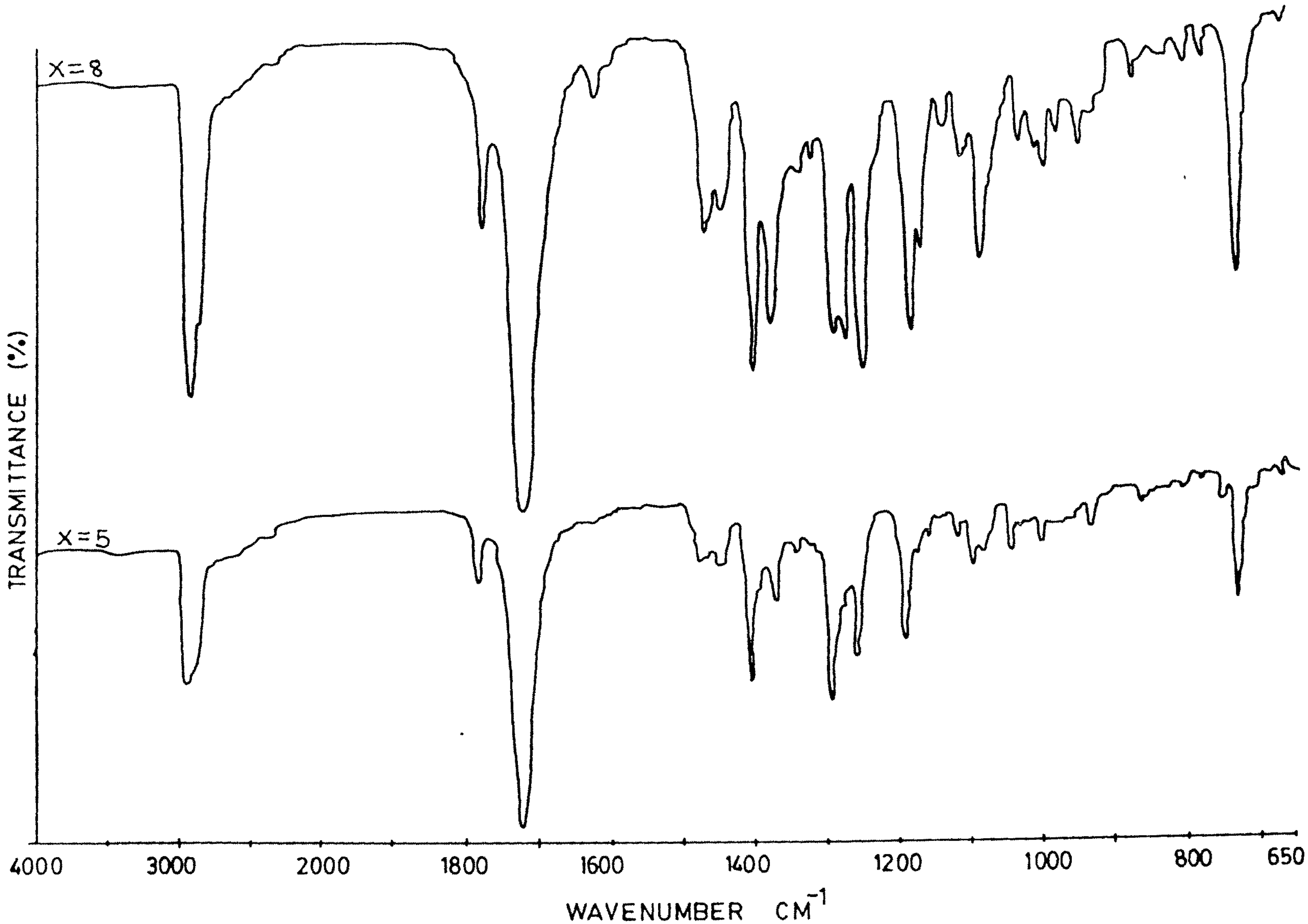


Fig: 41·a

IR Spectra of Mesogens of Series-VII

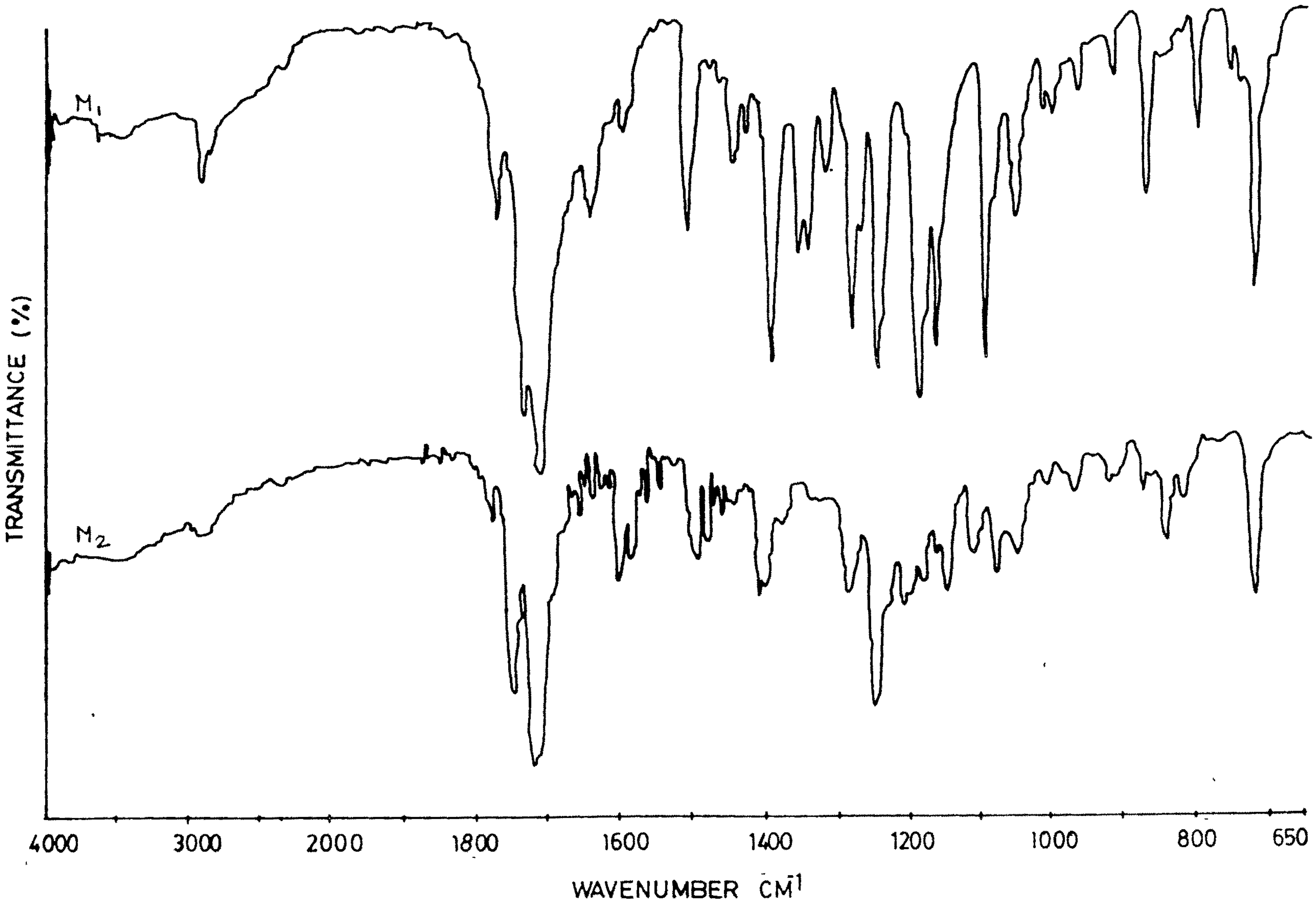


Fig: 41·b

IR Spectra of M_1 & M_2

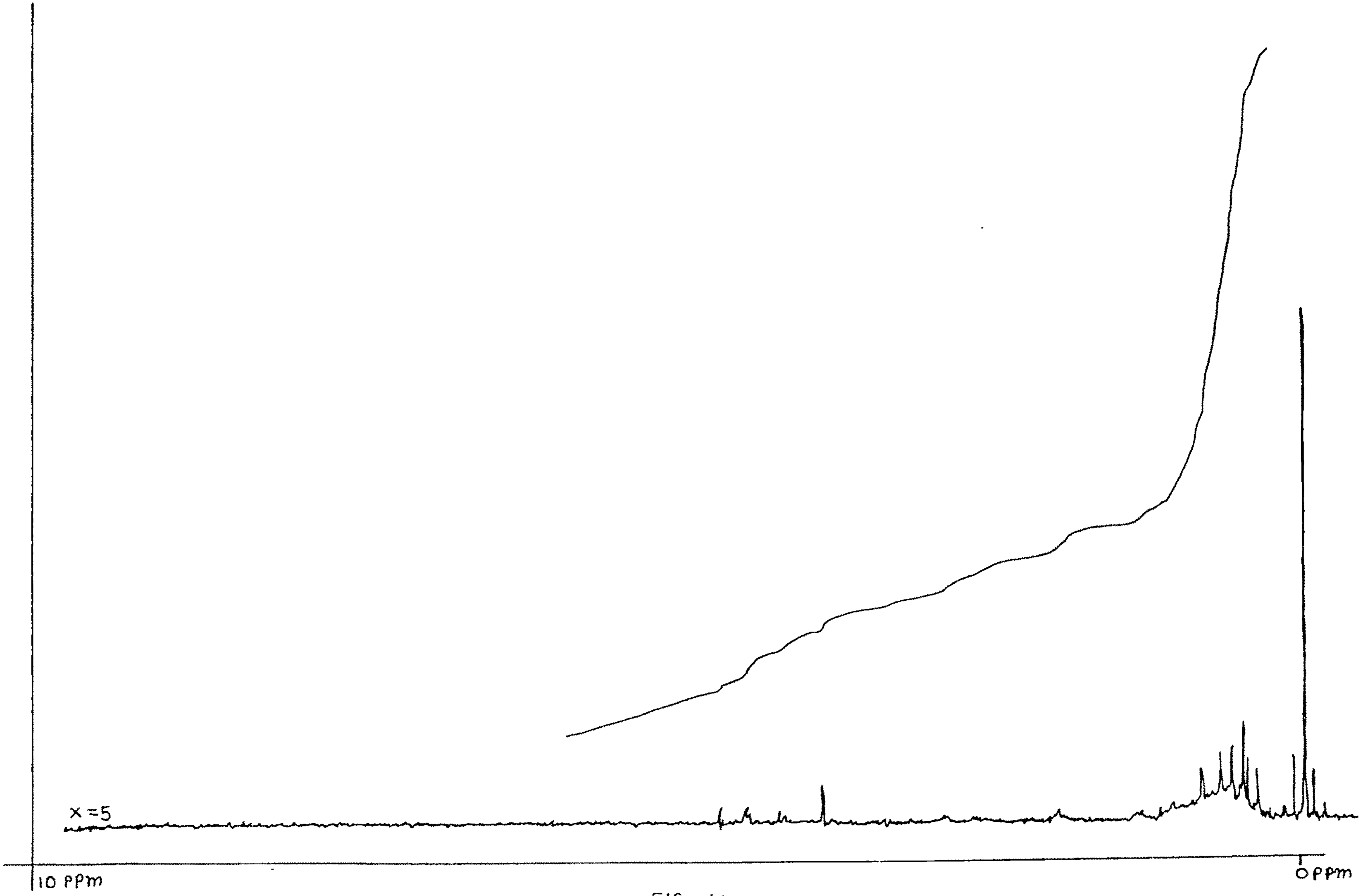


FIG 41.C

NMR Spectra of Mesogen of Series-VII

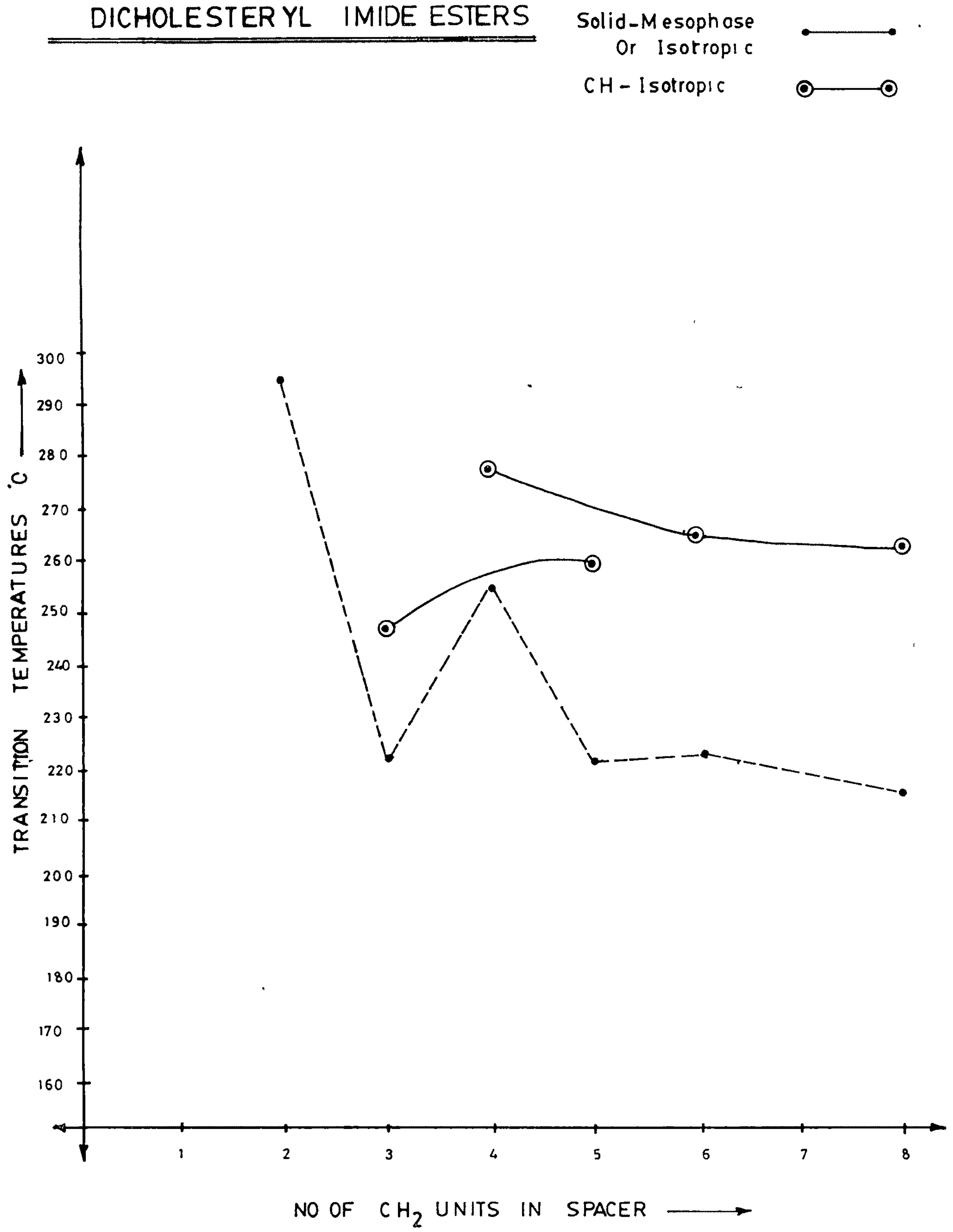

DICHOLESTERYL IMIDE ESTERS
Solid-Mesophase Or Isotropic
CH - Isotropic
TRANSITION TEMPERATURES °C
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
1
2
3
4
5
6
7
8
NO OF CH_2 UNITS IN SPACER

FIG:- 42

as for solid - cholesteric transition temperatures. The odd-even effect is much pronounced in solid - cholesteric or isotropic transition temperatures compared to cholesteric - isotropic transition temperatures. This indicates that number of methylene spacer plays an important role in the structure of crystals of these compounds. The geometry of series - VII is given in Fig. 39.b.

The geometry shows very complex structure. It incorporates two imide linkages where carbonyl groups contribute to the lateral attractive forces. Two ester linkages add to the flexibility of the molecules over and above the methylene spacers. The higher thermal stability of cholesteric phases can be attributed to the presence of two imide linkages and two cholesteryl units. Cholesteryl derivatives with other aromatic units are known to exhibit mesomorphism of higher thermal stability. The non-mesomorphism of first compound with two methylene spacers can be attributed to high melting point of the compound originating from less flexibility due to short spacer length. Some of the mesogens exhibit vivid colours in cholesteric phase. Blue phase is not detected in these mesogens.

To understand the role of cholesteryl units and the central N, N' - alkane -α,ω-diylbis (trimellitimide) segment in promoting mesophase, two model compounds were synthesized by condensing p-cresol (M_1) and 4-ethoxy-4'-

hydroxy azobenzene (M_2) with diacid chloride of N, N$'$ - hexane - α,ω - diyl bis (trimellitimide), M_1 is non-mesogenic but M_2 exhibits nematic phase of very-high thermal stability. This indicates that the length and polarizability of ester linkage is quite important in exhibition of mesomorphism when there is a flexible spacer and a broad molecule in the central core of the molecules, compared to cholesteryl moiety $H_5C_2O-C_6H_4-N = N-C_6H_4-O-\underset{\underset{O}{\|}}{C}-$ will be more linear and polarizable, this reflects into very high thermal stability of model compound M_2. The length and polarizability of one phenyl group at both the ends having methyl terminal substituent is not sufficient to induce mesomorphism. May be diesters with longer alkoxy phenyl group may exhibit mesomorphism. This work is taken up for further studies to evaluate the effect of structural changes on the mesomorphism mono and di-esters of trimellitimides. Initial results are highly encouraging.

3

CHIRAL ESTER AMIDES

3. Chrial Ester Amides :

Series VIII : S(+)-4(4'-β-Methyl butoxy benzoyloxy) -4"-n-alkoxy benzoyloxy benzanilides :

A number of mesogenic homologous series are reported having - COO-, -CH=N-, -N=N-, -CH=CH-, -CH=CH-COO-, -C=C-, -C≡C- etc. groups as central linkages. Many mesogenic homologous series contain two cetral linkages, both of them may either be ester (244, 366) or azomethine groups (332) or one of them may be ester and the other azomethine (347, 367). However, to the best of our knowledge, the first homologous series containing (-NH-CO) amide group as one of the central linkages was reported from our laboratory by Vora and Gupta (368) in 1981. Soon after that Kalyvas and McIntyre (369) and vora and Patel (229) reported a symmetrical homologous series having an ester and amido central linkages.

Neither Brown and Show (370) in their review on "mesomorhic state" nor Gray (218) in his classical monograph on liquid crystals have suggested amide group to be conducive to mesogenic properties. This may probably be the reason for rarity of mesogens with amide linkage. Gray (20) in the review of structural requirements for mesogens has expressed the options that if there are more than two benzene rings and one of the middle group is conducive to mesomorphism, then the introduction of a group like - NH-CO- would result in a thermally less stable liquid crystals

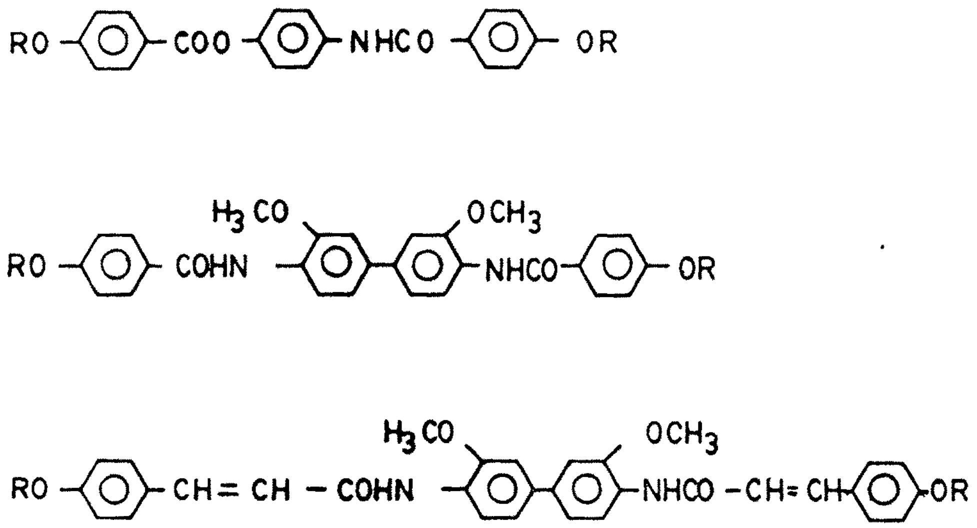

RO
COO
NHCO
OR
H3 CO
OCH3
RO
COHN
NHCO
OR
H3 CO
OCH3
RO
CH= CH – COHN
NHCO –CH= CH
OR

Fig: 43

compared to others where both the middle linkages are conducive to mesogenic character. Brown (142) has also mentioned that compounds with -CONH- may exhibit mesomorphism.

As discussed earlier the liquid crystalline order in polymers is of greater interest and importance. Many of these polymers have amide linkage. Model compounds exhibiting mesomorphism and having an amide group would be of interest to understand the mesogenic behaviour of such compounds and of polymers having amide linkage.

Vora et al (360) and Gupta (371) took up the study of number of mesogenic series with ester and amide central linkages and also of mesogenic series having two amide linkages as reported in fig. 43.

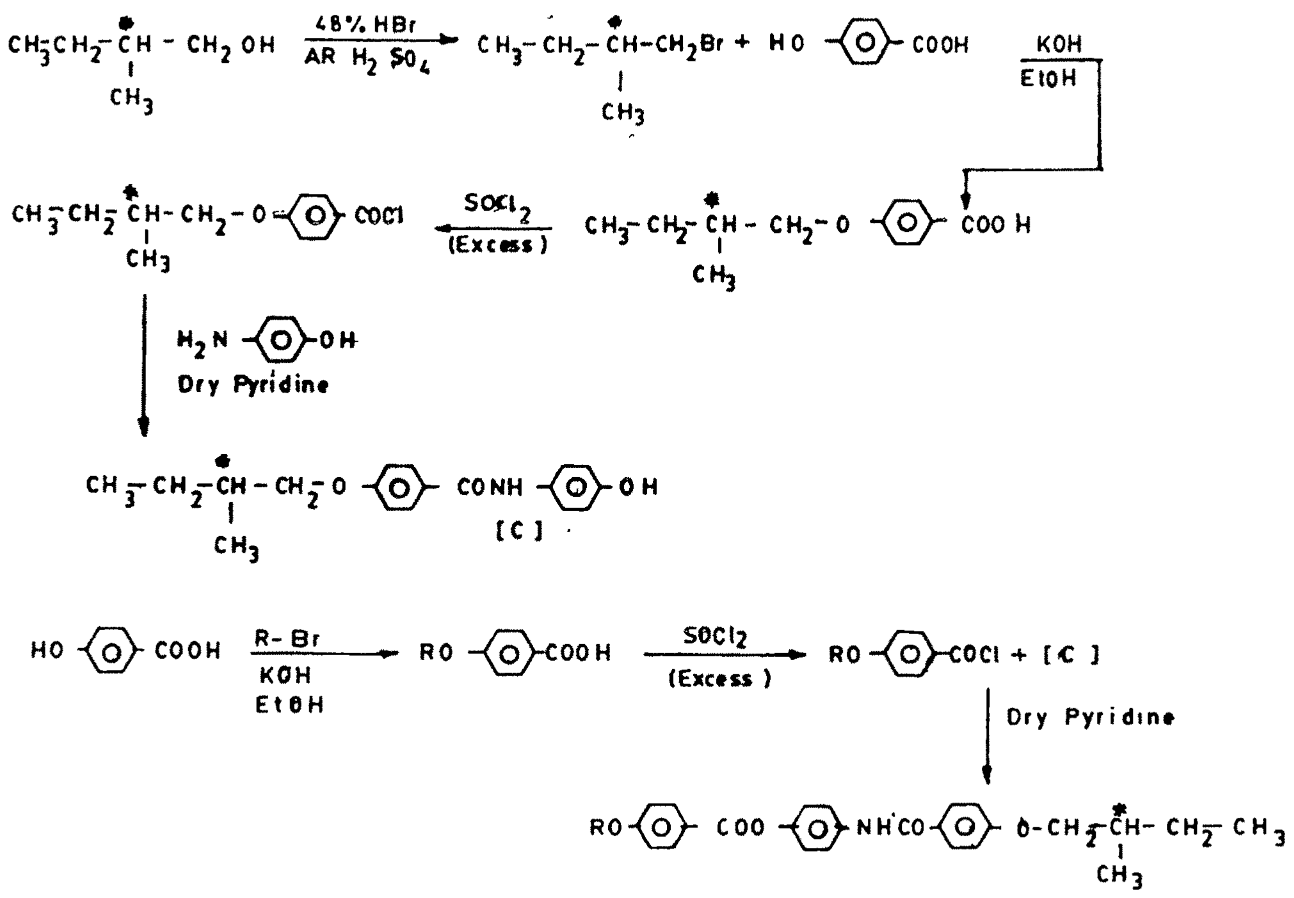
The observations of Vora et al (360) and Gupta (371) made it clear that compared to an ester and azomethine linkage, amide - central linkage enhances smectic and nematic phases and enhancement is always more in case of smectic mesophase.

In continuation of our laboratory's work on mesogenic homologous series containing amide central linkage, it was thought of interst to synthesize a chiral homologous series with amide central linkage with a view to study the effect of such changes on cholesteric and smectic phases of homologous series.

Series VIII was synthesized by the route as shown in fig. 44. Cholesteric mesophase commences from the n-butoxy derivative as monotropic phase, n-pentyloxy to n-decyloxy derivatives exhibit enatiotropic cholesteric phases. n-Dodecyloxy derivative exhibits smectic phases (SmA, SmB) and cholesteric phase. n-Tetradecyloxy to n-octadecyloxy derivatives exhibit Sm*C and Sm A phases. The plot of transition temperatures versus carbon atoms (fig. 46) does not exhibit any odd-even effect for cholesteric-isotropic transitions. This may be due to the non-mesomorphism of the first few homologues. The odd-even effect is more pronounced upto five or seven homologues (327). Smectic A- isotropic transition temperature curve exhibits a smooth trend. Sm*C - Sm A transition temperature curve falls initially than shows rising tendency as expected in the higher homologues (218).

Homologous series exhibits narrow mesomorphic range of cholesteric and smectic phases. All the members of the homologous series have strong tendency to crystallize on cooling a few degree below the solid - mesogenic transition temperatures.

The following text deals with the correlation between the structural aspect and mesogenic behaviour of series VIII in relation to other structurally related homologous series. Table 38 summarises the average nematic or cholesteric and smectic thermal stabilities and the points of commencement of the smectic mesophase in these series.



R= C_nH_{2n+1} , n = 3 to 8, 10, 12, 14, 16, 18.

SYNTHETIC ROUTE TO SERIES VIII

FIG:-44

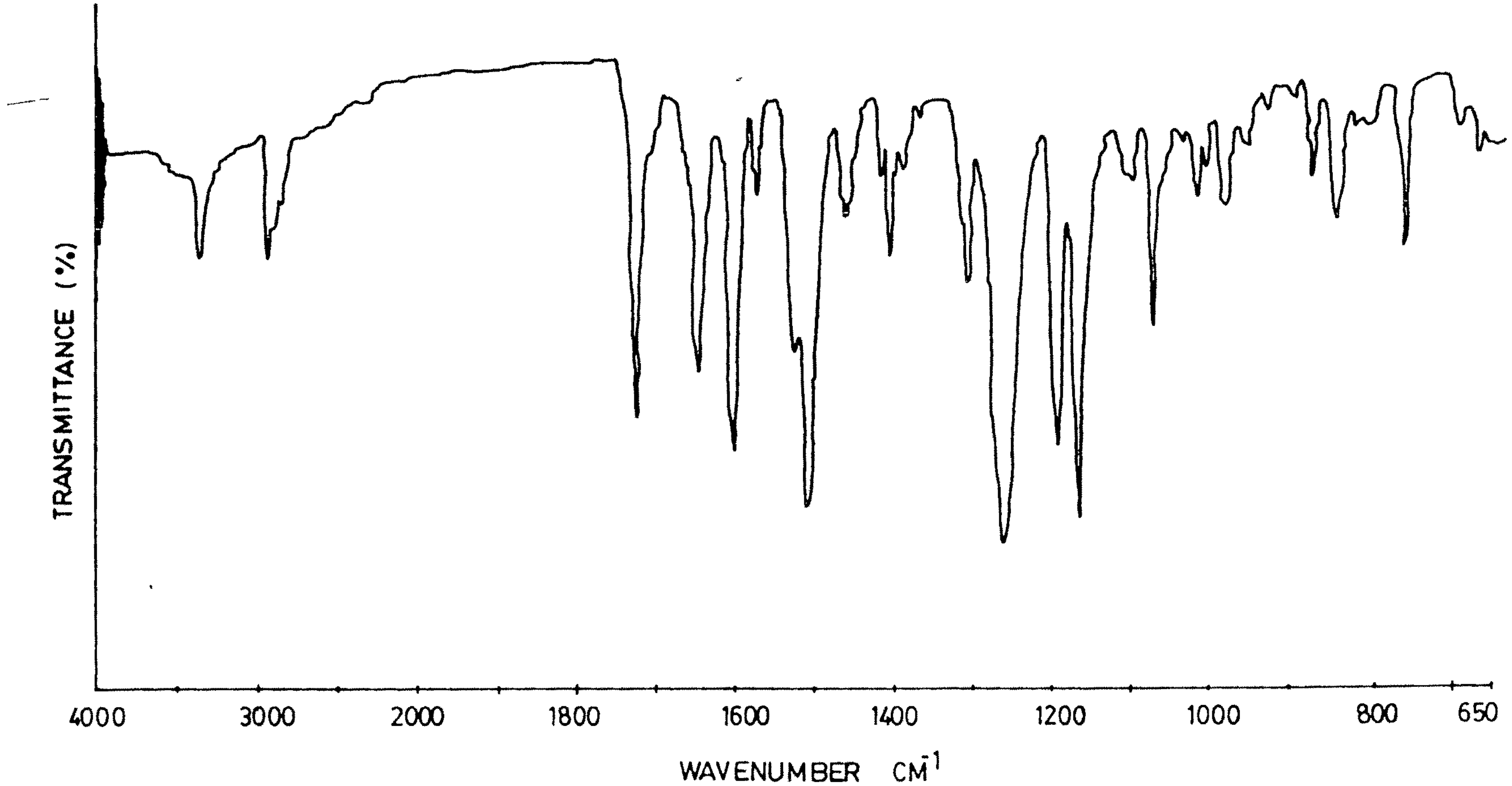


Fig: 45·a
IR Spectra of Compound [C]

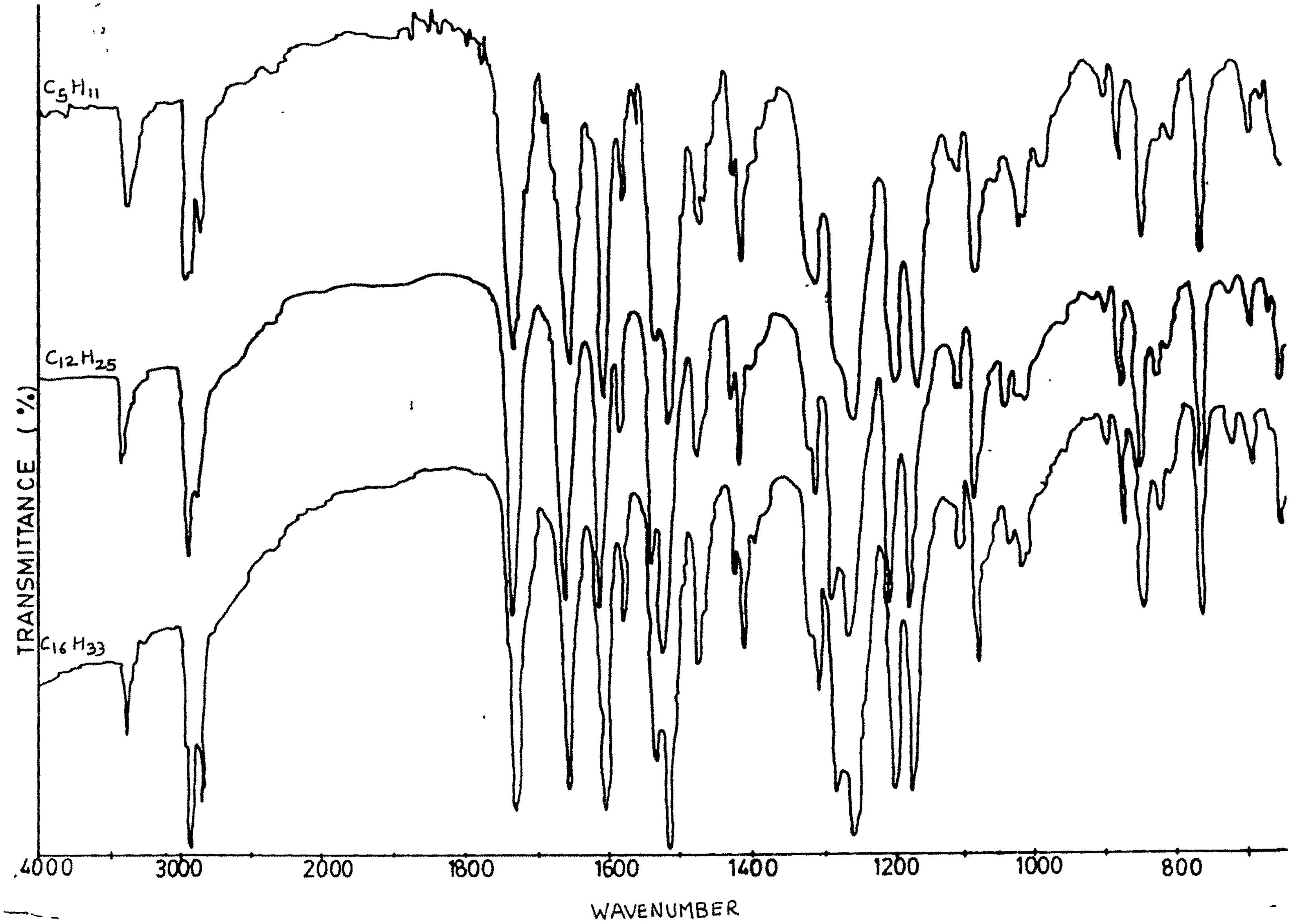


Fig: 45·b

IR Spectra of Mesogens of Series VIII

4 (4'-β METHYL BUTOXY BENZOYLOXY)- 4'-n-ALKOXY BENZOYLOXY BENZANILIDES

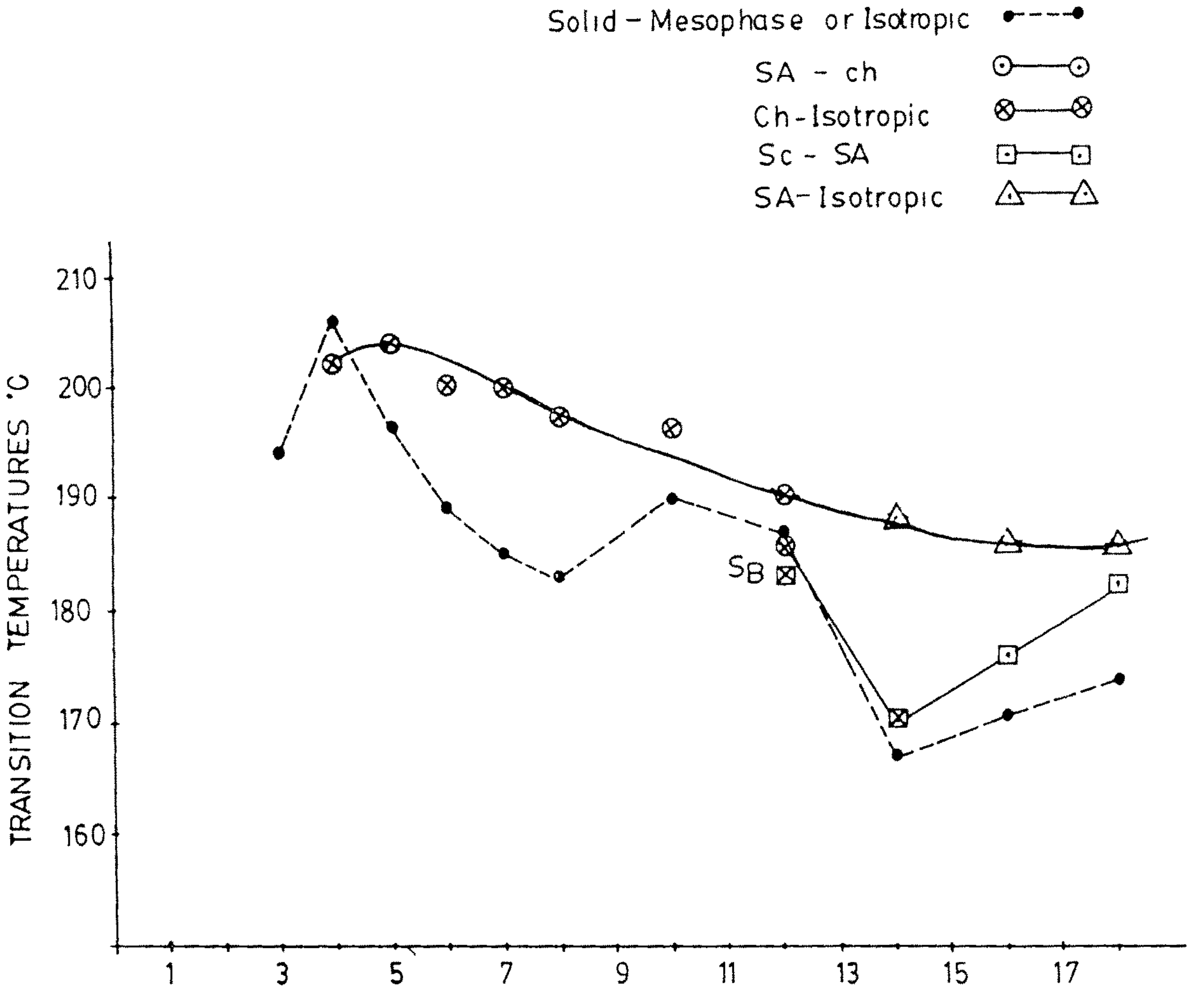
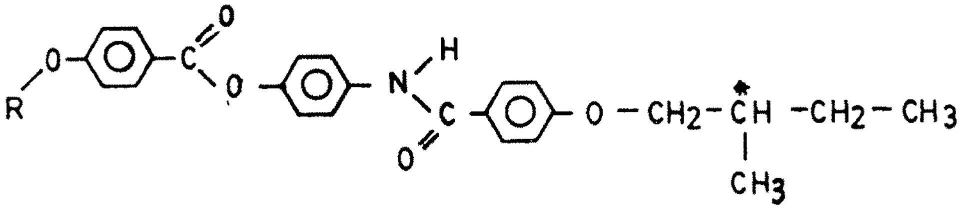
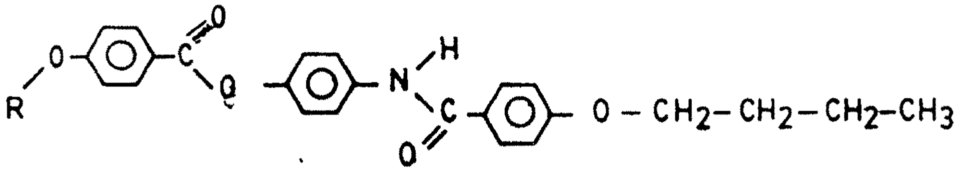


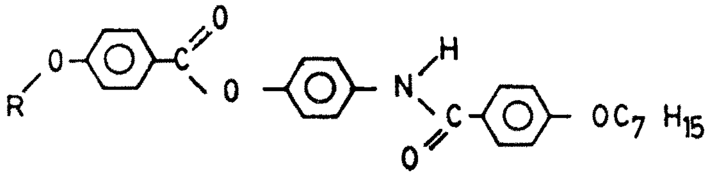
FIG : 46



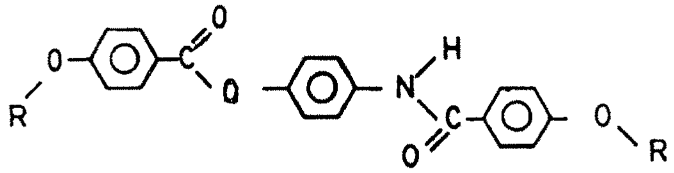
VIII



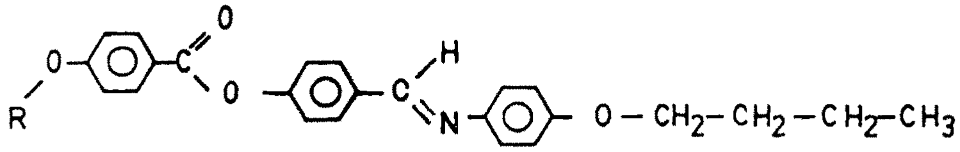
A



B



C



D

Fig : 47

TABLE - 38

Average Thermal Stability °C

Series	VIII	A	B	C	D
Ch or N-Isotropic Isotropic-Ch or N C_4 - C_{12}	198.43	253	225.78	$\frac{235.8}{C_4\text{-}C_8}$	233.57
Sm-Ch/Isotropic or Sm-Isotropic	186.5	-	209.13	$\frac{196.13}{C_{12}\text{-}C_{16}}$	170.37
Commencement of smectic mesophase	C_{12}	-	C_2	C_6	C_7

(1) S(+)-4(4'-β-methyl butoxy benzoyloxy) -4"-n-alkoxybenzoyloxy benzanilides - VIII and are compared with those of

(2) 4(4'-n-Alkoxybenzoyloxy)-4"-n-butoxy benzanilides A (372)

(3) 4(4'-n-Alkoxy benzoyloxy)4"-n-heptyloxy benzanilides B (368)

(4) 1,4-Bis(4'-n-Alkoxybenzoyloxy) Amino phenols C (229,369)

(5) 4(4'-n-Alkoxy benzoyloxy) benzylidene-4"-n-butoxy anilines D (347)

Reference to table 38 shows that the cholesteric thermal stability of series - VIII is much lower compared to that of series A. Reference to geometry (fig. 47) shows that both the series differ only in the terminal group at one end. Molecules of series VIII has a chiral 2-methyl butoxy group as terminal substituent whereas in the case of series A, n-butoxy group is present at that end.

Normally, branching affects smectic as well as nematic mesophases. The branched methyl group on second carbon must be responsible in decreasing cholesteric thermal stability of series - VIII compared to that of series A.

The methyl group on chiral carbon will not have just breadth increasing effect as it will be with methyl substituent on achiral carbon. In the case of chiral carbon, the methyl group does not lie on the same plane as other linear carbons are lying (352).

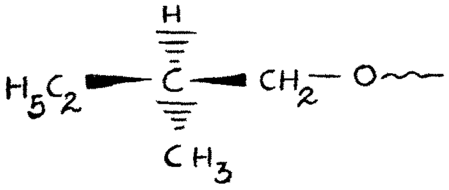


Fig. 22.c

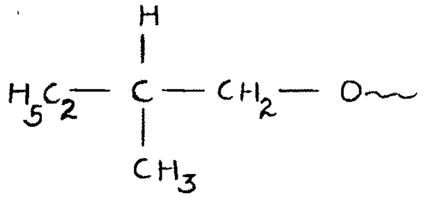


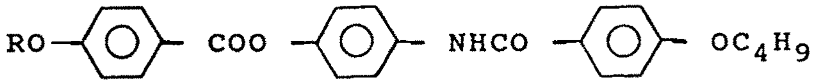
Fig. 22.d

Reference to figure 22.c shows that in the chiral molecule - H and $-CH_3$ group attached to chiral $^*C$ are not in the plane of linear alkyl chain whereas in the case of achiral compound (fig. 22.d) the -H and $-CH_3$ group, both lie in the same plane of alkyl chain. Naturally, this difference in conformation of chiral and achiral alkyl chain will influence the stability and even the commencement of the smectic phase. It seems that geometry of the chiral carbon affects the stability of the mesophase more adversely compared to the linear alkyl group present in series - A.

The molecules of series VIII are chiral, hence they arrange in layers on melting at the solid - cholesteric transitions. The geometry of chiral carbon of alkoxy group affects cholesteric phase more adversly because the geometry of molecules of series - VIII will create disturbance in the twisted layer structure of cholesteric phase (fig. 12) this must be the reason for the lower cholesteric thermal stability of series - VIII.

In the case of series A, the alkoxy chain is linear. Naturally the breadth increasing effect of β - Methyl group of chiral carbon is absent in the molecules of series - A. Due to this reason nematic thermal stability of series - A is much higher than that of series - VIII. An interesting mesogenic behaviour of series - A is that smectic mesophase does not commence up to the last member of the series. One would think that 2-Methyl group of chiral molecules of series VIII will be more deterrent to smectic phase. It seems that the behaviour of chiral carbon having two groups imparting acoplanarity to the molecules is not much understood. Even though - NHCO - group considered as conducive to smectic and nematic phases, the smectic phase is absent in series - A. The absence of smectic phase in series A has been disucssed by Vora et al (368) based on the effect of the length of terminal alkoxy group present at one end of the molecules where -NHCO- central linkage is present. Vora et al (372) have also obtained the threshold value of terminal group on the exhibition of smectic phases in the homologous series.

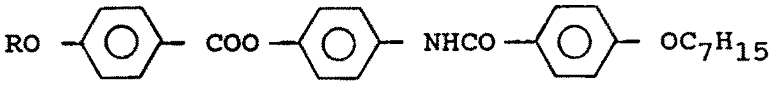
The comparison of isomorphous compound throws very good light on their mesogenic behaviour



A

Nematic

R $=nC_7H_{15}$



B

$R = n\text{-}C_4H_9$

Predominantly smectic (Sm - N)

Vora et al (368) have pointed out that heptyloxy group is more polarizable hence the molecules of series B - will be more polarizable. Naturally it will enhance smectogenic tendencies. However, the comparision of esteramides mesogens throw good light on the role of n-alkoxy group at one end of the homologous series like compound A and B.

It can be seen that here in these two compounds there is only interchange of end alkoxy groups, when n-butoxy group is present in the acid moiety forming amide linkage, eventhough at the other end heptyloxy group is present the smectic mesophase does not make its appearance. Whereas when the acid moety forming amide linkage contains the heptyloxy group, and on the other end only butoxy group is present, the molecules exhibit both smectic as well as nematic mesophases. This shows that eventhough one may have alkoxy group on the other end of the molecules up to octadecyloxy, the alkoxy end group present in the acid moiety forming amide linkage plays a major role and when the length of that alkoxy group crosses certain threshold value which may be -OC_9H_{11}, -OC_6H_{13} OR -OC_7H_{15}. To evaluate the threshold value of the fixed alkoxy chain at one end on the appearance of the smectic mesophase, two more compounds were synthesized by Vora and Dixit (372). Keeping n-OC_4H_9 group on the ester moiety, compounds with n-pentyloxy and n-hexyloxy group at the other end exhibited only nematic mesophase, this indicated that threshold value of fixed alkoxy group to induce smectic phase is n-heptyloxy group, if on the ester moiety n-butoxy group is fixed.

This type of behaviour in isomorphous compounds having unsymmetrical linkages is not generally observed. One can expect little difference in thermal stabilities as was observed by Vora and Chhangawala (373) when they studied the effect of end group on isomorphous compounds having unsymmetrical linkages. Over and above the threshold value of linear alkoxy group in the ester-amide homologous series in exhibition of smectic phases, series - VIII has added one more factor that a chiral carbon having 2-methyl lateral substituent also induces smectic phases in such homologous series.

It has been pointed out in previous section that chiral carbon having β-methyl or γ - methyl lateral substituent have enhanced smectogenic tendencies in number of homologous series (352).

The cholesteric and smectic thermal stabilities of series - VIII are lower than nematic thermal stability of series - B. Both the series have identical structure except the terminal substituent at one end of the molecules. Molecules of series VIII have a chiral 2 - methyl - butoxy group at one end and the molecules of series B have n-heptyloxy group at that end. The longer and linear heptyloxy group will enhance the nematic and smectic thermal stability of series B compared to series - VIII which has shorter alkyl group with branching (218).

The molecules of series - C are symmetrical (fig. 47) whereas the molecules of series VIII are unsymmetrical having fixed chiral 2 - methyl butoxy group at one end. In the case of series C, the length and polarizability of the molecules will be higher from fourth homologues compared to that of series - VIII. It is known that increase in the length and polarizability enhances the smectic and nematic thermal stabilities (218). This is reflected in the enhanced thermal stabilities of series - C compared to those of series VIII (Table - 38).

The difference in the molecules of series D and series VIII is in one of the central linkage and the terminal alkoxy group (fig. 47). Molecules of series - D have -CH=N- central linkage and the molecules of series VIII have -CONH- linkage. The molecules of series D have n-butoxy group at one end where as molecules of series VIII have - chiral 2-methyl butoxy group at that end.

It has been observed by Vora et al (368) that compared to schiff base linkage -CH=N-, the -NH-CO- linkage enhances smectic and nematic thermal stabilities. This suggests that decrease in the cholesteric thermal stability of series - VIII should be attributed to branched chiral alkoxy group. This is justifiable because as discussed in the begining, the cholesteric thermal stability of series VIII is much less compared to that of series A where both the series differ only in the terminal alkoxy group and the difference in terminal alkoxy group of series VIII and A is similar to that in series VIII and D.

The interesting aspect in series VIII and series - D is that the smectic thermal stability of series VIII is higher compared to that of series D eventhough the trend is opposite in cholesteric and nematic thremal stability. This observation further supports the previous observation of Vora et al (368), that -CO-NH- linkage enhances smectic mesophase much more compared to nematic mesophase in system differing in amide (- CONH-) and schiff base (-CH=N-) linkages.

In the forgoing discussion liberty is taken to compare effect of chemical constitution on cholesteric as well as nematic phases as if they are identical in nature. Dave et al (310, 364) have pointed out that effect of chemical constitution on cholesteric phase (observed in cholesteryl derivatives) is similar to the one observed in nematic phases. In the present work the chiral nematics (Cholesterics) are structurally more similar to nematogenic compounds. Naturally the comparision will be justifiable in understanding the role of chemical constitution on both the mesophases though there will be little difference in the absolute conformation of molecules in two phases.

4

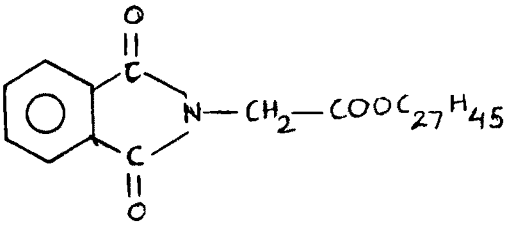
NEW MESOGENS WITH TYPICAL STRUCTURAL UNITS.

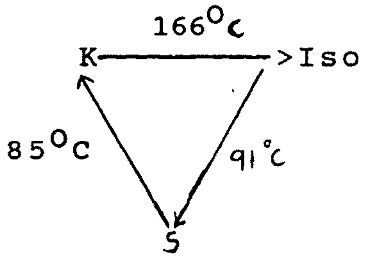
4.0 : New Mesogens with Typical structural units :

The mesogenic properties of cholesteryl devivatives of trimellitimide prompted to incorporate phthalimide nucleus and study the mesogenic properties of a few compounds to explore the mesogenic tendencies of such molecules.

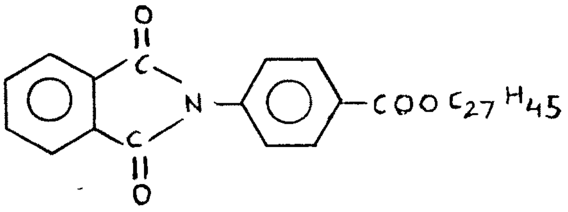
With this in view following two cholesteryl esters were synthesized and their meosgenic properties were evaluated.

MT_1 - Cholesteryl ester of N - phthaloyl glycine
[cholesteryl 2 - amino (N - phthaloyl) acetate]





MT_2 -Cholesteryl ester of N - Phthaloyl 4 - amino benzoic acid, [cholesteryl 4 - amino (N - phthaloyl) benzoate]



$K \xrightarrow{210^{\circ}C} Ch \xrightarrow{322^{\circ}C} Iso\ (d)$

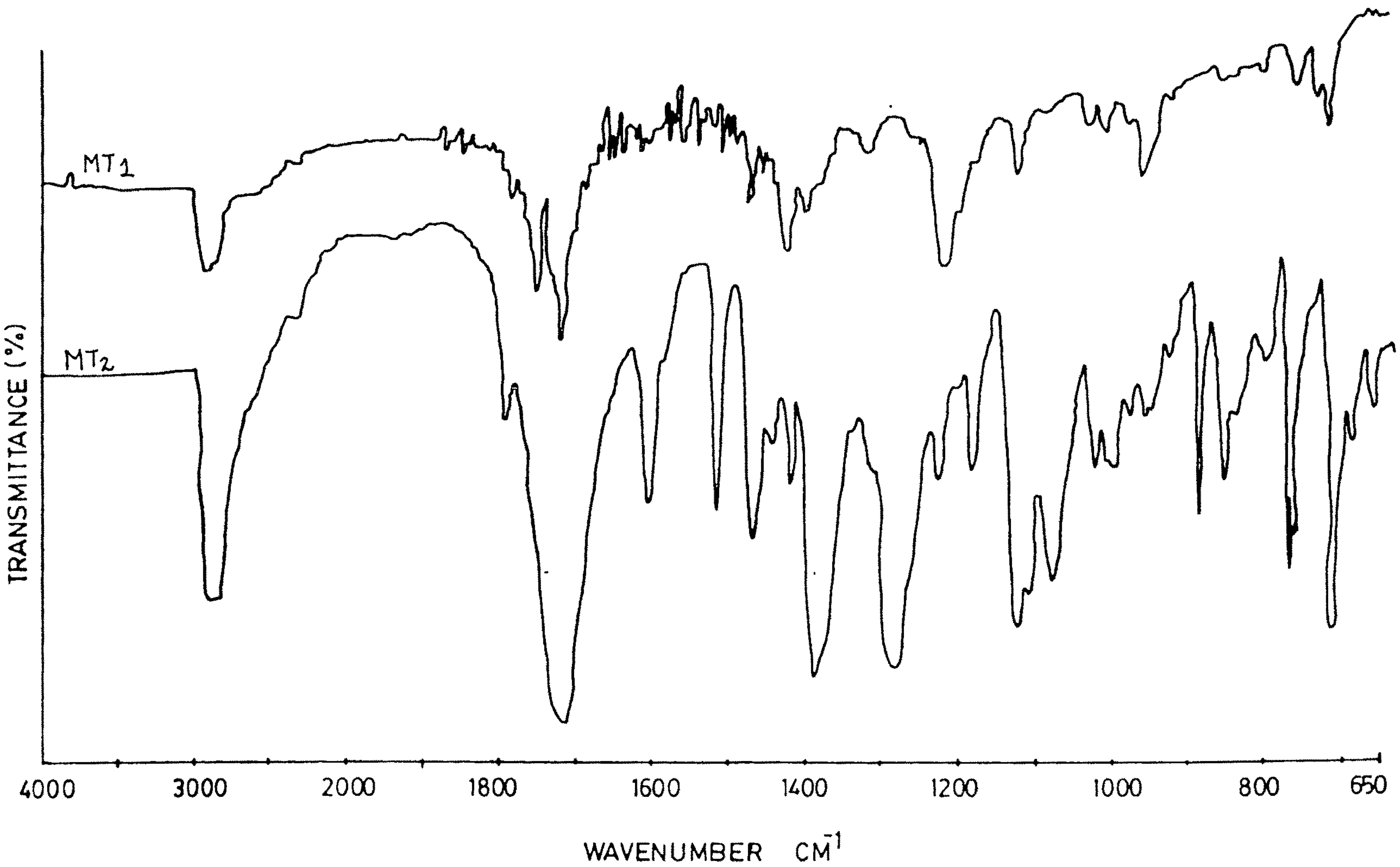


Fig. 47.a

IR Spectra of MT_1 & MT_2

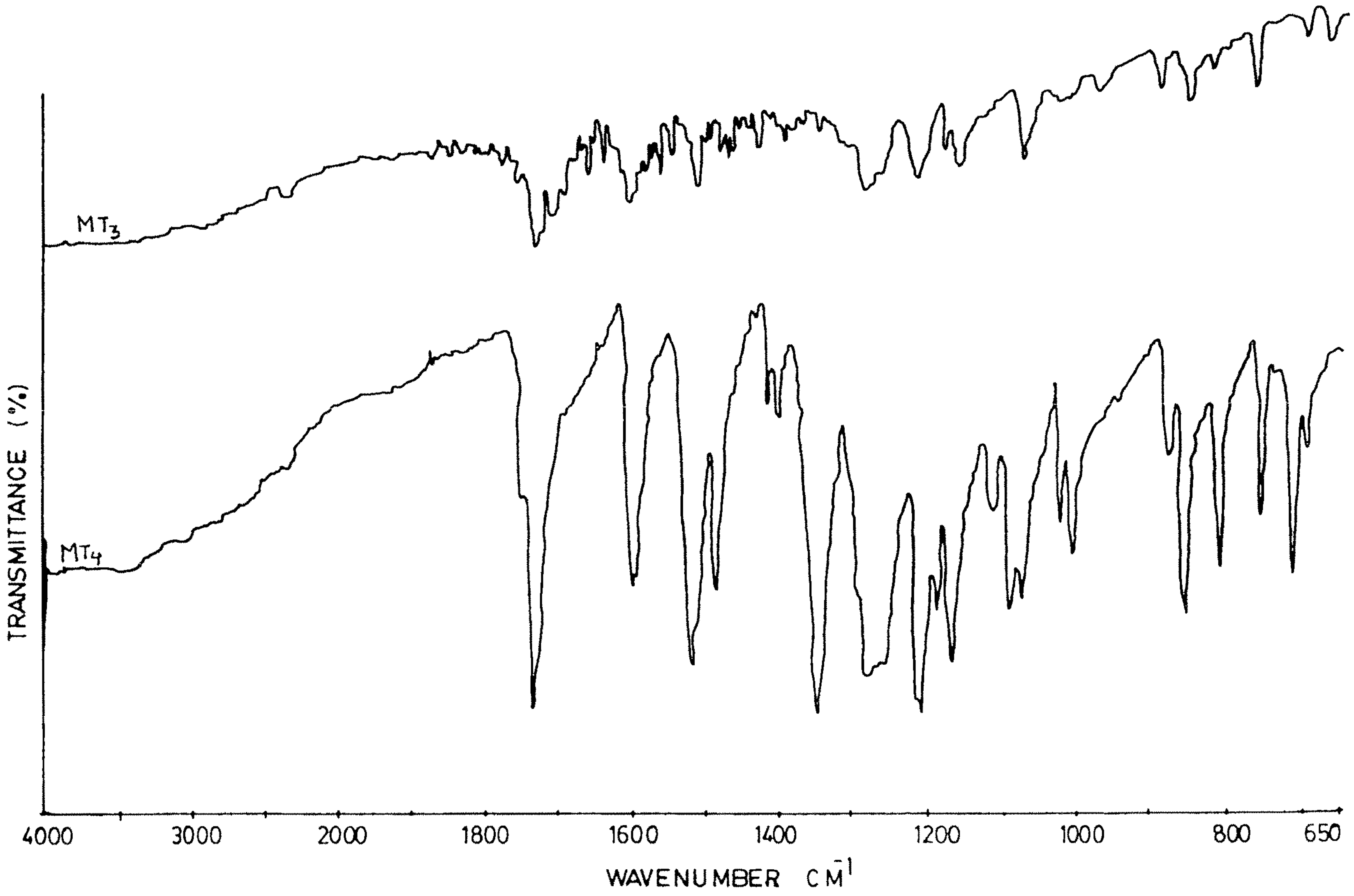
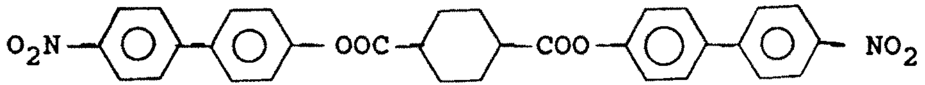


Fig: 47·b

IR Spectra of MT$_3$ & MT$_4$

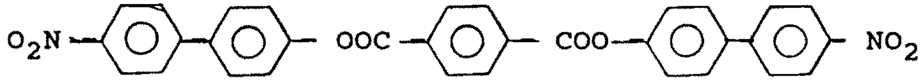
Both the model compounds exhibit mesomorphism. MT_1, exhibits monotropic smectic phase. This monotropic nature must be due to the steric interaction due to the short methylene spacer in the molecule. The transition temperatures of MT_2 can be attributed to the incorporation of phenyl ring in the molecules compared to the molecules of MT_1. It has been known that with the incorporation of polarizable phenyl ring mesomorphism is enhanced (218).

MT_3 : Di - (4 Nitrobiphenyl)-trans-1, 4-cylohexane dicarboxylate



$$K \xrightarrow{307^{\circ}C} N \xrightarrow{>360^{\circ}C} Iso(d)$$

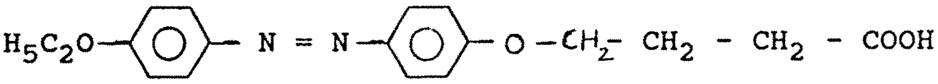
MT_4: Di - (4-Nitrobiphenyl) - terephthalate

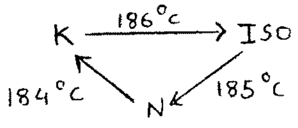


$$K \xrightarrow{315^{\circ}C} N \xrightarrow{>360^{\circ}C} Iso(d)$$

Both the compunds MT_3 and MT_4 exhibit nematic phases of very high thermal stability. This is expected as molecules of both the compounds posses two biphenyl moiety having terminal nitro ($-NO_2$) substituent. Even the central trans - cyclohexane ring does not reduce the nematic - isotropic transition temperature of MT_3 compared to MT_4 which has a central 1, 4 - phenylene nucleus. This indicates that trans conformation of 1, 4 - cyclohexyl derivative does not affect N-isotropic transition temperature adversely.

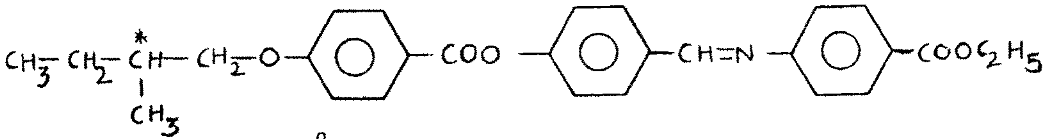
MT_5: 4-Ethoxy -4'- carboxypropoxy azobenzene

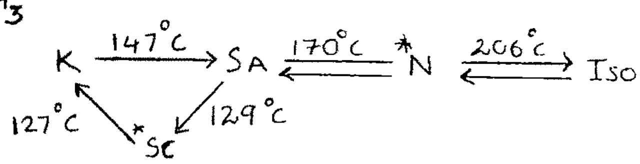




The monotropic phase is followed by crystalization. Number of other compounds are now being synthesized by other researchers of the group in the laboratory based on this initial findings of MT_5.

MT_6 : Ethyl 4(4' - β - methyl butoxy benzoyloxy) benzylidene - 4" amino benzoate.





A chiral compound was synthesized having an ester and the schiff base linkage to initiate work in this direction. MT_6 exhibits monotropic smectic *C, SmA and cholesteric phases. This has opened up the avenue for the synthesis of chiral mesogens exhibiting smectic *C phase and cholesteric phases with simpler structure.

5

FLUORESCENT MESOGENIC POLYMERS WITH CHALCONE LINKAGE.

5.0 : Fluorescent Mesogenic Polymers with Chalcone linkage :

The rarity of mesogenic compounds having chalcone linkage and potential of polymers with this linkage for application prompted Vora and Sheth (374) to study the polymers with chalcone linkage. Recently Chudgar and Shah have reported a mesogenic homologous series with chalcone linkage for the first time(375)

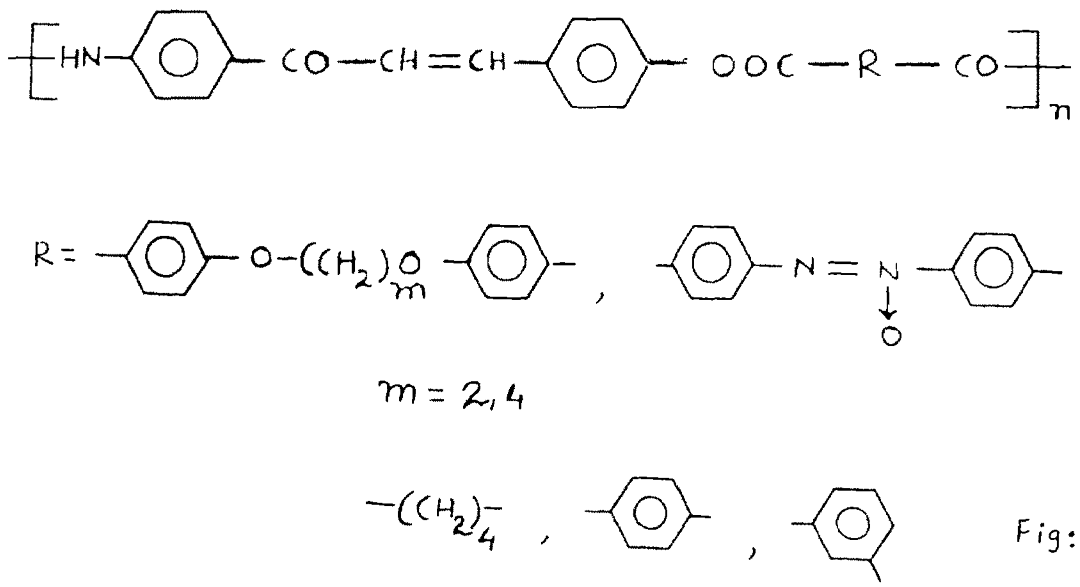


Fig:48.a

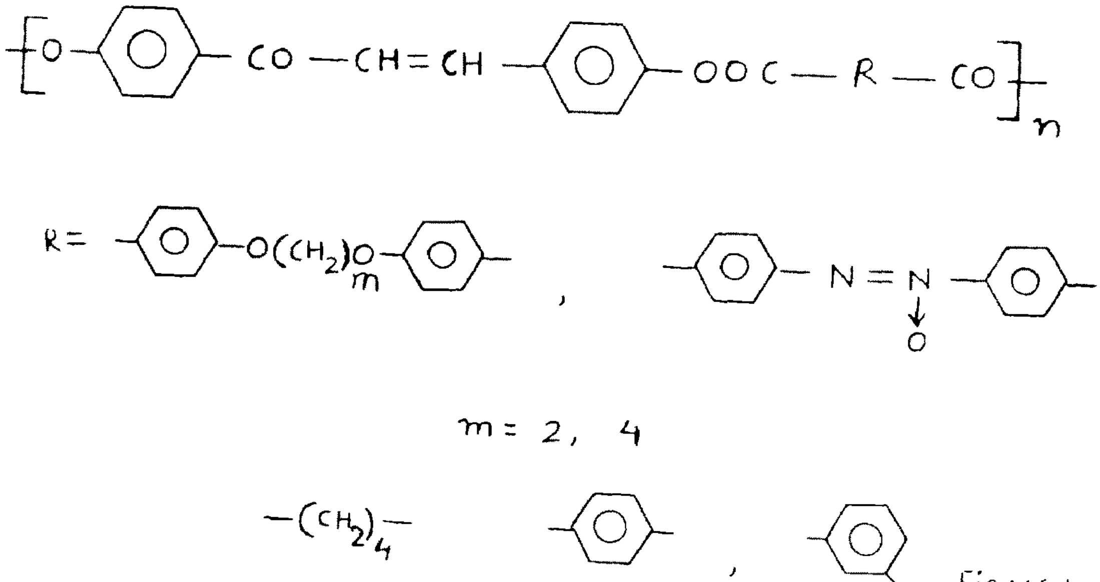


Fig:48 b

Vora and Sheth (374) studied polyesters and polyester amides by varying flexible methylene spacers from $(-CH_2-)_2$ to $(-CH_2-)_4$ and they also varied dicarboxylic acid chlorides having rigidity and flexibility as shown in fig. 48.a,b.

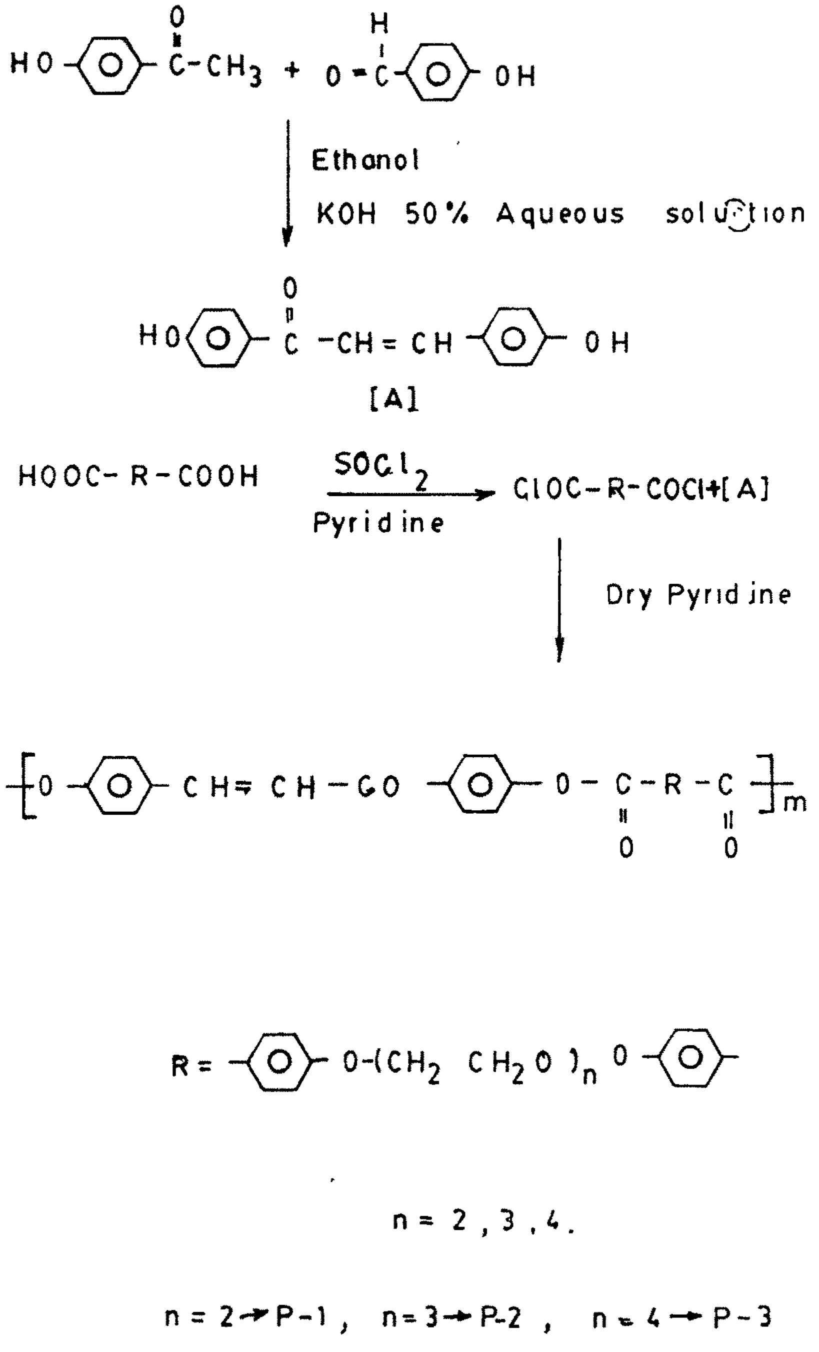
It was proposed in the present study to vary the length of oxyethylene flexible spacers in the acid moiety to evaluate the effect of increased flexibilities on mesogenic properties of polymer.

With this in view three polyester.chalcones are synthesized by the route given in fig. 49.

Reference to table 39 indicates that polymers P_1 and P_2 exhibit nematic phases. Polymer P_3 does not exhibit birefringence, but the polymer melt on slight disturbance exhibits intense birefringence. The polymer P_3 on cooling solidifies as a glassy material. The nematic phase of the polymer exhibits marble texture. (Microphotographs No K to M).

The comparision of mesogenic properties of different polymers is a difficult task as the mesogenic properties of polymers depend not only on the chemical constitution but also on the molecular weight and polydispercity of the system.

In the present study the structures of all the three polymers vary uniformly hence intrinsic viscosity values (η) are taken to compare the properties of polymers. Due to the solubility pararmeters of the polymers GPC study could not



SYNTHETIC ROUTE TO POLYMERS P_1 TO P_3

FIG:- 49

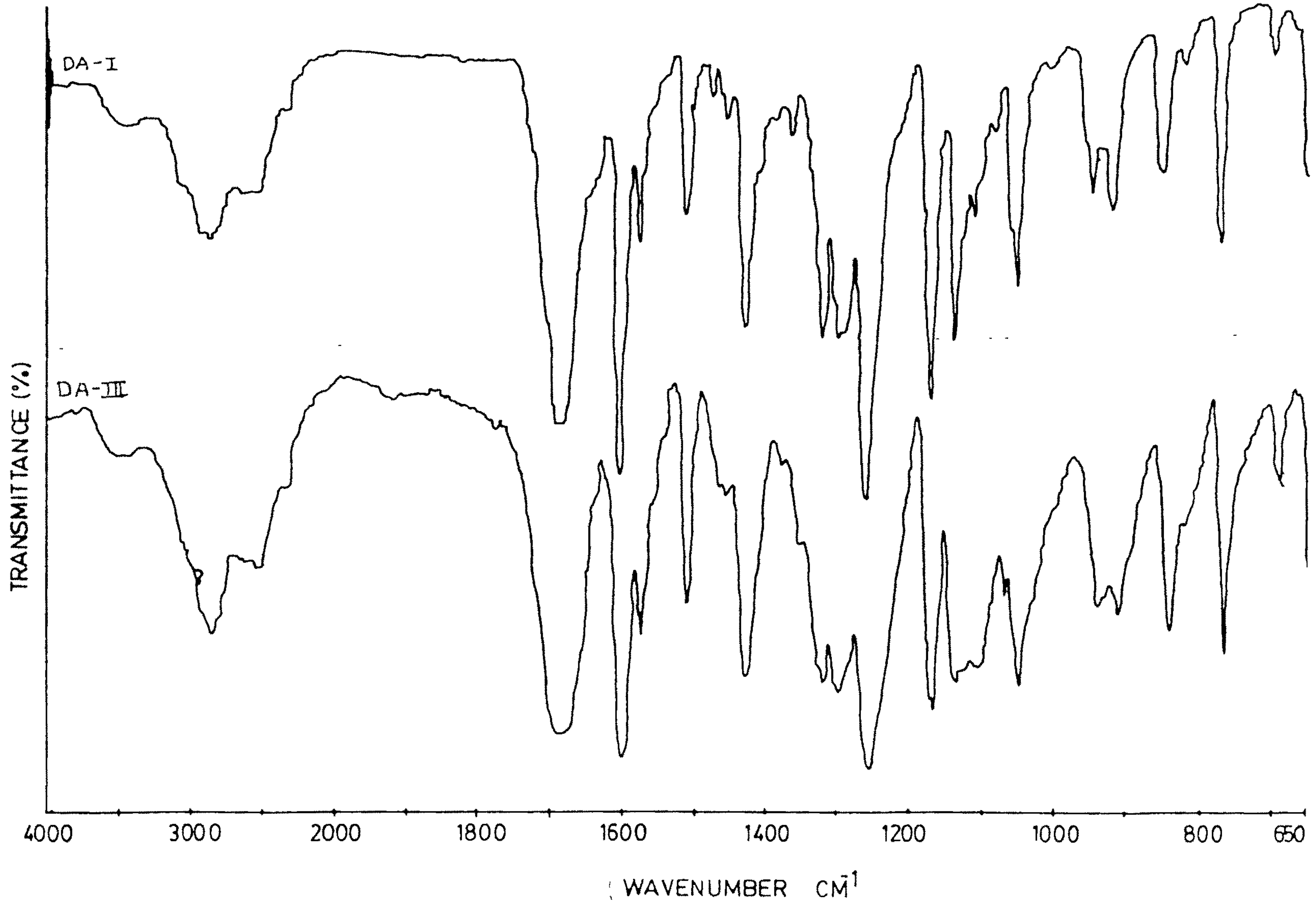


Fig: 50.a

IR Spectra of DA-I & DA-III

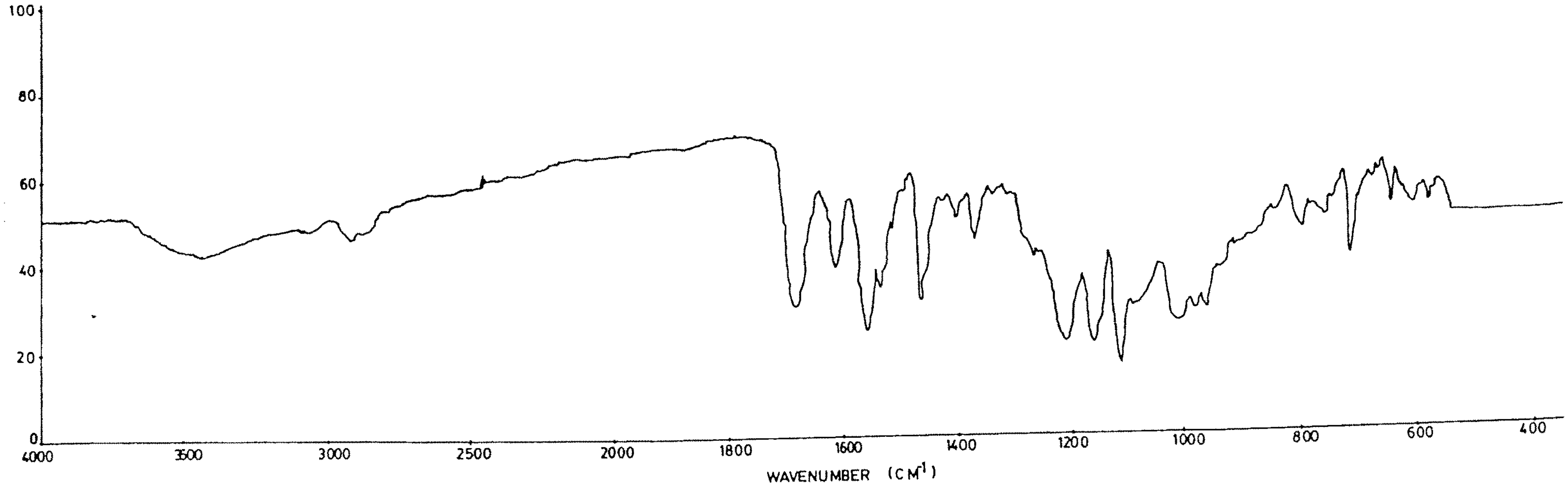


FIG 50·b

IR Spectra of P_1

PLOT OF $n_{sp/c}$ VERSUS CONCENTRATION

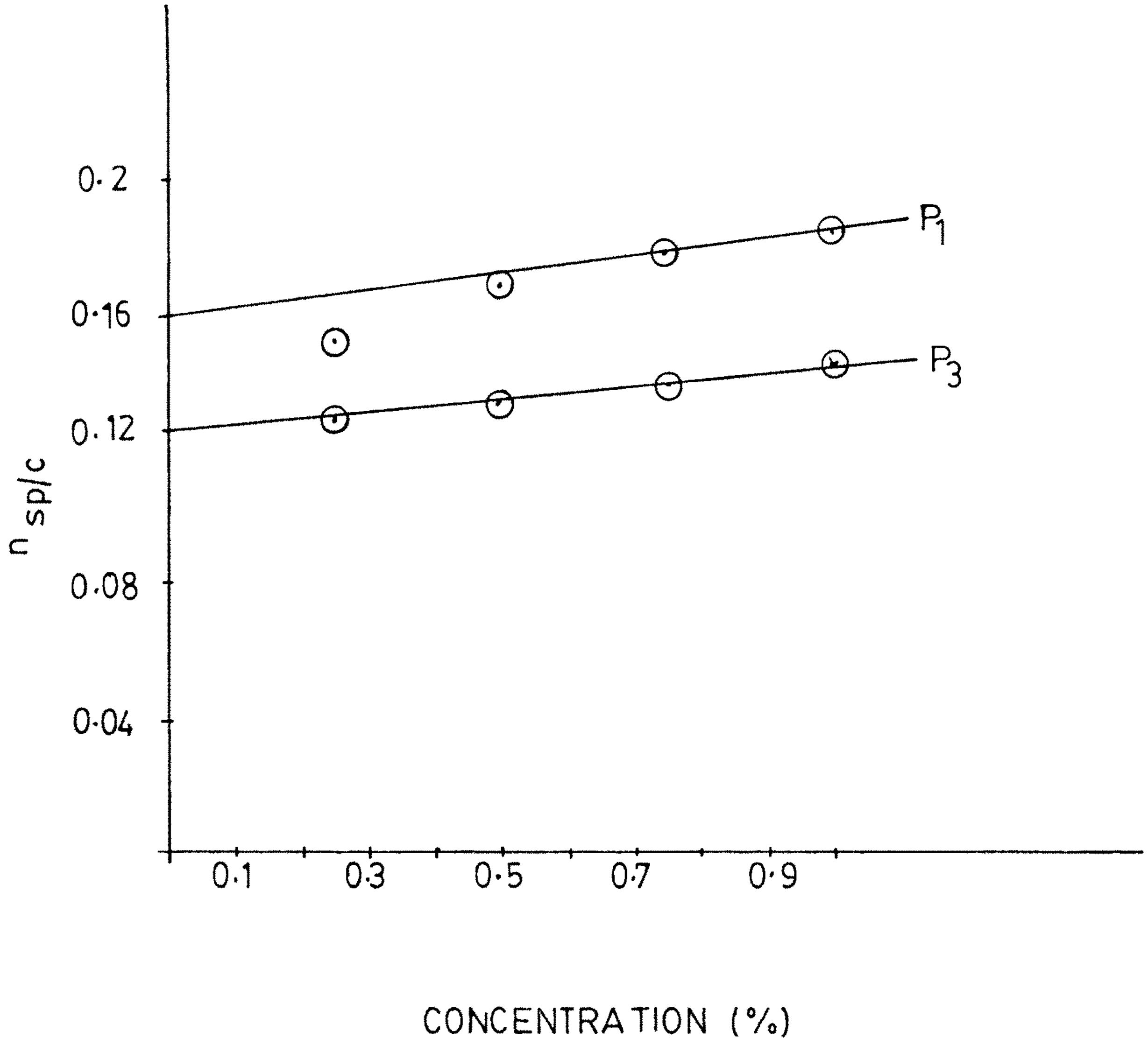
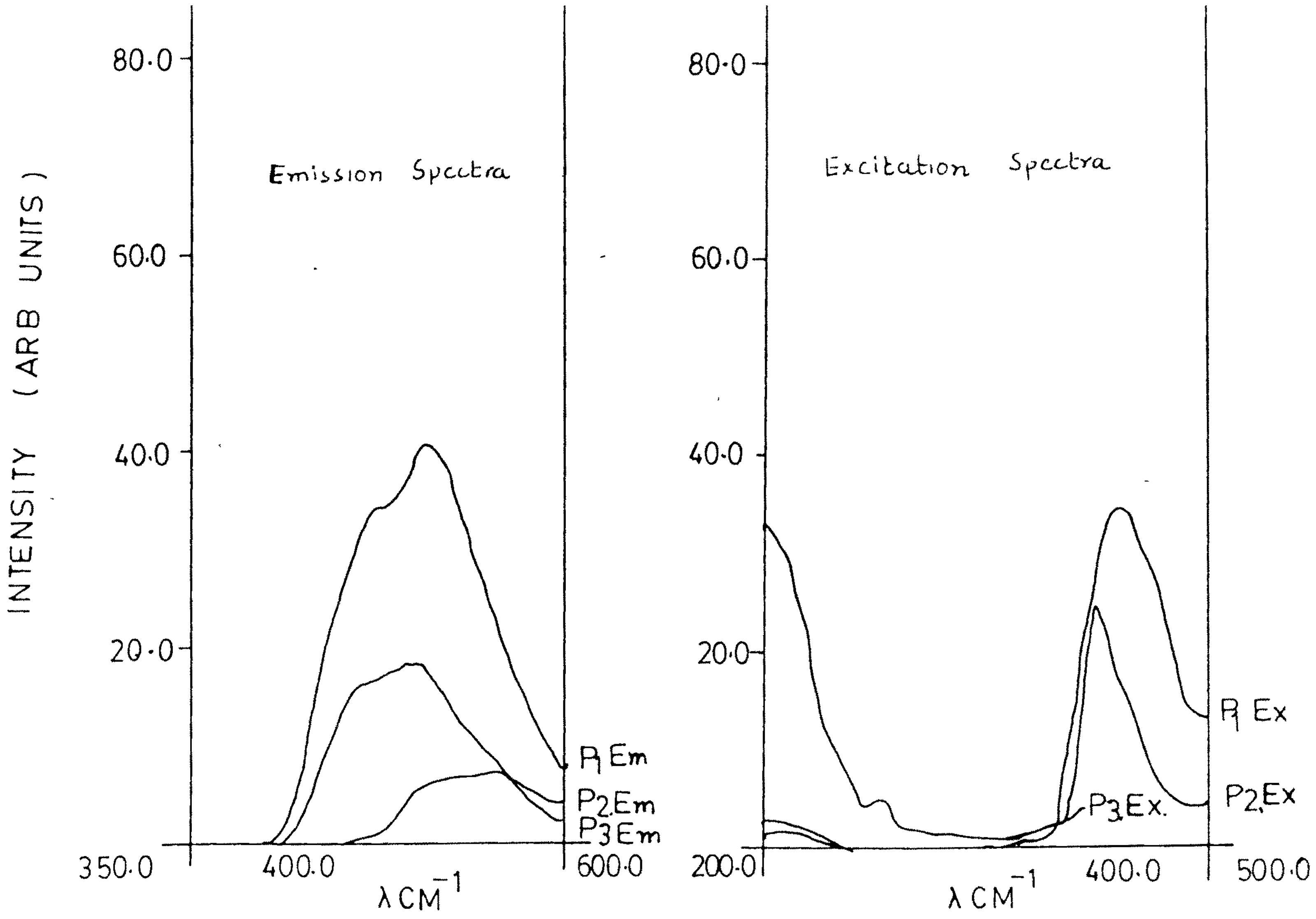


FIG. :- 51



FLUORESCEMENT SPECTRA OF THE POLYMERS P_1, P_3

FIG. - 52

be carried out. The mesogenic trend in P_1 to P_3 indicates (Table-39) that as the flexibility increases mesogenic properties decreases. Polymer P_2has very low solid - nematic and nematic - isotropic transitions compared to polymer P_1. Polymer P_3 is non-birefringent.

This indicates that addition of each oxyethylene linkage adversely affects the transition temperatures and mesomorphism in the system. This can be attributed to the increased flexbility of the system resulting from the addition of each "oxyethylene" ($-CH_2-CH_2-O-$) unit.

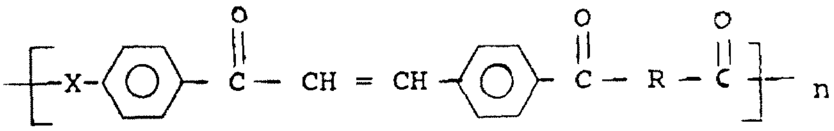
The comparision of the transition temperatures of the present system with the systems studied by Vora and Sheth (374) will be quite interesting.

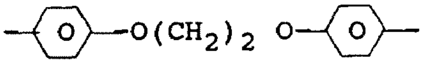
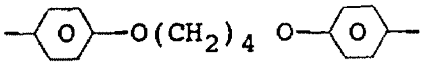
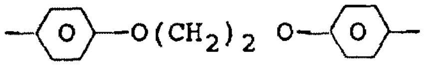
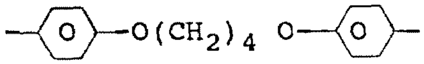
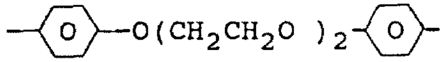
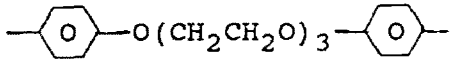
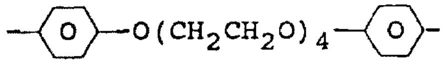
The comparision of transition temperatures is given in table 39.

The reference to table 39 indicates that present system exhibits nematic phases of lower thermal stability compared to the system having methylene flexible spacers (fig. 48.a,b). Not only this, the AHC, HC systems with $-(CH_2)_2-$ and $(CH_2)-_4$ flexible spacers exhibit smectic phases alongwith nematic phases. The difference in the present system and the AHC and HC system is in the type and number of flexible groups. It has been observed in low molecular system that increase in flexibility in the central linkage decreases solid mesomorphic and/or mesomorphic -isotorpic transitions and in some cases eliminates mesophases (218).

TABLE - 39

Transition Temperatures °C



Polymer	X	R	Transition	Temperatures°C	
			S	N	Iso
AHC-1	NH		140	205	274
AHC-2	NH		101	170	255
HC-1	O		142	190	>300(P)
HC-2	O		155	205	252
P1	O		-	162	201
P2	O		-	77	139
P3	O		-	-	76+

+ Gives intense birefringence upto 106°C, Solidifies as glass

The flexibility of `oxyethylene ' two and three units means introduction - CH_2-CH_2-O-CH_2-CH_2 five and eight atoms including oxygen in the central linkage. Naturally the increased flexibility decreases the mesogenic tendencies of the present system. The absence of smectic phase also can be attributed to the increased flexibility. The (η) value of the present system is little higher but that is not sufficient to increase the thermal stability of the mesophases. Graph of ηsp/c vs c is shown in the fig. 51.

It will be interesting to study the polyesteramides of chalcones with oxyethylene spacers.

The polymers P_1 to P_3 are screened for fluorescent properties (fig. 52).

The further work is contemplated to study the effect of ordered structure on the fluorescent behaviour of the polymers.

6

TEXTURES OF DIFFERENT PHASES.

6.0 : Textures of Different Phases and Characterization of Smectic Phases :

The microscopic method of characterization is by observing textures of different phases. Many times the polymorphism of smectic phases posses problems due to their identical textures or due to slight change in texture of the phase. In such (26, 223) cases classification is carried out by miscibility studies. The contact method has been applied for studying the miscibility behaviour. It is known that like phases are miscible with each other in all proportions whereas the unlike phases are only partially miscible. This technique was pioneered by Sackmann and Demus (26) and has been used by number of workers (223) in the field and is quite reliable. However, the calorimetry (139) and X-ray analysis (139) etc. are used to confirm the types of smectic phases and the molecular arrangement in the phases.

In the present study the types of the smectic mesophases are inferred from the textures observed under polarizing micrscope as well as by studying the miscibility behaviour of phases with the labelled smectic compounds.

Following labelled compounds were used for the characterization :-

(A) Smectic A labelled compounds :-

(i) 4(4'-n Hexadecyloxybenzoyloxy) benzylidene -2" - amino phenol (376)

$K \xrightarrow{77^{\circ}C} SA \xrightarrow{135^{\circ}C} Iso$

(B) Smectic C labelled compounds :-

(i) 4-n-Octadecyloxy benzoic acid (240)

$K \xrightarrow{103^{\circ}\ C} SC \xrightarrow{131.5^{\circ}C} Iso$

1. Cholesteric Texture :-

Classical texture exhibited by cholesteric compounds is focal-conic similar to a smectic texture which on slight distrubance or with a pressure on coverslip changes to the plane texture which normally exhibits vivid colours. Many times in cholesteric plane texture, certain typical broad -, thread like lines are observed which are called oily streaks.

The different textures of cholesteric phases exhibited by different compounds prepared in the present work are given in fig. A to F.

Photograph `A' exhibits appeareance of focal-conic texture from isotropic liquid on cooling. Other photographs exhibit plane textures including the one exhibiting oily streaks. Some of these compounds exhibit vivid colours which can be seen from the photographs.

2. Nematic Textures :-

2.1 Nematic Textures in simple liquid crystals :-

The nematogens exhibit classical threaded texture and the marble texture. The photographs of different nematogens are taken in the nematic phase which exhibits both types of textures
(Photographs G to J).

2.2 Nematic texture observed in polymers :

The classical textures of smectic and nematic phases are difficult to observe in masogenic polymers. Many times a slide is kept on the heating stage for a longer period at fixed temperature to develop the classical textures more so for the focal-conic smectic texture.

In the present study polymer P_1 and P_2 exhibited nematic texture without any difficulty. Photographs K and L are showing nematic phase observed in polymer P_1. Photograph M shows birefringence observed in polymer P_3.

3. Textures of smectic phases and the labelling of smectic phases by miscibility studies :-

The smectogens studied in the present work exhibit either focal-conic (fan-shaped) or schlieren texture. Focal conic texture suggest the presence of Sm_A phase (photographs N to Q) whereas schlieren texture indicates the presence of

Smectic C (30.a,b) phase photograph. S

3.1 : Characterization of Smectic phases :

Series I 4(4'-n- Alkoxy benzoyloxy)-4" nitro biphenyls

Smectogens = n-butoxy to n-octadecyloxy derivatives.

Series II 4-(n-Alkanoyloxy) -4'-nitrobiphenyls.

Smectogens = n-nonyl to n - hexadecyl derivatives.

Series III 4-n- Alkoxy -4'-nitrobiphenyls.

Smectogens = n-heptyloxy to n-hexadecyloxy derivatives.

Series VI Cholesteryl 4-n alkoxy phenylcarbamates

Smectogens = Methoxy to n-Octadecyloxy derivatives.

Smectogens of respective homologous series were studied for intermiscibility. Above mentioned homologues for series I-III and series VI were intermixed by contact method. The results indicated that each series exhibits same kind of smectic mesophase.

The representative smectogens of different series were selected for further characterization. The textures exhibited by all the smectogens were observed under the microscope as discussed earlier. The characterization was further carried out by using a labelled smectogen for contact study. The miscibility study was carried out first by labelled smectic A compound, as all the smectogen exhibited focal-conic (fan-shaped) texture characteristic of smectic A phase. The smectic mesophase of the respective smectogens of different series exhibited continous miscibility with smectic A mesophase of labelled smectogens. This indicated that smectogens of series I-III and VI exhibited smectic A phases.

As per the prescribed method the miscibility of representative semectogens was also studied with labelled smectic C-compound. The smectic phases of above homologoues do not mix with the smectic C phase of the labelled compound.

The study indicated that the smectogens of series I-III and VI exhibit smectic A type mesophase confirmed by miscibility studies and texture phenomena.

3.2 : Exhibition of `Filament or Ribbon like' Texture :

An interesting observation was found during miscibility study. The isotropic melt of smectogen of series I (octyloxy derivative) and labelled smectic -C compound 4-n-octadecyloxy benzoic acid on cooling gave `Filaments' or `Ribbon' like texture which coalesce to focal-conic texture. Filaments grow to a certain size and then suddenly bundle up in a focal-conic texture. Such phenomena was observed by Arora et al (76.a), in their study of mesophases exhibited by the Cyanobiphenyl esters. However, later on they reported that the phenomena is observed when impurities are present in the smectogen (76.b). With the above background it was thought to study the phenomena in more detail.

The mixture of n-octyloxy derivative exhibiting smectic A phase and n-octadecyloxy benzoic acid exhibiting smectic C phase gave `Ribbon' like texture on cooling the isotropic phase. As the concentration of smectic C compound increased, phenomena was more intense. Similarly, behaviour was observed in the binary mixture of n-octyloxy derivative of series I, n-tridecyl derivative of series II, with n-Octadecyloxy benzoic acid exhibiting smectic C phases. To confirm that such behaviour is observed by the impurities, n-heptyloxy phenol was added to n-octyloxy derivatives of series I, the melt did not give any ribbon like texture. The study indicated that when two components of a binary system are exhibiting smectic A and smectic C phases and the smectic C phase component has higher alkoxy group than the isotropic melt of the mixture exhibits ribbon type texture before giving focal-conic texture of smectic A phase.

Before arriving to final conclusion more binary systems will be studied to observe the filament formation in such systems.

3.3 : Smectogens of Series VIII :

Series VIII is chiral one and the exhibition of Sm*C is an important phenomena as this phase gives ferro-electric properties.

C_{14} to C_{18} members of the series exhibit texture classical of smectic*C phases. The range of Smectic*C phase is relatively short hence the contact method is not much useful in ascertaining the smectic*C phase in this compounds. These compounds are quite stable and exhibit Sm *C phase at higher temperatures hence can be good candidates for enhancing the transition temperatures of ferroelectric mixtures used for applications in electronic displays.

3.4 : Chiral smectogen (*MBBNB) :

S(+) 4(4"-β methyl butoxy benzoyloxy) 4'-nitrobiphenyl.

This smectogen exhibits two smectic phases S_1 and S_2 , S_1 exhibits focal conic texture and has tendency to become homeotropic (Photograph P, Q). On further heating S_1 phase exhibits typical texture of S_2 at 205°C temperature (Photograph R) which is precisely reversible. Texture of S_2 phase is similar to the one reported by Goodby et al (351) as chiral Sm A^* phase. Further characterization is contemplated on this compound to establish the nature of smectic phase of S_2.

This study shows that most of the smectogens reported above exhibited "smectic A" phases, whereas a few of them exhibited chiral smectic *C phases.

The labelling was easier for the above compounds, as the reference compounds with labelled smectic mesophases and overlapping mesophase range could be traced and synthesized.

A. Microphotograph of cholesteric phase which exhibits appearance of focal- conic texture from isotropic liquid of S (+) 4(4'-β-methyl butoxy benzoyloxy)-4"-n dodecyloxy benzanilides on cooling at 188°C.

B. Microphotograph of cholesteric phase exhibits focal conic texture of S(+) 4(4'-β-methylbutoxy benzoyloxy)-4"-n-dodecyloxybenzanilides on cooling at 187°C.

C. Microphotograph of cholesteric phase with plane texture of compound CC-1 on cooling at 113°C.

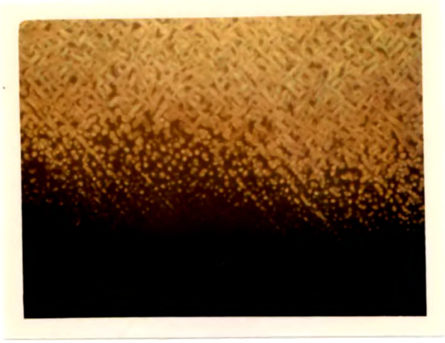
D. Microphotograph of cholesteric (chiral nematic) phase with oily stricks of S(+) -4(4'-β-methyl butoxy benzoyloxy) -4"-n-dodecyloxy benzanilides on heating at 188°C.

E. Microphotograph of cholesteric (chiral nematic) phase with oily stricks of 4(4"-β-methyl butoxy benzoyloxy)-4'-nitrobiphenyl on heating at 217°C.

F. Microphotograph of cholesteric (chiral nematic) phase with oily stricks of 4(4"-β-methyl butoxy benzoyloxy)-4'-nitrobiphenyl on heating at 220°C.

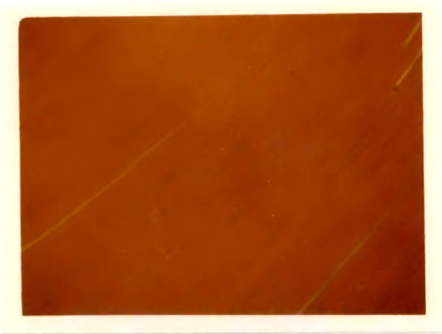
* All the photographs taken under cross polarizers.

* Magnification 20 x 10



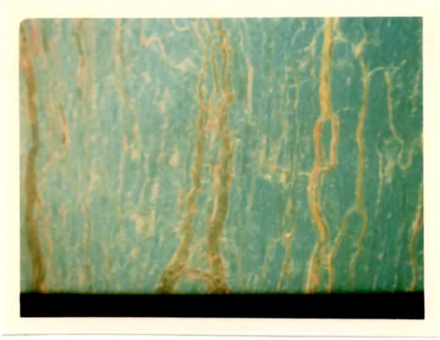
A

B



C

D



E

F

G. Microphotograph of nematic schlieren texture of 4(4"-n-butoxy benzoyloxy)-4'-nitrobiphenyl on heating at 192°C.

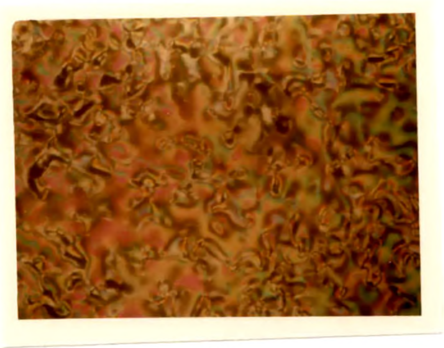
H. Microphotograph of nematic marble texture of 4(4"-n-Heptyloxy -benzoyloxy) 4'- nitrobiphenyl on heating at 228°C.

I. Microphotograph of nematic marble texture of 4(4"-n-propoxy benezoyloxy)-4'- nitrobiphenyl on heating at 180°C.

J. Microphotograph of nematic marble texture of 4(4"-n-propoxy benzoyloxy)-4'- nitrobiphenyl (when cover glass was pressed) on heating at 250°C.

* Photographs taken under cross polarizers.

* Magnification 20 x 10



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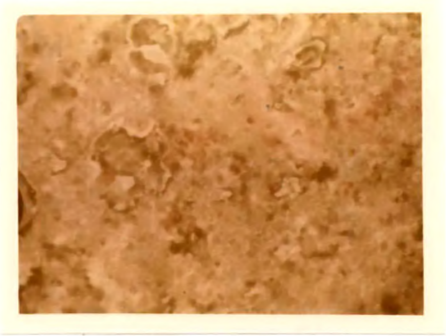


H

I

J

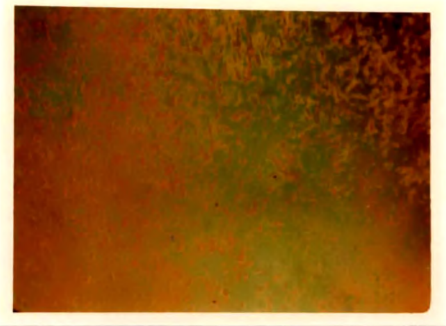
K. Microphotograph of nematic marble texture of polymer P_1 on heating at 193°C.

L. Microphotograph of nematic marble texture of polymer P_1 on cooling at 176°C.

M. Microphotograph of polymer P_3 showing intense birefringence during heating at 73°C on pressing the coverslip.

* All the photographs taken under cross polarizers.

* Magnification 20 x 10



K

L

M

N. Microphotograph of smectic A texture of 4(n-Undecanoyloxy)-4'- nitrobiphenyl on heating at 65°C.

O. Microphotograph of smectic A texture of Cholesteryl 4-n-Octyloxy phenyl carbqmate on cooling at 168°C.

P Microphotograph of smectic A texture of 4(4"-β-methyl butoxy benzoyloxy)-4'-nitrobiphenyl on heating at 179°C.

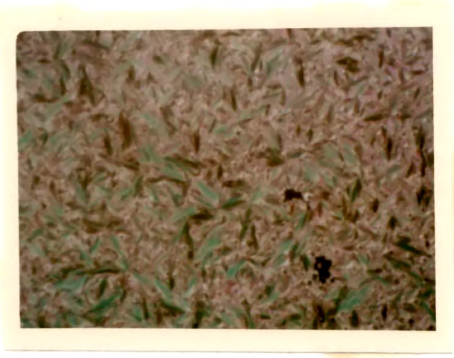
Q. Microphotograph of smectic A homeotropic texture of 4(4"-β-methyl butoxy benzoloxy)-4'-nitrobiphenyl on heating at 181°C.

R. Microphotograph of smectic X (S$_2$) texture of S(+) 4(4'- β-methyl butoxy benzoyloxy)-4'-nitrobiphenyl on heating at 206°C.

S. Microphotograph of smectic C schlieren texture of S(+) - 4(4'- β- methyl butoxy benzoyloxy) -4"-n- octadecyloxy benzanilide on cooling at 174°C.

- * All the Photographs taken under cross polarizers

- * Magnification 20 x 10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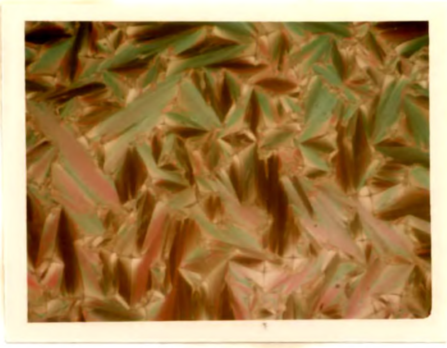
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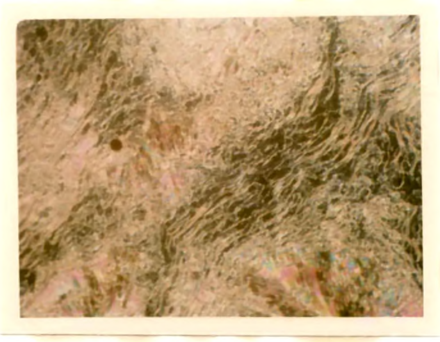
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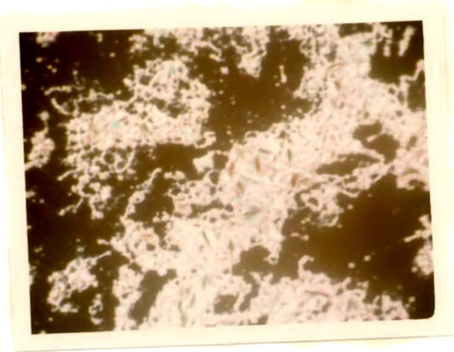
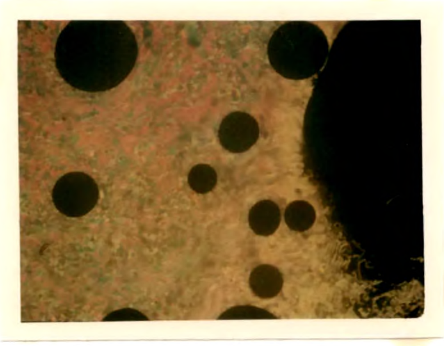

Q


R


S

7

CALORIMETRIC STUDY.

7.0 : Calorimetric Study :

Thermal analysis plays an important role in the characterisation of mesomorphic substances and in the elucidation of structure property effects. Calorimetry is a valuable help to detect polymorphism and can yield some clues to phase transition. A knowledge of both the temperature and heat of transition is necessary if the principles of physical analysis are to be applied to mesophase forming systems. From this information the transation entropy may be calculated which acts as a key for evaluating the type and degree of order present in systems involving phase changes.

The melting process can be characterized by the entropy change on fusion (377). We can break the overall entropy of fusion ΔS_f into the three approximate parts : positional,, orientational and conformational entropy of fusion.

$$\Delta S_f = \Delta S_{pos} + \Delta S_{or} + \Delta S_{con}$$

Crystals of spherical motifs such as noble gases and metals show only positional disordering. Independent of the molecular size, ΔS_f is usually between 7 and 14 J/(K mol^o) (378). This is the rule of Richards (379), analogous to Trouton's rule for entropies of evaporation. Similarly, one finds for crystals which seperate on melting into small, non-spherical rigid motifs, that the entropy of fusion consists of positional and orientational contribution. In this case one finds a ΔS_f between 30 and 60 J/(K mole^{o}) (378) as first observed by Walden (380). Again, ΔS_f is size-independent. As soon as a molecule can show conformational disordering, it has additional contribution to ΔS_f. This conformational contribution is dependent on the number of bonds around which conformational disordering is possible. The paraffins represents a well documented series of molecules with increasing fractions of conformational entropy of fusion (378). The practically spherical methane shows a final ΔS_f of 10.3 J/(K mole^{o}) which is largely positional. Nonspherical ethylene which undergoes no conformational isomerism, has a ΔS_f of 32.2 J/(K mole^{o}), consisting of positional and orientational contributions. The straight-chain n-decane has a ΔS_f of 118.2 J/(K mole^{o}) because of its large conformational entropy in the melt. Camphor, which is nearly spherical and rigid, in turn, is similar in numbers of atoms to n-($C_{10}H_{16}O$ versus $C_{10}H_{22}$), but has a ΔS_f of only 14.3 J/(K mole^{o}). It cannot contain conformational or orientational contributions. Linear flexible macromolecules finally have, because of their large size, only negligible positional and orientational contributions per mole of repeating units. Their entropy of fusion is dominated by conformational contributions. Analysis of equilibrium data on fusion of many macromolecules has revealed that ΔS_{conf} is about 9.5 J/(k mole^{o}) (378) for each mole of bonds around which conformational freedom is attained on fusion. The devitrification process shows no change in entropy.

Thermally, an increase in heat capacity is observed. The exact temperature range of this increase is dependent on cooling and heating rate. The glass transition is dynamic in nature. Empirically, one could observe that molecule of similar size and number of motifs that starts moving on devitrification have similar increase in heat capacity, ΔC_p. For small motifs one finds a ΔC_p of about 11.3 J/(K mole^{o}) (381). For large motifs, such as phenylene or larger ring structures, the contribution may be two to three times this amount (382). As one can judge from entropy increase on fusion the gain of disorder, one can judge from heat capacity increase on devitrification, the gain of mobility.

Based on this simplified description of the melting and glass transitions, it is possible to propose number of mesophases. It is possible to keep orientational order, but lose positional order. These "positionally disordered" crystals or "orientationally ordered" liquids (383) are widely known as liquid crystals (140).

Next is group of materials with a mesophase which shows "orientational disorder", but positional order. These materials are widely known as plastic crystals (384), because of the ease of deformation of such crystals. This name is well accepted and much less cumbersome than "orientationally disordered" crystals (383).

The third group of mesophase materials represents the "conformationally disordered" crystals, called `condis crystals'. The physical properties of `condis crystals', which largely maintain positional and orientational order, change in much too subtle a way from the fully ordered crystals so that a common property could be attached to their name.

The difference between the three mesophase crystals are largely based on the geometry of the molecules. We can expand on the summary of Smith (383) who compared liquid and plastic crystals and states : The molecules of liquid crystals always have a rigid, mesogenic group which is rod or disc like and causes a high activation energy to rotational reorientation (1). The molecules of plastic crystals, in contrast, are compact and more globular, so that their reorientation is not opposed by a high activation barrier. The `condis crystals', in turn consist of flexible molecules which can undergo relatively easily hindered rotation to change conformation without losing positional or orientational order.

It was planned to carry out calorimetric study of some homologous series to find enthalpy and entropy changes by using DSC technic at phase transations. Following six homologous series were selected for thermal study.

(1) 4-(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyl

(2) 4(n-Alkanoyloxy)-4'-nitrobiphenyl

(3) 4-n-Alkoxy-4'-nitrobiphenyl

(4) Dicholesteryl carbonates with rigid and flexible spacers.

(5) Cholesteryl 4-n-alkoxy phenyl carbonates.

(6) S(+) 4-(4'-β-methyl butoxy benzoyloxy) -4"-(n-alkoxybenzoyloxy) benzanilides.

(i) 4-(4"-n-alkoxy benzoyloxy)-4'-nitrobiphenyl.

Total thirteen members (C1 to C8, C10 - C18) were screened by DSC method. All the members exhibit prominent endothermic peaks for solid-mesogenic transitions, small peaks for Smectic nematic and mesogenic isotropic trasnition (fig.52.a)

In this series propoxy, octyloxy, decyloxy and dodecyloxy derivatives exhibit additional endothermic peaks for the solid-solid transition.

Enthalpy and entropy data are given in table 29. first two members of the series exhibit two sharp endothermic peaks for solid- nematic and nematic-isotropic transitions. Fourth homologue also exhibited sharp peaks for solid-nematic and nematic-isotropic transitions. The microscopic studies have indicated that n-butoxy derivative exhibits monotropic smectic phase. Due to this reason, the DSC was also run on cooling the sample. An additional exothermic peak for the nematic-smectic transition was obtained on cooling before crystallization which confirmed the microscopic observation of monotropic smectic phase. From n-pentyloxy to n-octyloxy derivatives three sharps endothermic peaks were obtained on heating, n-decyloxy to n-octadecyloxy derivatives, exhibited two peaks for solid-smectic and smectic to isotropic transitions.

(ii) 4-alkanoyloxy-4'- nitrobiphenyl

Six members of this series from C7 to C15 were screened by DSC method. Members exhibit endothermic peaks on heating for solid-mesogenic and mesogenic-isotropic transitions. Monotropic phases were confirmed by running the samples while cooling where exothermic peaks were obtained.

The enthalpies and entropies data are given in table 30. DSC Thermograms Fig. 52. b

(iii) 4-n-Alkoxy-4'-nitrobiphenyl

Five members were screened by DSC method. All the five members were showing endothermic peaks for solid-mesomorphic and mesomorphic-isotropic transitions. The enthalpy and entropy data are given in table 31. (Fig: 52. C)

(iv) Dicholesteryl carbonates with flexible and rigid spacers.

Ten compounds of this series have been studied by calorimetric method. Compounds CC-1, CC-4 and CC-8 show endothermic peaks for solid - solid modifications. Members of this series exhibit endothermic peaks for solid - Isotropic, solid-mesogenic and mesogenic - isotropic transitions. Monotropic phases were confirmed by running the sample while cooling where exothermic peaks were obtained. In compound CC-11 only one broad endothermic peak was obtained, it was due to the overlapping of two transitions. Colorimetric data are given in table 32. (Fig: 52. d-f)

(v) Cholesteryl 4-n-Alkoxy phenyl carbamates

All the thirteen members were screened by DSC method. Though first member exhibits monotropic smectic phase inferred from the microscopic reading, no DSC peak was obtained when the sample was run on cooling before the onset of crystallization. The propoxy derivative also exhibits monotropic smectic phase. In case of n-butoxy derivative enantiotropic smectic and cholesteric phases were also not detceted. Only one peak was observed. This single peak was due to the overlapping of two transitions which are seperated by 2°C span only. n-Propoxy, n-hexyloxy to n-Octyloxy, n-dodecyloxy and n-octadecyloxy derivatives of the series exhibit additional endothermic peaks which were due to solid-solid transitions. This phase change was also detected under microscope observations. All the members are showing endothermic peaks for phase transitions. Enthalpy and entropy values are recorded in table 33.(Fig. 52-9)

(viii) S(+) 4-(4'-β-methyl butoxy benzoyloxy)-4"-n-
alkoxy benzoyloxy benzanilides.

Seven members of this series were studied by DSC method. (C_4 to C_6, C_8 - C_{16}). n-Decyloxy derivative exhibits endothermic peak for solid-solid modification. n-Butoxy derivative exhibited exothermic peak for monotropic cholesteric phase. In case of n-pentyloxy and n-Hexyloxy derivatives endothermic peaks for solid-cholesteric transition could not be obtained. It may be due to overlapping of two phases which are separated by span of about 5°-10°C. In case of n-octyloxy and n-decyloxy derivatives, endothermic peaks were obtained for solid-mesophase and mesophase to isotropic transitions. n-Dodecyloxy derivative did not show exothermic peaks for monotropic smectic phases. It may be due to the short range of smectic phases. n-Hexadecyloxy derivative also did not exhibit endothermic peaks for enantiotropic smectic phase. Only single peak was obtained which was due to overlapping of two transitions. Calorimetric data are given in table 34. (Fig: 52:h)

For all the series, enthalpies, entropies and total entropies were plotted against number of carbon atoms in alkoxy or alkyl chain or $-CH_2$ $-CH_2O$-Units. (Fig : 53-67)

In case of series - I enthalpies and entropies exhibit odd-even effects for nematic - isotropic transitions.

In the case of series-II, solid-mesomorphic transition enthalpies and entropies exhibit odd - even effect from C_7 to C_9 homologues but enthalpies for nematic/smectic - isotropic transitions do not exhibit such alte~~r~~nations.

In case of series VI, enthalpies and entropies for solid - mesogenic transitions exhibit usual alte~~r~~nation for odd-even members.

The enthalpy and entropy changes exhibit variations in the case of series IV and for series VIII. Total entropies were plotted against number of carbon atoms in alkoxy chain also shows variations as one ascends the series.

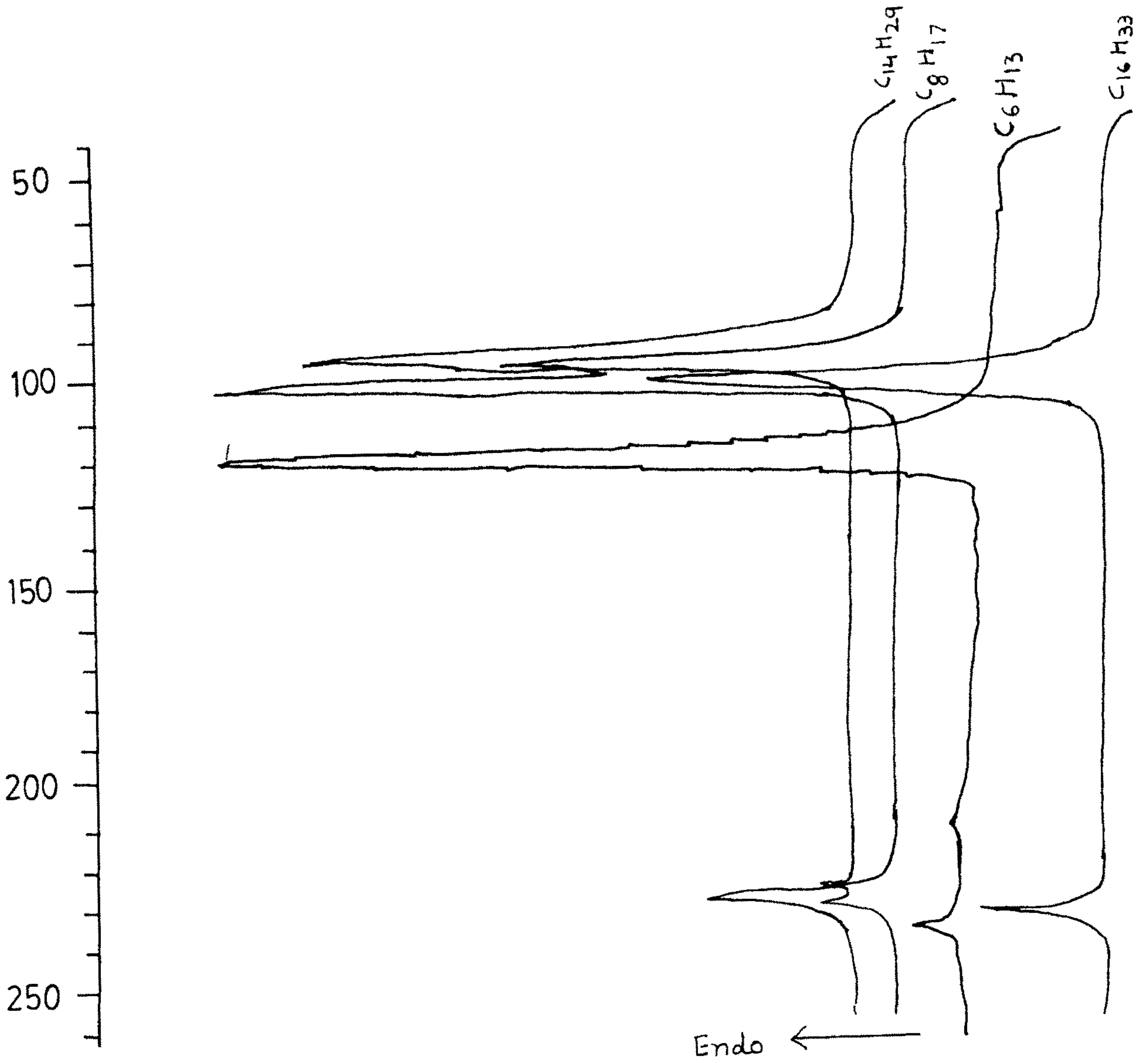


FIG.: 52a

DSC Thermograms of Mesogens of Series - I

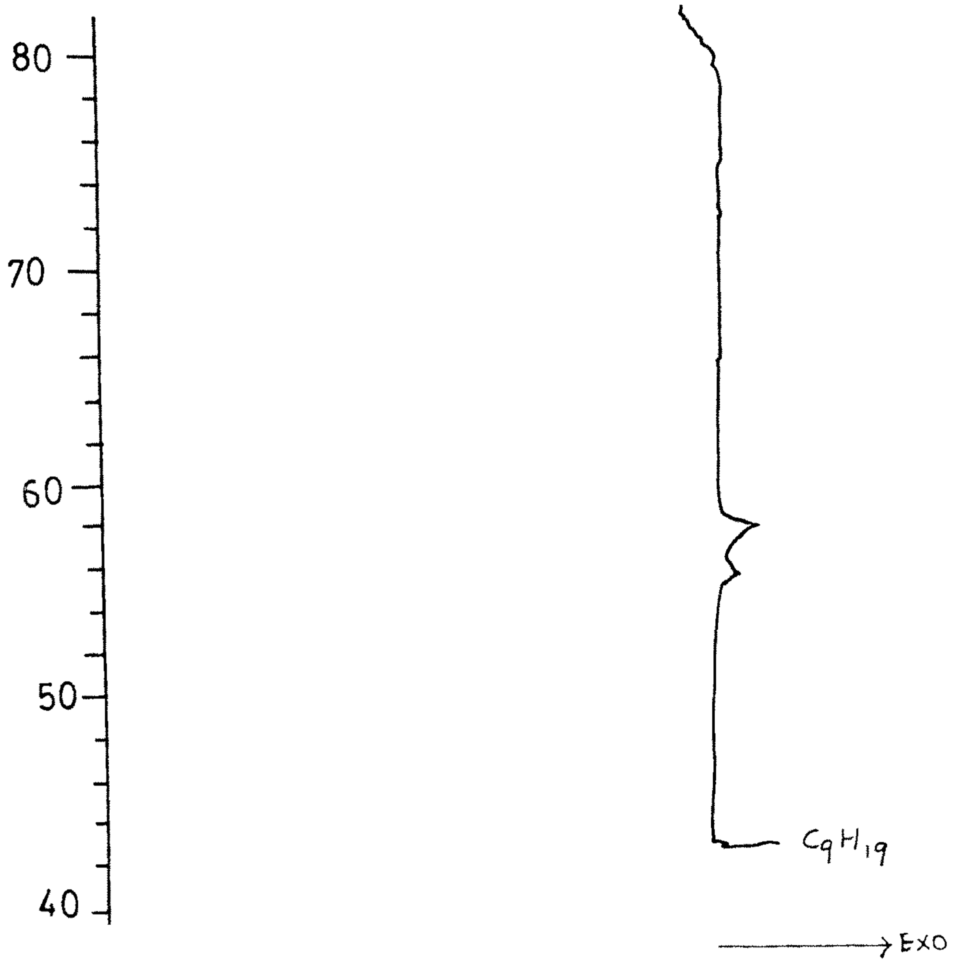


FIG. :- 52·b

DSC Thermogram of mesogen of series-II

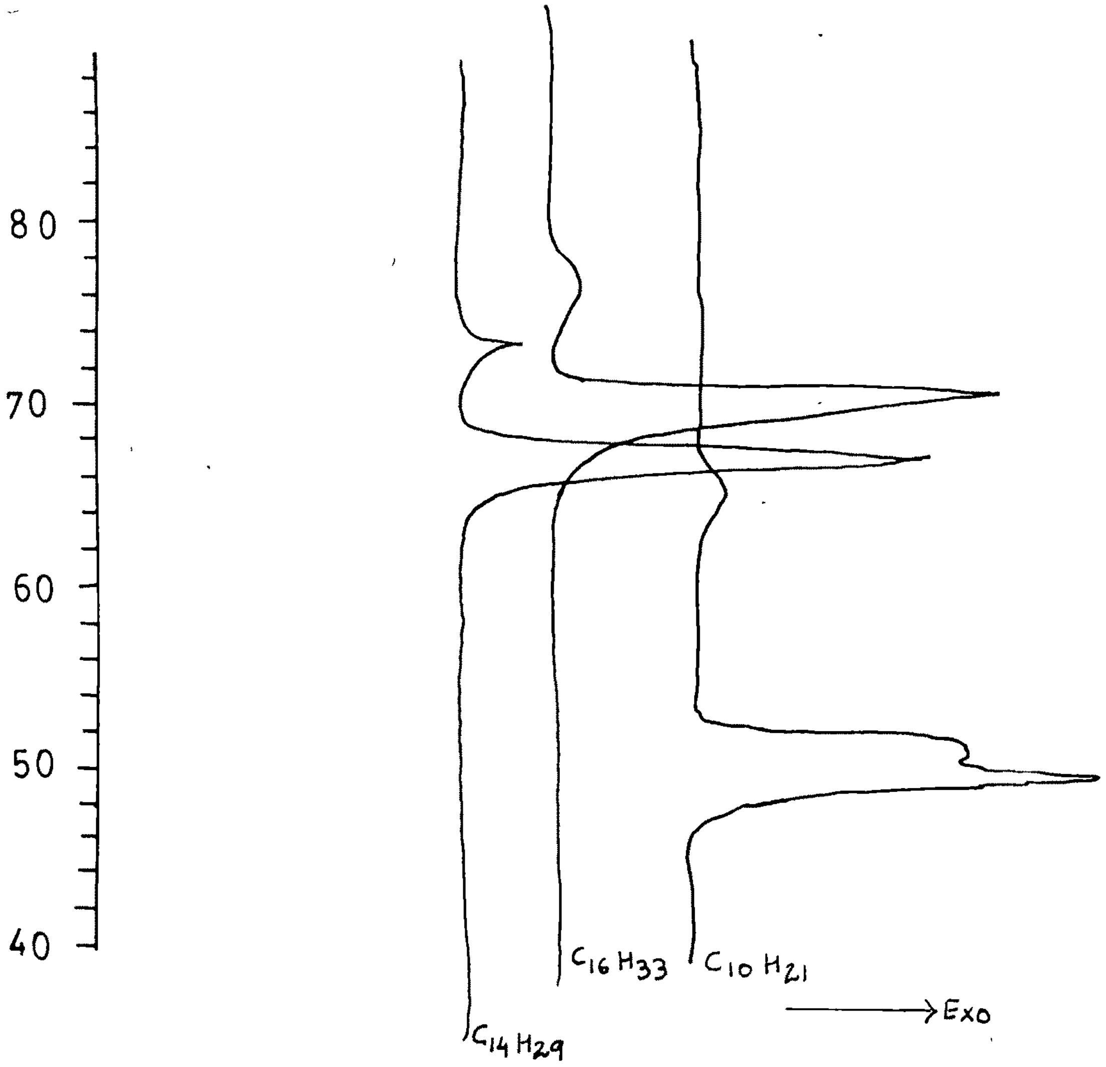


FIG. :- 52·C

DSC Thermograms of Mesogens of series-III

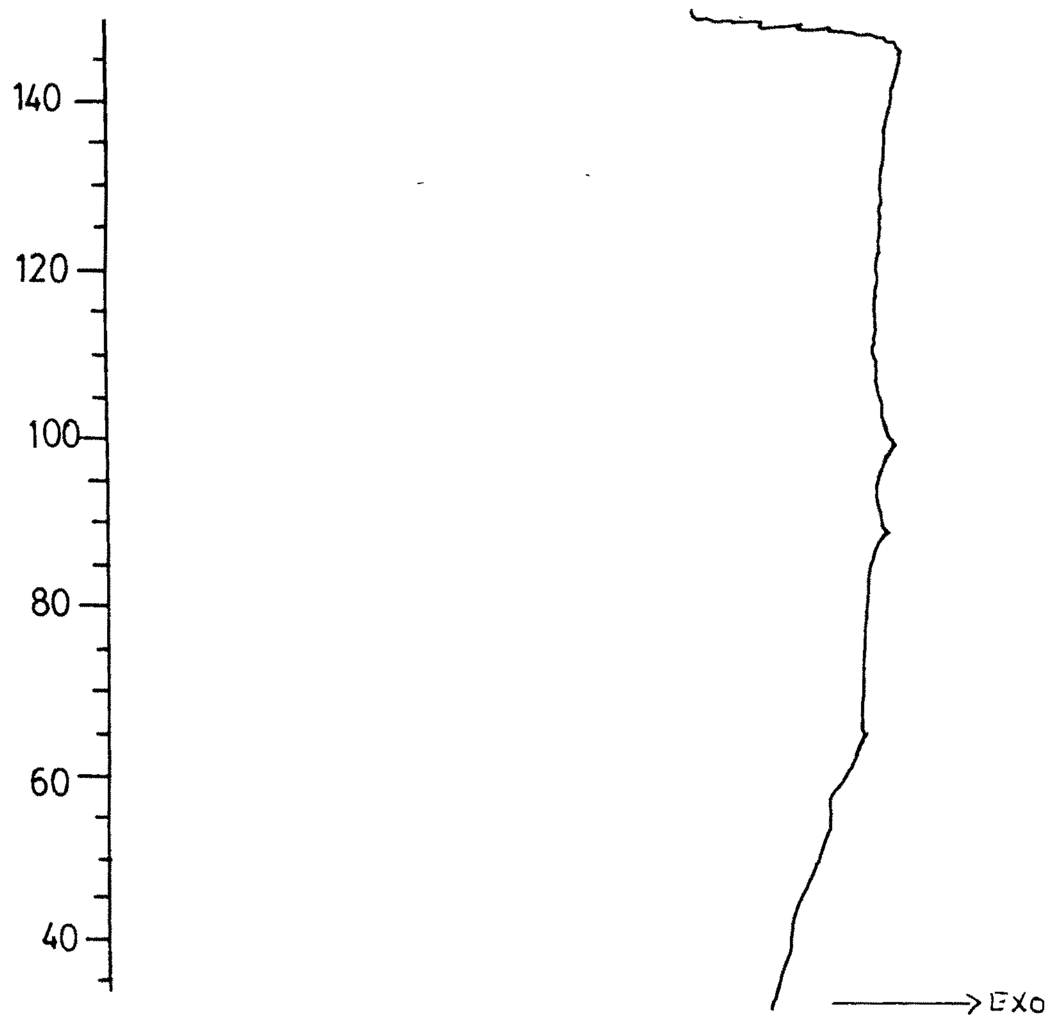
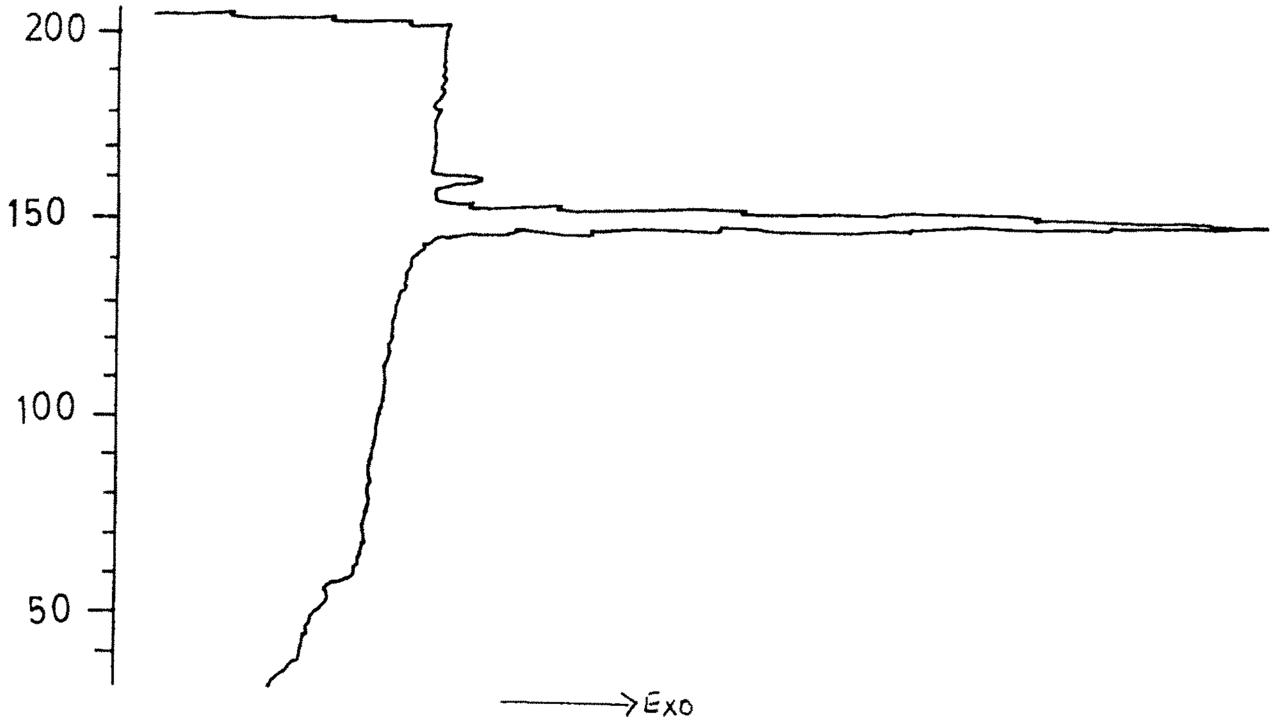


FIG:-52-d

DSC Thermogram of CC-3



FIG·52·e

DSC Thermogram of CC-4

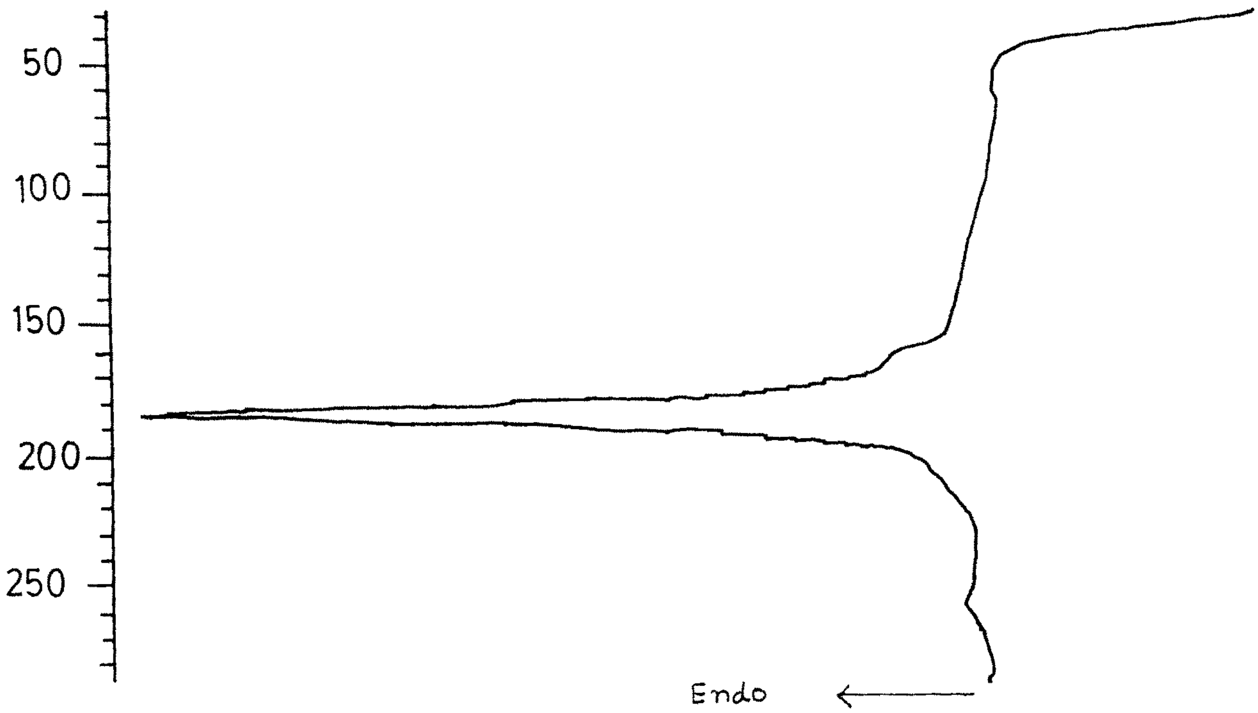


FIG. :- 52.f

DSC Thermogram of CC-6

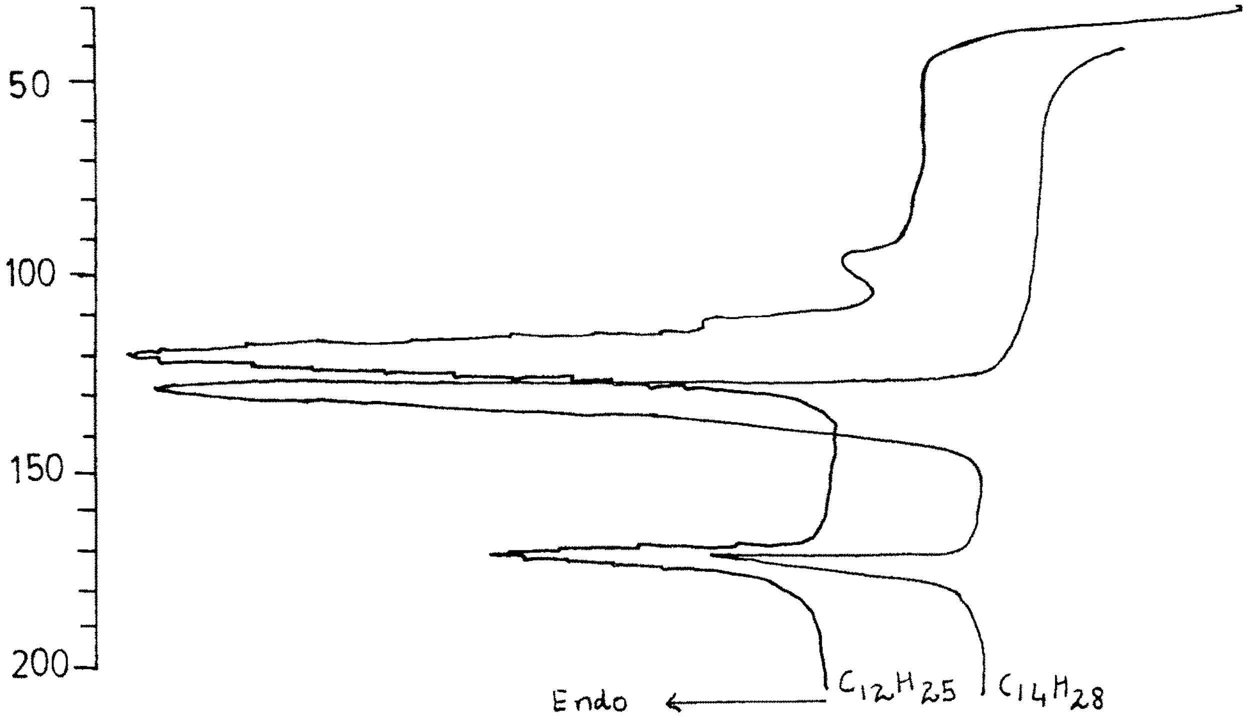


FIG :- 529

DSC Thermograms of Mesogens of
series - VI

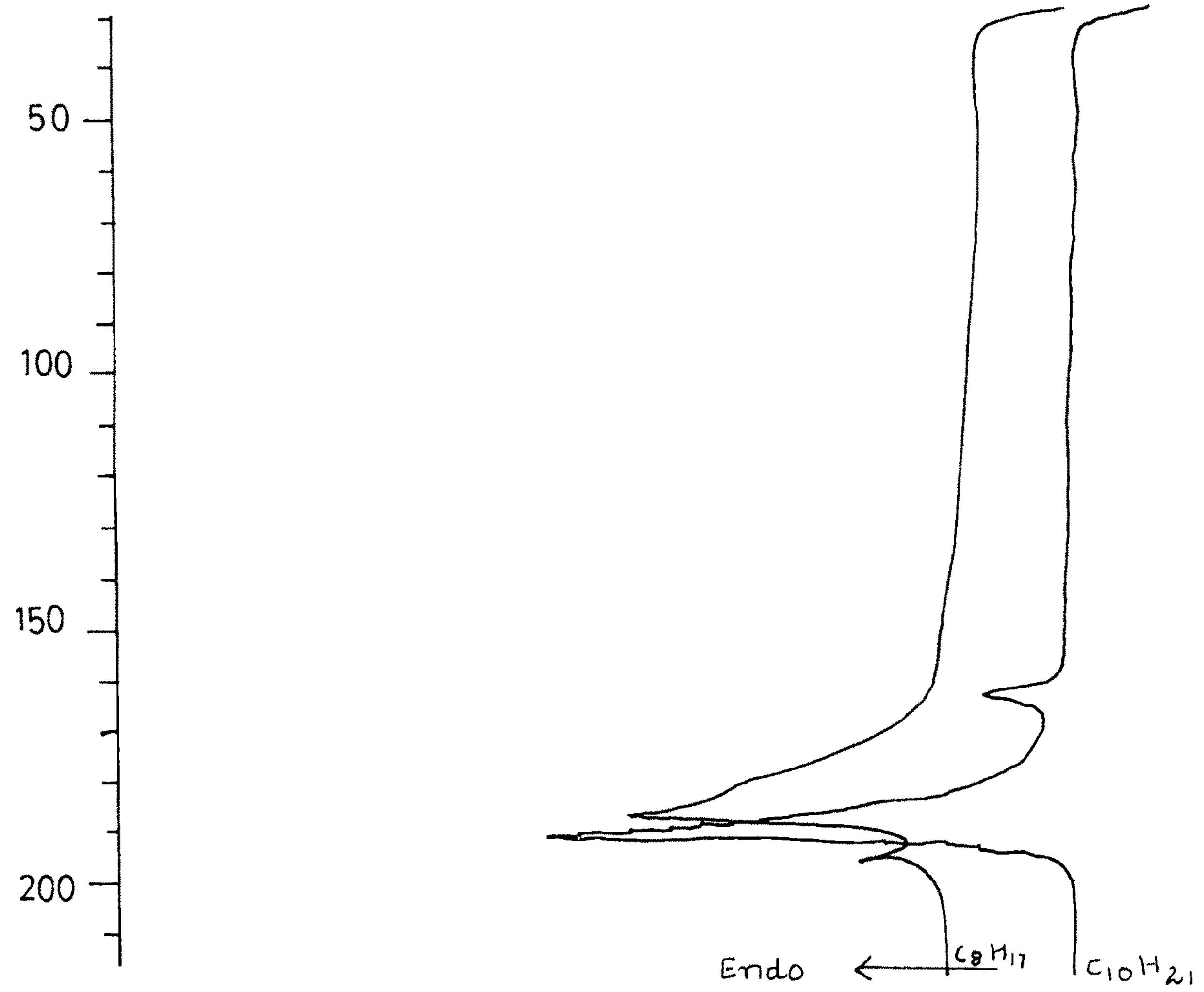


FIG ·52·h

DSC Thermograms of Mesogens of Series - VIII

ENTHALPY CHANGES ΔH OF 4-(4″-n ALKOXY BENZOYLOXY)-4′-NITROBIPHENYL

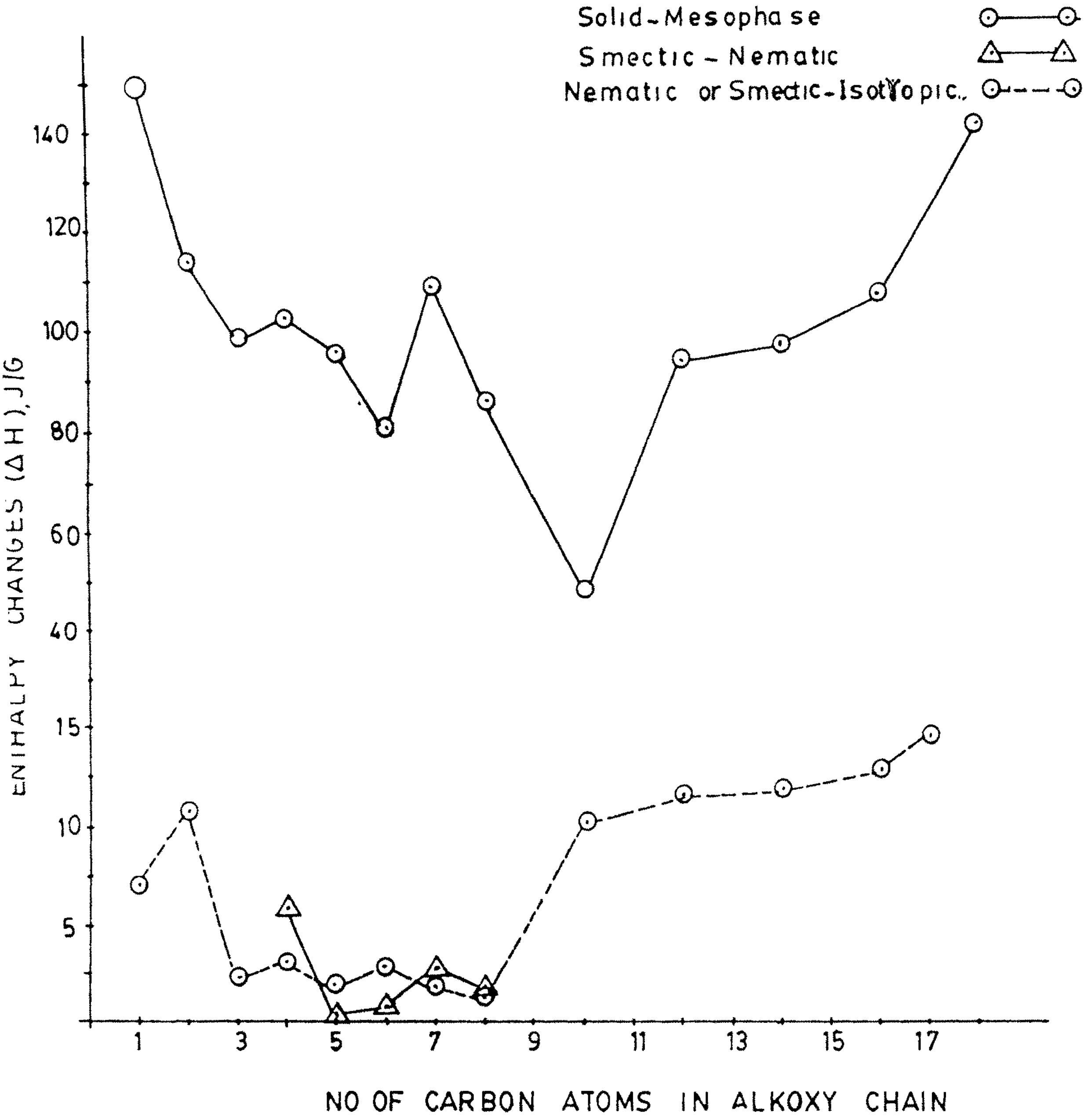


FIG.-53

ENTROPY CHANGES ΔS OF 4-(4''-n-ALKOXY BENZOYLOXY)-4' NITROBIPHENYL

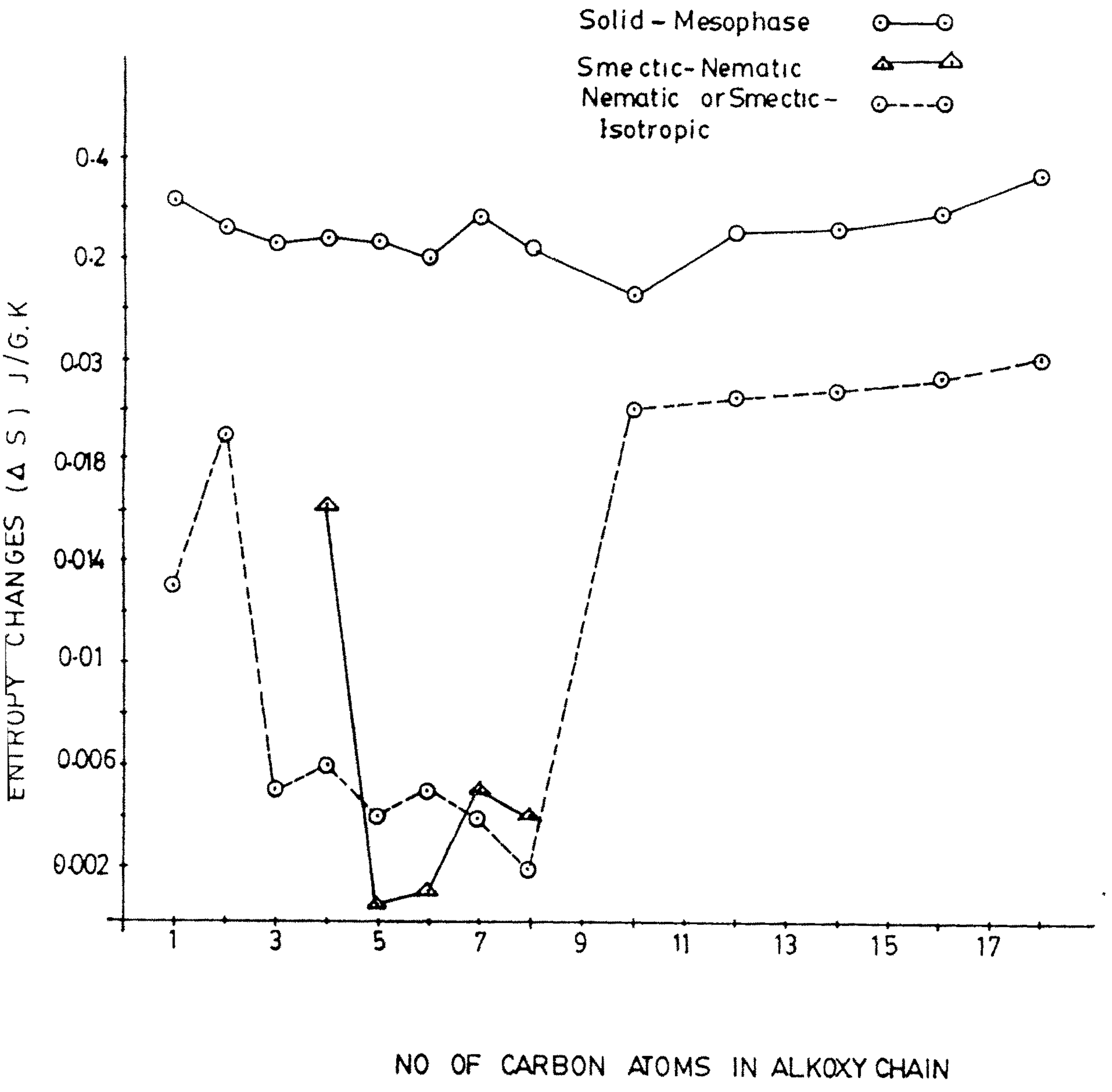


FIG : 54

TOTAL ENTROPY CHANGES ΔS OF 4-(4''-n-ALKOXY BENZOYLOXY) -4'-NITROBIPHENYL

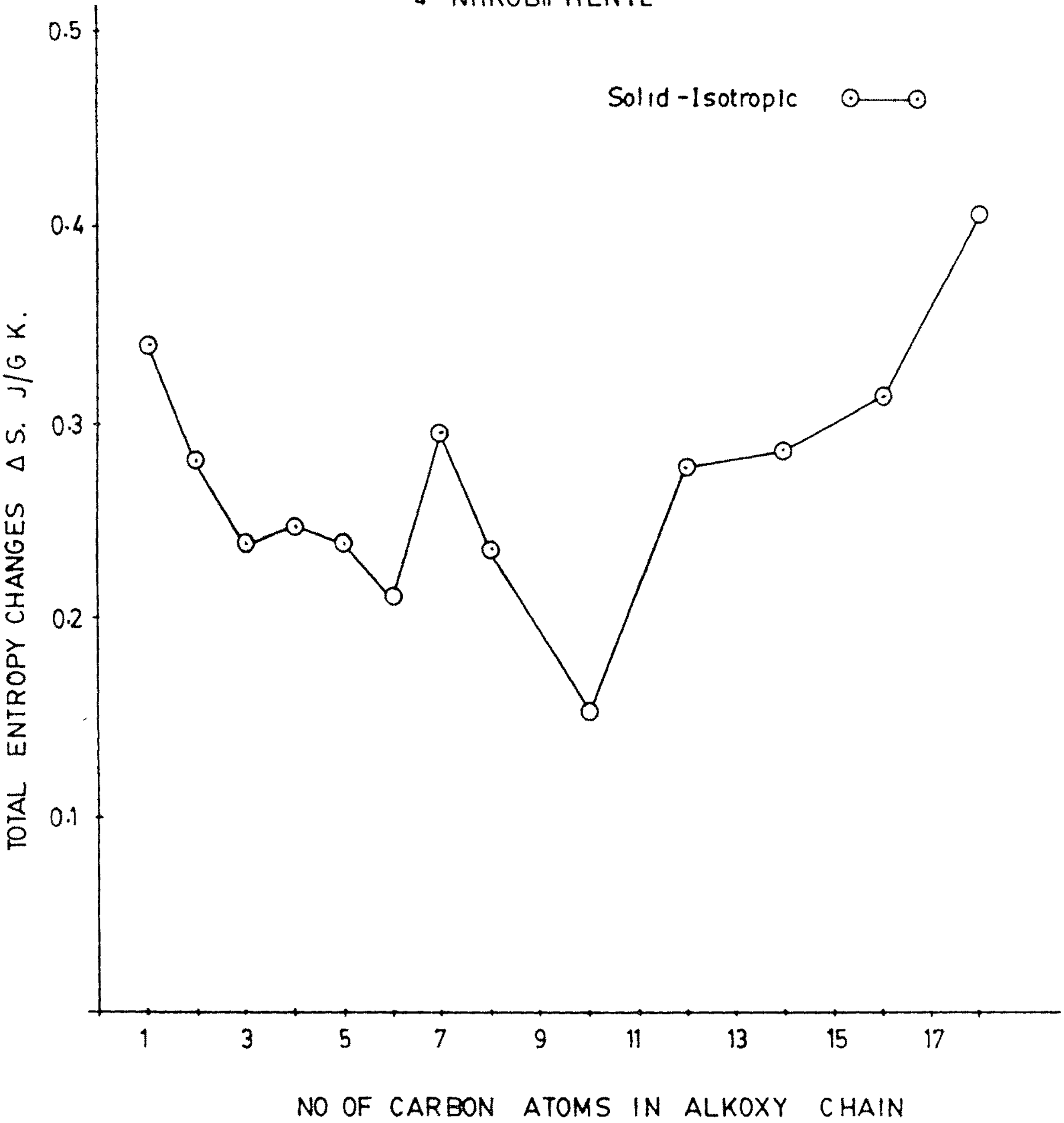


FIG. :- 55

ENTHALPY CHANGES ΔH OF 4 (n-ALKANOYLOXY) 4'- NITROBIPHENYL

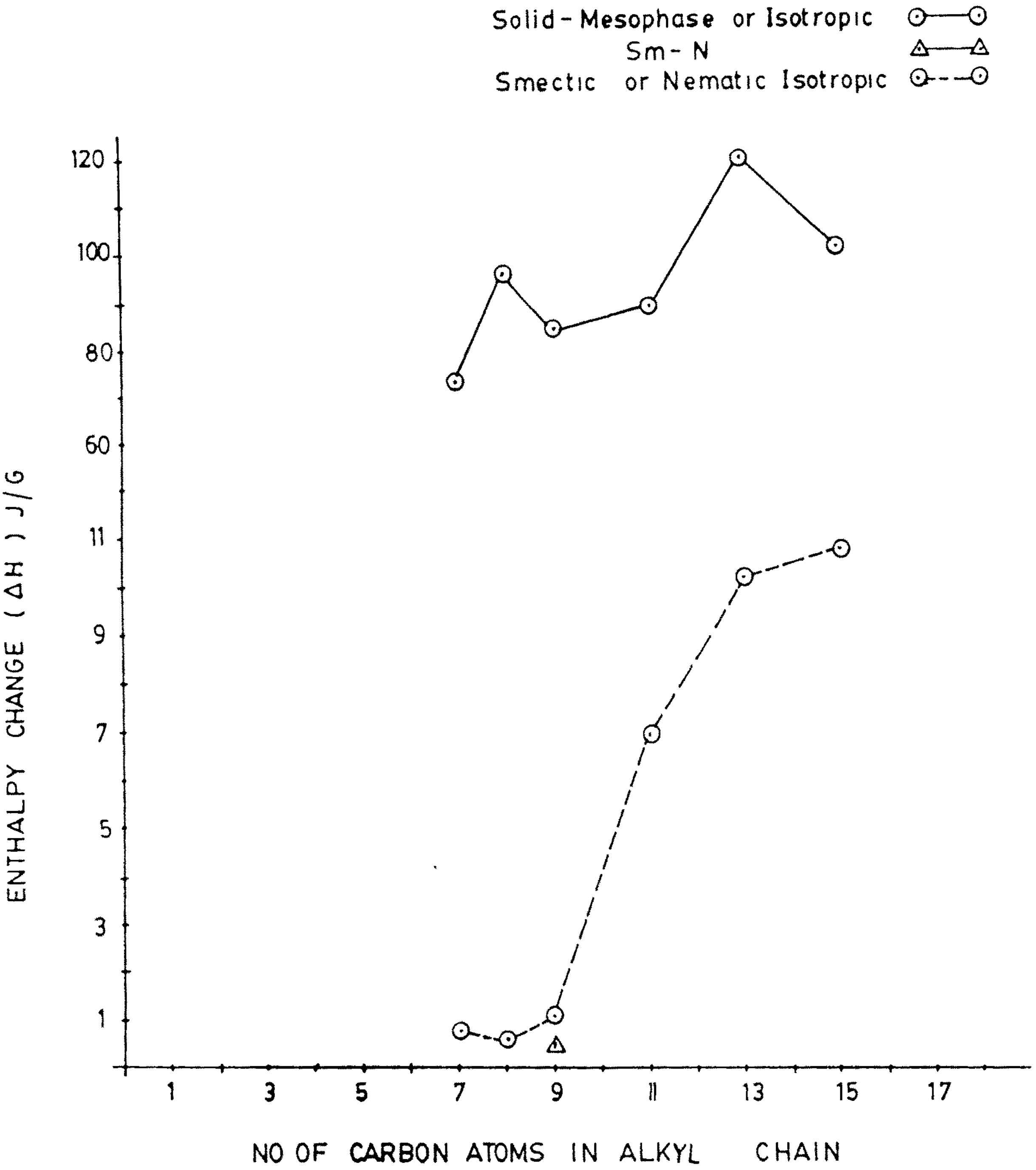


FIG · 56

ENTROPY CHANGES ΔS OF 4-(n-ALKANOYLOXY) 4'-NITROBIPHENYL

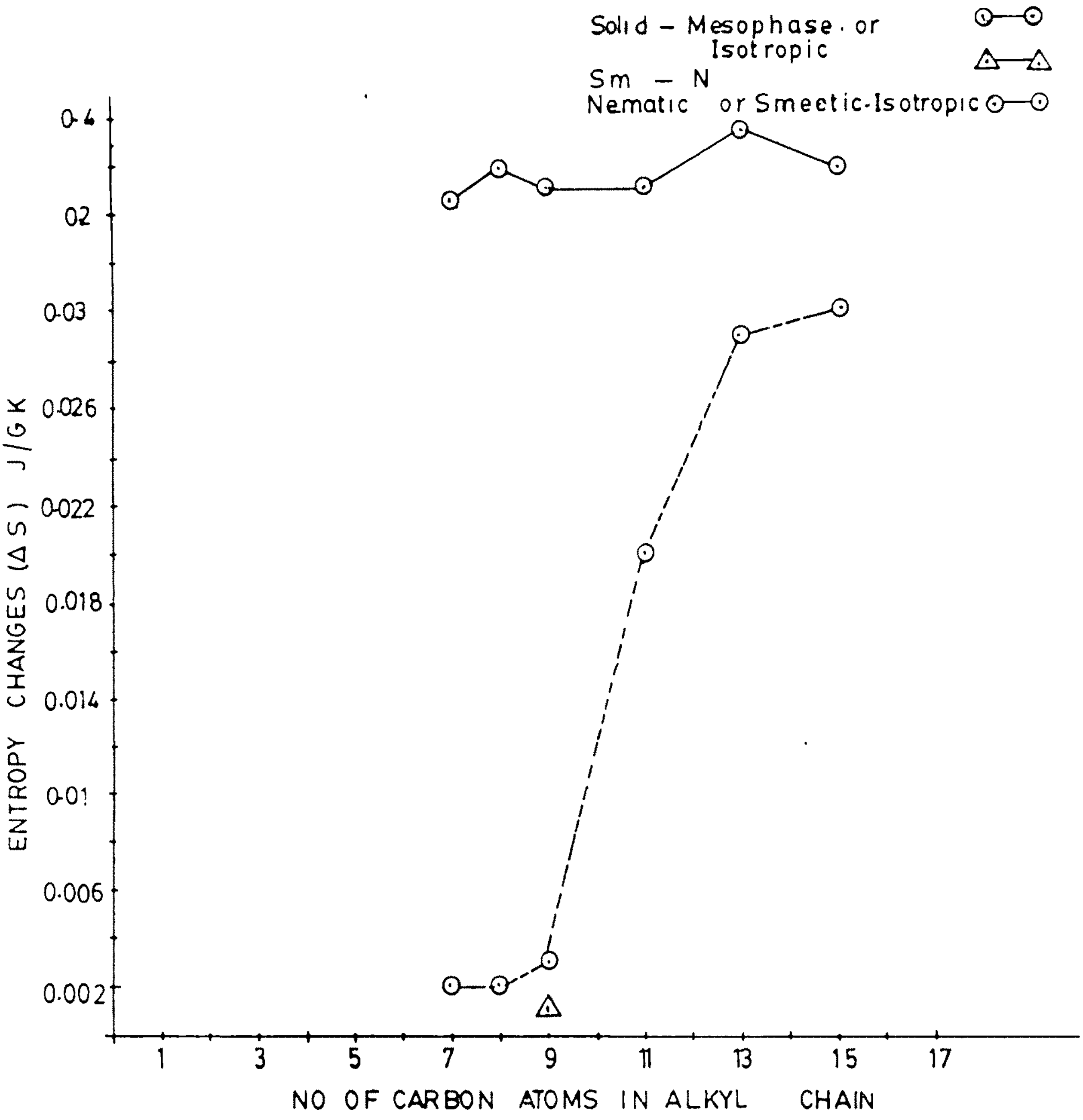


FIG:57

TOTAL ENTROPY CHANGES ΔS OF 4(n-ALKANOYLOXY) 4'-NITROBIPHENYL

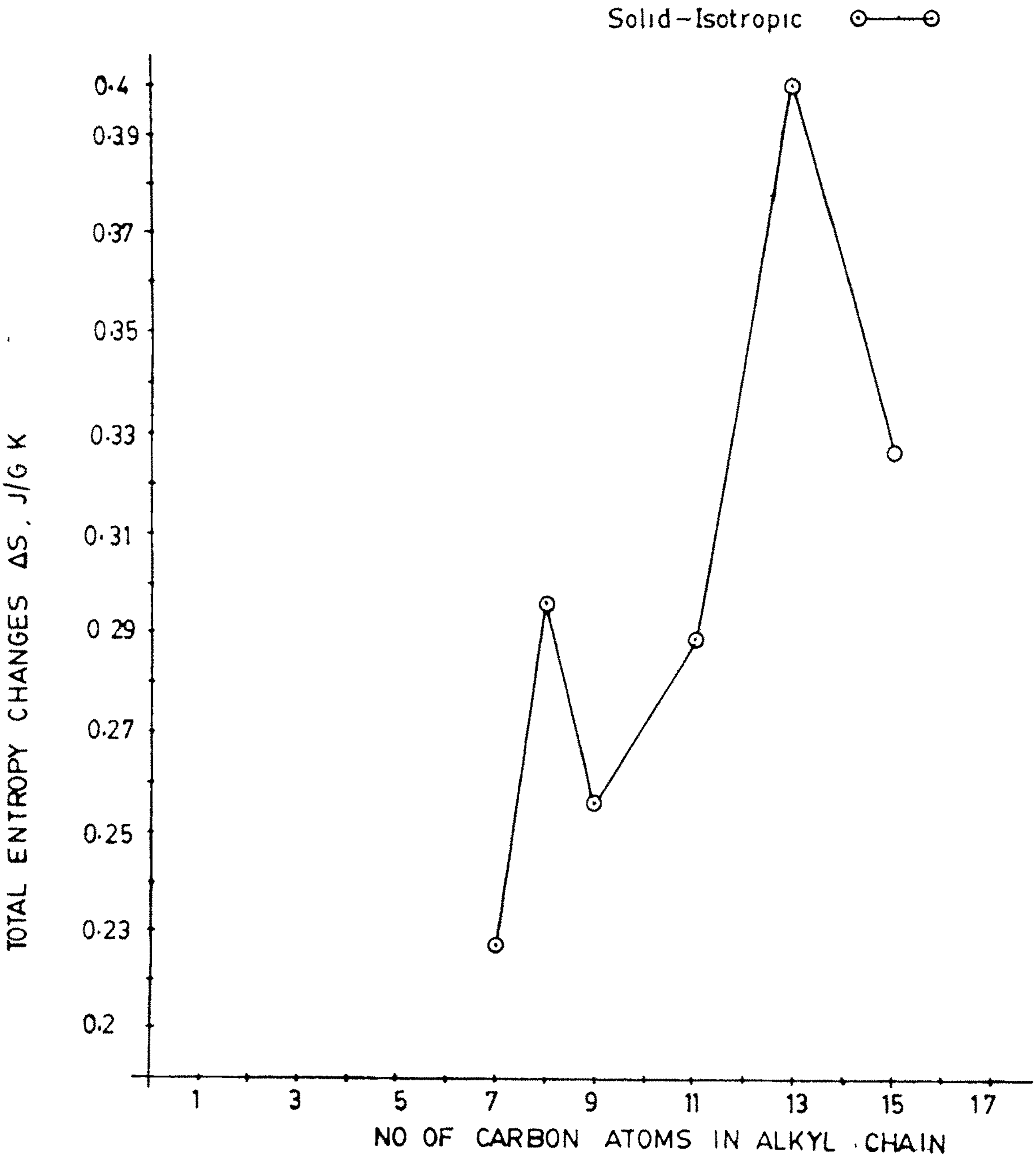


FIG · 58

ENTROPY CHANGES ΔS OF 4-n-ALKOXY-4'-NITROBIPHENGL

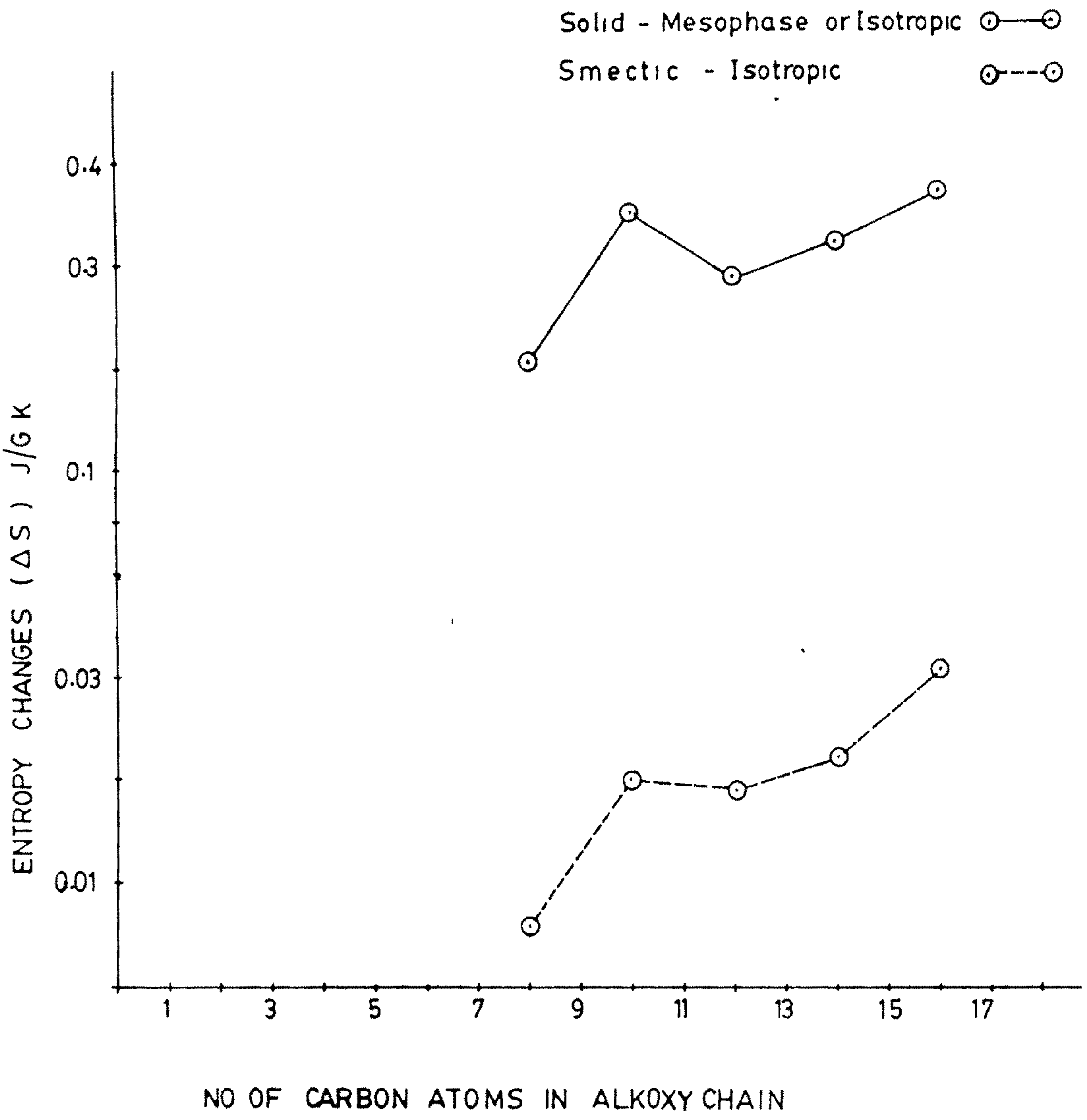
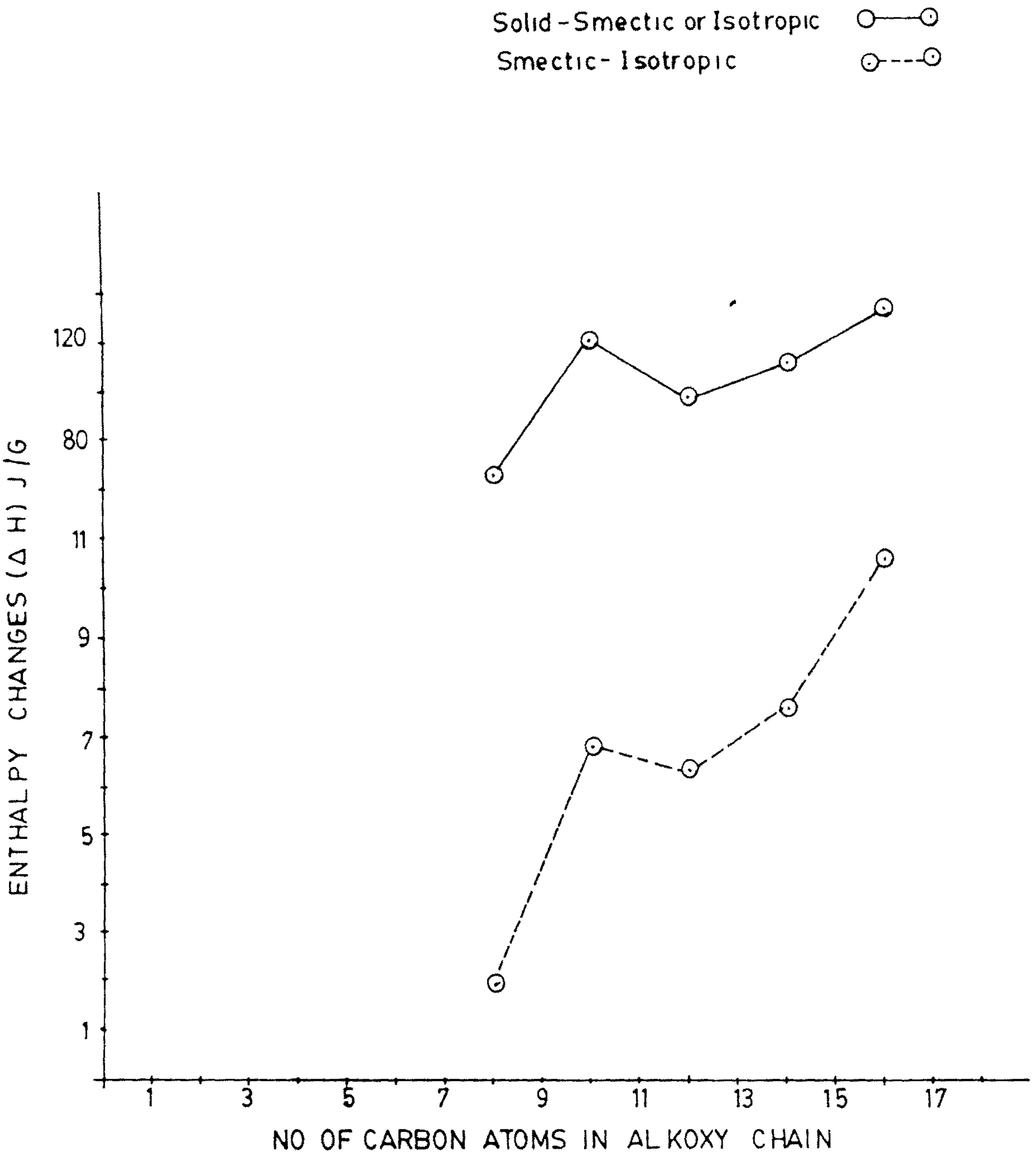


FIG.:- 59

ENTHALPY CHANGES ΔH OF 4-n ALKOXY -$4'$-NITROBIPENYL



FIG·· 60

TOTAL ENTROPY CHANGES ΔS OF 4-n ALKOXY-4'-NITRO BIPHENYL

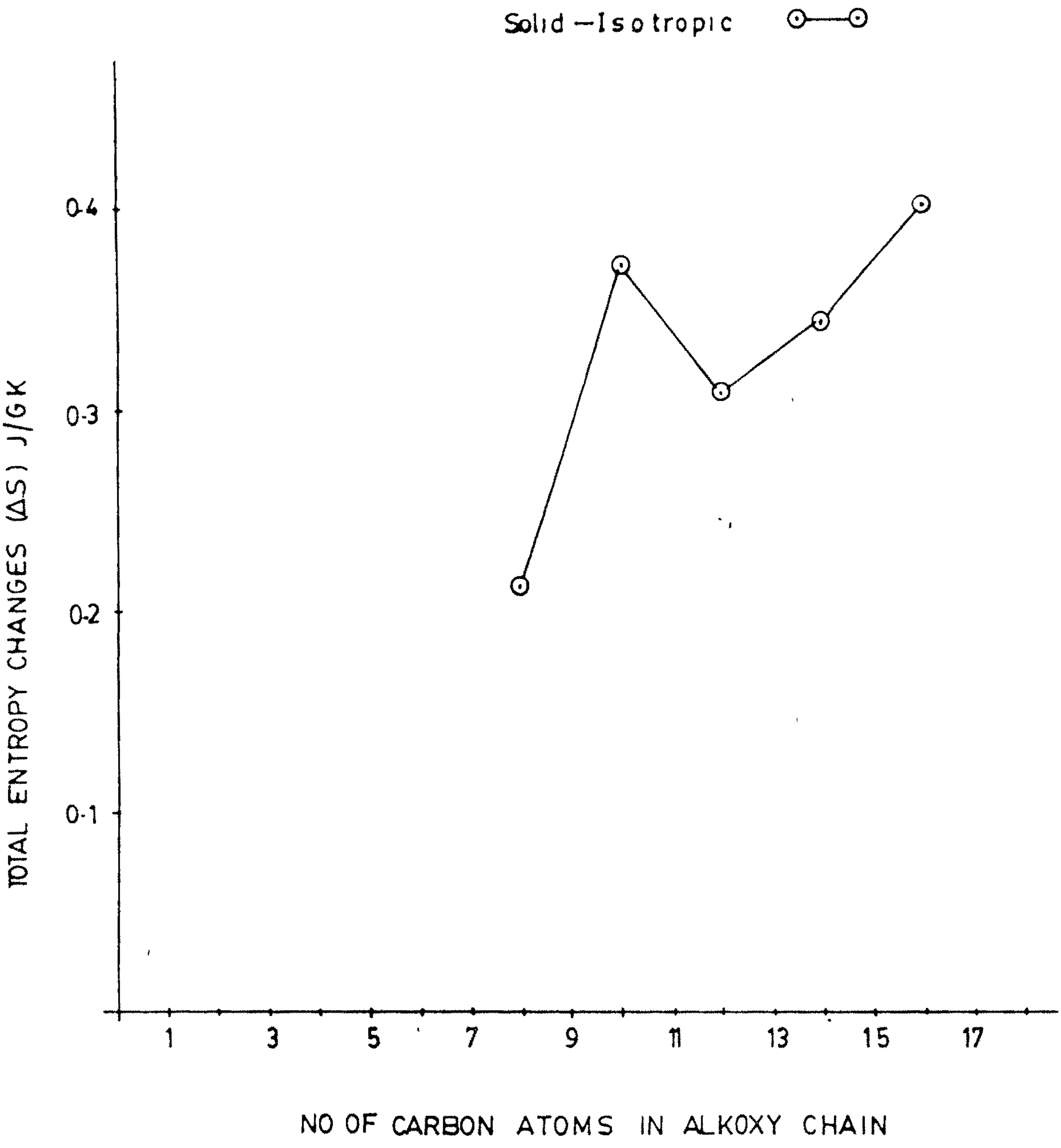


FIG. :- 61

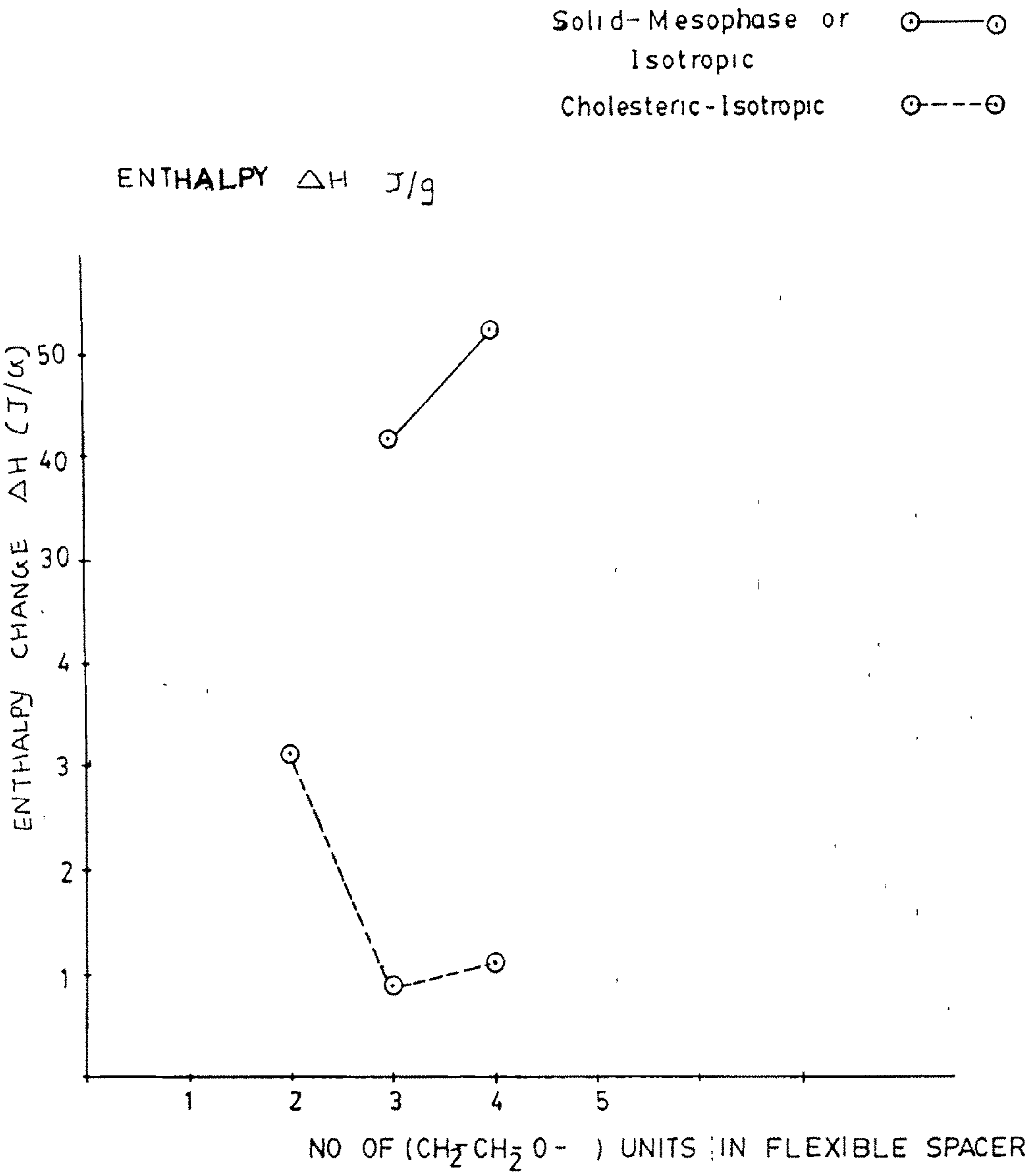


FIG. 62

Series: IV

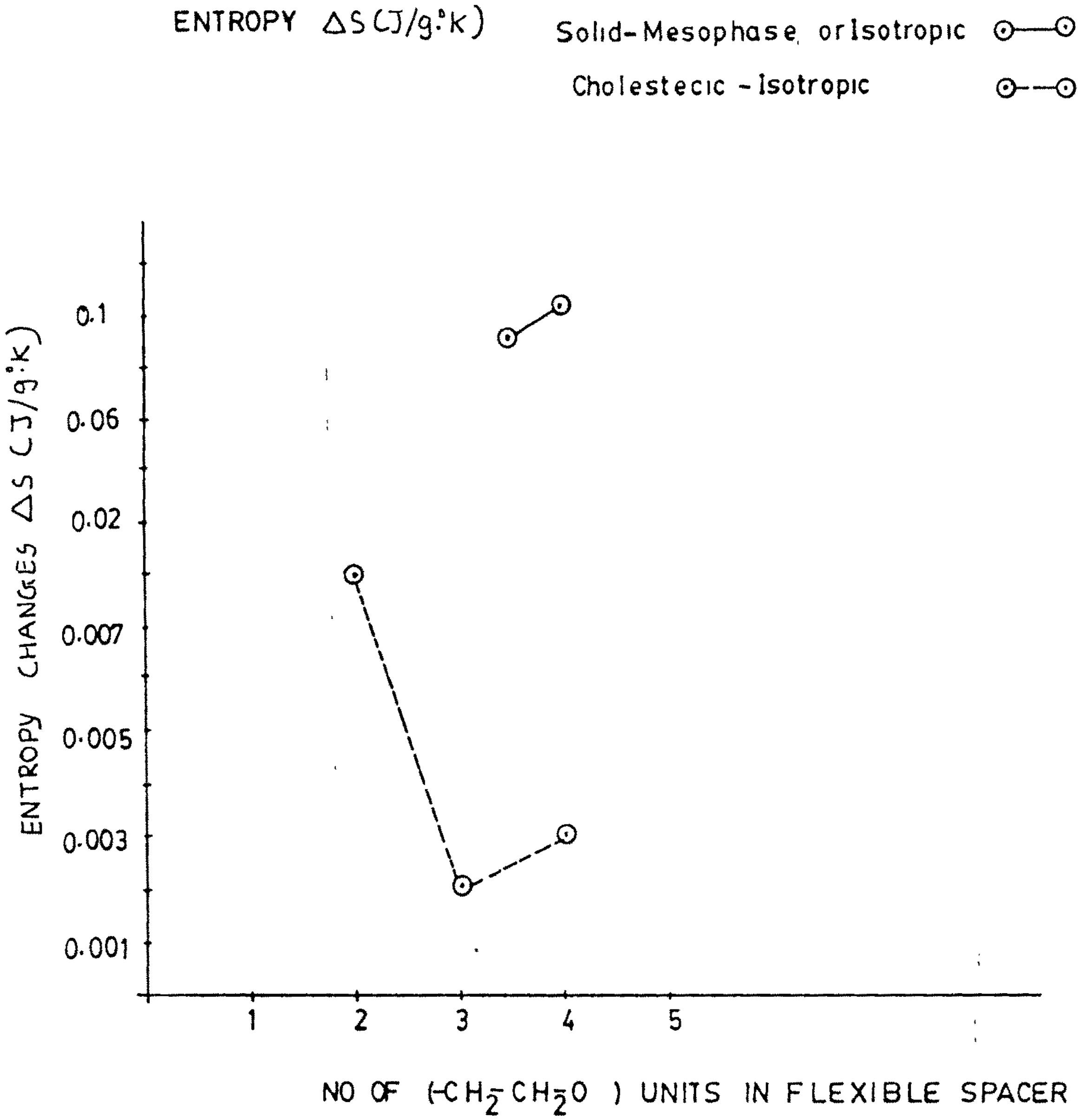


FIG: 63

Series: IV

TOTAL ENTROPY ΔS J/g.°K

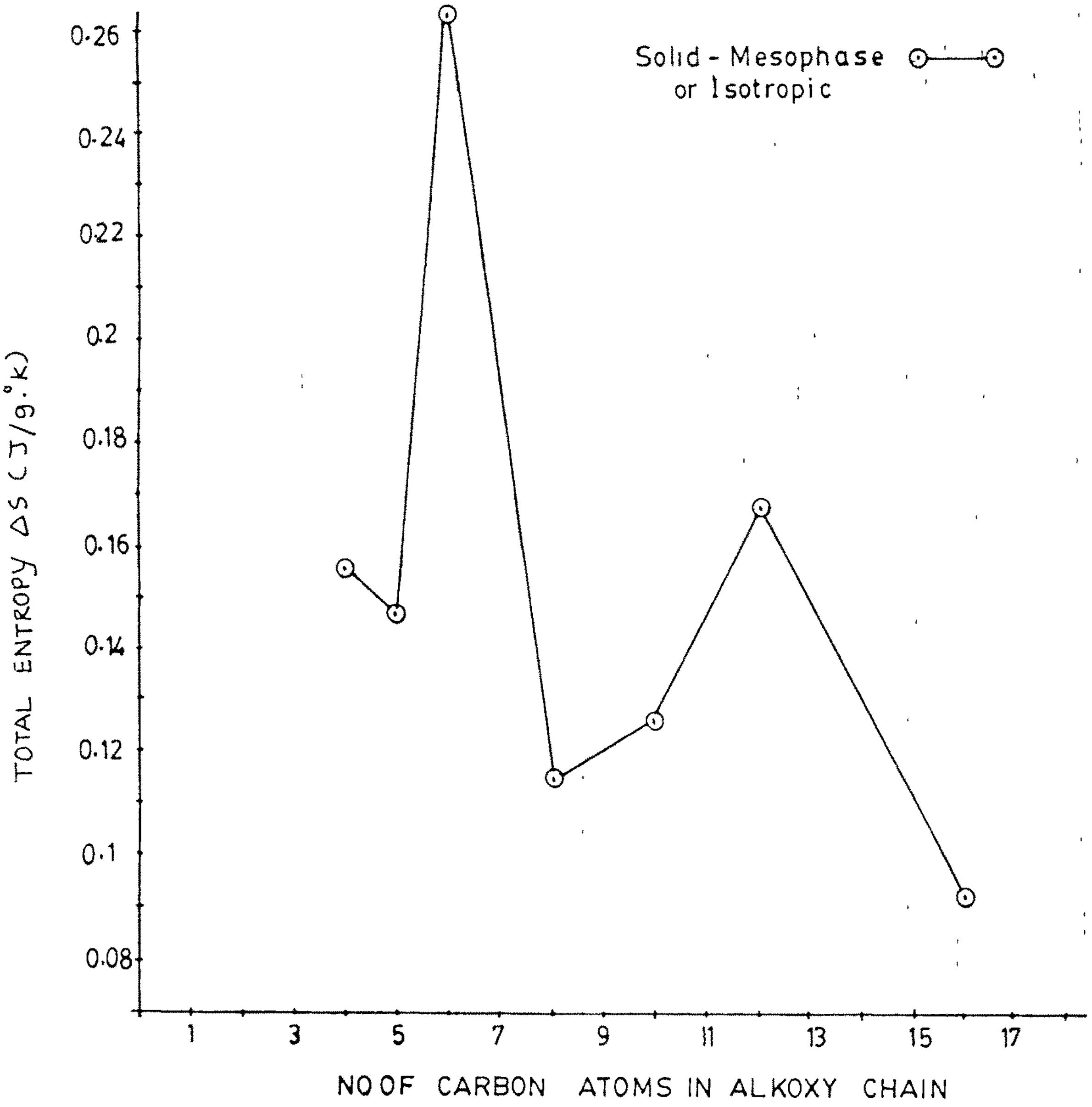


FIG 64

Series- VIII

ENTHALPY CHANGES ΔH OF CHOLESTERYL 4-n-ALKOXY PHENYL CARBAMATE

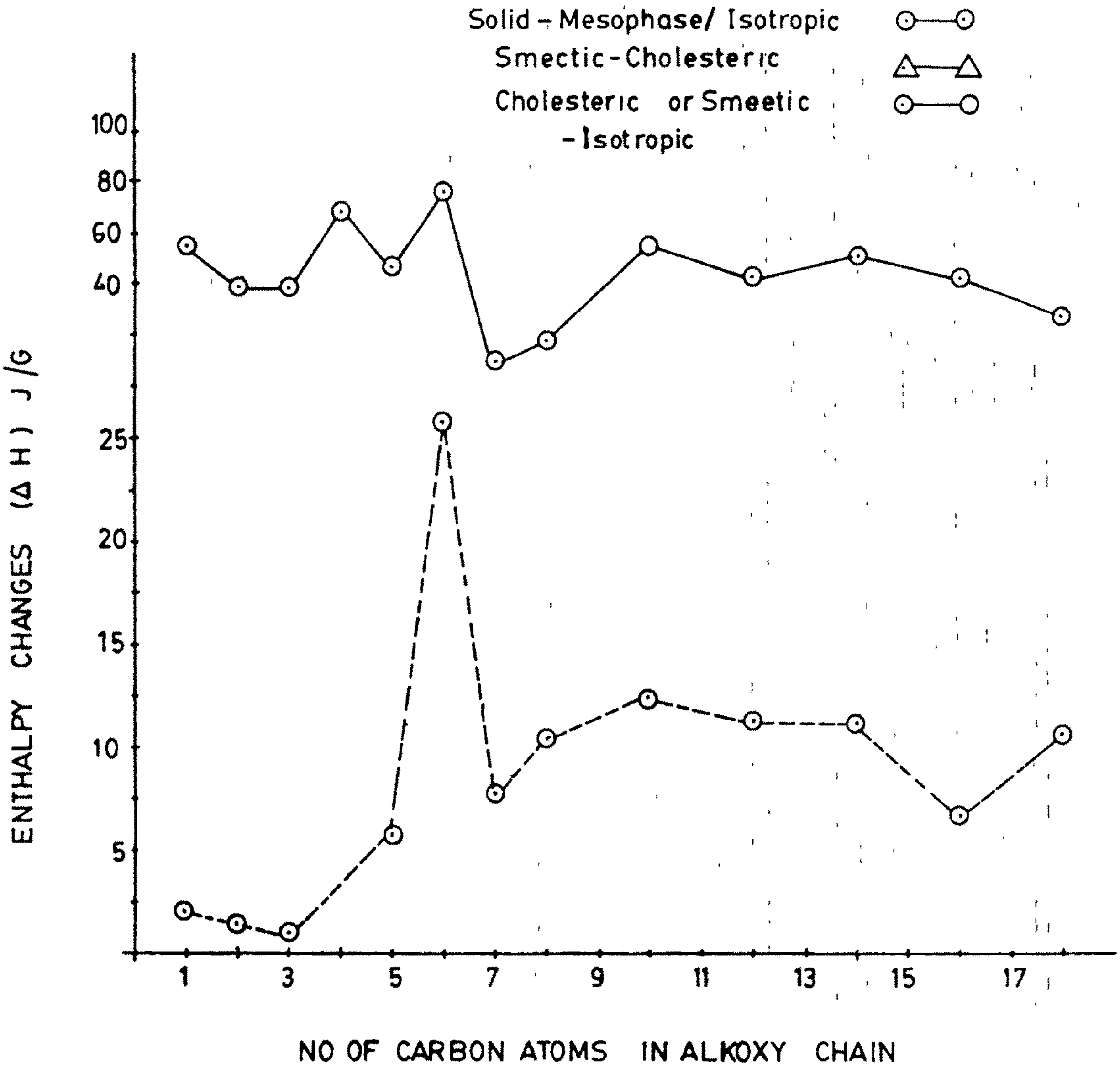


FIG.:- 65

ENTROPY CHANGES (ΔS.) OF CHOLESTERYL 4-n-ALKOXY PHENYL CARBAMATES

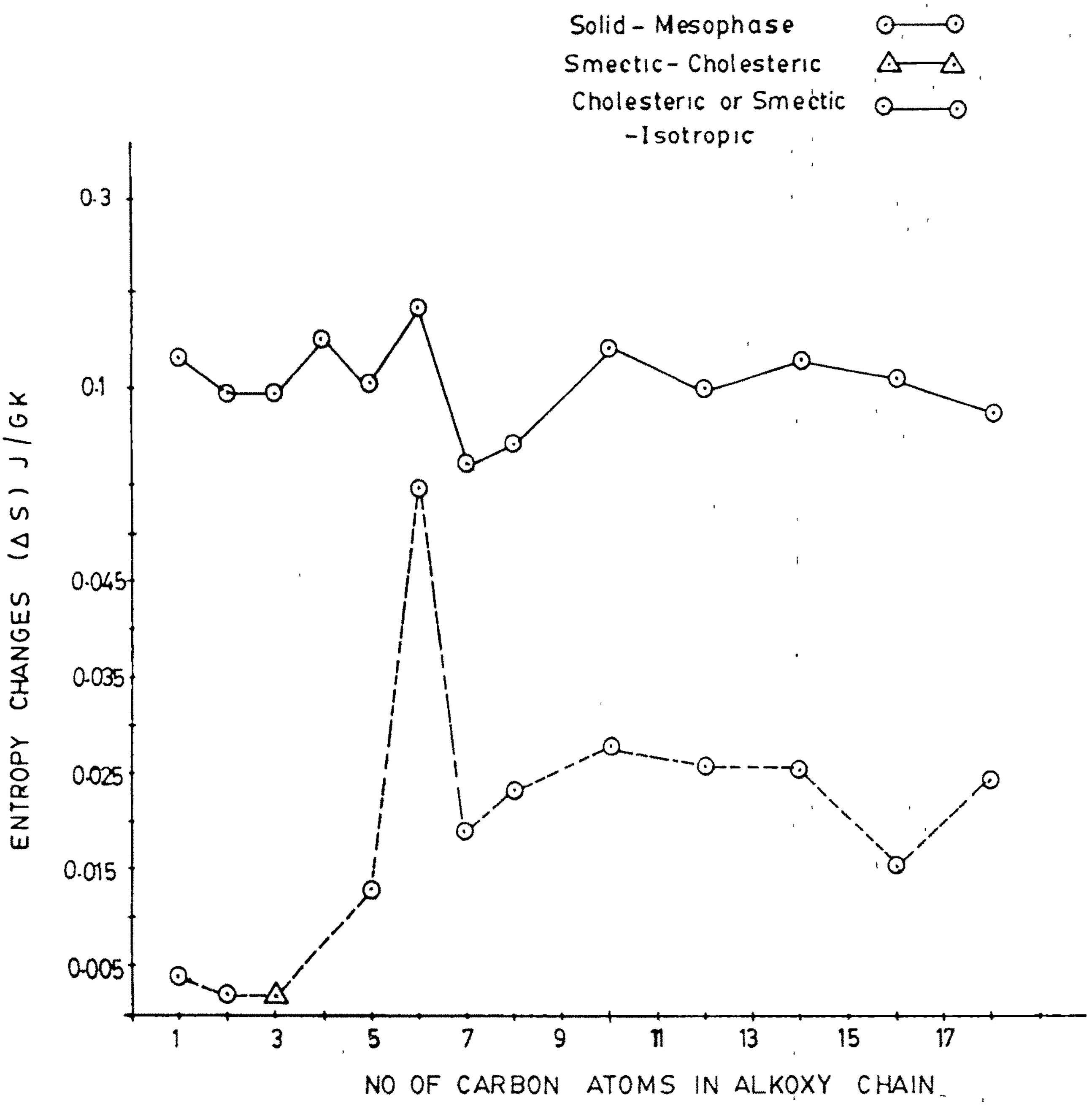


FIG:- 66

TOTAL ENTROPY CHANGES ΔS OF CHOLESTERYL -4-n-ALKOXY PHENYL CARBAMATES

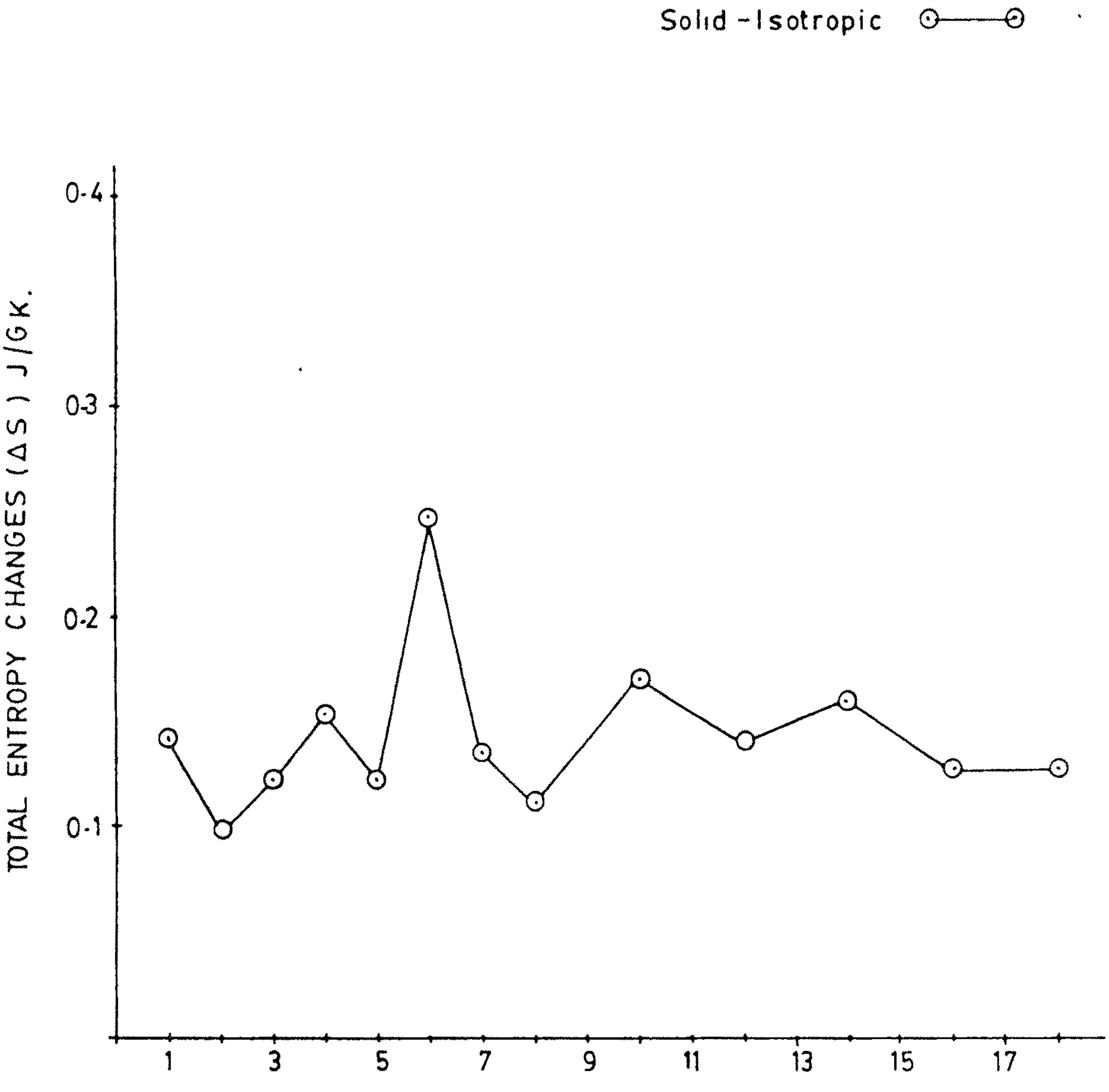


FIG.:- 67