RESULTS AND DISCUSSION

1.0 LOW MELTING SMECTOGENIC ESTERS WITH BROKEN ALKOXY CHAIN.

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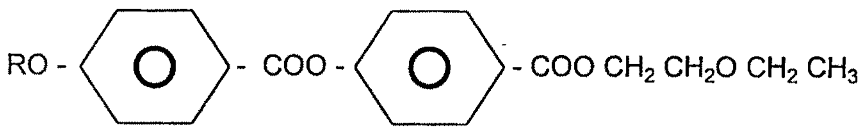
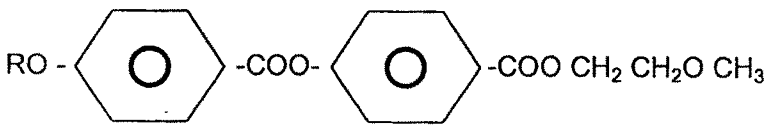
1. LOW MELTING SMECTOGENIC ESTERS WITH BROKEN ALKOXY CHAIN.

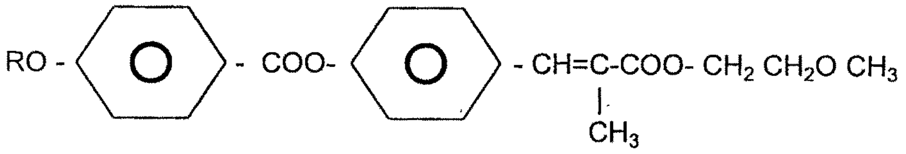
The advent of applications of liquid crystals in optical display devices led to an upsurge in the synthesis of room temperature nematic liquid crystals. Subsequently it was established that smectic A phases as well as chiral smectic C phases have applications in advanced liquid crystal displays. This led to the design of molecules which exhibit low melting smectic A phases and smectic C phases. Esters normally induce smectic phases. Aromatic esters with broken alkoxy chain in the ester linkage are less exploited. Rajput and Vora (242) have reported alkyl esters of 4-n-cinnamoyloxy benzoic acids which exhibit low melting smectic mesophases. Van Meter and Klanderman (243) and Tatsuta et al (244) have reported some of the alkyl esters of 4-n-alkoxy benzoyloxy benzoic acids. Broken alkoxy ester chain in 4-n-alkoxy benzoyloxy benzoic acid is expected to bring down mesophases at lower temperatures. With this expectation following three homologous series were synthesized.



Series - I



Series - II



Series - III

The route of synthesis for series I - III is given in Scheme - 1 - 3, respectively

Series - I : Ethoxyethyl 4-(4'-n-alkoxybenzoyloxy) - benzoates.

Twelve compounds have been synthesized and their mesogenic properties are evaluated. The melting points and transition temperatures are recorded in Table 1

First four members are non-mesogenic. n-Hexyl and n-octyl members exhibit enantiotropic smectic A phase whereas rest of the members exhibit monotropic smectic A phases.

Series - II : Methoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates.

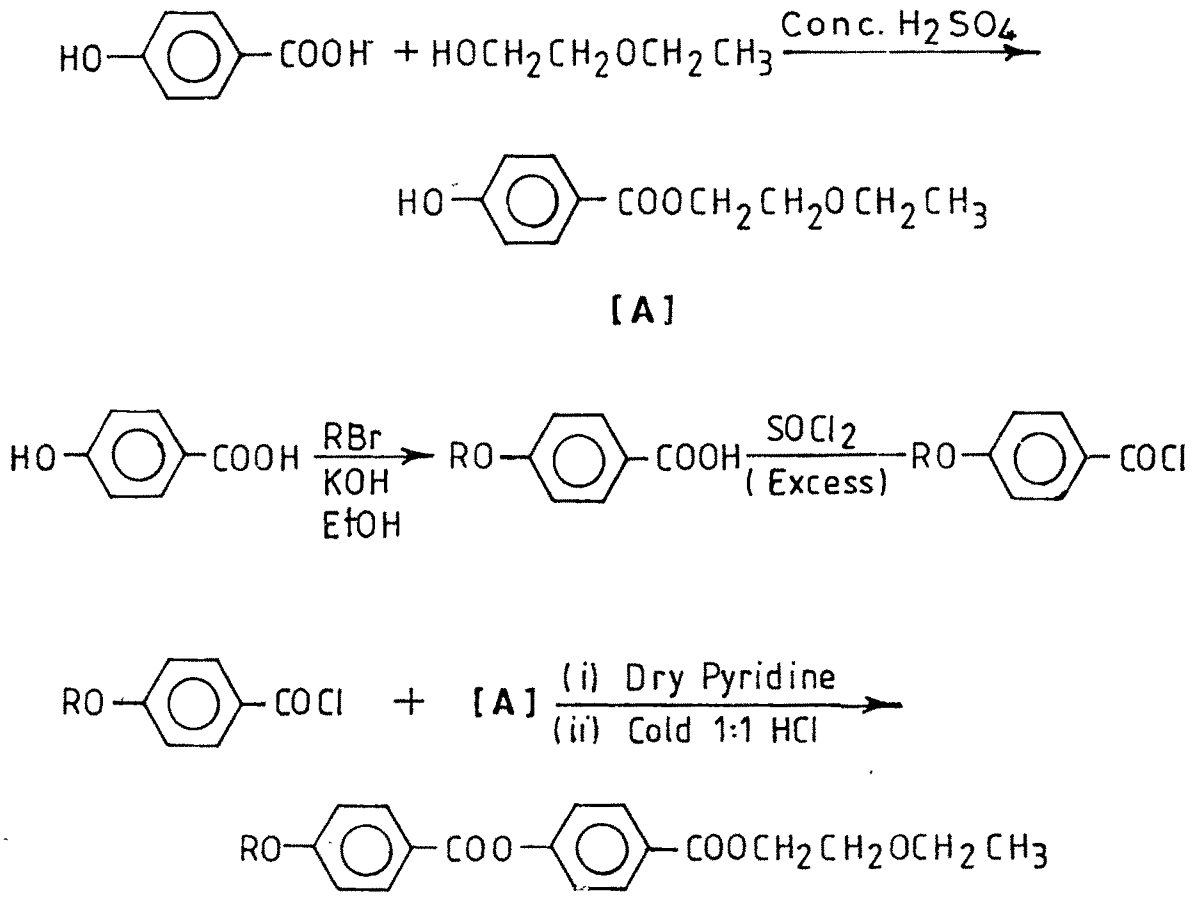
Twelve compounds have been synthesized and their mesogenic properties are evaluated. The melting points and transition temperatures are recorded in Table 3.

First four members are non-mesogenic, n-pentyl and n-hexyl derivatives exhibit monotropic smectic A phase, whereas rest of the members exhibit enantiotropic smectic A phases.

Series - III : Methoxyethyl *trans* -4(4'-n-alkoxybenzoyloxy)-α- methyl cinnamates.

Nine compounds of the series with alkoxy group from n-butoxy to n-octyloxy, n-decyloxy, n-dodecyloxy, n-tetradecyloxy and n-hexadecyloxy have been synthesized Lower members are non-mesogenic, n-heptyl derivative exhibits monotropic smectic A phase whereas rest of the higher members are enantiotropic smectic A.

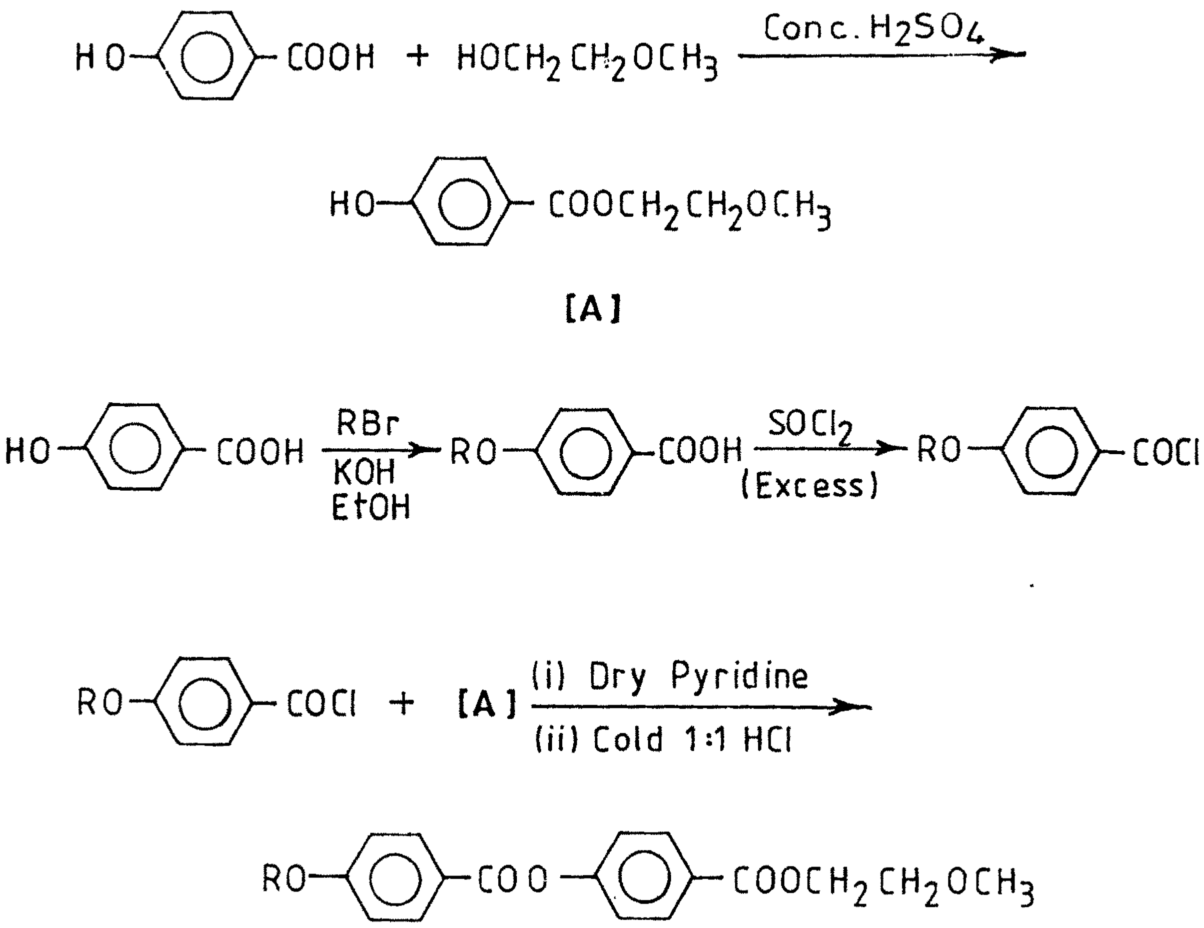
The melting points and transition temperatures are recorded in Table 5



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

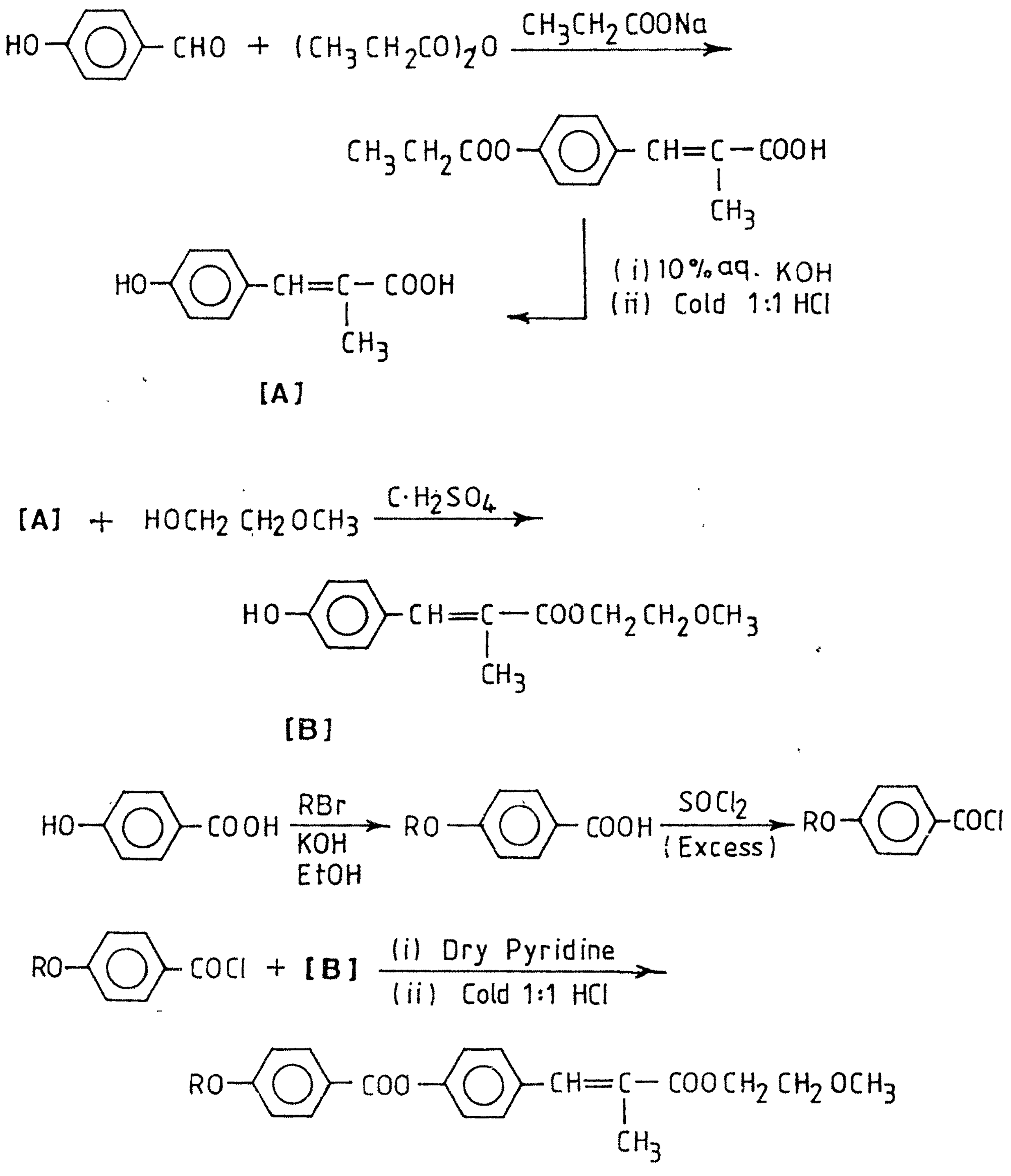
SYNTHETIC ROUTE TO SERIES – I

SCHEME-1



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

SYNTHETIC ROUTE TO SERIES — II
SCHEME-2



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

SYNTHETIC ROUTE TO SERIES – III

SCHEME-3

1.1 Common Features of Series I, II & III.

All the three series are smectogenic in nature and exhibit smectic A mesophases. The plot of transition temperatures against number of carbon atoms in the alkoxy chain, shows odd-even effect for only series - I (Fig. 45) whereas series - II (Fig. 46) and series - III (Fig. 47) do not show any odd-even effect. All the three series exhibit rising tendency for smectic - isotropic transition tempertures, which levels off for the higher homologues, except in the case of series - III. Gray (183) has explained the rising tendency of transition temperatures in low melting homologous series. Addition of each methylene group increases the polarizability and length of the molecules which raise the mesomorphic-isotropic transitions. Gray has also explained odd-even effect in the smectic - isotropic transitions.

The reference to Fig. 45 shows that series I exhibits odd-even effect for the smectic-isotropic transition temperatuers. Reference to Fig. 46, shows that in the case of series - II, smectic - isotropic transitions rise steeply. Gray (183) has explained that homologous series where smectic - isotropic or smectic - nematic transitions rise steeply the odd-even effect is not observed as the rise in successive transitions is greater than odd-even difference. Reference to the graph of series - III (Fig. 47) indicates that mesophase commences from n-heptyloxy derivative and subsequently there are only even members, hence one can not observe any odd-even effect in this series.

The above discussion makes it clear that though there is structural similarities between series I to III, only series-I exhibits odd-even effect for the smectic - isotropic transition temperatures.

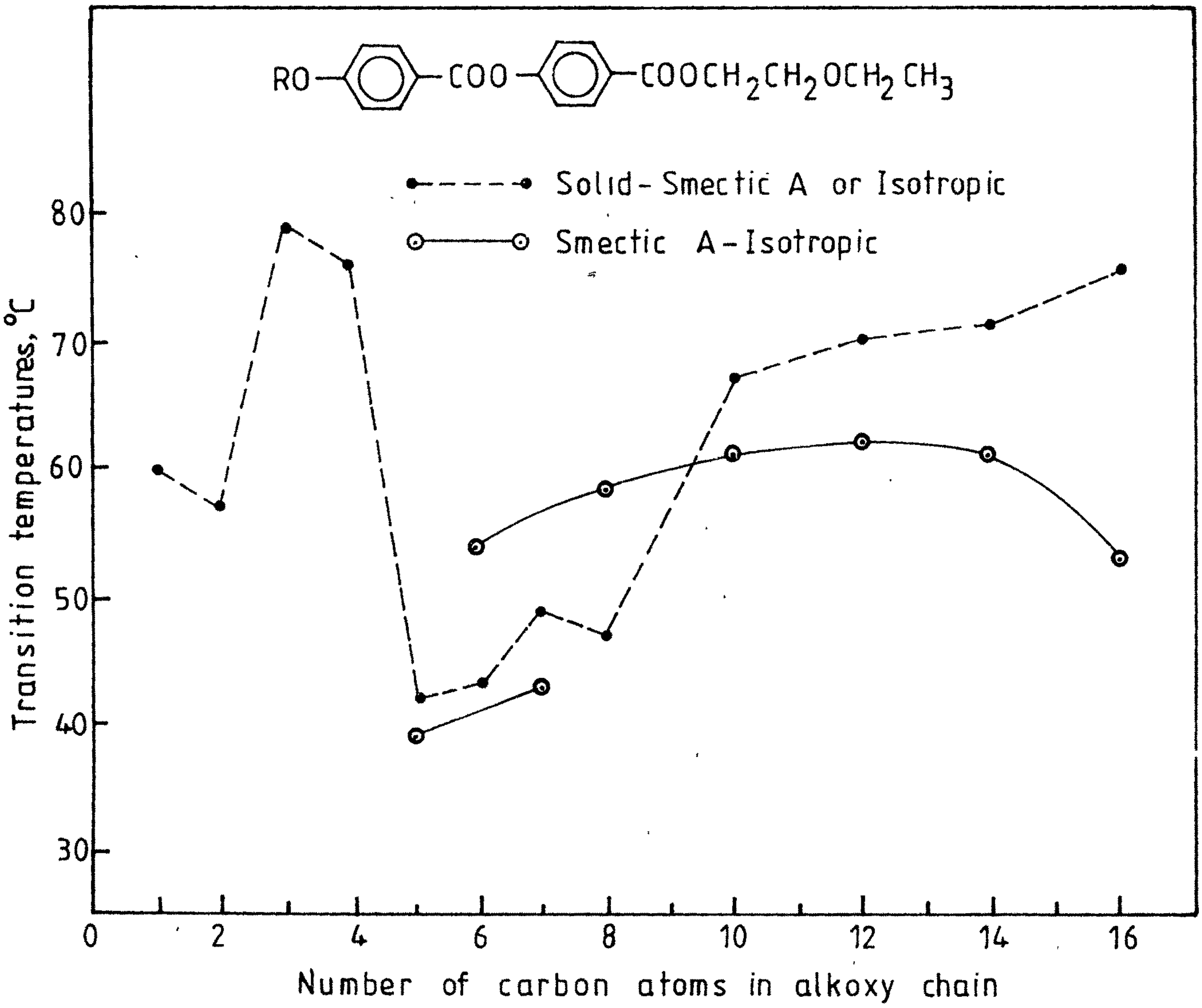

RO—⟨○⟩—COO—⟨○⟩—COOCH₂CH₂OCH₂CH₃
Solid - Smectic A or Isotropic
Smectic A - Isotropic
Transition temperatures, °C
30
40
50
60
70
80
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 45

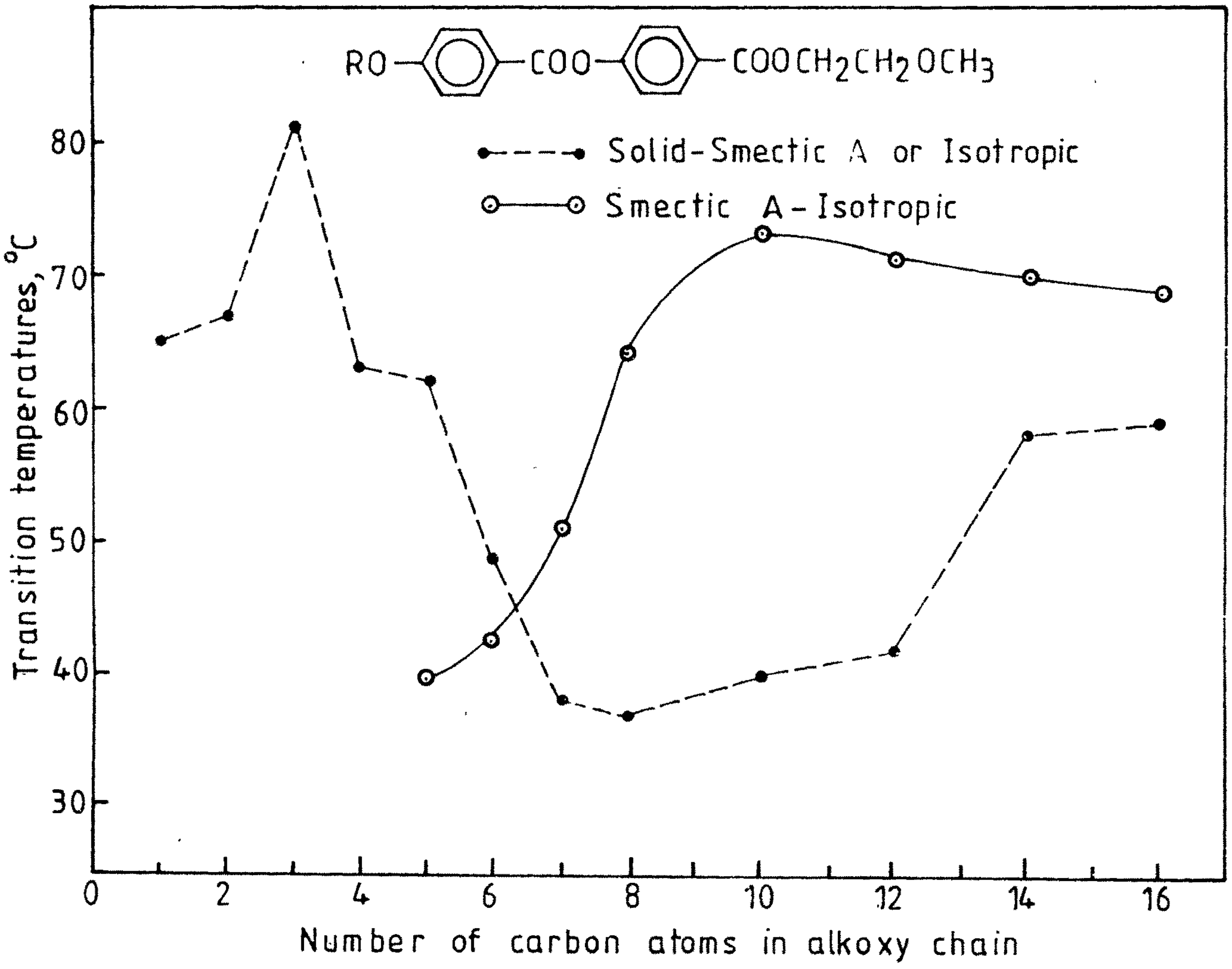

RO–C6H4–COO–C6H4–COOCH2CH2OCH3
Solid-Smectic A or Isotropic
Smectic A-Isotropic
Transition temperatures, °C
80
70
60
50
40
30
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 46

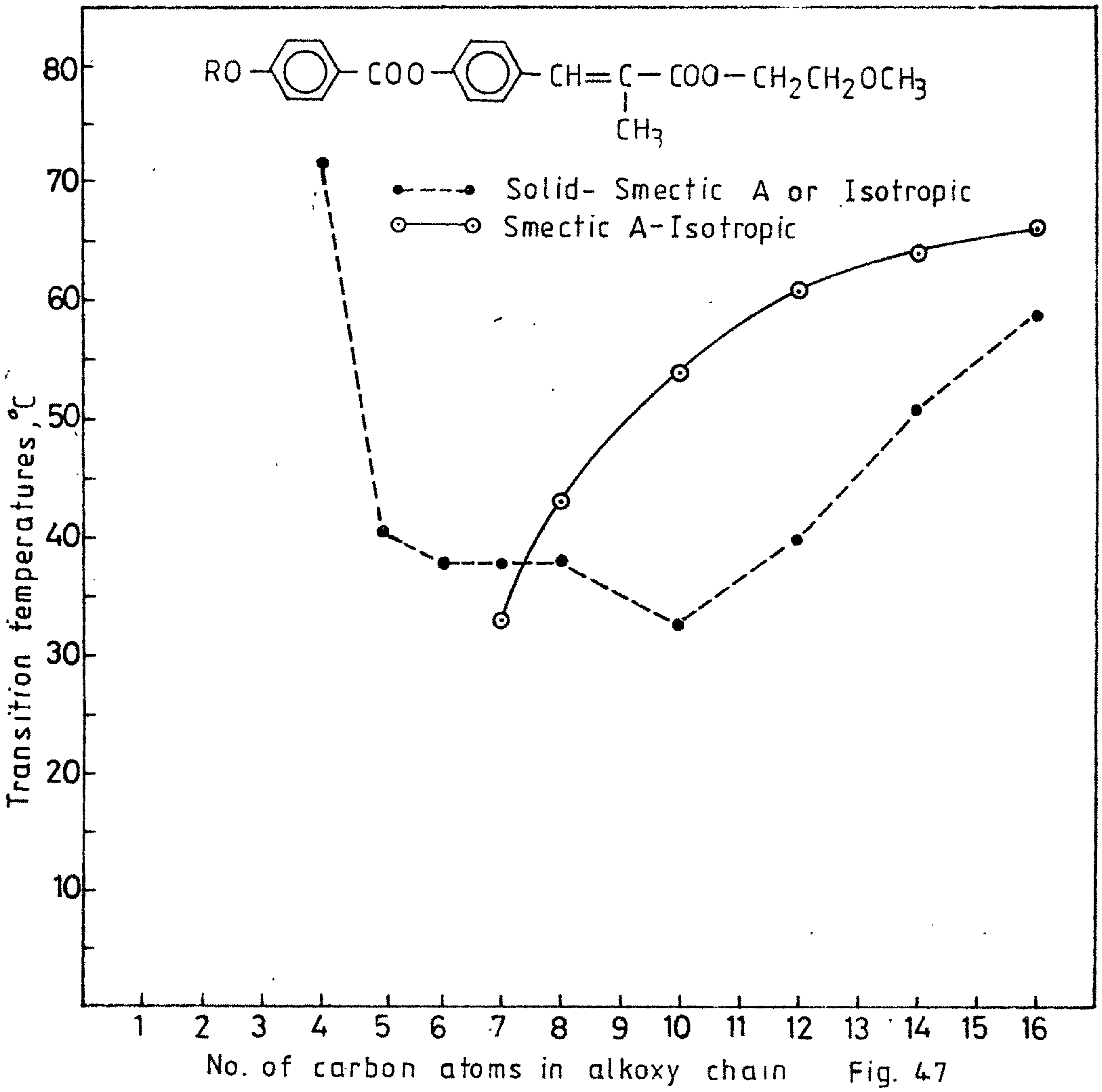

RO–C6H4–COO–C6H4–CH=C(CH3)–COO–CH2CH2OCH3
Solid- Smectic A or Isotropic
Smectic A-Isotropic
Transition temperatures, °C
80
70
60
50
40
30
20
10
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
No. of carbon atoms in alkoxy chain

Fig. 47

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

Table 39, summarises the average thermal stabilities of different mesogenic homologous series synthesized i.e.

i) Ethoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates I.
ii) Methoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates II.
iii) Methoxyethyl *trans*-4(4'-n-alkoxybenzoyloxy) -α-methyl cinnamates III.

They are compared with each other and with those of

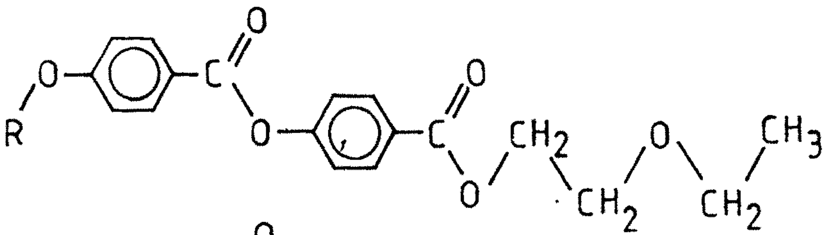
iv) β-Chloroethyl 4(4'-n-alkoxybenzoyloxy) benzoates A. (245)
iv) 4-n- Butyl(4'-n-alkoxycinnamoyloxy) benzoates B. (246)
v) Propyl 4(4'-n-alkoxyphenylazo) benzoates C. (247)

It is interesting to note that none of the present series - I to series - III exhibits smectic - C phase. They exhibit smectic-A phase. Series-II exhibits enantiotropic S_A phase except a few members which are monotropic. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain indicates that solid to mesomorphic or isotropic transition temperatures exhibit minima in the middle members of series-I, then they exhibit steep rising tendency which results in pronounced monotropic nature of smectic phases in the higher homologues of series-I. In the case of series-II, solid to mesomorphic or isotropic transition temperatures fall steeply and cover larger area and rise steeply for the higher homologues. Higher homologues exhibit predominantly enantiotropic smectic phases in series-II.

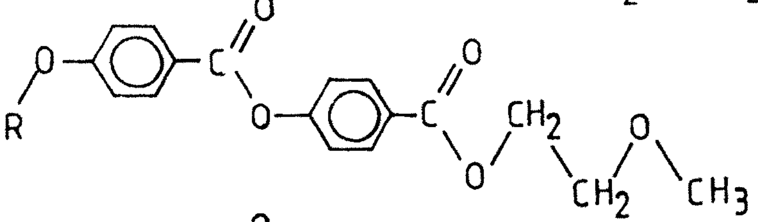
Table - 39

Average Termal stabilities (^{o}C)

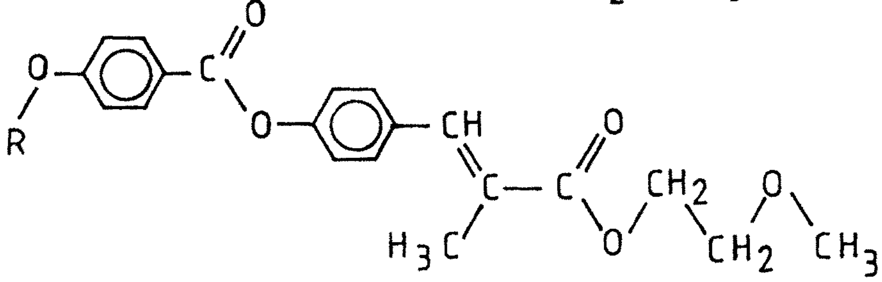
Series	**I**	**II**	**III**	**A**	**B**	**C**
Smectic-Isotropic (C_7 - C_{16})	56.33	66.33	53.5	83.83	106.17	94.5
Commencement of Smectic Phase	C_5	C_5	C_7	C_6	C_2	C_4



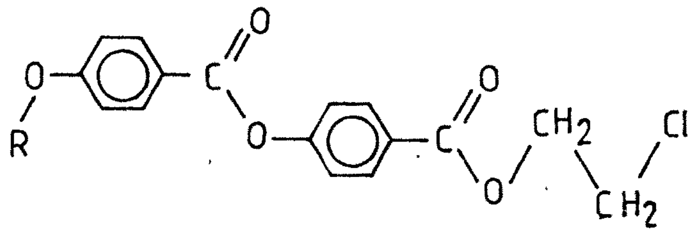
I



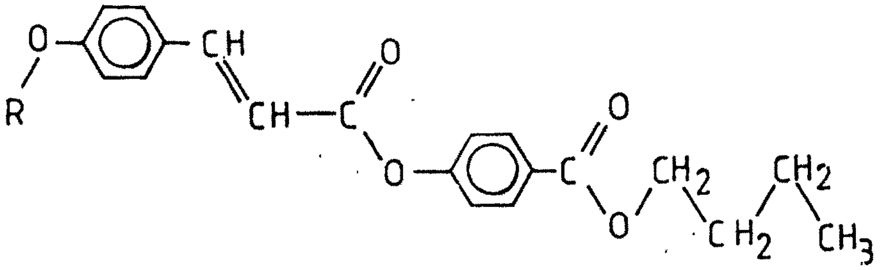
II



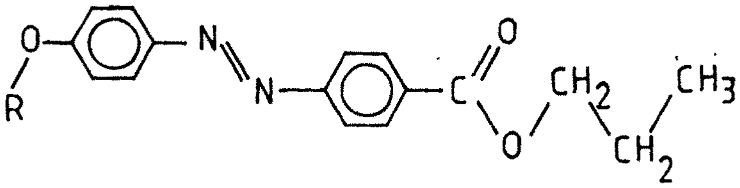
III



A



B



C

Fig. 48

The reference to geometry of series-I and series-II (Fig. 48) indicates that they differ in the terminus, series-I has $-OC_2H_5$ at the terminus where as series-II has $-OCH_3$ group at the terminus.

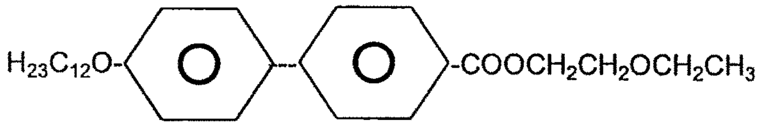
It has been normally observed that solid to mesomorphic or isotropic transitions normally do not exhibit set trends but behave irratically, mesomorphic- mesomorphic or mesomorphic - isotropic transition temeperatures exhibit regularity (183). However, it has been observed that lateral substituent or branching lowers the melting point in many cases. Extension of methylene spacer beyond certain number lowers the transition temperatures in many cases. In the present two series the solid to mesomorphic or isotropic transition temperatures are decreased markedly in series -I compared to series-II. Smectic - isotropic transition temperatures are slightly decreased. As mentioned earlier the difference between the two series is in the terminus. $-OCH_2 - CH_3$ (I) and $-OCH_3$ (II) It seems number of spacer groups and position of terminal $-OCH_3$ group adversely affects the solid-mesogenic/isotropic properties of series-II resulting in lower melting points and lower average smectic thermal stability.

The molecules of series - III are little longer (Fig. 48) and more polarizable compared to molecules of series - I and series - II, However, they also possess *trans* α-methyl group in the side chain which contributes towards the increase in the breadth of the molecules. It has been observed that increase in the breadth of the molecules adversely affects the smectic phase compared to nematic phase. It seems that α-methyl group has out balanced the effect of increased length and polarizability of molecules of series-III by reducing its average smectic-Isotropic thermal stabilities.

The reference to Table 39 indicates that the average thermal stability of series-II is lower than that of series-A. Molecules of both the series are almost identical except on the one side of terminus. Series-I has broken ethoxy methanol group where as series-A has ω - chloro ethoxy group. ω - Chloro group enhances polarizability of the molecules of series A, whereas broken alkoxy group adversely affect the smectic thermal stabilities of series-II, resulting in to enhanced smectic thermal stability of series-A.

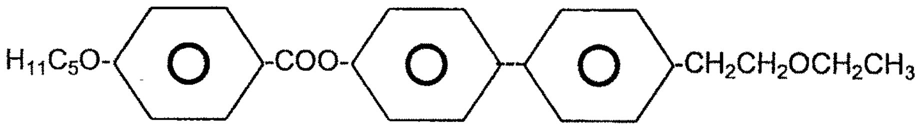
Molecules of series B are little longer and more polarizable compared to those of series-I (Fig. 48). Moreover, molecules of series B have n- butyl ester linkage at one terminus against broken alkoxy terminus in the molecules of series-II. Both these factors will enhance the smectic thermal stability of series-B compared to series-II which is the case. Molecules of series-C have an azo central linkage and n-propyl ester linkage at the ester terminus. Compared to this series II has an ester linkage and a broken alkoxy group at the ester terminus. As disccussed above broken alkoxy group will affect the smectic thermal stability of series-II adversely resulting in lower thermal stability.

Two compounds having the following structure were synthesized to evaluate the effect of biphenyl moiety devoid of ester central linkage compared to series - I



Compound (I)

k60.0S$_A$ 73.0I



Compound (ii)

K90.0S$_A$166.0I

On comparing the structure of molecules of series-I, in the compound (i) the ester linkage between the two phenyl rings is eliminated. This enhances the polarisability of the compound (i) as compared to that of molecules of series-I. The n-dodecyl homologue of series-I exhibites monotropic smectic A phase where as the compound (i) exhibits enantiotropic smectic A phase having slightly more thermal stability.

Compound -(ii) exhibits much higher thermal stability compred to n-pentyloxy homologue of series-I. This is as expected because the molecules of compound (ii) have one phenyl ring more which is the part of biphenyl linkage.

1.2 Mesogenic Binary Systems.

In general binary systems exhibiting mixed mesomorphism can be of three types (i) where both the components are mesomorphic (ii) where only one component is mesomorphic (iii) where both the components are non-mesomorphic. Here we describe mixed mesomorphism of the first and the third type.

System A : Component a: Ethoxyethyl 4(4'-n-butoxybenzoyloxy) benzoate.
-Non-mesogenic
Component b: β-Chloroethyl -4(4'-n-butoxybenzoyloxy) benzoate.
-Non-mesogenic

Reference to binary phase diagram (Fig. 49) shows that monotropic smectic A phase is exhibited from 9.78 to 89.79 mole % concentration of component a except at ~ 50 mole % of component a where it exhibits enantiotropic smectic A phase This is due to the highly depressed eutectic point around 50 mole % of component a.

System B : Component a : Methoxyethyl 4(4'-n-butoxybenzoyloxy) benzoate.
-Non-mesogenic
Component b: β-Chloroethyl 4(4'-n-butoxybenzoyloxy) benzoate.
-Non-mesogenic

The mixtures exhibit purely monotropic smectic A phase. Reference to binary phase diagram (Fig. 50) indicates that the monotropic smectic A phase is induced between 10.08 - 80.26 mole % of component a.

System C : Component a : Ethoxyethyl 4(4'-n-hexyloxy benzoyloxy) benzoate.
Mesogenic
Component b : Methoxyethyl 4(4'-n-decyloxy benzoyloxy) benzoate.
Mesogenic

Reference to phase diagram (Fig. 51) shows that on both the sides as the concentration of either of the component increases melting point exhibits marked depression. In the region of 42.35 mole % to 72.01 mole % of component a mesophase persists up to 0 °C.

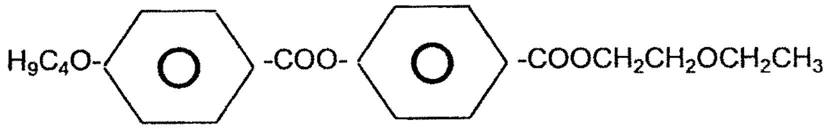
As the mixtures exhibit smectic A phase below room temperatures they have potential applications in display devices.

Most of the mixtures exhibit homogeneous phase only in few cases where two phase region is observed, for simplicity the highet temperatures are considered for drawing binary phase diagrams.

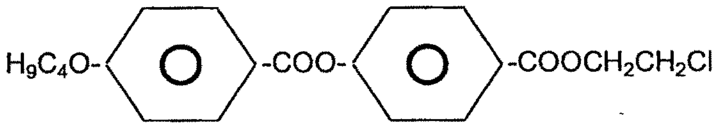
Table - 33

SYSTEM - A

Component : a



Component : b



Transition Temperatures °C

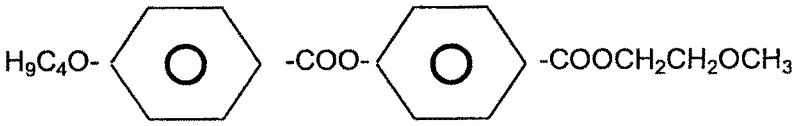
Sr. No.	Mole % of a	Transition Temperatures °C S_A	I
1	0.00	-	75.0
2	9.78	(64.0)*	75.0
3	19.61	(60.0)	69.0
4	29.48	(58.0)	66.0
5	39.41	54.0	57.0
6	49.37	50.0	54.0
7	59.4	(53.0)	66.0
8	69.49	(51.0)	67.0
9	79.60	(50.0)	70.0
10	89.79	(48.0)	73.0
11	100.0	-	76.0

( )* Monotropic Value

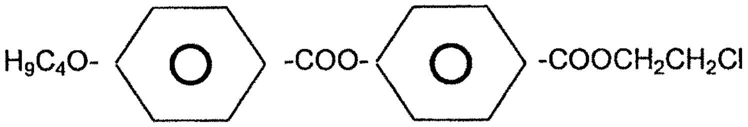
Table - 34

SYSTEM - B

Component : a



Component : b



Transition Temperatures °C

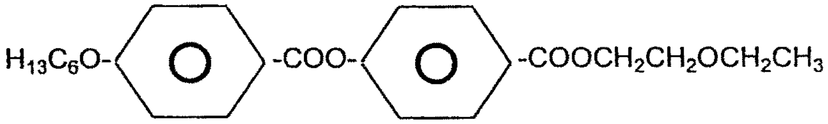
Sr. No.	Mole % of a	Transition Temperatures °C	
		S_A	I
1	0.00	-	75.0
2	10.08	(60.0)*	74.0
3	20.18	(59.0)	72.0
4	30.24	(59.0)	71.0
5	40.29	(60.0)	70.0
6	50.29	(52.0)	67.0
7	60.28	(56.0)	65.0
8	70.26	(51.0)	63.0
9	80.26	(49.0)	62.0
10	90.13	-	62.0
11	100.0	-	63.0

( )* Monotropic Value

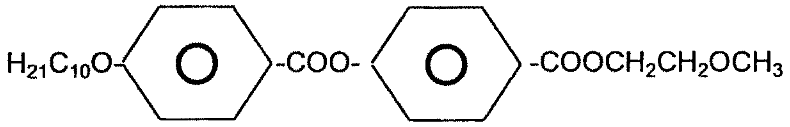
Table - 35

SYSTEM - C

Component : a



Component : b

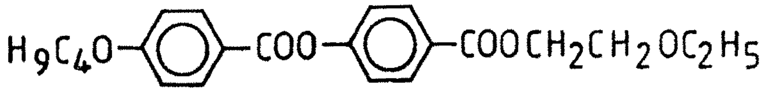


Transition Temperatures °C

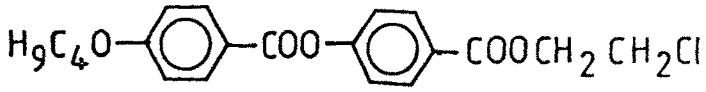
Sr. No.	Mole % of a	Transition Temperatures °C	
		S_A	I
1	0.00	40.0	73.0
2	10.88	38.0	63.0
3	21.59	31.0	62.0
4	32.05	29.0	58.0
5	42.35	Mixtures remain smectic on quenching even at 0 °C	56.0
6	52.41		56.0
7	62.29		55.0
8	72.01		52.0
9	81.52	29.0	50.0
10	90.84	39.0	48.0
11	100.0	43.0	54.0

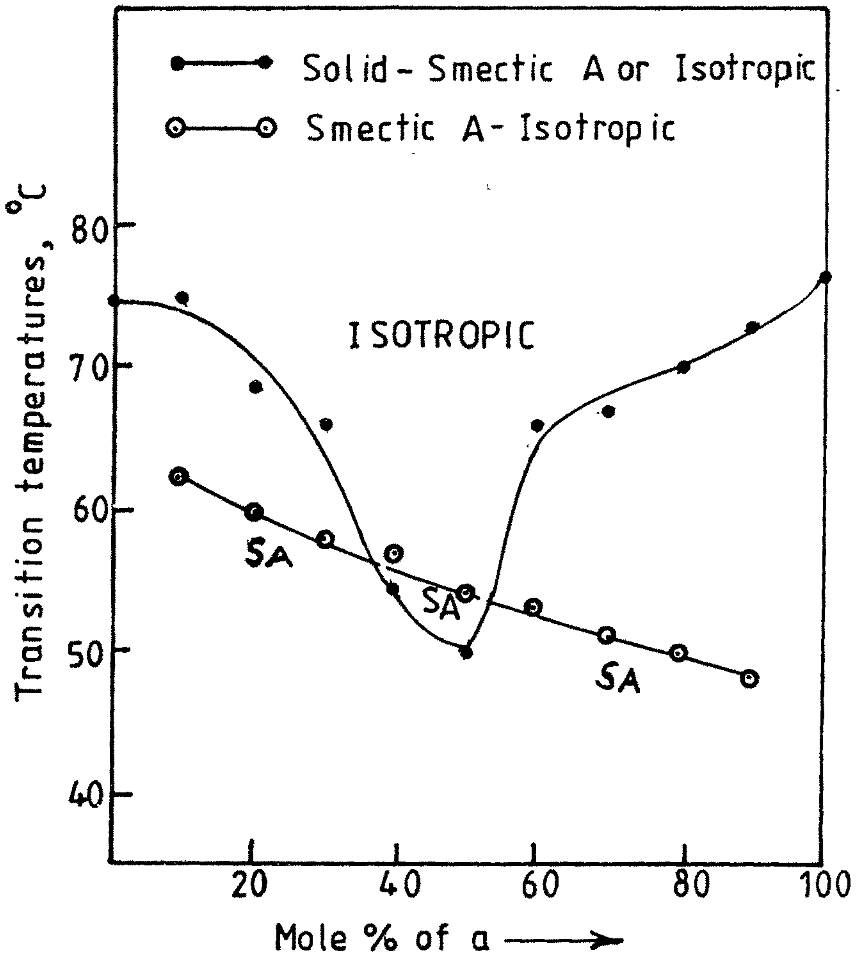
( )* Monotropic Value

Component a



Component b

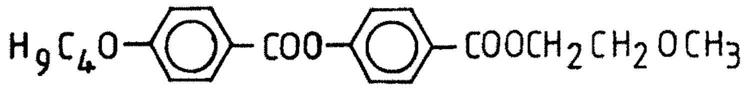




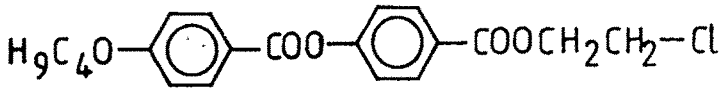
System A

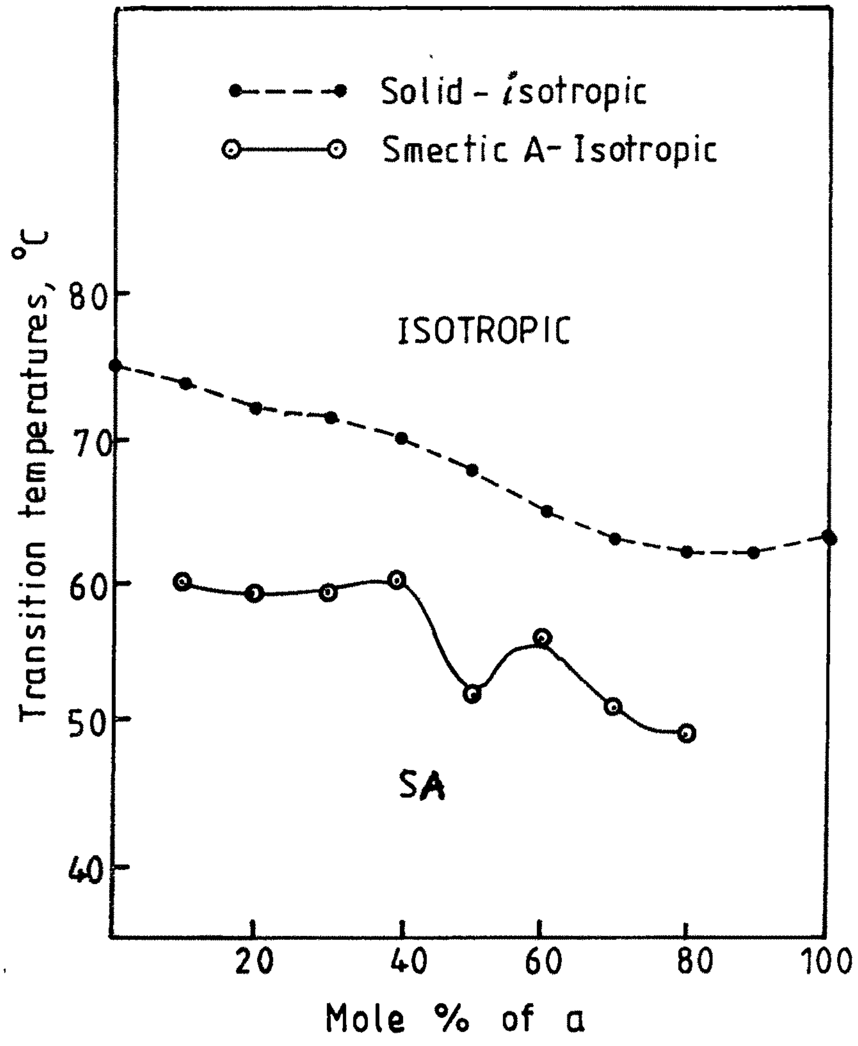
Fig. 49

Component a



Component b

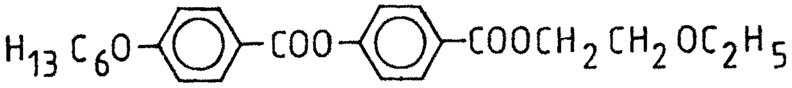




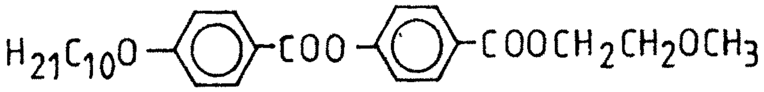
System B

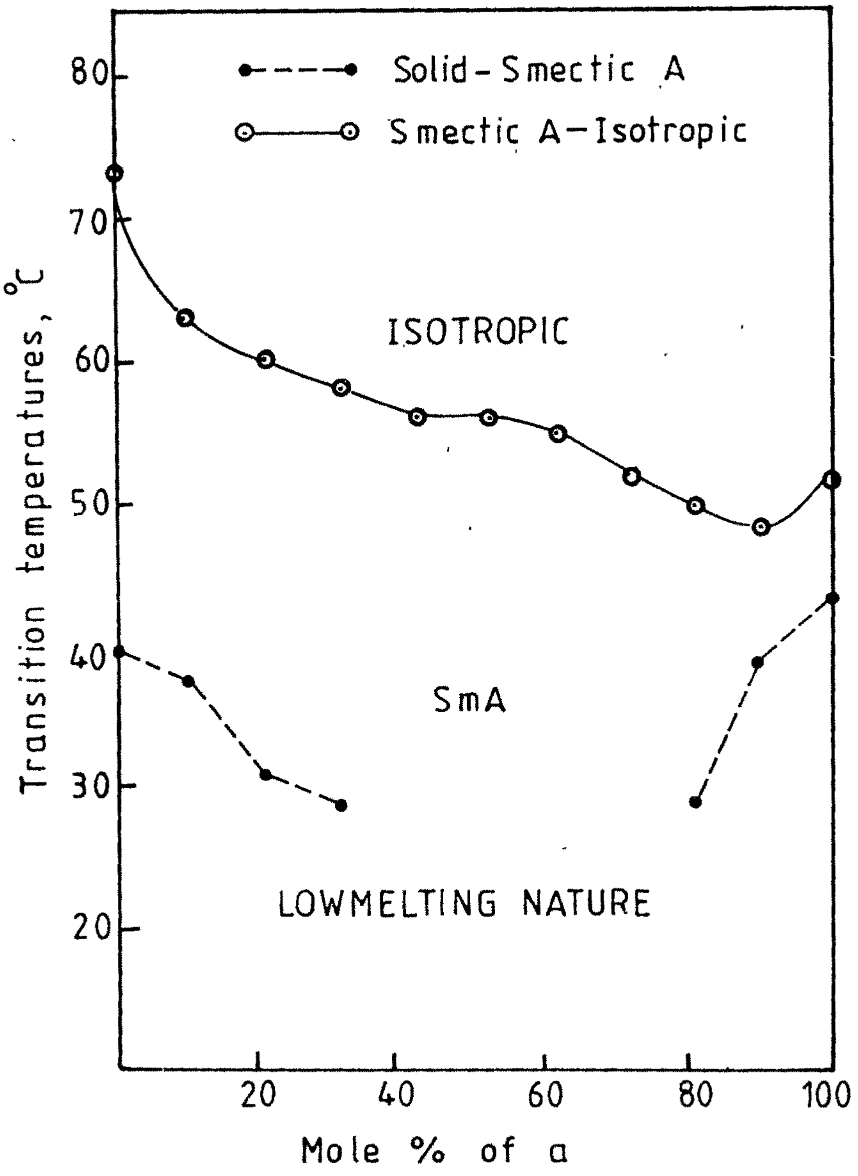
Fig. 50

Component- a



Component- b





System- C

Fig. 51

2.0 LIQUID CRYSTALLINE SCHIFF BASES WITH NAPHTHALENE NUCLEUS AND AZOMESOGENS

2.0 LIQUID CRYSTALLINE SCHIFF BASES WITH NAPHTHALENE NUCLEUS AND AZOMESOGENS

In their study to establish the co-relation between broad nucleus and cholesteryl derivatives and their effect on mesomorphism, Dave et al (248, 249) synthesized number of Schif base homologous series having naphthalene moiety. Wiegand (195) has also reported a few liquid crystalline compounds with naphthalene moiety.

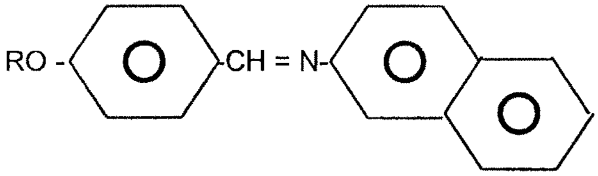
The effect of chemical constitution on 1,4-,1, 5- and 2,6- substituted naphthalene derivatives has also been studied (183,194 - 197, 250).

It seems,the interest in naphthalene nucleus is again revived in last decade and number of research papers published have mesogens with naphthalene nuclei. (251 - 258)

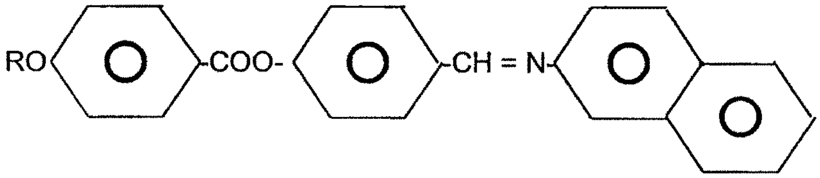
Polymeric liquid crylstals with naphthalene moiety have been studied extensively and patents also have appeared in the literature. (259, 259a)

The mesomorphic compounds incorporating a phenolic or a primary amino end group are rare (260-263). Schroeder and Schroeder (264) reported few such mesogenic compounds. Mesogenic compounds with terminal alcoholic group (265) and amino group (266) are of interest, lately. Vora et al. (267) for the first time reported two extensive homologous series containing terminal and lateral phenolic group. The laterally substituted thiol mesogens are yet to be reported. Gray (183) has explained that the rarity of such mesogenic compounds may be due to intermolecular hydrogen bonding and the broadening of the molecules. In order to investigate the influence of the lateral thiol groups on mesmorphism first extensive mesogenic homologous series of Schiff base esters with lateral thiol group (Series - VI) has been also synthesized.

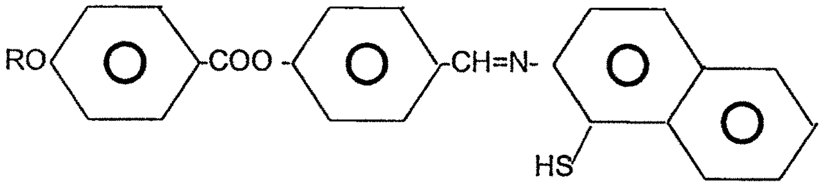
Six homolgous series, containing azo or azomethine central linkage of the following structural formulae are synthesized.



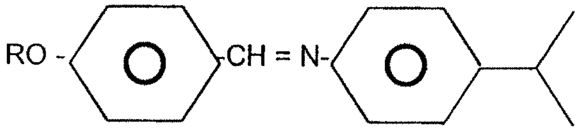
Series IV



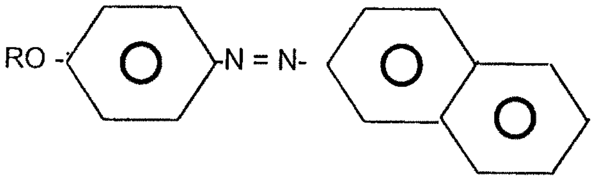
Seires V



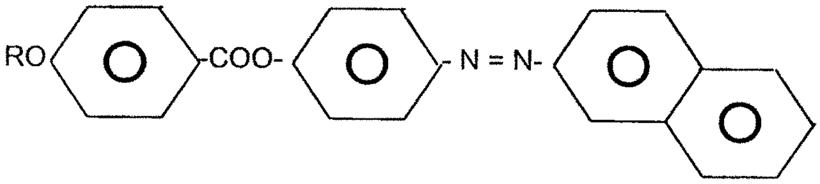
Series VI



Series VII



Series VIII



Series IX

The route of synthesis for series IV - IX is given in Scheme 4-9, respectively.

Series - IV : 4-n-alkoxybenzylidene -2'-aminonaphthalenes.

Twelve compounds have been synthesized and their mesogenic properties are evaluated. The melting points and transition temperatures are recorded in Table 7.

The n-hexyloxy to n-Decyloxy derivatives exhibit monotropic nematic phases. n-Dodecyloxy derivative exhibits monotropic SmA as well as monotropic nematic phase. Rest of the members are non-mesogenic.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Fig. 52) exhibits a tendency of rising nematic-isotropic transition in ascending series.

Series - V : 4(4'-n-alkoxybenzoyloxy benzylidene) -2'-aminonaphthalenes.

All the twelve members synthesized exhibit enantiotropic nematic phase. SmC mesophase commences from the n-heptyloxy derivative as a monotropic phase n-decyloxy to n-Hexadecyloxy derivatives exhibit enantiotropic SmC phase the transition temperatures are recorded in Table 9

Series - VI : 4(4'-n-alkoxybenzoyloxy benzylidene) -2'-aminonaphthalene -1"- -thiols

All the twelve members synthesized exhibit enantiotropic nematic phase SmC mesophase appears from the n-dodecyloxy derivative as a monotropic phase and the n-tetradecyloxy and n-hexadecyloxy homologues exhibit enantiotropic SmC phases. The transition temperatures are recorded in Table 11

Series - VII : 4-n-alkoxybenzylidene -4'-isopropylanilines.

Twelve compounds have been synthesized and their mesogenic properties are evaluated. The melting points and transition temperatures are recorded in Table 13.

The n-octyloxy and n-dodecyloxy derivatives exhibit enantiotropic smectic A phase whereas n-decyloxy and n-tetradecyloxy derivatives exhibit monotropic smectic A phases. Rest of the members are non-mesogenic.

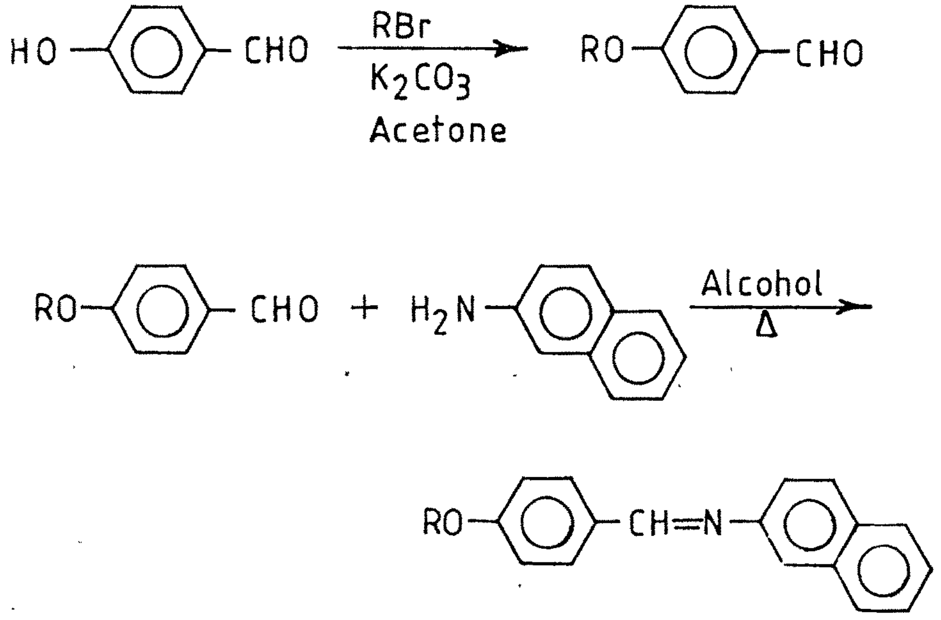
Lower homologues as well as higher homologues of two series are non-mesogenic. This indicates that isopropyl terminal group disturbs the order when molecules do not have sufficient chain length or very long chain length. Interesting aspects is that even the isopropyl terminal group is present the homologues (C_8-C_{14}) exhibit Smectic mesophase.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Fig. 55) exhibits a tendency of rising smectic - isotropic transition in ascending series. Fig. 55 also indicates the steep rising tendency of solid - smectic or isotropic transition for n-decyloxy and n-tetradecyloxy derivatives which results in pronounced monotropic smectic nature.

Series - VIII : 4-n-alkoxyphenyl azo -2'-naphthalenes.

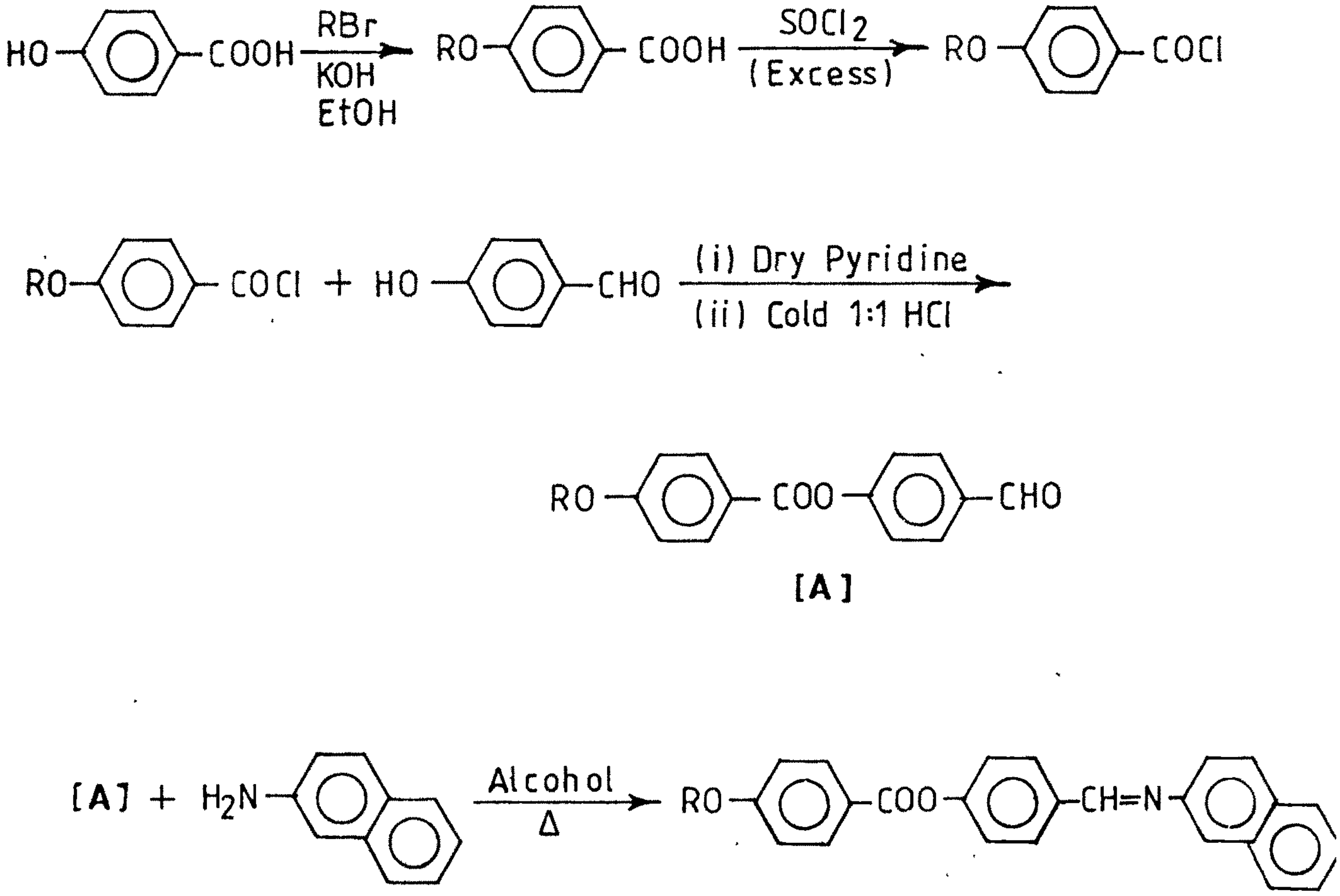
Seven compounds have been synthesized. All the compounds are non-mesogenic (Fig. 56) Melting points are recorded in Table 15.

Series - IX : 4(4'-n-alkoxybenzoyloxy) phenylazo -2'-naphthalenes.



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

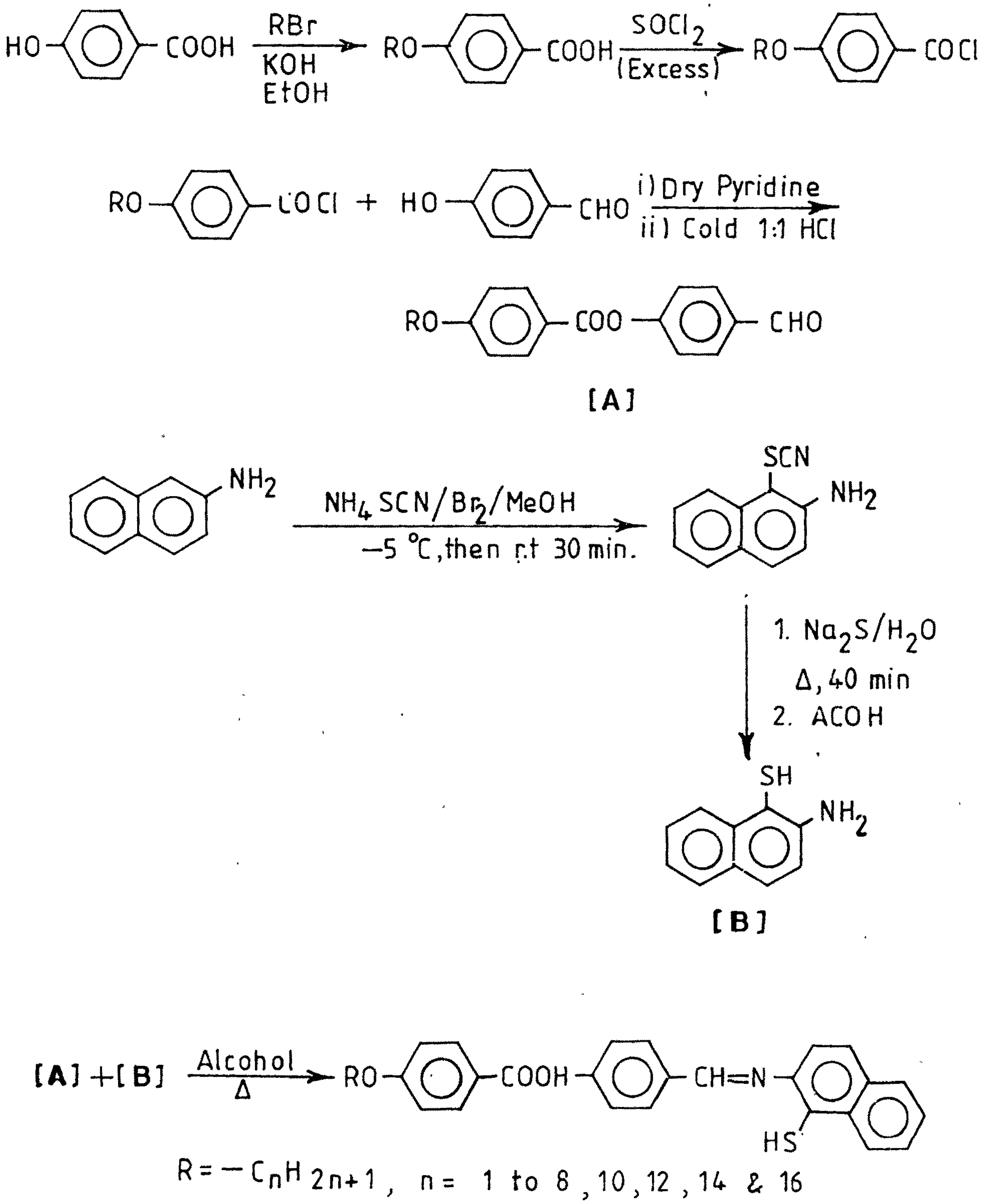
SYNTHETIC ROUTE TO SERIES-IV
SCHEME-4



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

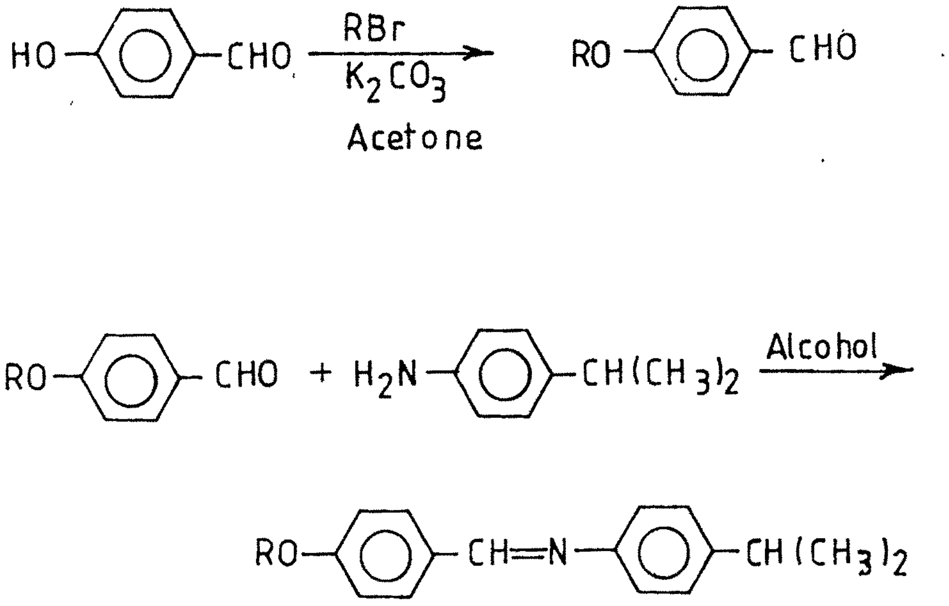
SYNTHETIC ROUTE TO SERIES-V

SCHEME-5



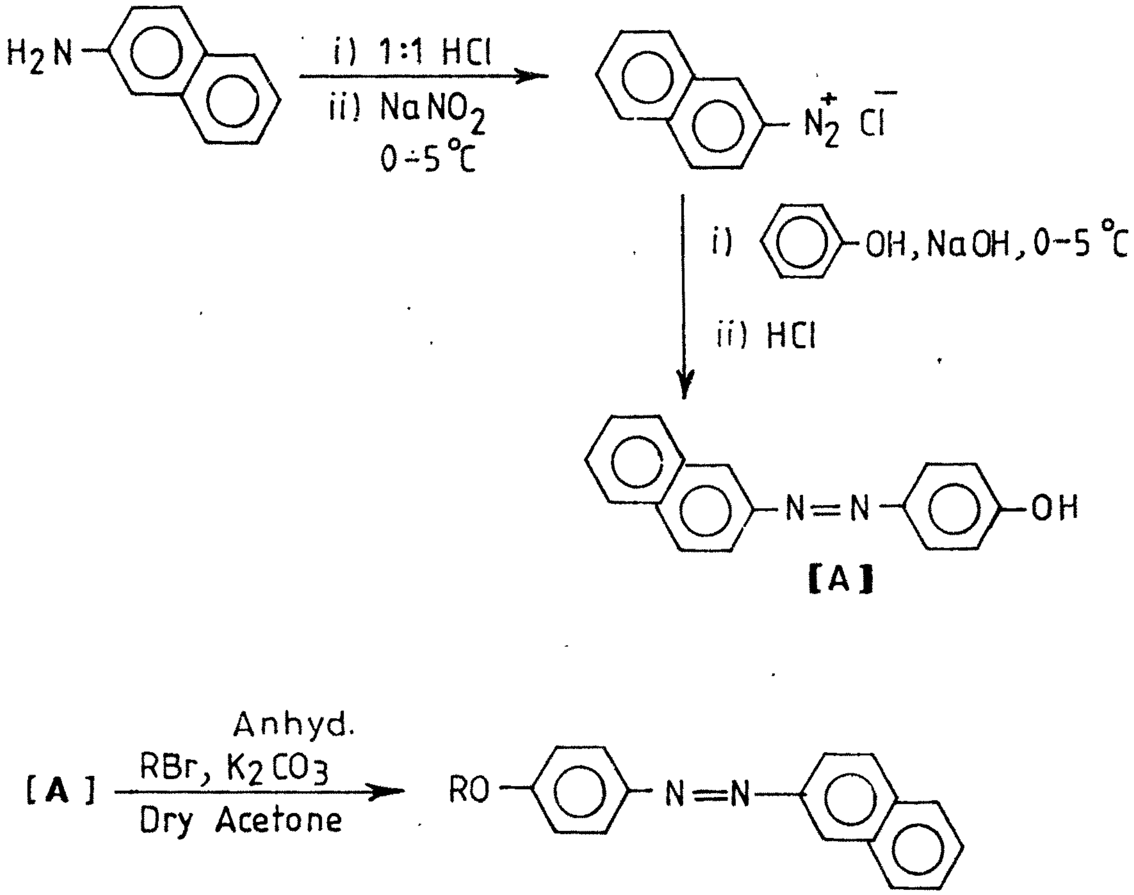
SYNTHETIC ROUTE TO SERIES – VI

SCHEME – 6



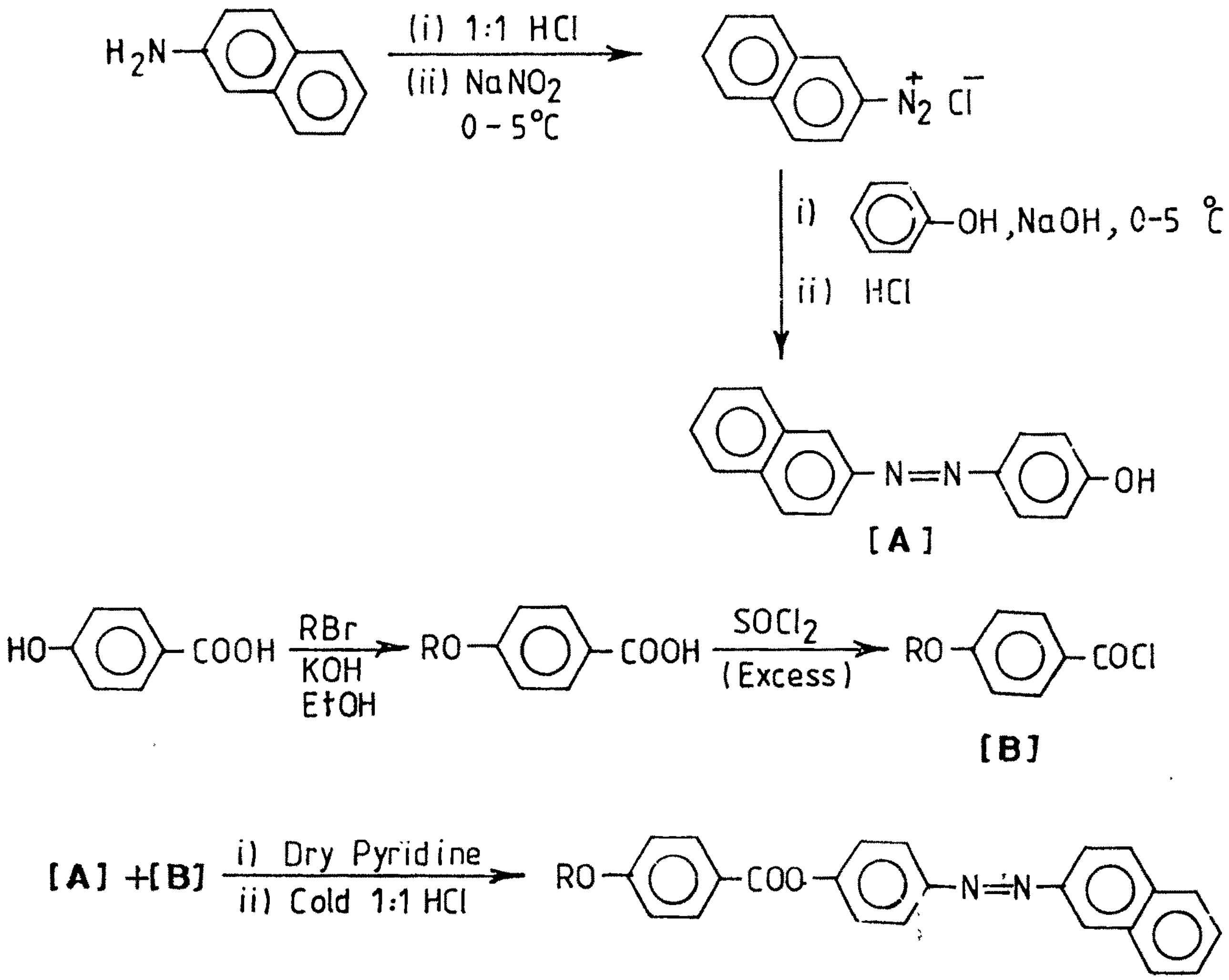
$R = -C_nH_{2n+1}$, n = 1 to 8, 10, 12, 14 & 16

SYNTHETIC ROUTE TO SERIES-VII
SCHEME-7



$R = -C_nH_{2n+1}$, n = 6, 7, 8, 10, 12, 14 & 16

SYNTHETIC ROUTE TO SERIES – VIII
SCHEME-8



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

SYNTHETIC ROUTE TO SERIES - IX

SCHEME - 9

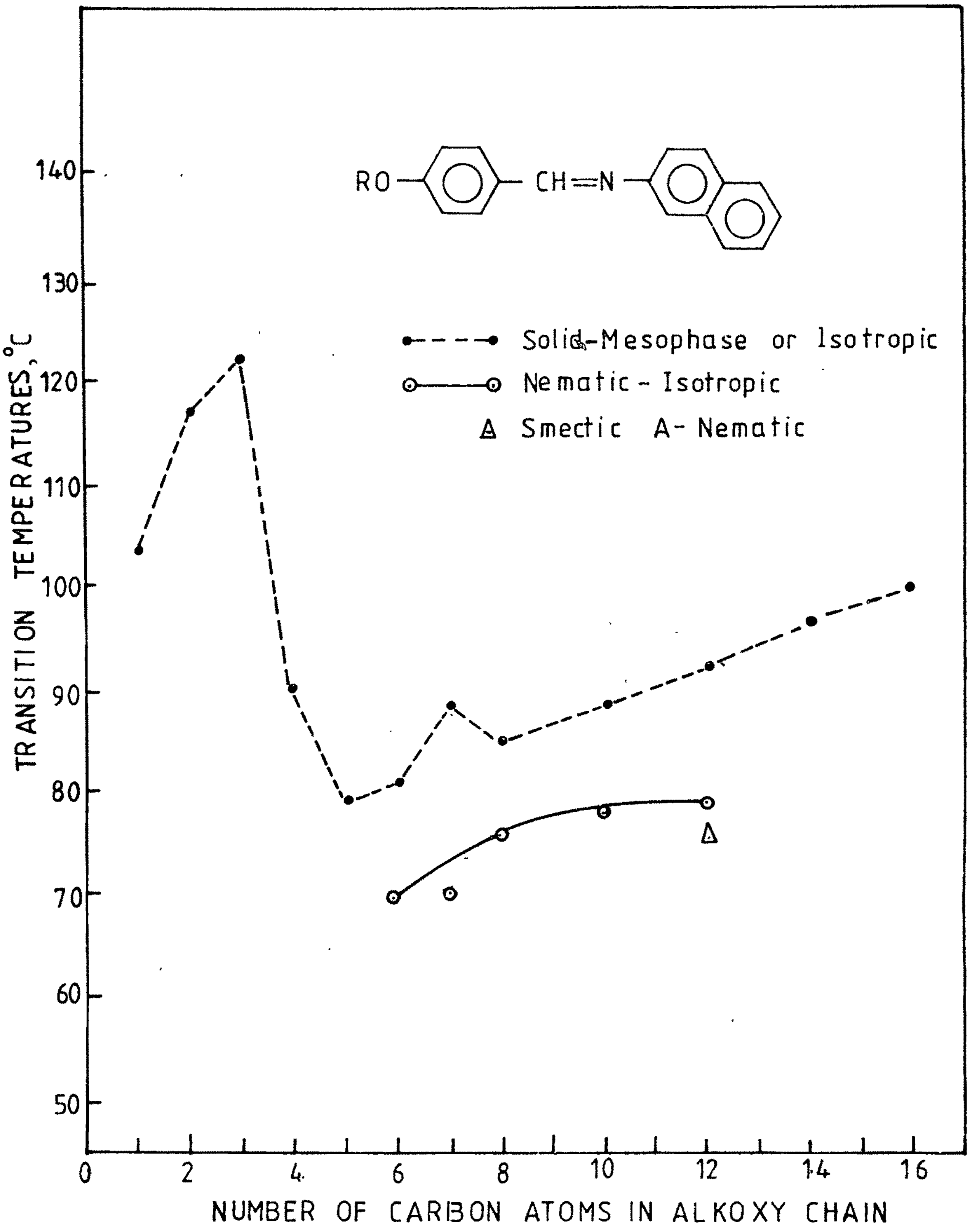

RO
CH=N
Solid-Mesophase or Isotropic
Nematic - Isotropic
Smectic A- Nematic
TRANSITION TEMPERATURES, °C
140
130
120
110
100
90
80
70
60
50
0
2
4
6
8
10
12
14
16
NUMBER OF CARBON ATOMS IN ALKOXY CHAIN

Figure 52

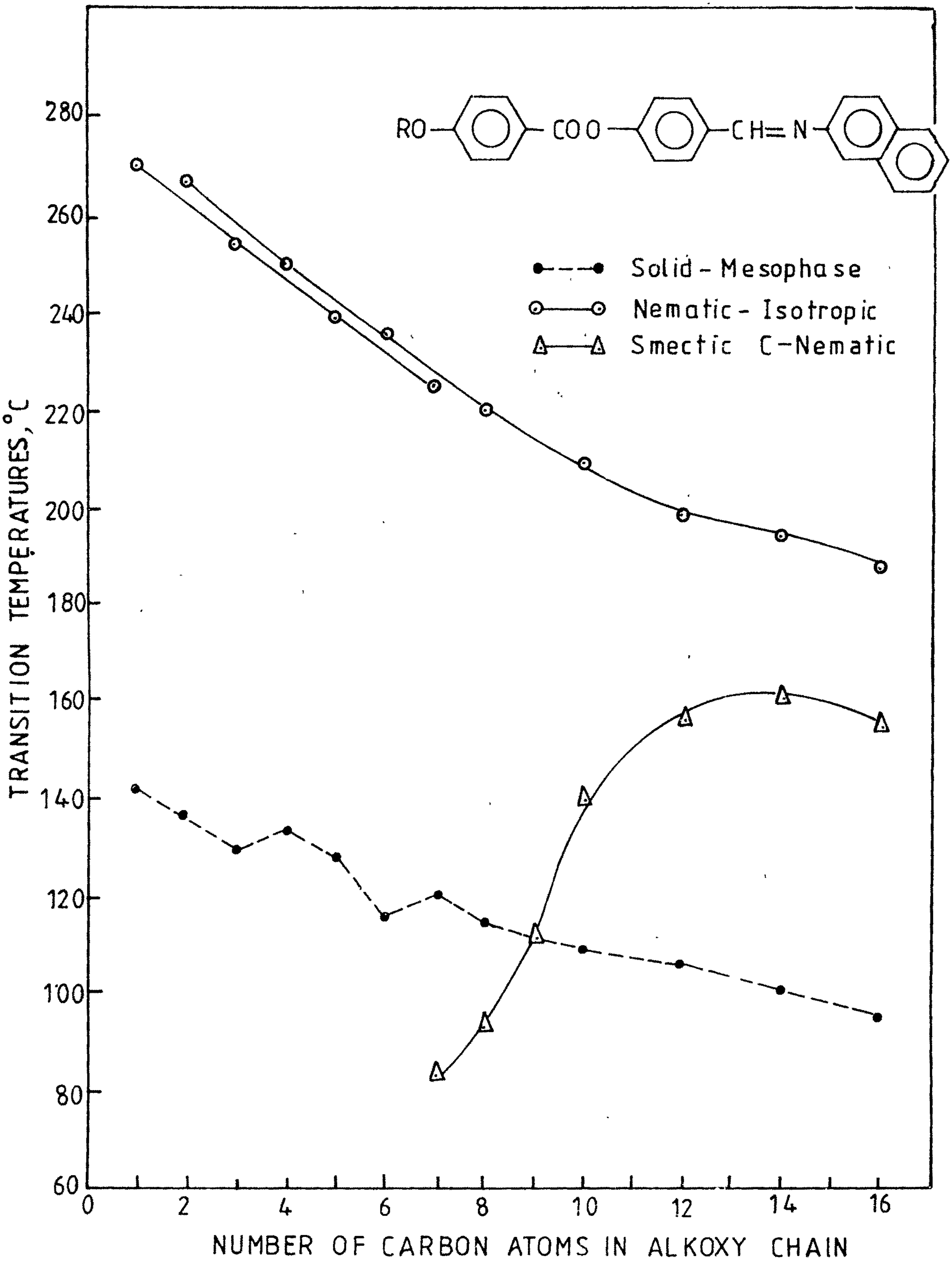

RO — COO — CH=N
TRANSITION TEMPERATURES, °C
280
260
240
220
200
180
160
140
120
100
80
60
0
2
4
6
8
10
12
14
16
NUMBER OF CARBON ATOMS IN ALKOXY CHAIN
●- - -● Solid - Mesophase
⊙——⊙ Nematic - Isotropic
△——△ Smectic C-Nematic

Figure 53

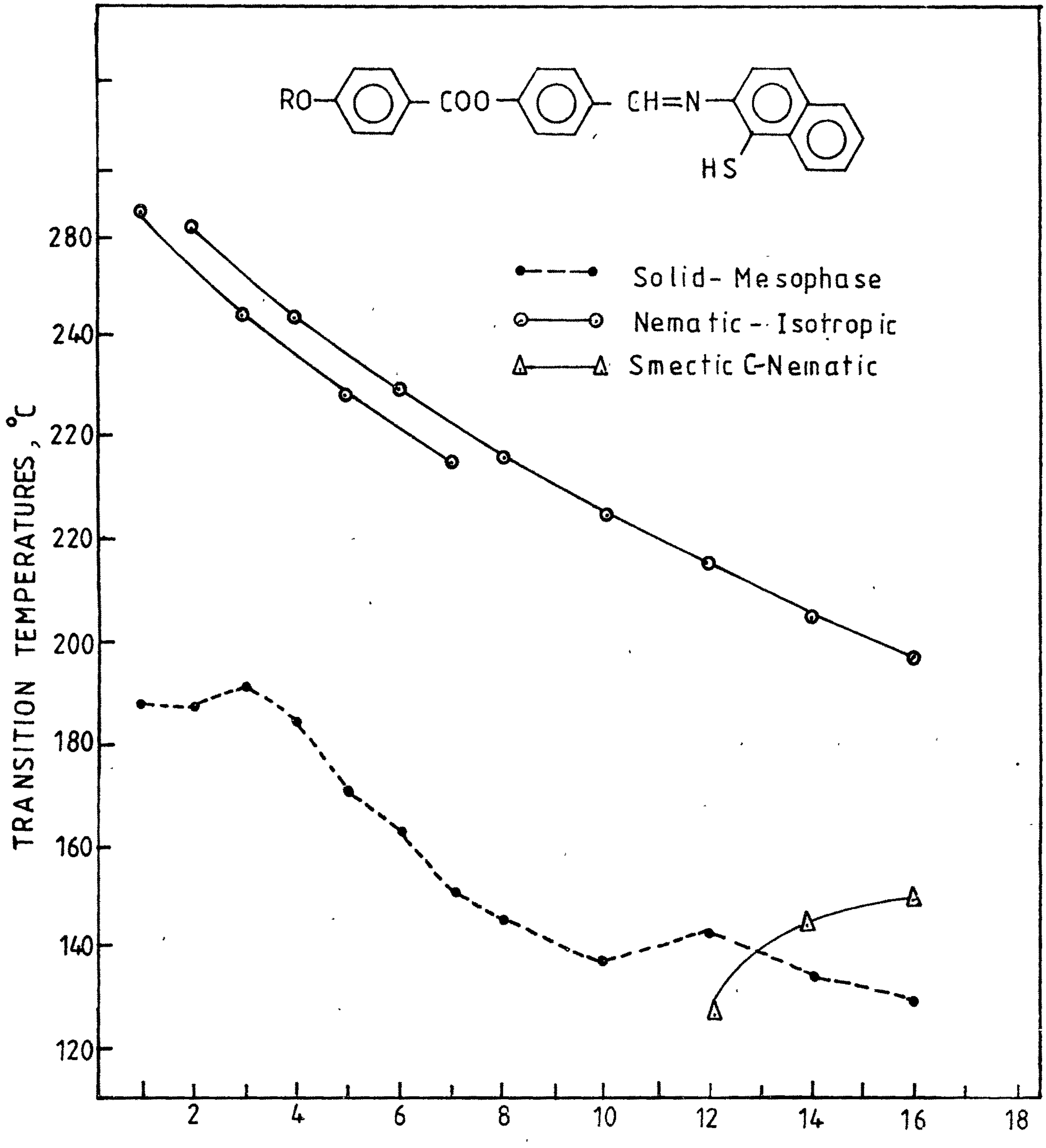

RO
COO
CH=N
HS
Solid- Mesophase
Nematic -- Isotropic
Smectic C-Nematic
TRANSITION TEMPERATURES, °C
280
240
220
220
200
180
160
140
120
2
4
6
8
10
12
14
16
18
NUMBER OF CARBON ATOMS IN ALKOXY CHAIN

Figure 54

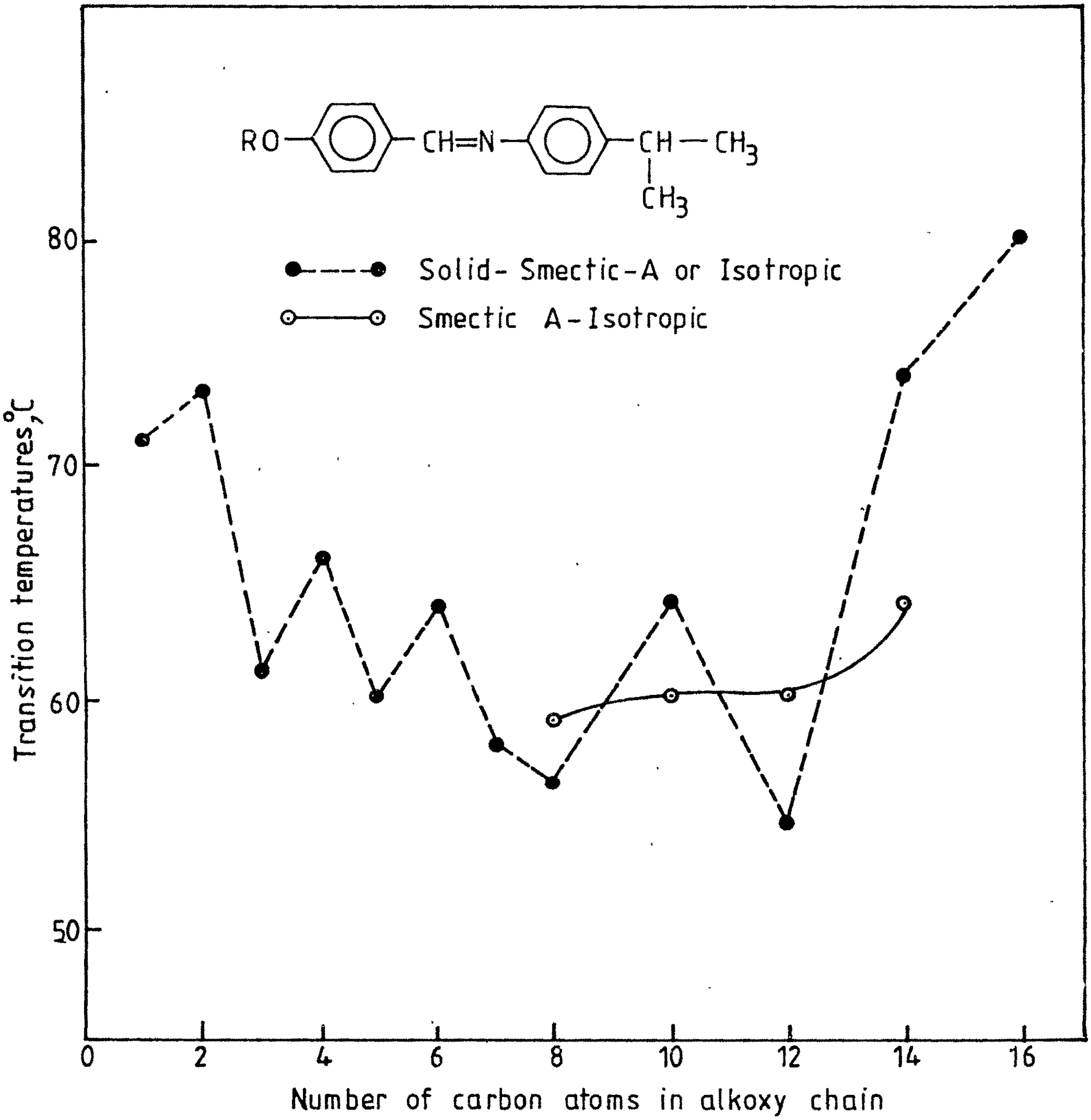

RO
CH=N
CH — CH3
CH3
Solid- Smectic-A or Isotropic
Smectic A-Isotropic
Transition temperatures,°C
80
70
60
50
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Figure 55

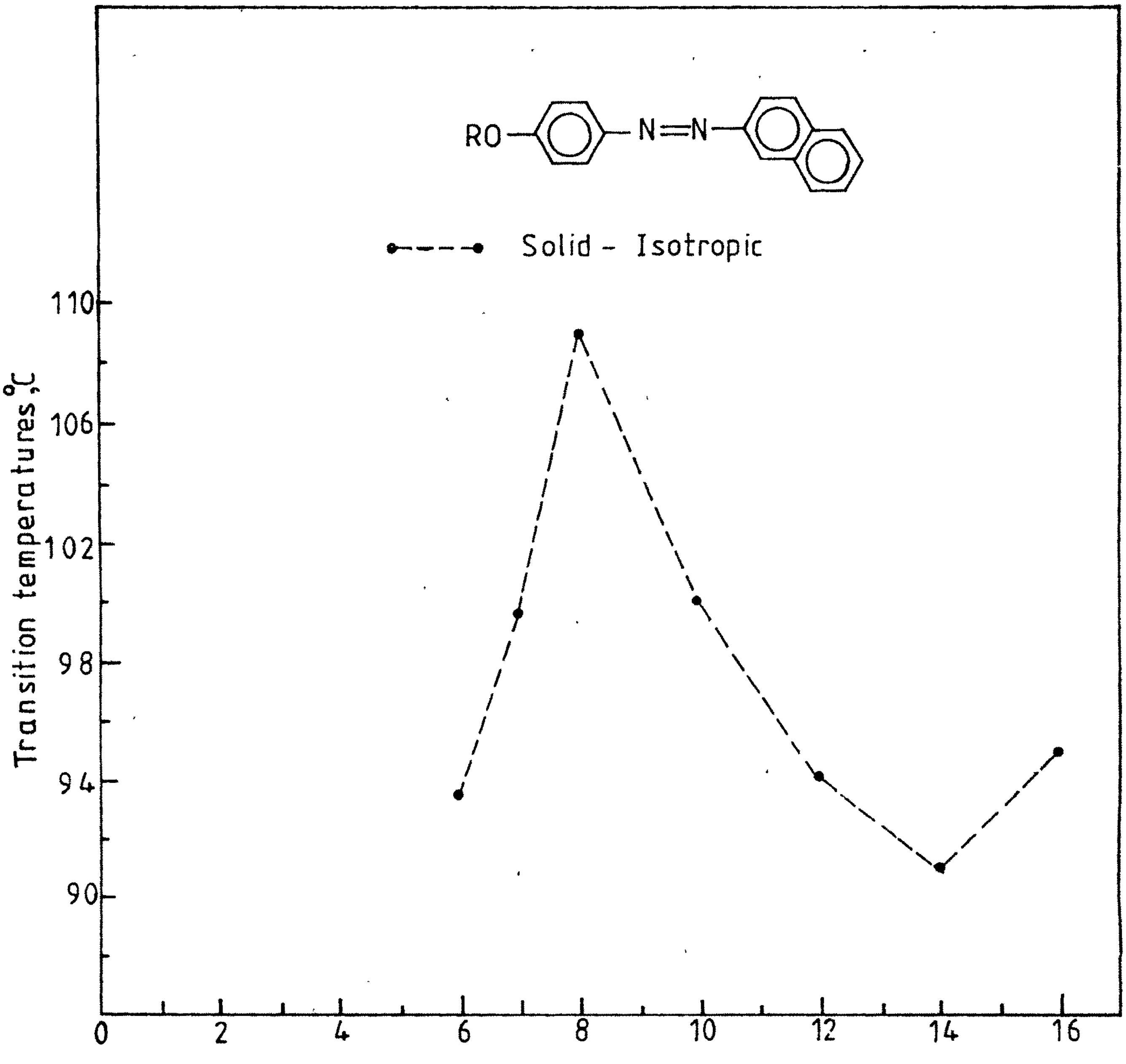

RO—N=N—
Solid - Isotropic
Transition temperatures,°C
110
106
102
98
94
90
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Figure 56

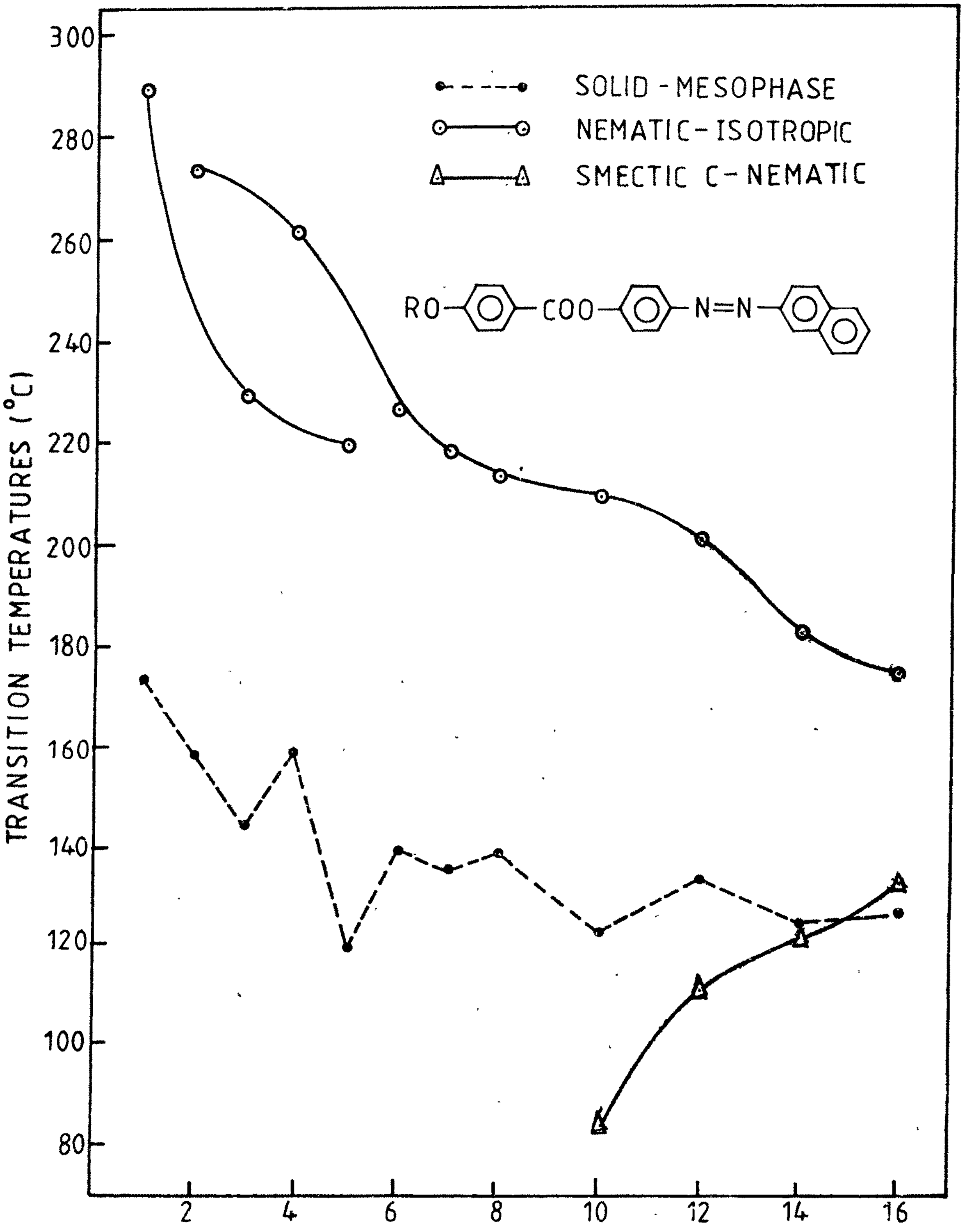

SOLID - MESOPHASE
NEMATIC - ISOTROPIC
SMECTIC C - NEMATIC
RO–⟨○⟩–COO–⟨○⟩–N=N–
TRANSITION TEMPERATURES (°C)
300
280
260
240
220
200
180
160
140
120
100
80
2
4
6
8
10
12
14
16
NUMBER OF CARBON ATOMS IN ALKOXY CHAIN

Fig. 57

All the twelve members synthesized exhibit enantiotropic nematic phase. SmC mesophase commences from the n-decyloxy derivative as a monotropic phase. The transition temperatures are recorded in Table 17.

2.1 Common Features of Series V, VI & IX.

All the three homologous series exhibit mesomorphism. The plot of transition tempertures against the number of carbon atoms in the alkoxy chain (Fig. 53, 54, 57) shows steady fall in nematic-isotropic transitions and exhibits marked odd-even effect It also exhibits a tendency of rising smectic - nematic transitions in ascending series. The rising smectic-nematic transitions slightly level off for higher homologues in series V. (Fig. 53).

Gray (183) has explained the alternation by assuming zig-zag conformation of the alkyl chian in the molecule. The absence of alternation in the smectic - nematic transition temperatures are explained by stating that in such a conformation the added methylene group does not affect the lateral transitions differently whether the chain is even or odd provided that the chain axes are normal to the interfaces. However, some homologous series are reported by Gray and Harrison (189) and by Fishel and Patel (268) where odd-even dffect is observed for smectic - nematic transition tempertures. Gray and Harrison (189) also observed high alternation for the nematic-isotropic transition temperatures in the ω - substituted alkyl arene esters. They have reported that smectic - nematic and smectic - isotropic transition temperatures alternate less markedly and in some systems, the alternation is negligible,and the smectic-nematic and smectic-isotropic transition temperatures fit in a single curve. From the above discussion it is reasonably evident that transition temperature changes in mesogens are a delicate balance of several factors such as molecular shape, conjugation, resonance, conformational preference of alkoxy chain, size and position of dipole etc.

This is further supported by some more studies. In the case of 4(4'-n-alkoxybenzoyloxy) -4"-aminoacetophenones (230), odd-even alternation is observed for the smectic-isotropic transition temperatures, whereas in the series 4(4'-n-alkoxybenzylidene) -4"-aminoacetophenones (269) no such alternation is observed for the smectic - isotropic transition temperatures. The difference between the two series is only in the central linkage. Vora (270) has also reported the absence of odd-even effect in the smectic-isotropic transition temperatures of series 4'-n-alkoxybenzylidene-4"-bromoanilines.

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 (272). For the mesogenic homologous series, Gray (8), 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 seperations, 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 the isotropic liquid phase. The

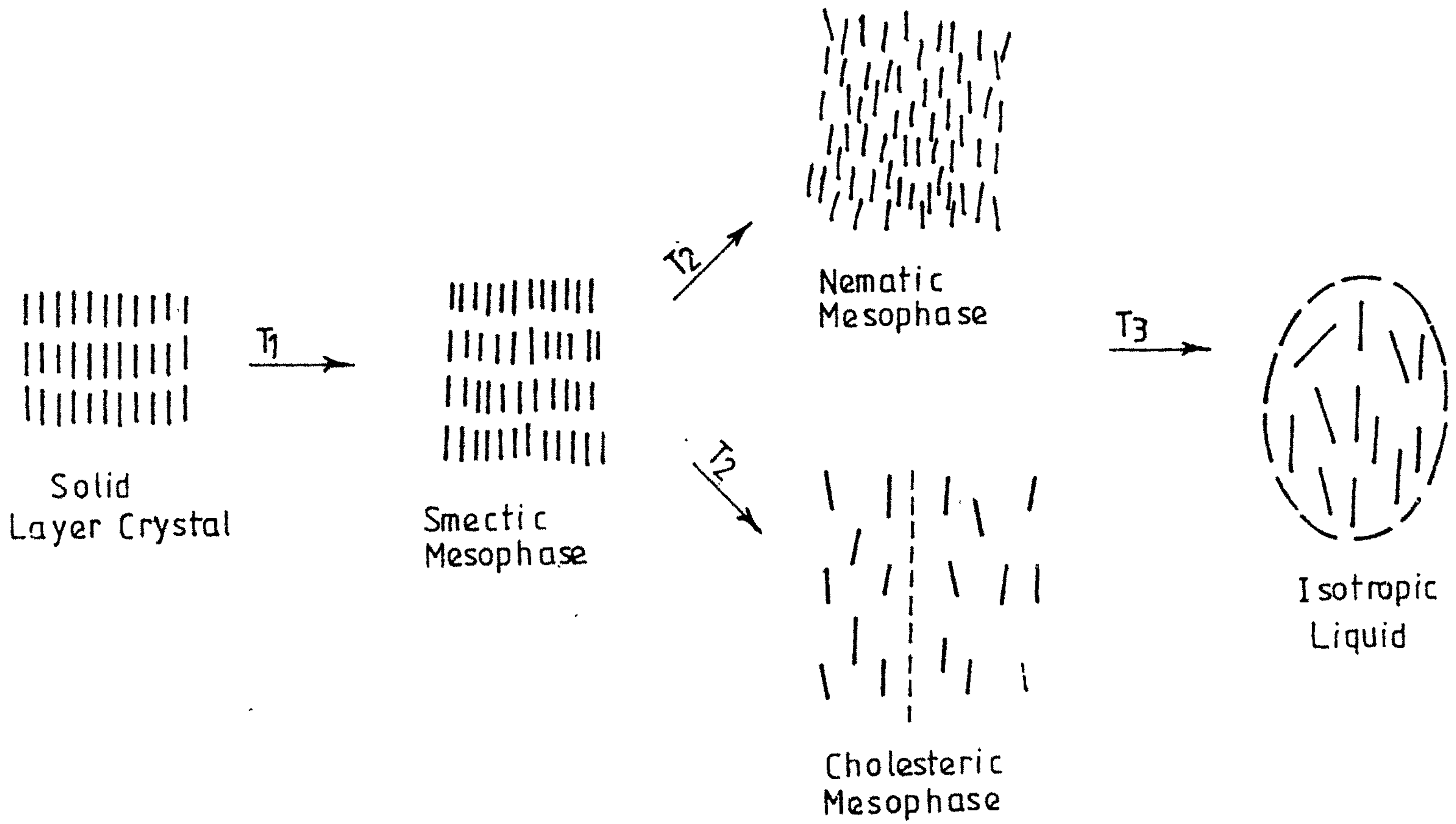

Solid
Layer Crystal
T1
Smectic
Mesophase
T2
T2
Nematic
Mesophase
Cholesteric
Mesophase
T3
Isotropic
Liquid

Fig. 58

molecular layer structure of the smectic phase occurs in temperature region 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 cohesions. On further heating all the Vander Waals forces are again broken down and the molecules pass into randomly arranged isotropic liquid state. These changes can be represented schematically as shown in the Fig. 58.

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 (183) 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 of the terminal intermolecular cohesions. However, Gray (183) and Maier and Baumgartner (273) have suggested that the addition of each methylene unit simultaneously increases the overall polarizability of the molecules and the lateral inter molecular attractions. The lower homologues are purely nematic, i.e. for the short chainlength compounds, the seperation 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 chainlength of alkyl group, no nematic mesophase would be observed and system would exhibit pure smectic phase. At this stage smectic mesophase will directly pass into isotropic liquid stage, presumably because the terminal intermolecular attractions 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 mesophase. In lower homolegues, the terminal cohesive forces are relatively strong, with the increase in alkyl chainlength, 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-alkoxybenzylideneamino fluorenones and 4-n-alkoxybenzylideneaminobiphenyls, having substitution in 2 or 3 positions (274) and 2-methyl -1, 4-phenylene bis(4'-n-alkoxybenzoates), (275) 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 noctadecyloxy derivative the smectic-nematic curve does not merge with the nematic - isotropic curve. Dave et al. (248, 249) 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 disordered 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 (183, 278-280). 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 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.

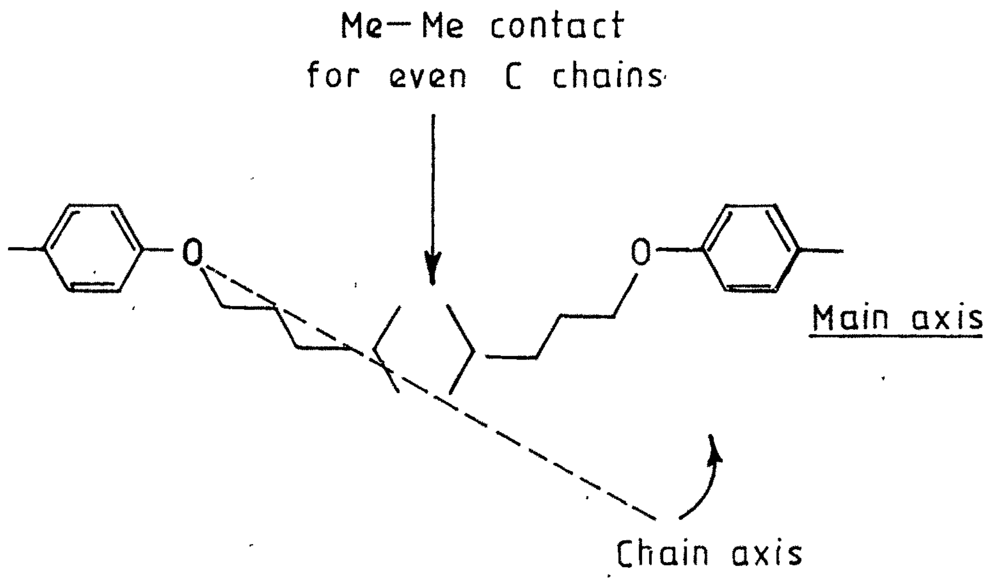


Fig.59

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 transition 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 groups in an end - to - end packing of the molecules of n-alkyl aryl ethers, such as p-n-alkoxybenzoic acids. For short alkyl chain, if the chain extends strictly along its own axis (dotted line in Fig. 59) 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 in temperatures.

With the higher homologues the alkyl chain may be forced (curved arrow in Fig 59) 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.

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

Table - 40 summarizes the average thermal stabilities of different mesogenic homologous series synthesized i.e.

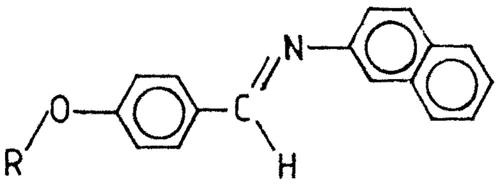
i)	4-n-Alkoxybenzylidene -2'-aminonaphthalenes	IV
ii)	4-(4'-n-Alkoxybenzoyloxy benzylidene) 2"-aminonaphthalenes.	V
iii)	4-(4'-n-Alkoxybenzoyloxy benzylidene) 2"-aminonaphthalene -1"-thio ls.	VI.
iv)	4-n-Alkoxyphenyl azo -2"-naphthalenes.	VIII
v)	4-(4'-n-Alkoxybenzoyloxy) phenylazo -2"-naphthalenes.	IX

are compared with each other and with those of

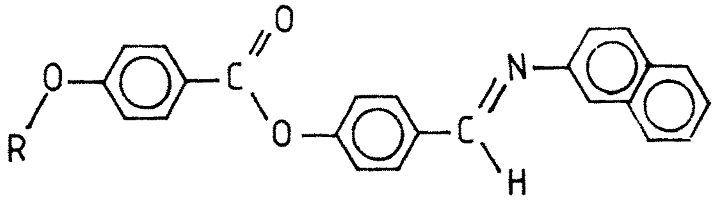
vi)	4-n-Alkoxybenzylidene anilines.	A	(274)
vii)	4-n-Alkoxybenzylidene -4-aminodiphenyls.	B	(274)
viii)	4(4'-n-Alkoxybenzoyloxy benzylidene) anilines.	C	(281)
ix)	4(4'-n-Alkoxybenzoyloxy benzylidene) -2"-aminophenols.	D	(267)

Reference to Table - 40 shows that middle members of series - IV exhibit monotropic mesophasses whereas series - A is non-mesogenic. This may be due to the terminal naphthalene nucleus, which enhances polarizability of the molecules of series -I compared to series - A, which contains terminal benzene nucleus. The molecules of series - IV and series - VIII differ in central linkage. Molecules of series - IV have central azomethine -CH=N- linkage whereas molecules of series - VIII have azo central linkage the reference to Table 40 shows that middle members of series - IV exhibits mesomorphism whereas series - VIII is non-mesogenic. This indicates that azomethine linkage -CH=N- is more conducive to mesomorphism as compared to azo -N=N- central linkage.

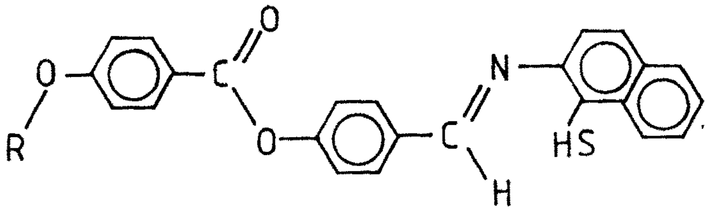
Reference to Fig. 60 shows that molecules of series - IV and series - B have the same molecular geometry except the terminal aromatic nucleus. Molecules of series -



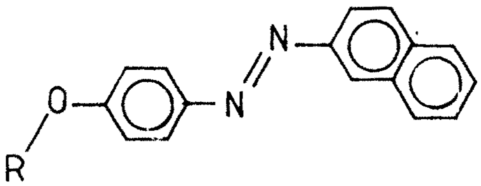
IV



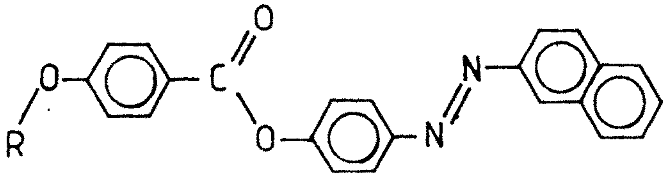
V



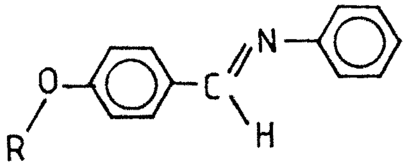
VI



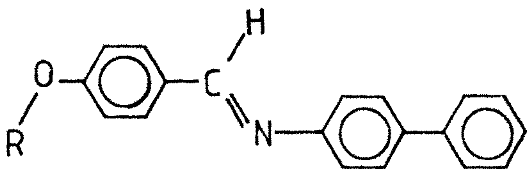
VIII



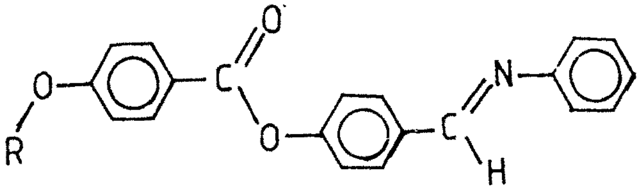
IX



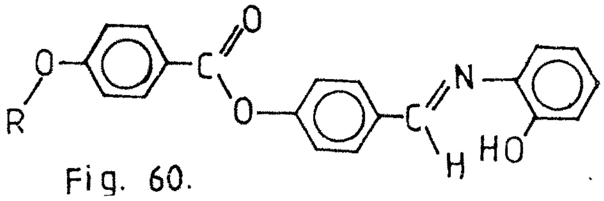
A



B



C



D

Fig. 60.

IV have terminal naphthalene nucleus wheras molecules of series - B have terminal biphenyl nucleus. It is known that the biphenyl nucleus enhances the mesophase thermal stabilities of the system (183) as it increases the length and polarizability of the molecules whereas naphthalene nucleus increases the breadth of the molecule which reduces the mesophase thermal stabilities. This is evident from the comparison of mesogenic thermal stabilities of series - IV and series - B (Table - 40). The smectic as well as nematic thermal stabilities of series - IV are much lower as compared to those of series - V. This can be attributed to the greater length and higher polarizabilty of series - V.

Reference to Table - 40 indicates that the smectic and nematic thermal stabilities of series - V are higher compared to those of series - C. Compared to series - C, the molecules of series - V are little longer and more polarizable, but have increased breadth due to naphthalene moiety.

Gray (183) has explained that if the molecules of mesogens have increased length and polarizability along with increase in the breadth the mesomorphic properties will be enhanced if fullest effect of increase in breadth is not felt by the molecules.

In the case of series - V the geometry of the molecules due to *trans* configuration results into very little breadth increasing effect because it is substituted in 2 position (β-position).

Naturally one would expect higher thermal stabilities of series - V compared to those of series - C which is the case.However, increase in the nematic thermal stability is of 77° C whereas increase in the smectic thermal stability is of 22° C. This further confirms that even little increase in the breadth of the molecules adversely affects the smectic mesophase.

The nematic thermal stability of series - V and series - IX are almost the same This is understandable as there is not much change in the geometry of the two series, the central linkage is changed from -CH=N to -N=N-, respectively. However, the smectic thermal stability of the series - V is higher compared to that of series - IX Generally incorporation of ester and azomethine linkage increases the acoplanarity of the system (24, 25). To reduce the steric interaction, terminal naphthalene ring goes little out of plane compared to phenyl ring. Naturally, series - V will be more acoplanar due to the presence of azomethine central linkage. Probably this acoplanarity gives such a packing to the molecules that the smectic thermal stability of series - V becomes higher than that of series - IX. This also reflects in series - IV and series - VIII where middle members of series - IV exhibit monotropic mesophases and series - VIII is non-mesogenic.

On comparing series - IX and series - C, it is evident that the nematic thermal stability of series - IX is much higher than that of series - C which is expected as the length of molecules of series - IX is little more than that of the molecules of series - C However, the smectic thermal stability of both the series is almost the same.

This may be attributed to two opposing effects in both the series. The acoplanarity imparted to the molecules of series - C enhances the smectogenic tendency. However, in the case of series - IX the little breadth increasing effect due to the presence of naphthalene moiety adversely affects the smectic mesophase. The net effect in each series is such that their smectic thermal stabilities coincide with each other.

Reference to Table - 40 shows that the average smectic thermal stability of series - VI is lower and the average nematic thermal stability is higher compared to that of series - V. The difference between the two series is only in a thiol substituent which is present in series VI. The reference to geometry shows that thiol substituent will have hydrogen bonding with azomethine linkage. Thus the nematic thermal stability of series VI is enhanced However, increased breadth effect due to naphthalene nucleus along with thiol group adversely affects the smectic mesophase that smectic thermal stability of series - VI is lower compared to series - V.

The molecules of series - VI and series - D differ only on the terminus. Molecules of series - VI has naphthalene nucleus whereas molecules of series - D have benzene nucleus. As discussed earlier the increase in the length and polarizability of series - VI due to naphthalene moiety increases nematic thermal stability of series - VI It has also been explained that presence of naphthalene mainly does effect adversely and decrease the enhancement in the smectic thermal stability. Probably this is the reason that the smectic thermal stability of series - D is about 11°C higher than that of series - VI.

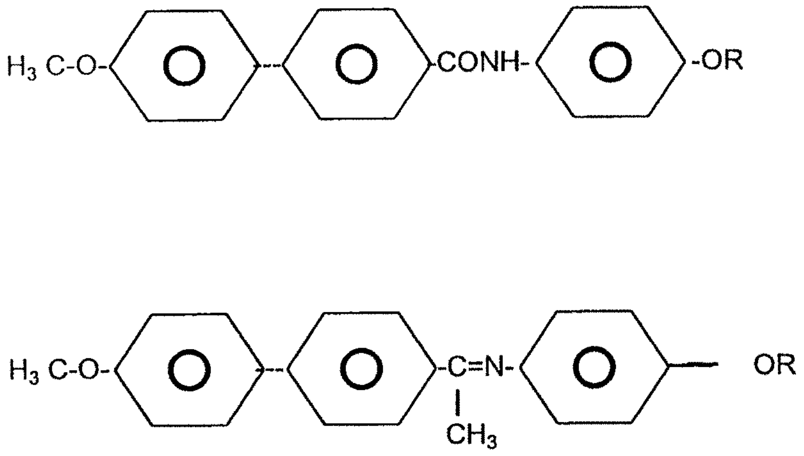
3.0 LIQUID CRYSTALLINE HOMOLOGOUS SERIES WITH BIPHENYL NUCLEUS

3.0 LIQUID CRYSTALLINE HOMOLOGOUS SERIES WITH BIPHENYL NUCLEUS

Biphenyl nucleus comprise one of the most interesting research areas in the study of relations between chemical constitution and mesomorphic properties The experience with the biphenyl structures points out that twisting often accompanies substitution in this and other molecules, and this, like the increase in molecular diameter, lowers the clearing temperatures. The mesomorphic properties graduallly disappear with increased twisting of the biphenyl, and this continues until mesomorphism disappears completely with 2, 2', 6, 6' tetra substitution.

Earlier amide linkage was considered to be non conducive to mesomorphism However, the first homologous series containig amide as one of the central linkages was reported from our laboratory by Vora and Gupta (282) in 1981. Soon after that Kalyvas and McIntyre (283) and Vora and Patel (284) reported a symmetrical homologous series having ester and amide central linkages.

In extension of this work homologous series of biphenyl moiety with an amide central linkage was synthesized. Another series containing an α-methyl - azomethine central linkage in place of the amide central linkage was synthesized to evaluate the effect of central linkage on mesomorphism. The structures of the series - X and series - XI are as follows.



Series - X

Series - XI

Fig - 63

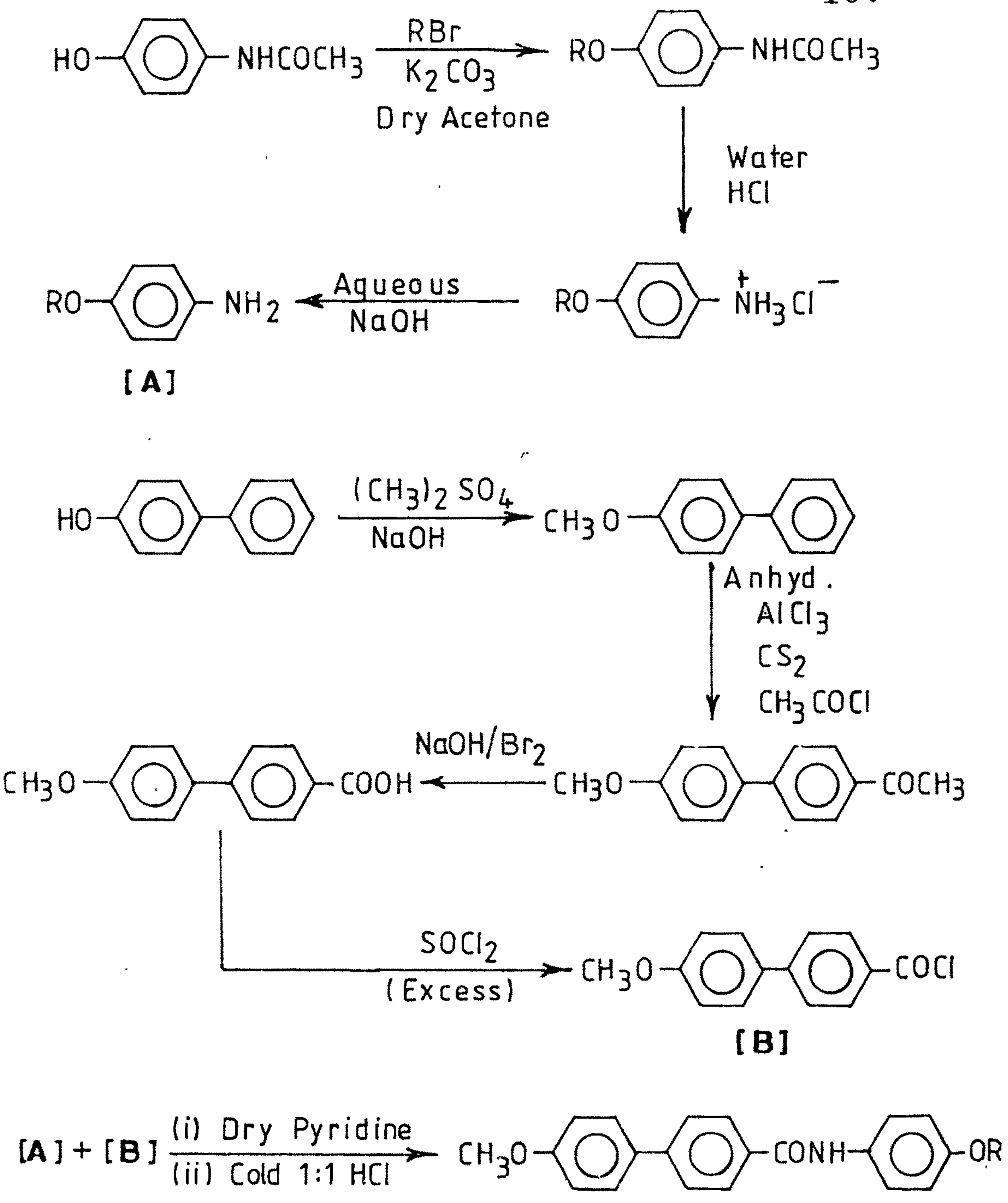
The route of synthesis for series - X and series - XI is given in scheme 10 and 11, respectively.

Series - X : 4(4'-methoxy phenyl) 4"-n-alkoxy benzanilides.

Twelve compounds have been synthesized and their mesogenic properties are evaluated. All the members exhibit enantiotropic mesomorphism. Methoxy derivative is purely nematogenic. Ethoxy to n-butyloxy derivatives exhibit enantiotropic smectic A as well as nematic mesophases. n-pentyloxy to -n-hexadecyloxy derivatives exhibit only enantiotropic smectic A mesophases. The transition temperatures are recorded in Table 19. The route of the synthesis for this series is shown in Scheme. 10.

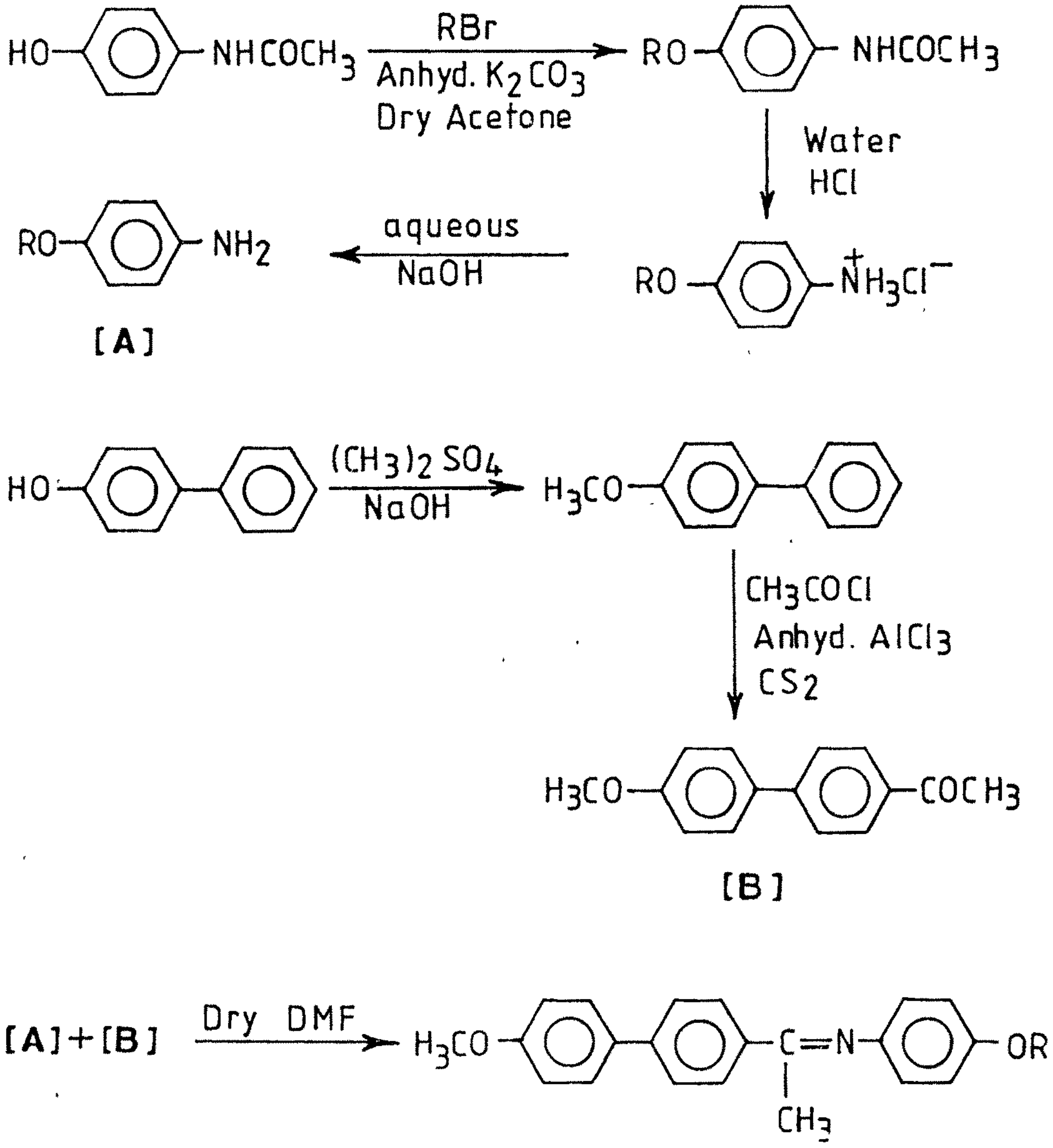
Series - XI : 4'- -methoxy -α- methyl biphenylidene -4"-n-alkoxy anilines.

Nine members of the series are synthesized. The route of the synthesis for this series is shown in Scheme - 11 and transition temperatures are recorded in Table 21 All the members synthesized exhibit enantiotropic nematic mesophase.



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

SYNTHETIC ROUTE TO SERIES – X
SCHEME–10



$R = -C_nH_{2n+1}$, $n = 1$ to 8 & 10

SYNTHETIC ROUTE TO SERIES-XI

SCHEME-11

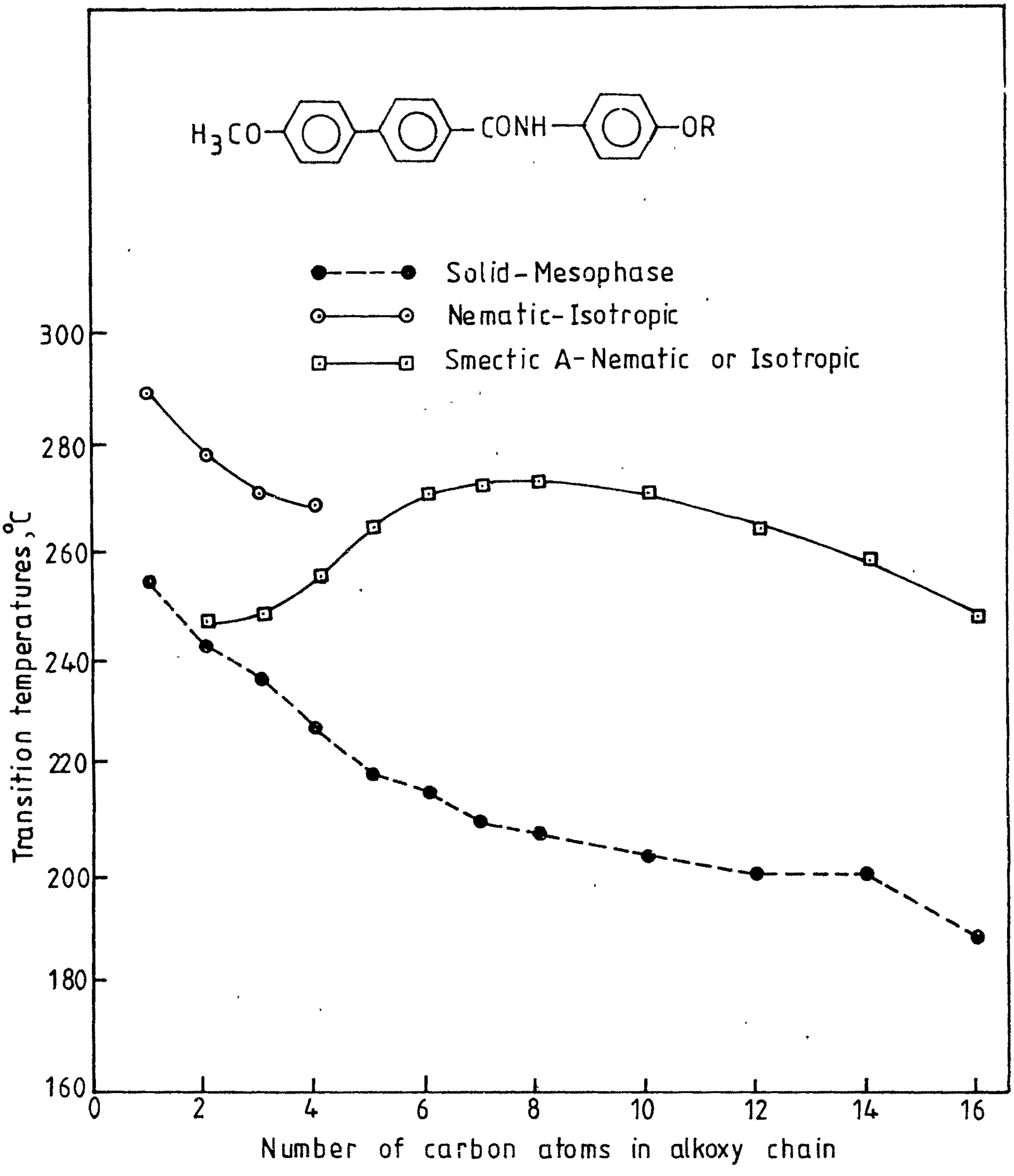

H3CO
CONH
OR
●- - - -● Solid-Mesophase
⊙——⊙ Nematic-Isotropic
⊡——⊡ Smectic A-Nematic or Isotropic
Transition temperatures, °C
300
280
260
240
220
200
180
160
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 61

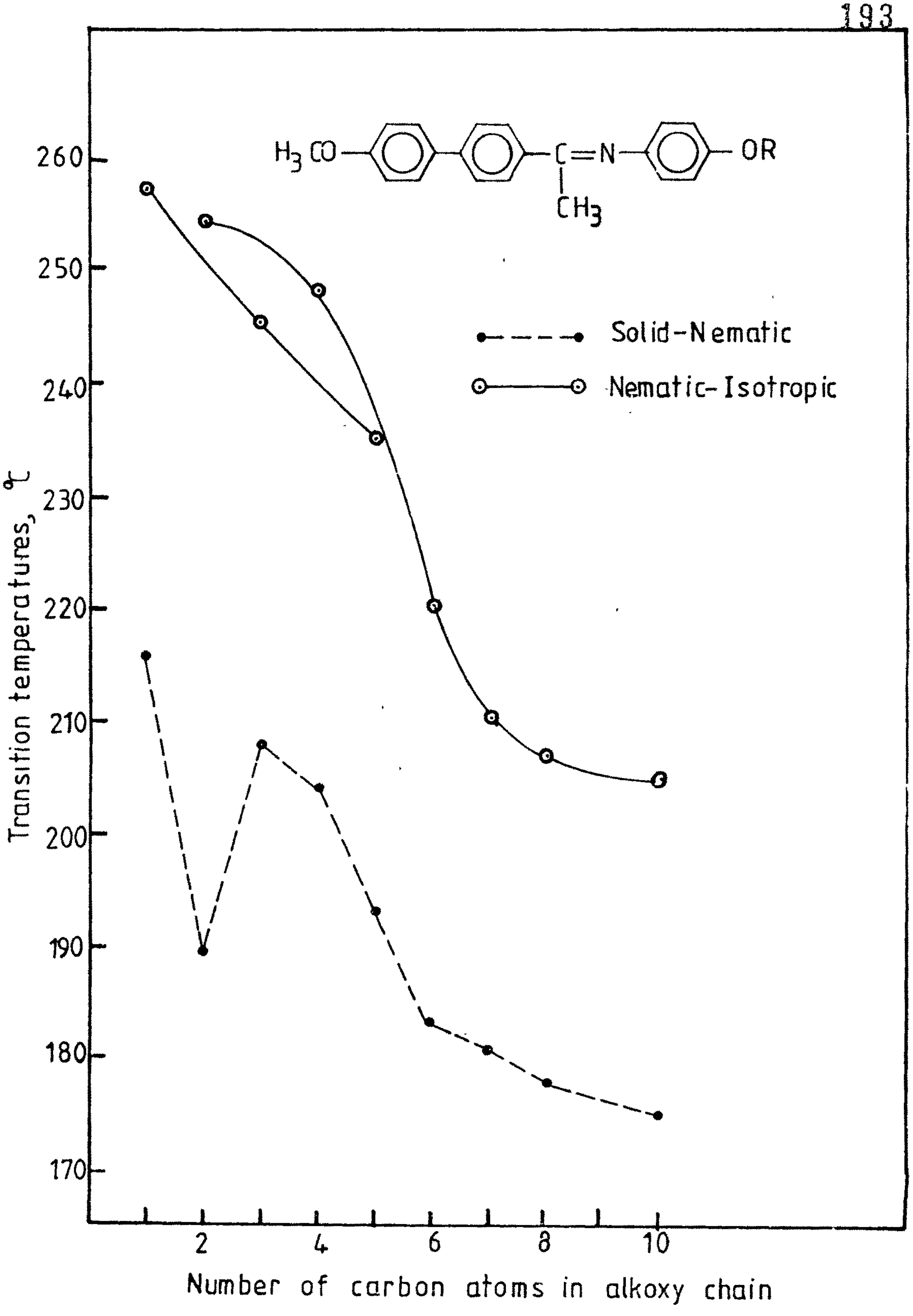

H3CO
C=N
CH3
OR
Solid-Nematic
Nematic-Isotropic
Transition temperatures, °C
260
250
240
230
220
210
200
190
180
170
2
4
6
8
10
Number of carbon atoms in alkoxy chain

Fig.62

3.1 Common Features of series - X and Series - XI

All the members of series - X and Series - XI exhibit mesomorphism. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain does not exhibit odd-even effect for nematic - isotropic or smectic - nematic transition temperatures though smectic phase is observed from the second member of the series - X (Fig. 61) whereas series - XI (Fig. 62) exhibtis usual odd-even effect for the nematic - isotropic transition temperatures.

It is difficult to explain absence of odd-even effect in phase diagram of series - X as other homologous series with -CONH- linkage exhibit odd-even effect.

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

Table - 41 summarizes the average thermal stabilities of different mesogenic homologous series synthesized i.e.

i)	4(4'-Methoxy phenyl) 4"-n-alkoxy benzanilides	X.
ii)	4'-Methoxy -α- methyl biphenylidene -4"-n-alkoxy anilines.	XI

Reference to Table 41 shows that average nematic thermal stability of series - X is higher than that of series - XI. In series - X there is an amide central linkage whereas

Table 41

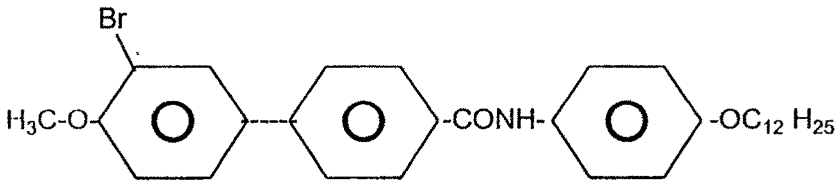
Average thermal stabilities °C

Series	**X**	**XI**
Nematic-Isotropic (C_1-C_4)	275.75	250.5
Smectic-Nematic or Isotropic (C_2-C_{16})	260.54	------
Commencement of Smectic mesophase	C_2	------

in the series XI there is an -α-methyl azomethine central linkage. Comparison of mesogenic properties of these two series indicates that amide linkage endows strong smectogenic tendency to the series - X whereas -α-methyl azomethine linkage destroys the smectic phase and imparts nematogenic tendency to the compounds of series - XI.

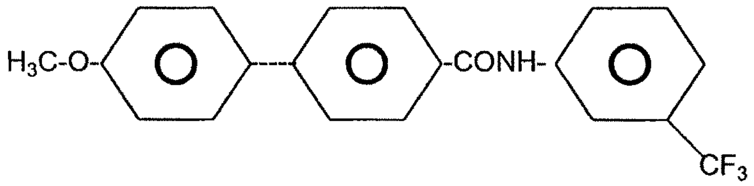
The observation of Vora et al. (282) and Gupta (285) made it clear that compared to an ester and azomethine linkage, amide-central linkage enhances smectic and nematic phases and enhancement is always more in the case of smectic mesophase. It seems that the -α-methyl group not only increases the breadth of the moleules of series - XI, but also increases the acoplanarity in the system due to steric interaction. Both these factors would be responsible to eliminate the smectogenic tendencies from such system.

A few odd compounds were synthesized (Fig. 63 a) to evaluate the effect of terminal or lateral substitution on mesomorphism which can be correlated with other homologues.



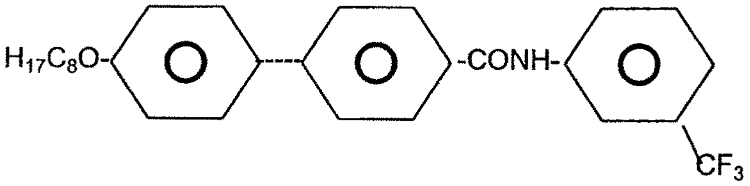
(i)

K188.0 S_A 218.0 I



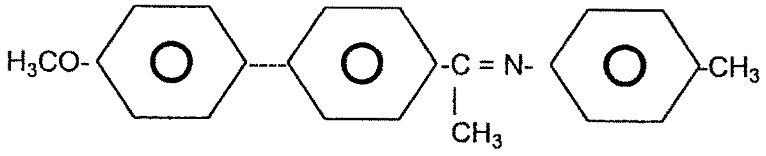
(ii)

K199.0 I



(iii)

K 159.0 I



(iv)

K239.0 I

Fig. 63a.

In compound (i) there is lateral -Br substituent which increases the breadth of the molecule. Naturally the thermal stability of the compound (i) is lower than the corresponding homologue of series - X. Similarly, there is a breadth increasing effect of the lateral -CF_3 group in compounds (ii) and (iii) and hence they are non-mesogenic. Even the n-octyloxy derivative (compound - iii) is non-mesogenic.

The compound (iv) is structurally similar to the molecules of series - XI. The only difference being in the terminal group. The presence of dipolar -OCH_3 group at the terminus of compounds of series - XI enhances the mesomorphism. Due to this compound (iv) is non-mesogenic whereas the corresponding homologues in series - XI exhibits mesomorphism.

4.0 DESIGNING MESOGENIC MATERIALS FOR NLO PROPERTIES.

4.0 DESIGNING MESOGENIC MATERIALS FOR NLO PROPERTIES.

Most thermotropic liquid crystals have a rigid core composed of two or more aromatic and/or alicyclic rings and one or more flexible terminal alkyl/alkoxy chains (286). Laterally substituted mesogens are of considerable interest because these compounds deviate from the classical rod-like shape. In general, a rigid, lateral substituent perturbs the orderings of liquid-crystalline phases (182,287,288), causing a significant depression in the clearing point, a reduction of the liquid crystal range, and a destabilization of ordered smectic phases. However, the effect of lateral, flexible substituent like an alkoxy or alkyl chain is quite different (289-291). A methyl or a methoxy substitutent causes a strong decrease in the melting and clearing temperatues, but as the chain length increases, the effect of the perturbation diminishes.

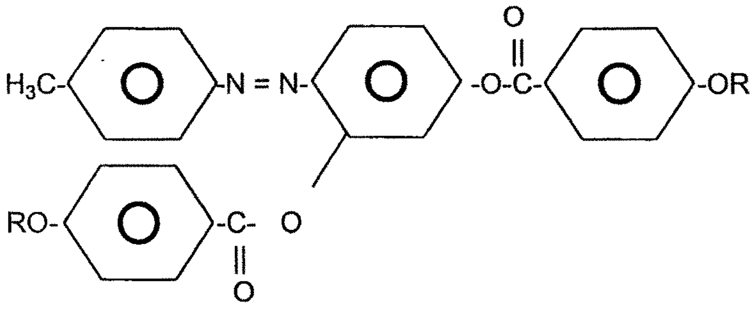
The type of liquid-crystalline phase formed by these compounds depends mainly on the position of the lateral chain. generally the nematic phase is preferred if the lateral chain is attached to an inner ring, but smectic phases are favoured if the lateral and terminal chains are attached to an outer ring in the meta and para positions, respectively.

Observation of number of researchers that introduction of aromatic rings in the lateral branch favours the smectic layer structures (S_A, S_C) is quite interesting (292-294).

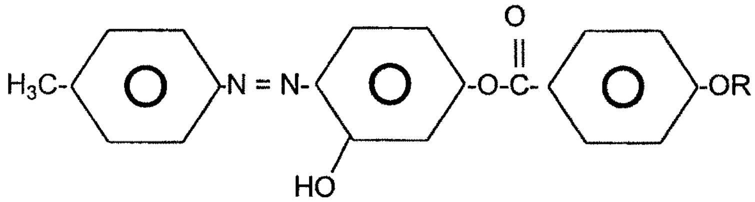
Non Linear Optical (NLO) materials should be assymetric in structure. They should have resultant higher dipole moment. Recently, organic molecules are being designed for NLO properties. However, mesogenic materials provide additional properties as they behave broadly as single crystals. If chirality is induced with smectic C phase, compounds exhibit strong NLO behaviour.

The search for Smectic C materials and asymmetric molecules with slightly polar groups was intended in the present work as prelude to introduce strongly polar groups at one of the terminus subsequently to induce strong NLO properties.

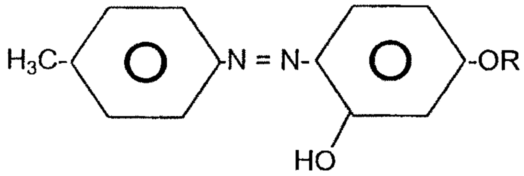
By keeping this in view and to explore the effect of lateral 'rigid' aromatic substituents on mesomorphism the following five homologous series were synthesized and their mesogenic properties are evaluated.



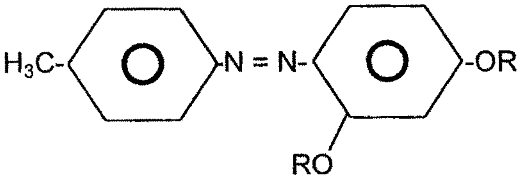
XII



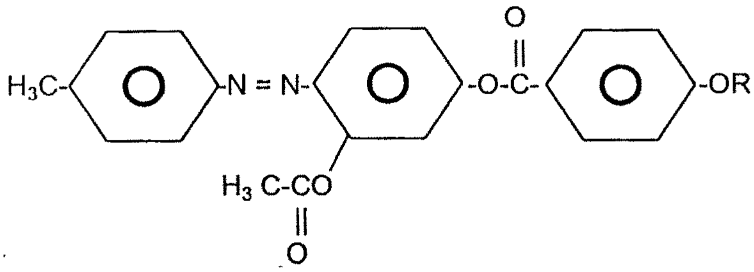
XIII



XIV



XV



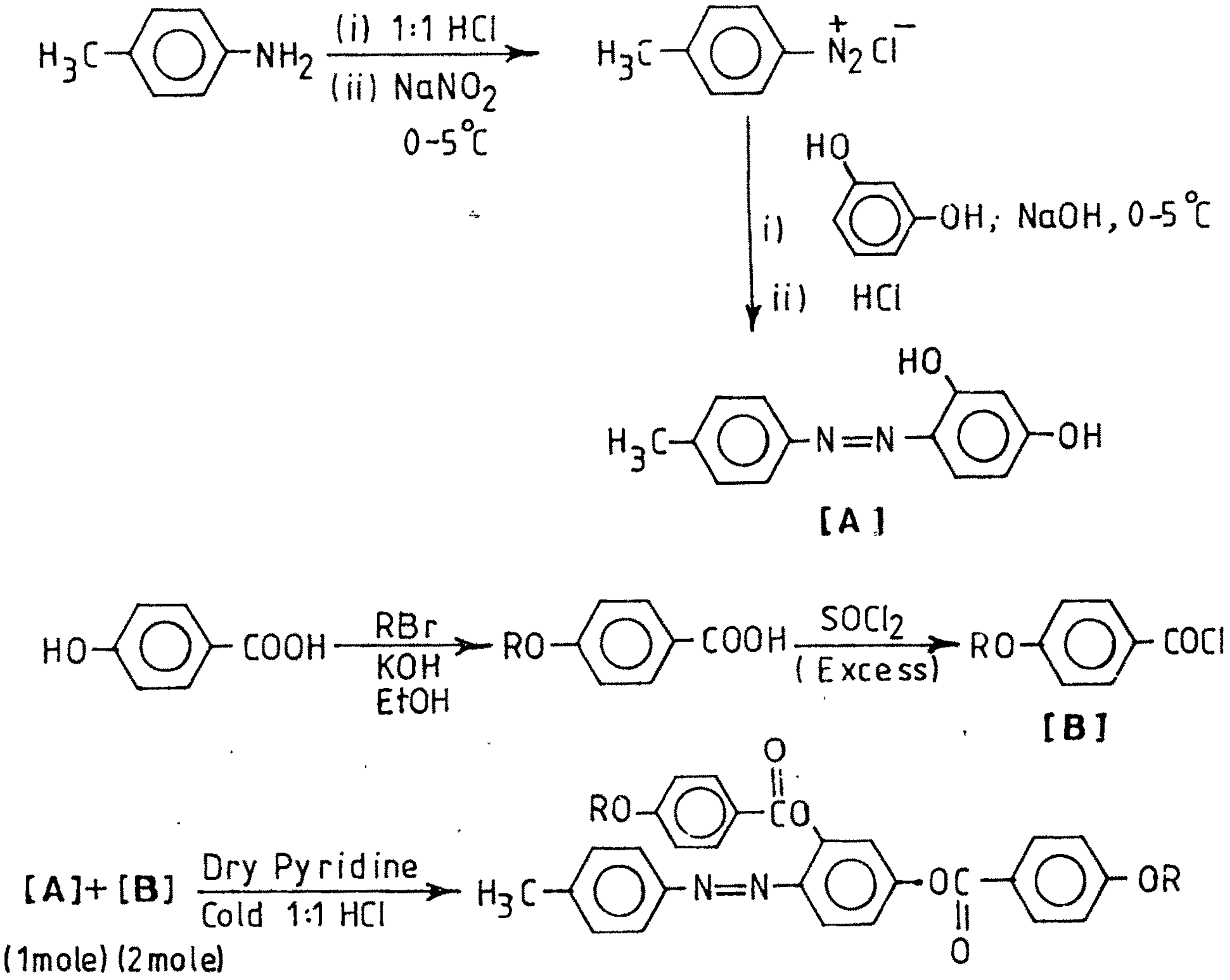
XVI

The route of synthesis for series XII - XVI is given in scheme 12 - 15 respectively.

Series - XII : 4-methyl 2'-4'-bis(4"-n-alkoxy benzoyloxy) azobenzenes.

Twelve compounds have been synthesized and their mesogenic properties were evaluated. n-Butyloxy to n-hexadecyloxy derivatives exhibit monotropic smectic C mesophase. The first three homologues are non-mesogenic. the melting points and transition temperatures are recorded in Table 23.

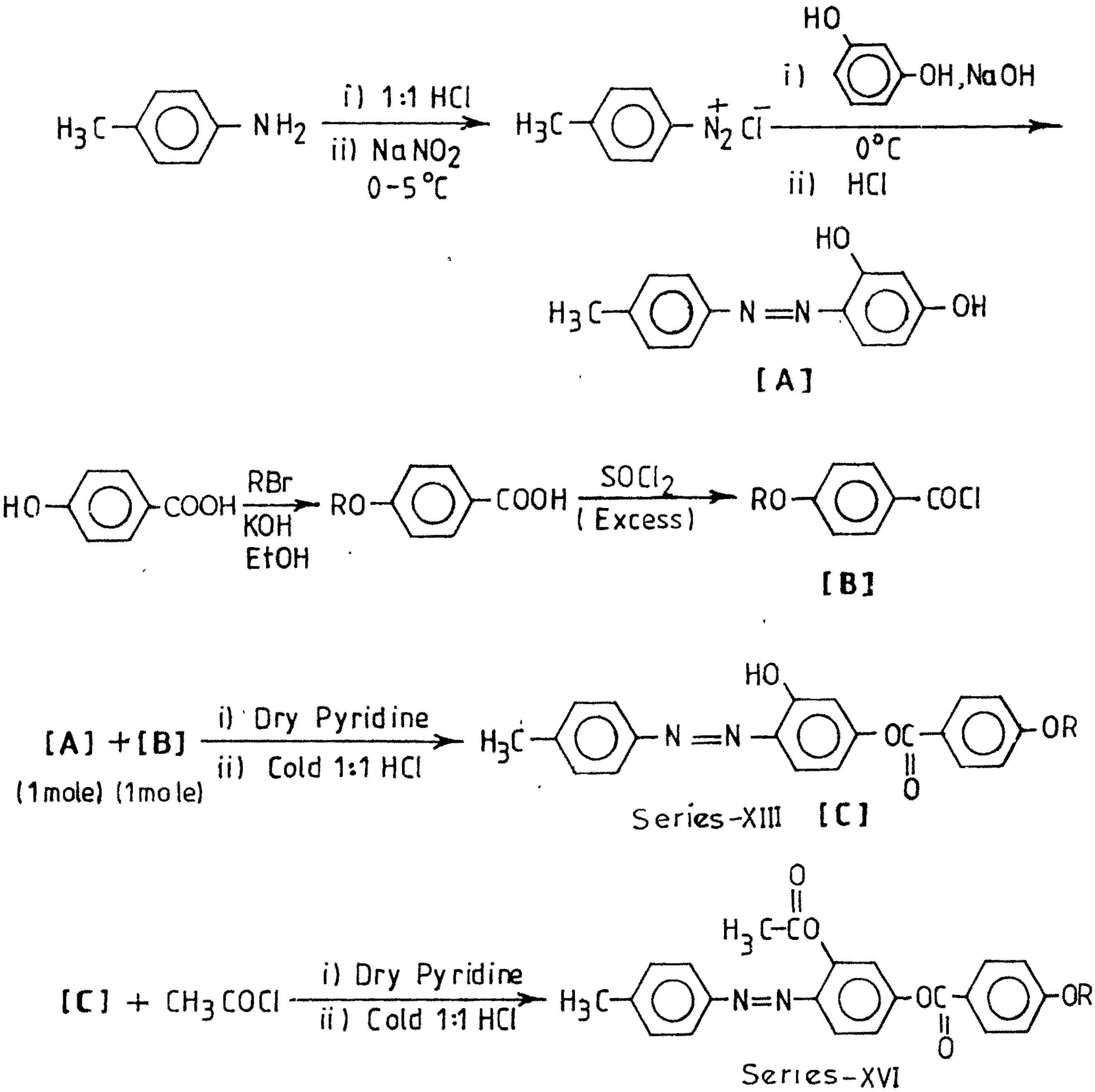
Series - XIII : 4-methyl 2'-hydroxy -4'-(4"-n-alkoxy benzoyloxy) azobenzenes.



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

SYNTHETIC ROUTE TO SERIES—XII

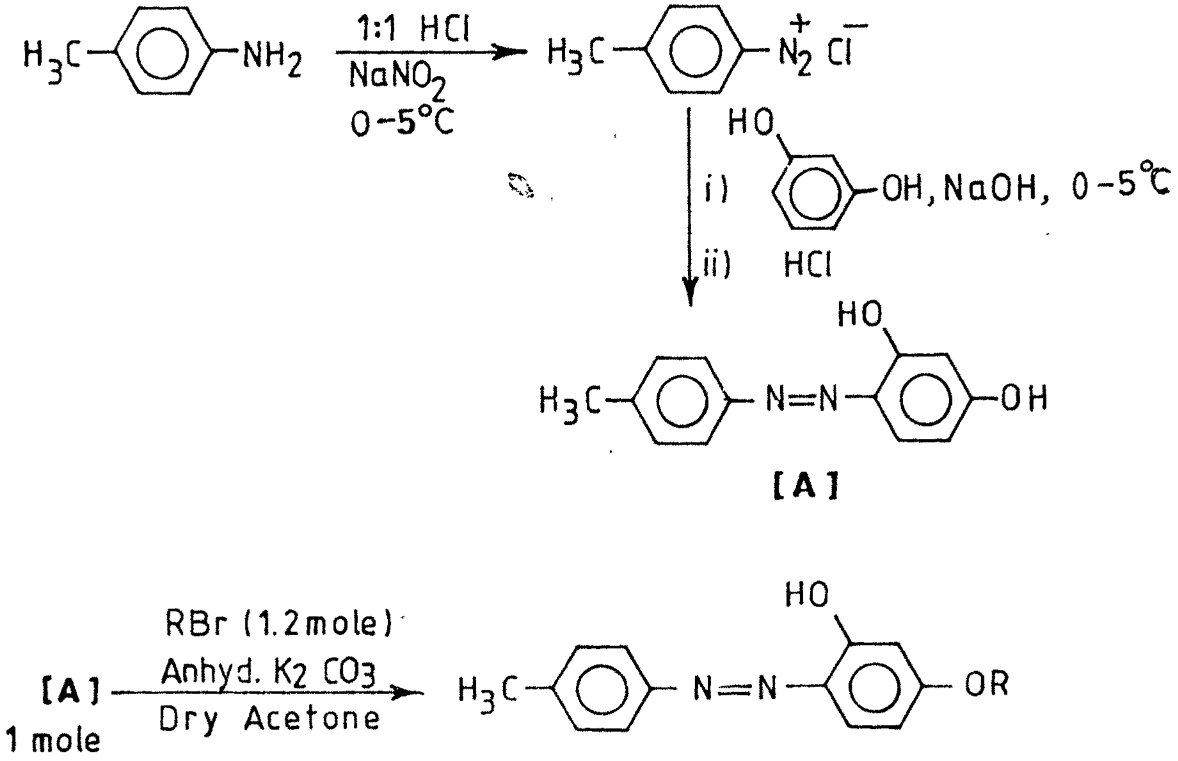
SCHEME-12



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

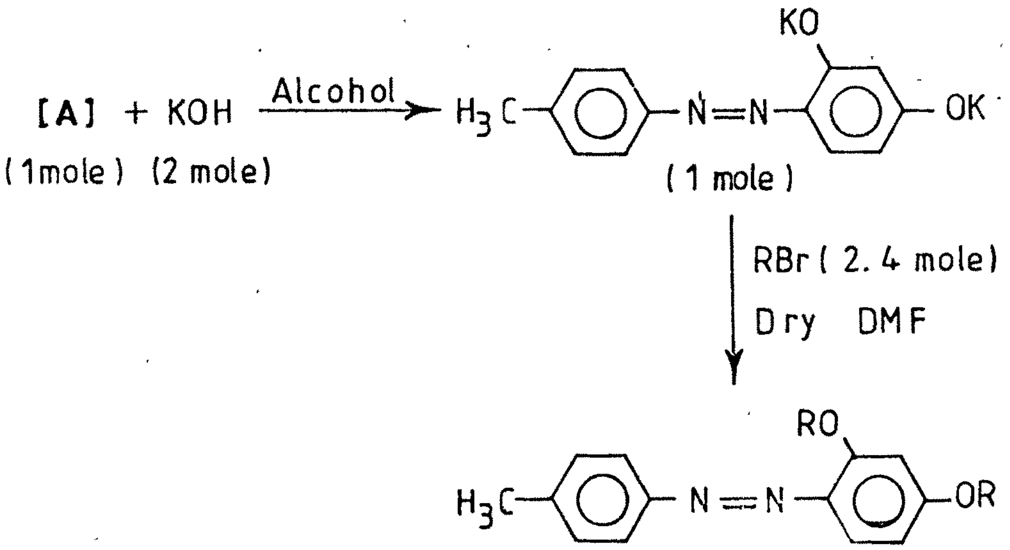
SYNTHETIC ROUTE TO SERIES– XIII & XVI

SCHEME-13



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

SYNTHETIC ROUTE TO SERIES – XIV
SCHEME – 14



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

SYNTHETIC ROUTE TO SERIES-XV
SCHEME-15

All the twelve homologues synthesized exhibit enantiotropic nematic mesophase This series has very high thermal stability. The transition temperatures are recorded in Table 25.

Series - XIV : 4-methyl 2'-hydroxy 4'-n-alkoxy azobenzenes.

This series is also purely nematogenic. n-Propyloxy derivative exhibits monotropic nematic phase. Higher members exhibit enantiotropic nematic phase. The transition temperatures are recorded in Table 27.

Series - XV : 4-methyl 2'-4'-di-n-alkoxy azobenzenes.

Nine compounds have been synthesized. All the compounds were found to be non-mesogenic (Fig. 67) with very low melting points. (Table 29).

Series - XVI : 4-methyl 2'-acetyloxy -4'-(4"-n-alkoxy benzoyloxy)azobenzenes.

Twelve homologues have been synthesized. They are purely nematogenic. All the homologues of this series exhibit monotropic nematic mesophase except the n-dodecyloxy and n-tetradecyloxy homologues which are enantiotropic nematic. The transition temperatures are recorded in Table 31.

4.1 Common Features of series XII - XIV and XVI.

All the four homologous series exhibit mesomorphism. The series XII exhibits monotropic low melting smectic C mesophase whereas rest of the series exhibit nematic mesophases. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Fig. 64-66 & 68) exhibits marked odd-even effect for the mesophase - isotropic transitions. Series - XII exhibits a tendency of rising smectic - isotropic transition in

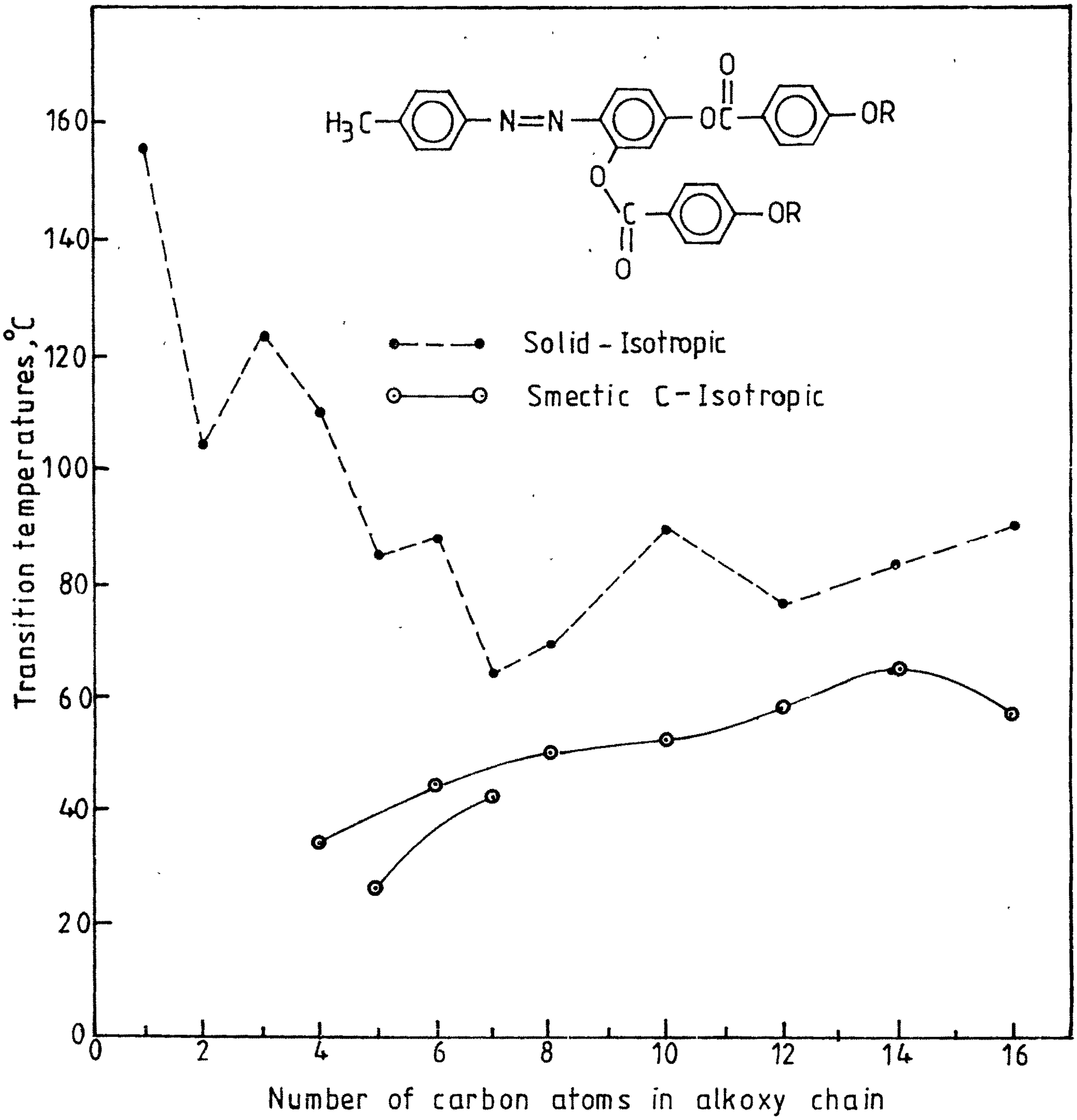

H3C
N=N
O
OC
OR
O
C
O
OR
Solid - Isotropic
Smectic C-Isotropic
Transition temperatures, °C
0
20
40
60
80
100
120
140
160
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 64

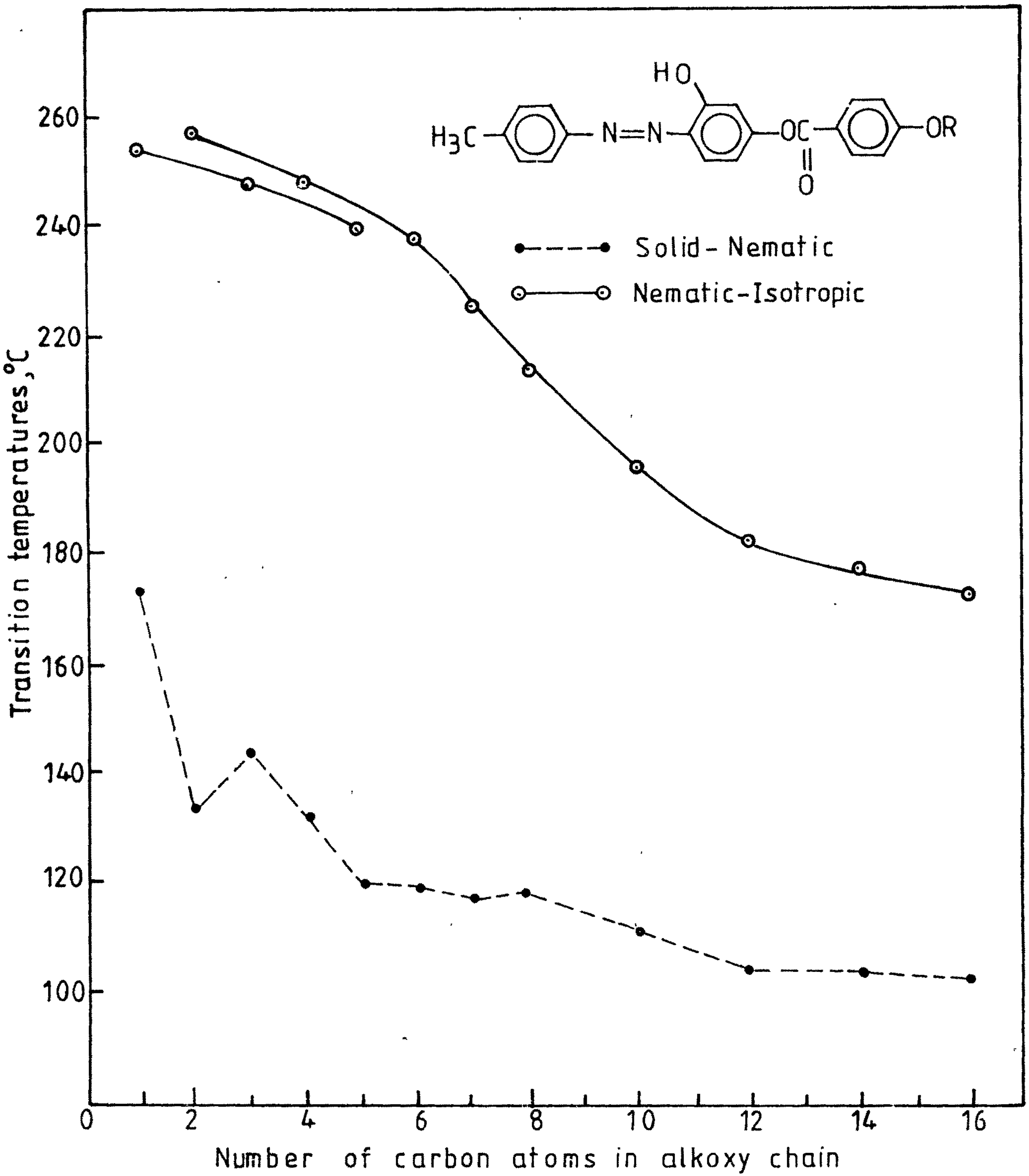

HO
H3C
N=N
OC
O
OR
Solid-Nematic
Nematic-Isotropic
Transition temperatures, °C
260
240
220
200
180
160
140
120
100
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 65

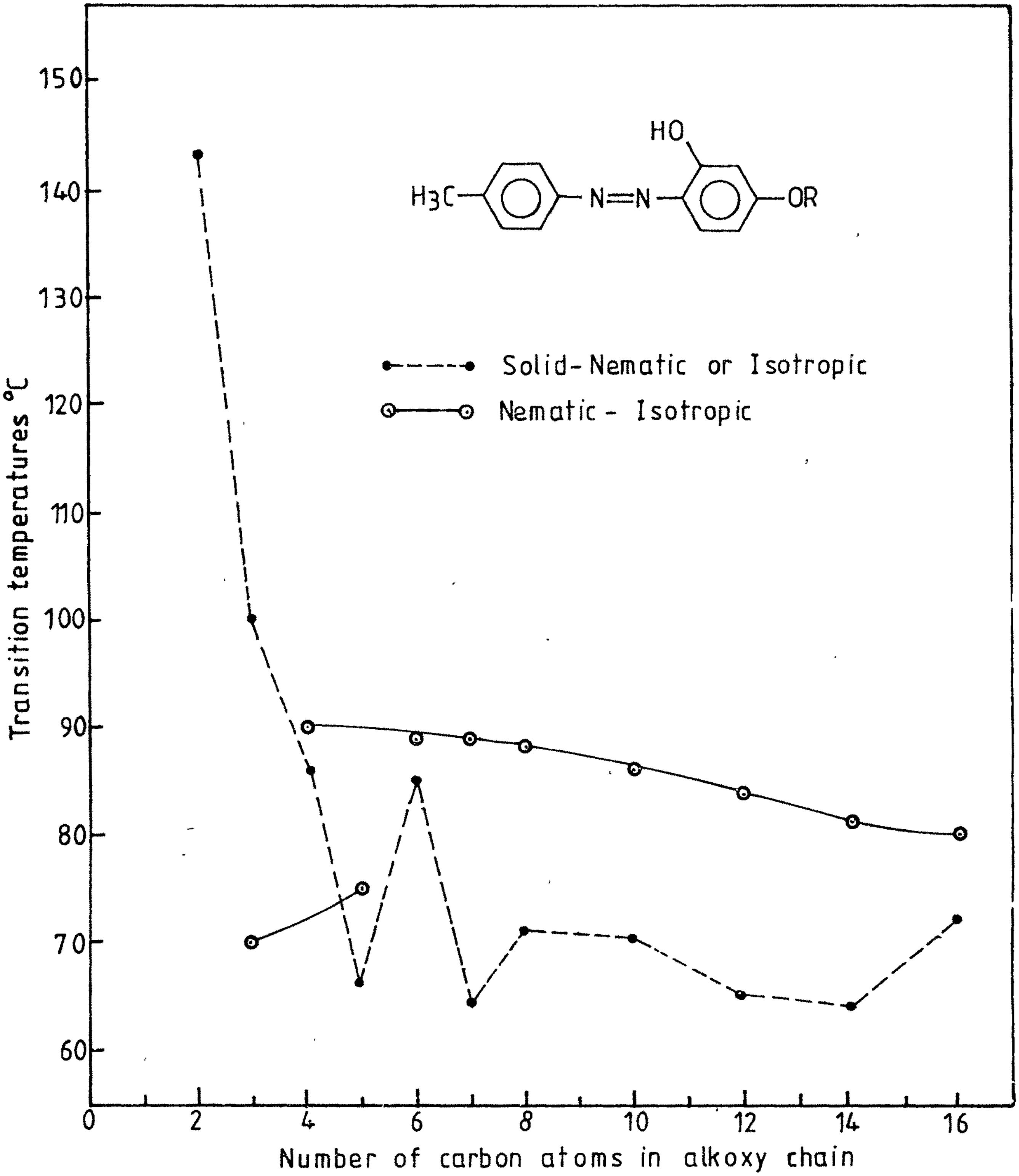

HO
H3C
N=N
OR
Solid-Nematic or Isotropic
Nematic - Isotropic
Transition temperatures °C
150
140
130
120
110
100
90
80
70
60
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 66

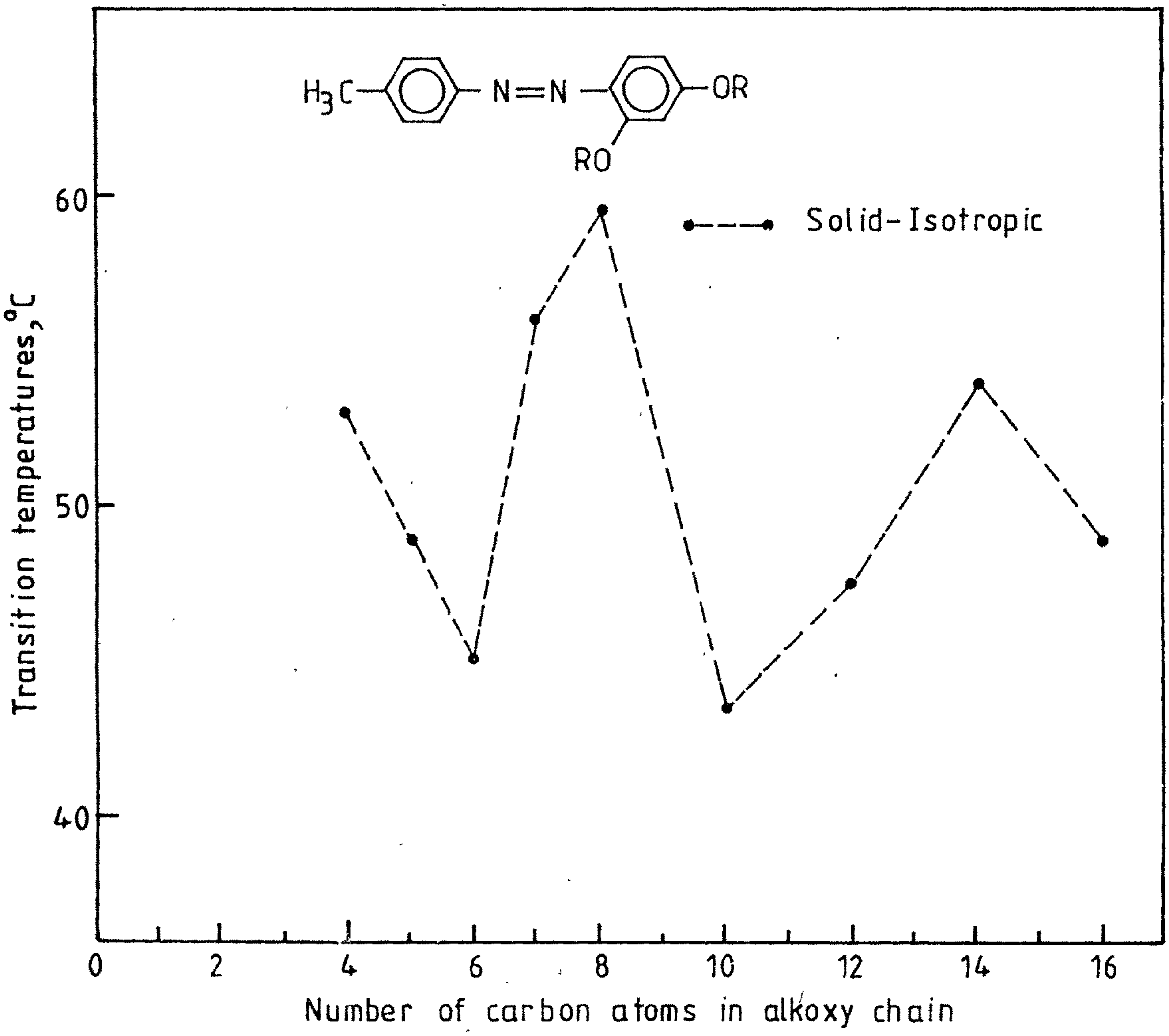

H3C, N=N, OR, RO
Solid-Isotropic
Transition temperatures, °C
40
50
60
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 67

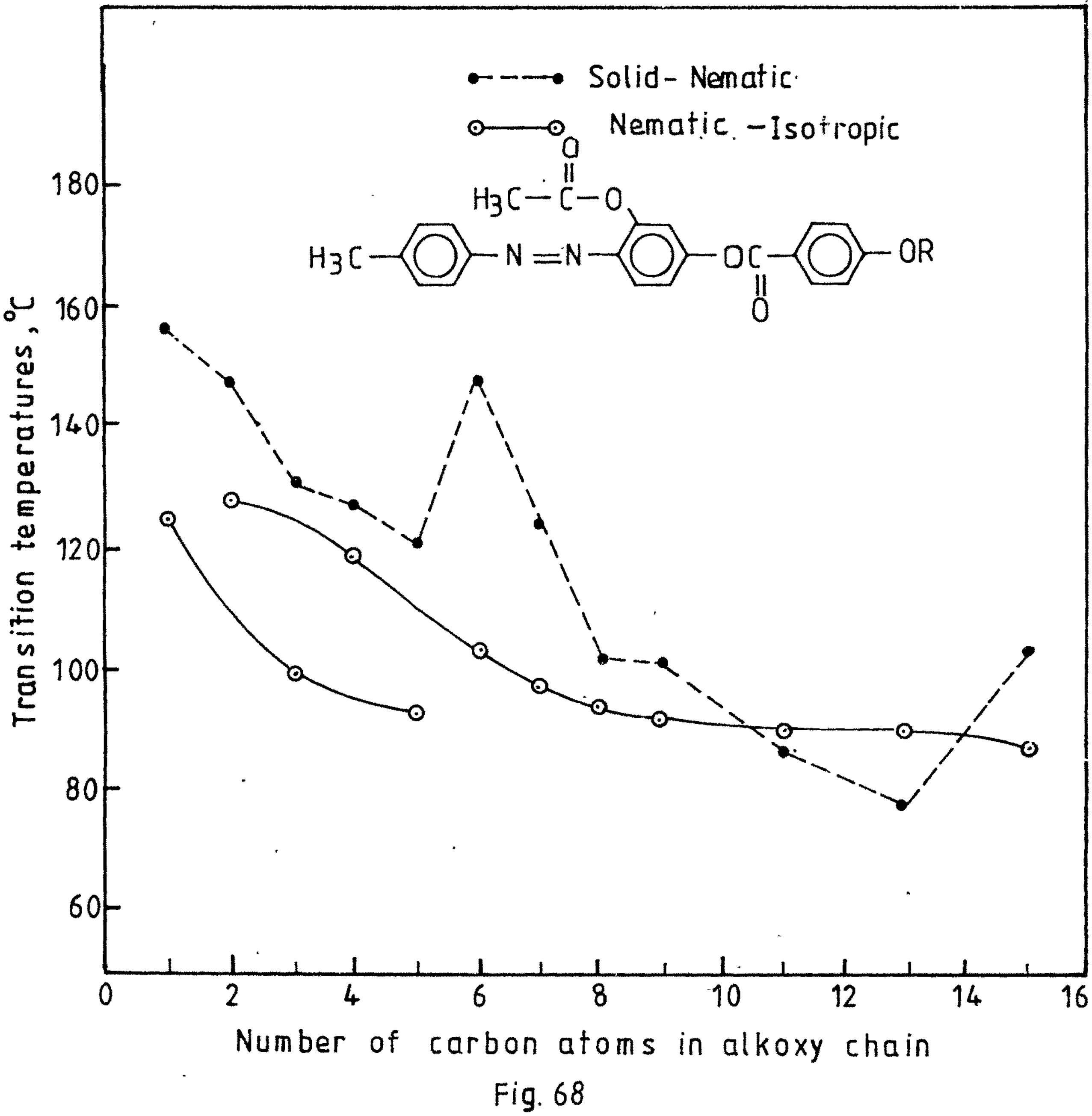

Solid- Nematic
Nematic -Isotropic
H3C
N=N
OC
O
OR
H3C—C—O
Transition temperatures, °C
180
160
140
120
100
80
60
0
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 68

ascending series (Fig. 54). Series - XII, XIV and XVI shows steady fall in nematic-isotropic transition except the odd derivatives of series - XIV (Fig. 56) which shows rising temdency.

As mentioned previously, thermal stability, a measure of mesomorphism can be correlated with the molecular consititution of the compounds.

Table 42 summarizes the average thermal stabilities of different mesogenic homologous series synthesized i.e.

i)	4-Methyl 2', -4'- bis-(4"-n-alkoxybenzoyloxy) azobenzenes.	XII	
ii)	4-Methyl 2' hydroxy -4'- (4"-n-alkoxybenzoyloxy) azobenzenes.	XIII	
iii)	4-Methyl 2' hydroxy -4'-n-alkoxy azobenzenes.	XIV	
iv)	4-Methyl 2' hydroxy -4'-di-n-alkoxy azobenzenes.	XV	
v)	4-Methyl 2'-acetyloxy -4'- (4"-n-alkoxybenzoyloxy) azobenzenes.	XVI	

are compared with each other and with those of

vi)	4-n-dodecyloxy -2', 4'-bis(4"-n-alkoxybenzoyloxy) azobenzenes.	A	(263)
vii)	4-n-Butyl 2'-hydroxy-4'-n-alkoxy azobenzenes.	B	(295)

Molecules of series - XIII have three phenyl rings joined by two central groups and have a lateral hydroxy group. Naturally intramolecular hydrogen bonding leading to π-electron delocalization as well as the presence (296) of three phenyl reings endow them with higher thermal stabilities.

None of the homologous series have both these features hence series - XIII exhibits highest thermal stbilities.

The series - XII exhibits monotropic smectic C phase whereas series XVI exhibits only nematic mesophase. Hartung et al (297) have suggested packing of such molecules in series XII. The two symmetrically independent molecules have a nearly perfect parallel alignment. The gap between two molecules, following one after the other in the direction of their long axes and so being members of a molecular row, is filled by the bulky lateral branch of a molecules belonging to the neighbouring row. In this way, the rows are interlocked and the principle of high economy of space is fulfilled. Another striking feature of the crystal structure is the strong intercalation of the molecules within the sheets by their alkyl chains.

The stacking of the sheets results in an overall molecular arrangement which can be interpreted as a layered structure, similar to the model of smectic liquid crystalline phases, with strong tilted molecules and an intercalation of the layers by the alkyl chains.

The Sc phase in the series - XII can be thus attributed to the lateral bulky chain comprising of an aromatic ring in addition to the alkoxy group. The molecules of series XVI have an acetyl lateral substituent which can not arrange as mentioned in above discussion However, it would disturb the formation of layer structure as observed in number of homologous series by Weiss flog et al. (298).

The above discussion clearly indicates that short aliphatic lateral chains can stabilise the nematic phase whereas long aromatic lateral substituents stabilise smectic phases.

Table 42

Average Thermal Stabilities

Series	XII	XIII	XIV	XV	XVI	A	B
Smectic-Isopropic	57.5 (C_{12},C_{16})	----	----	----	----	54.05 (C_{12},C_{16})	----
Nematic-Isotropic	----	221 (C_1-C_{16})	83.85 (C_3-C_{10})	----	102.04 (C_1-C_{16})	70.32 (C_4,C_8,C_{12},C_{16})	77 57 (C_3-C_{10})
Commencement of smectic mesophase	C_4	----	----	----	----	C_{12}	----

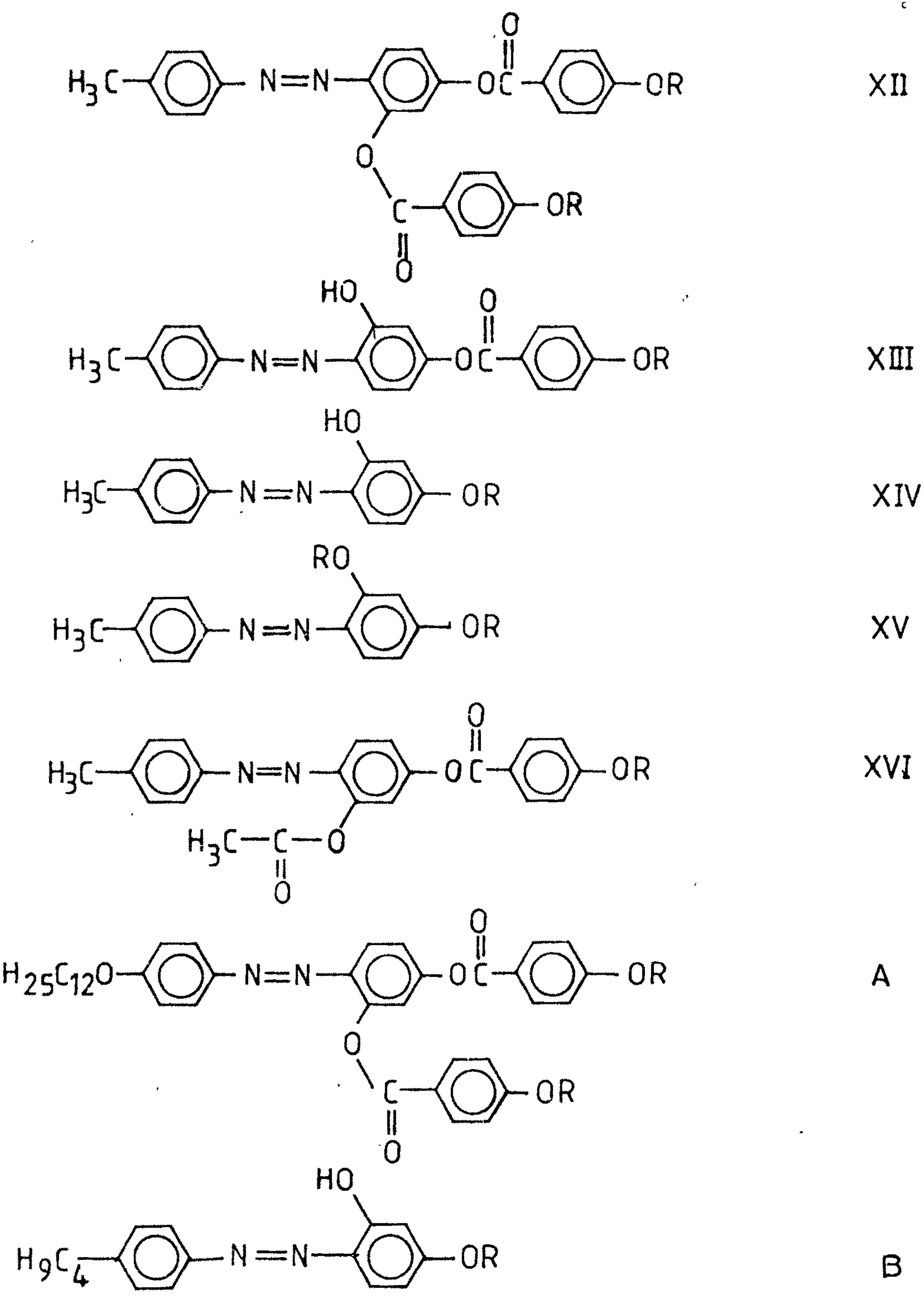


Fig. 69

Series - XIV is nematic whereas series - XV is non-mesogenic. This is quite expected as the lateral alkoxy chain in the molecules of series - XV depresses the nematogenic tendency of the system so much so that the nematic phase altogether disappears. In the series - XIV however, the lateral -OH group due to intramolecular hydrogen bonding imparts the molecules of series - XIV some structural order and hence enantiotropic nematic mesophase with good thermal stability is obtained.

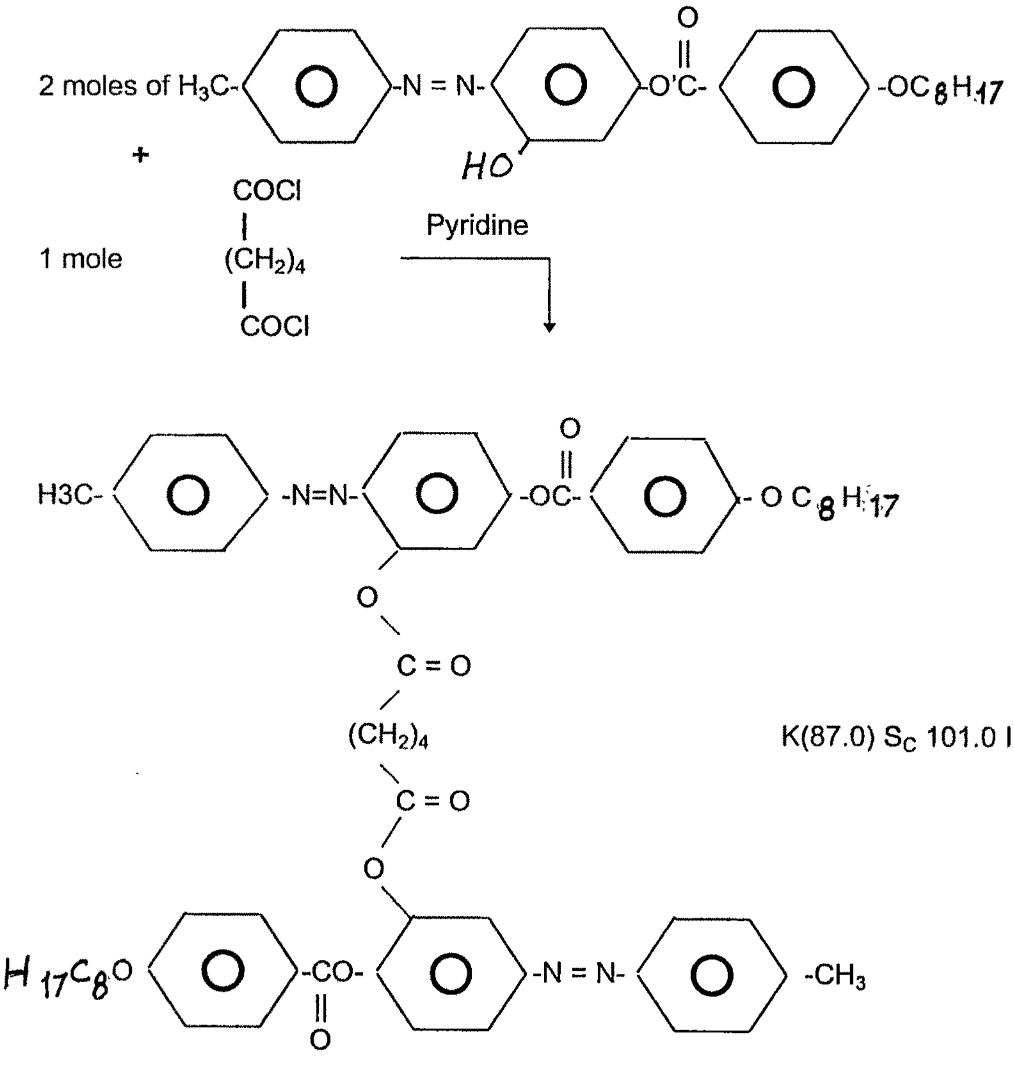
Bayle et al. have reported only a few homologues of series - A which exhibit smectic as well as nematic mesophases. Couple of higher homologues exhibit smectic - C phase. The mesogenic thermal stabilities are comparable with series - XII. It is quite surprising that even with dodecyloxy group fixed at one terminus, system does not exhibit strong smectogenic tendency in series - A.

The average nematic thermal stablility of series - XIV is slightly more than that of series - B. This is as expected because of the difference in the terminal alkyl chian. In series - XIV there is a terminal -CH_3 chain whereas in series - B there is terminal n-C_4H_9-chain.

The study has provided room temperature smectic C phases with azo - and ester linkages with unsymmetric molecular arrangement. Further study in the direction to induce NLO properties at one terminus of series - XII, -NO_2 and other strongly polar groups are introduced. Chirality is also being introduced to obtain Sm*C phases. Initial results are highly encouraging.

Siamese Twins :

The exhibition of smectic phases by the homologues of series -XII and exhibition of high temperature nematic phases by the homologues of series - XIII gave us an idea that if flexible spacer is attached through lateral -OH group joining molecules of series - XIII on both the sides we may obtain a Siamese twin which might exhibit mesomorphism. With this in view following reaction was carried out.

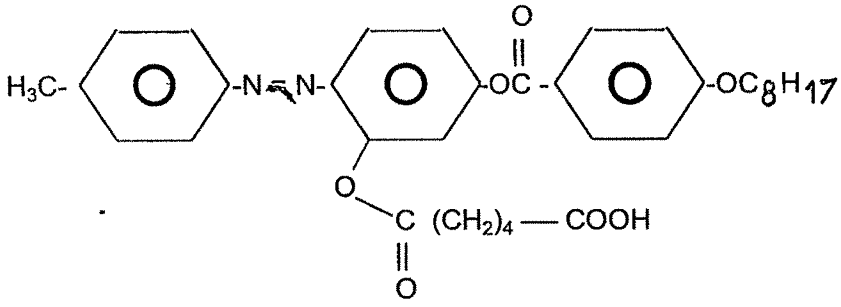


K(87.0) S$_C$ 101.0 I

ST - I

The reaction gave two components and they were separated. ST-I was identified by IR, NMR and elemental analysis which is recorded in experimetal section 4.6c.

The second component seems to be monoester of adipic acid. This was separately synthesised by taking excess of adipoyl chloride and hexadecyloxy homologue of series XII. Following compound was obtained.



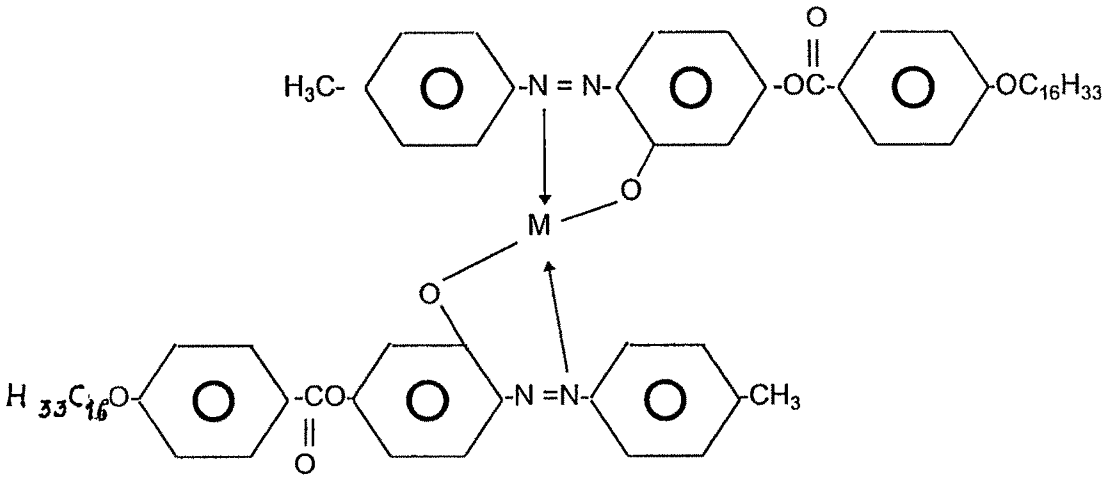
K 154.0 I

The compound with flexible tail and terminal carboxylic group does not exhibit mesomorphism.

The compound is characterised by elemental analysis, IR and NMR spectra (Expt. sect. 4.7c).

These results indicate that these molecules are very interesting. It has been planned to introduce different rigid and flexible spacers and obtain Siamese twins to evaluate the effect of these parameters on mesomorphism.

Homologues of series XIV with lateral hydroxy group having ortho phenolic group also provides a centre for metal chelation. Tempted by this idea the study was initiated in this direction by synthesizing two metal complexes of following structure.



M = Ni : K 182.0 N 203 I

M = Cu : K 185.0 I

The copper (II) complex does not exhibit mesomorphism. However, the Nickel (II) complex exhibits nematic mesophase with much higher thermal stabilities.

Both complexes are characterised by elemental analysis and IR spectra.

The initial results are highly encouraging. Further study of these metal complexes are planned with other homologues where the H_3C- terminus is changed to higher n-alkoxy group whereby the transition temperatures may come down and induction of smectic mesophase can be possible.

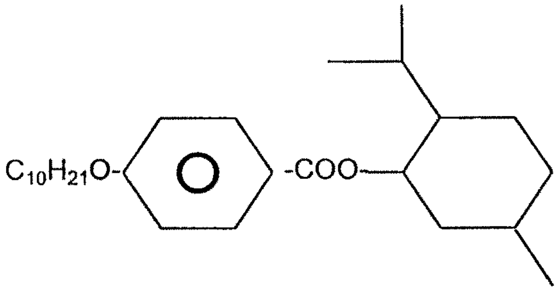
Induction of chirality by doping mesogens with menthol derivative.

Number of researchers have tried to induce chirality in the achiral mesogens by doping it with naturally occuring chiral compounds or their derivatives (299).

Natural menthol is readily available in Baroda hence it was proposed to prepare derivative of chiral natural menthol.

Following menthol derivative was synthesized.

I)



M_1

Binary mixtures were prepared by doping homologues of series IX.

Three binary phase diagrams were developed by doping menthol derivative M_1 with n-decyloxy, n-tetradecyloxy and n-hexadecyloxy homologues of series IX by adding dopant maximum upto 50%.

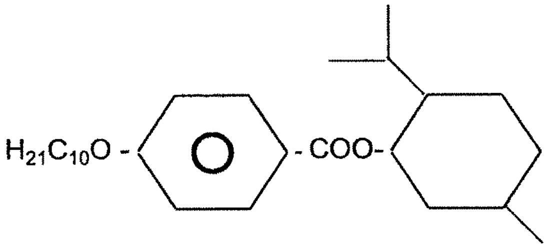
The reference to Table - 36 (Fig. 70) indicates that chiral dopant induces chiral smectic C phase and chiral nematic phase (*N) in all the three systems. However, induction of chiral smectic *C is more in the higher homologues of series - XII.

The *N-I transitions decrease in a regular manner as the concentration of dopant increases.

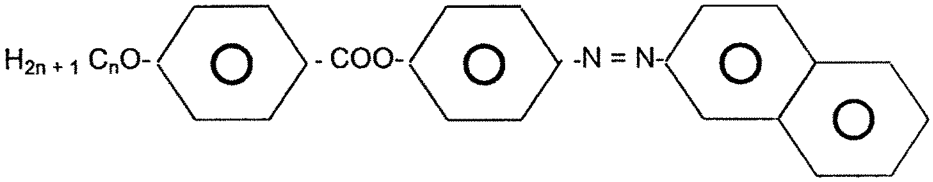
The study provides a mean to induce Sm*C and cholesteric phase (*N) in the system by doping it with the derivative of naturally occuring chiral menthol.

Table 36

Component : a



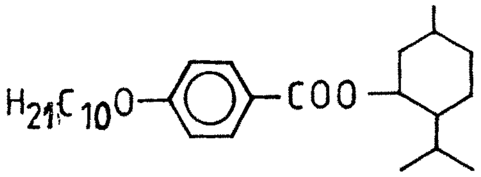
Component : b

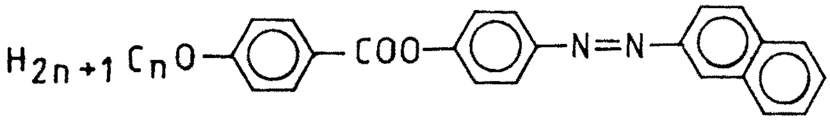


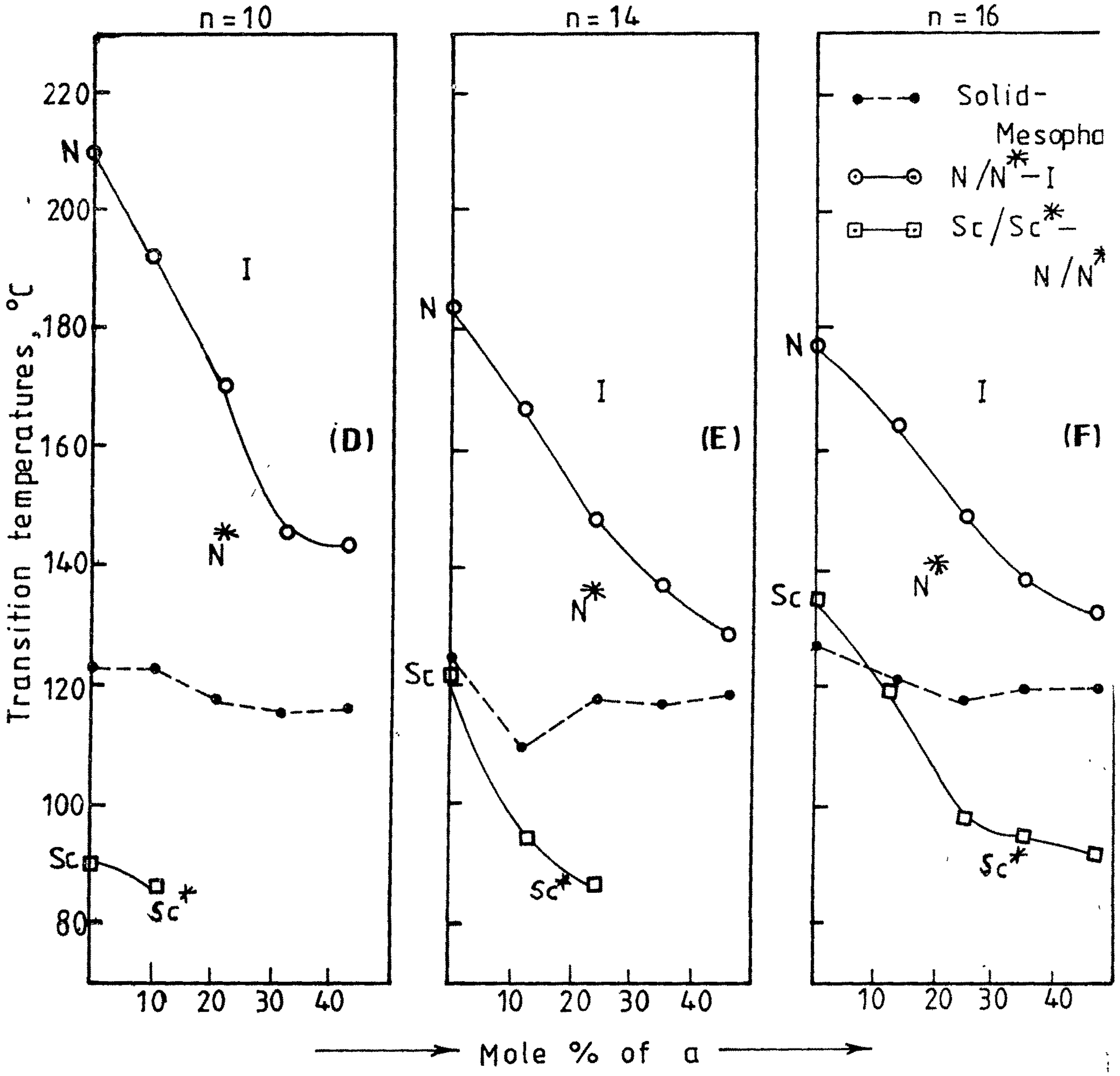
SYSTEM - D

Mole % of a	n			Transition Temperatures oC		
		SmC	SmC*	N	N*	I
0.0	10	(90.0)*	-	123.0	-	210.0
11.27	10	-	(86.0)	-	123.0	192 0
22 23	10	-	-	-	118.0	170 0
32 89	10	-	-	-	116.0	146 0
43 25	10	-	-	-	116.0	144.0
			SYSTEM - E			
0 0	14	(121.0)	-	125.0	-	183.0
12 43	14	-	(94.0)	-	119.0	166.0
24 22	14	-	(86.0)	-	118.0	148.0
35.39	14	-	-	-	117.0	137.0
46.01	14	-	-	-	119.0	129 0
			SYSTEM - F			
0.0	16	127.0	-	134.0	-	177.0
12 97	16	-	(120.0)	-	121.0	164 0
25 11	16	-	(98.0)	-	118.0	149 0
36 39	16	-	(95.0)	-	120.0	138 0
47 22	16	-	(92.0)	-	120.0	133 0

( )* Monotropic Value

Component a


Component b




System- D- E-F

Fig. 70

TEXTURES OF DIFFERENT PHASES

5.0 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 textures of the phase. In such 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 (7) and has been used by number of workers (300) in the field and is quite reliable. However, the calorimetry (301) and x-ray analysis (301) ect 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 microscope as well as by studying the miscibility behaviour of phases with labelled smectic compounds.

Following labelled compounds were used for the characterization.

A] Smectic A labelled compounds

i) 4-Nitro 4'-n-decyloxy benzoate. (302).

K 55.0 S_A 77.5 I

ii) Terephthal bis 4-n-hexyloxy aniline (303).

K 159.0 S_B 176.0 S_C 232 .0 S_A 239.0 N 262 0 I

iii) 4'-n-Heptyloxy benzylidene-4-azobenzene (303, 304).

K 105.0 S_3 111.5 S_B 125.5S_A 150.5 N 167.5 I

B] Smectic C labelled compounds

i) 4 -n-Hexadecyloxy benzoic acid (223).

K 85.0 S_C 132.2 I

C] Nematic labelled compounds

4(4'-n-Tetradecyloxy benzoyloxy) -3-methoxy benzylidene 4"-anisidine. (198)

K 81.0 N 120.5 I.

1. 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 S_A phase (photographs A-D, F, I) whereas schlieren texture indicates the presence of S_C phase (photographs E, G, L, M).

1.1 Characterization of smectic phases of series I - III, V, VI, IX, X, XII.

Smectogens of homologous series were studied for intermiscibility.

Homologues of series I-III were also intermixed with one another by contact method. The results indicated that each series exhibits same kind of smectic mesophase

In order to characterise the type of smectic phase, in these three series, n-octyloxy homologue of series - II was used Labelled smectic A compound (i) and n-octyloxy homologue of series II were mixed. The smectic mesohase exhibited continuous miscibility with the smectic A mesophase of labelled smectogen. This indicated that smectogens of series I-III exhibited smectic A phase.

The smectogens of series V, VI and IX exhibit the same kind of smectic mesophase To determine the type of smectic mesophase n-tetradecyloxy derivative of series V. was mixed with smectic A labelled compound (iii) However it was seen that the two phases were not miscible which indicated that the type of phase was not smectic A or smectic B Further, the same derivative was mixed with smectic C labelled compound (i) Here it was seen that the phases are completely miscible. Hence all the smectogens of series V, VI and IX exhibit smectic C mesophase.

From texture the smectogen of series X appear to exhibit a focal - conic texture of smectic A phase. The n-hexyloxy homologue of series X was mixed with smectic labelled compound (ii). This labelled compound exhibits smectic A, smectic B and smectic C phases in addition to nematic phase. When the two compounds were mixed it was seen that the smectic mesophase of the n-hexyloxy homologue is miscible only with the smectic A mesophase of the labelled compound. Therefore it was concluded that smectogens of series X exhibit smectic A mesophase.

2 *characterization of Nematic phase.*

The schliren texture of smectic C mesophase and nematic phase appear quite similar hence the nematic phase showing threaded texture was charaterised using nematic labelled compound (i).

Series XVI 4-Methyl 2'-acetyloxy 4'(4"-n-alkoxy benzoyloxy) azobenzenes

The n-dodecyloxy homologue of series XVI was mixed with nematic labelled compound (i). The nematic mesophase exhibited continuous miscibility with the nematic mesophase of labelled nematogen.

The n-dodecyloxy derivative was also mixed with smectic C labelled compound (i) where in it was found that the two mesophases do not mix.

CHAPTER - 1

A. Microphotograph of smectic A texture of ethoxyethyl 4(4'-n-octyloxy benzoyloxy) benzoate on heating at 53 °C.

B. Microphotograph of smectic A texture of methoxyethyl 4(4'-n-tetradecyloxy benzoyloxy) benzoate on cooling at 65 °C.

C. Microphotograph of smectic A texture of methoxyethyl *trans* -4(4'-n-dodecyloxy) -∝- methyl cinnamate on cooling at 48 °C.

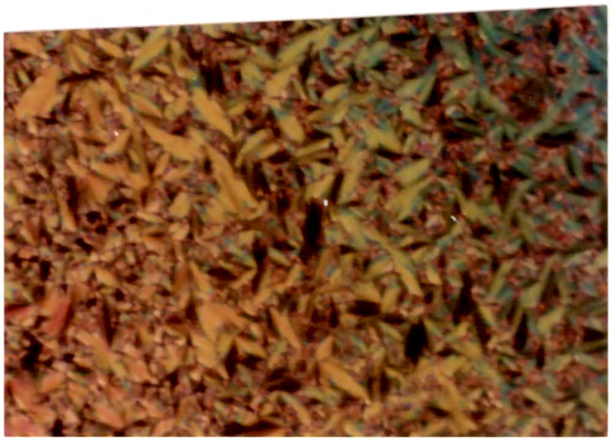
D. Microphotograph of smectic A texture of methoxyethyl *trans* -4(4'-n-dodecyloxy) -∝- methyl cinnamate on cooling at 45 °C when doped with 10% by weight of chiral dopant -(1R, 2S, 5R) - (-)- menthyl 4-n-dodecyloxybenzoate (exhibiting vivid colours).

All the photograhs taken under cross polarizers.

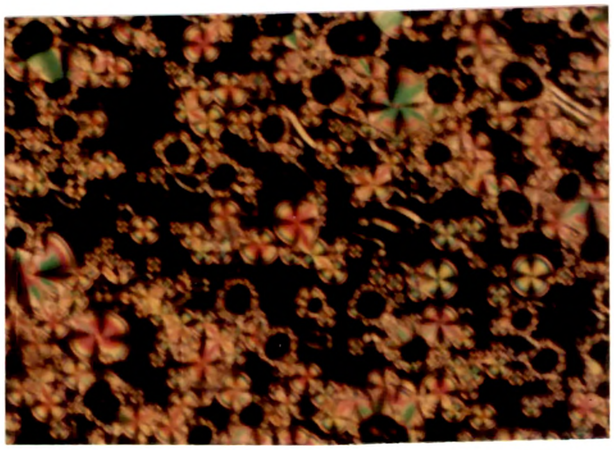
Magnification 20 X 10.

(A)

(B)



(C)



(D)

CHAPTER - 2

E. Microphotograph of smectic C texture of -4(4'-n-tetradecyloxy benzoyloxy benzylidene) 2" -amino naphthalene 1" -thiol on heating at 140 °C.

F. Microphotograph of smectic A texture of 4'-n-dodecyloxy -4'-n-isopropyl aniline on cooling at 57 °C.

G. Microphotograph of smectic C texture of -4(4'-n-hexadecyloxy) phenylazo -2"-naphthalene on heating at 130 °C

H. Microphotograph of cholesteric (chiral nematic) phase with oily stricks of -4(4'-n-hexadecyloxy) phenylazo -2"- naphthalene on heating at 125 °C when doped with 10% by weight of chiral dopant (1R, 2S, 5R) -(-)- menthyl 4-n-decyloxybenzoate.

All the photograhs taken under cross polarizers.

Magnification 20 X 10.

(E)

(F)

(G)

(H)

CHAPTER - 3

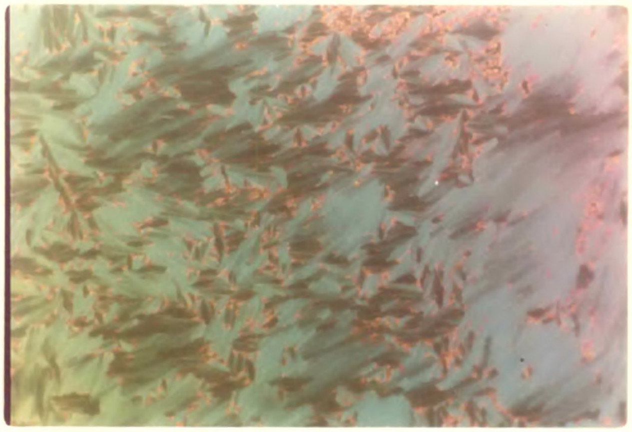
I. Microphotograph of smectic A texture of -4(4'-n-methoxyphenyl) 4"-n-propyloxy benzanilide on heating at 242 °C.

J. Microphotograph of nematic marble texture of 4(4'-n-methoxyphenyl) 4"-n-propyloxy benzanilide on heating at 255 °C.

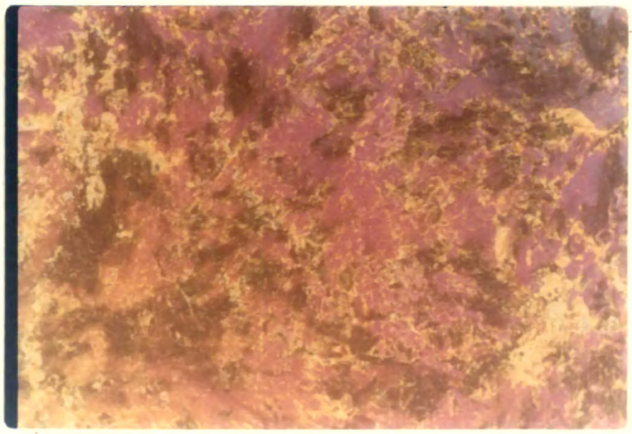
K. Microphotograph of nematic marble texture of 4' methoxy -α- methyl biphenylidene 4"-n-octyloxy aniline on heating at 190 °C.

All the photograhs taken under cross polarizers.

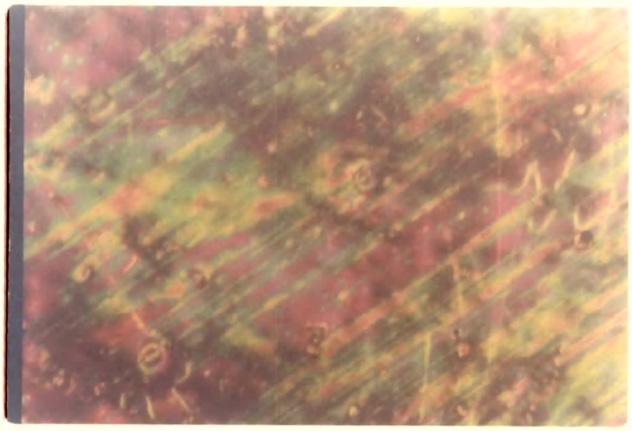
Magnification 20 X 10.



(I)



(J)



(K)

CHAPTER - 4

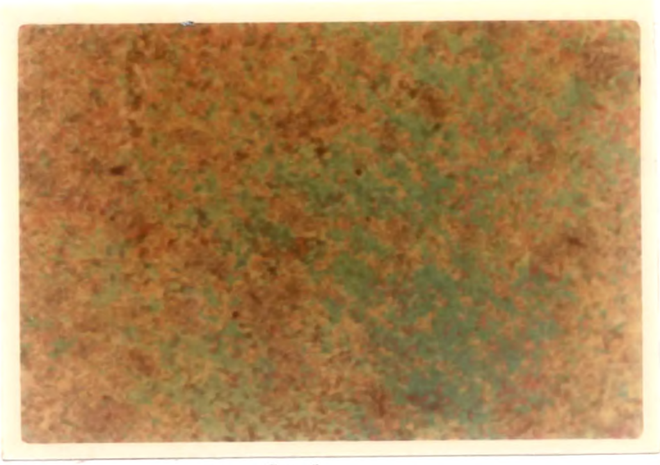
L. Microphotograph of smectic C texture of 4'-methyl -2', 4'-bis(4"-n-decyloxybenzoyloxy) azobenzene (when cover glass was pressed) on cooling at 47 °C.

M. Microphotograph of smectic *C texture of 4'-methyl -2', 4'-bis(4"-n-decyloxybenzoyloxy) azobenzene on cooling at 30 °C when doped with 10% by weight of chiral dopant (1R, 2S, 5R) -(-)- menthyl-4-n-dodecyloxybenzoate.

N. Microphotograph of nematic threaded texture of 4-methyl 2'-hydroxy 4'-n-tetradecyloxy azobenzene on cooling at 68 °C.

All the photograhs taken under cross polarizers.

Magnification 20 X 10.



(L)

(M)

(N)

DIFFERENTIAL SCANNING CALORIMETRY

6.0 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 transition 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 (305) 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 °) (306) This is the rule of Richards (307), analogous to Trouton's rule for entropies of evaporation. Similarly, one finds for crystals which separate on melting into small, non-spherical rigid motifs, that the entropy of fusion consists of positional and orientational contribution. In this case one finds ΔS_f between 30 and 60 J/(K mol °) (306) as first observed by Walden (308). 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 represent a well documented series of molecules with increasing fractions of conformational entropy of fusion (306). 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 smiliar in numbers of atoms to n-(C_{10} H_{16} O versus C_{10} H_{22}), but has 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 may macromolecules has revealed that ΔS_{conf} is about 9.5 J (K mole ^{o}) (306) 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}) (309). For large motifs, such as phenylene or larger ring·structures, the contribution may be two to three times this amount (310). 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 "orientaltionally ordered" liquids (311) are widely known as liquid crystals. (312).

Next is group of materials with a mesohase which shows "orientational disorder", but positional order. These materials are widely known as plastic crystals (313), because of the ease of deformation of such crystals. This name is well accepted and much less cumbersome than "orientationally disordered" crystals. (311).

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 (311) 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. 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 homologous series and a few typical mesogens to find enthalpy and entropy changes by using DSC technic at phase transitions Following nine homologues of mesogenic 4-methyl 2'-hydroxy 4'-(4"-n-alkoxy benzoyloxy) azobenzenes (Table-37) and other thirteen homologues of different homologous series (Table-38) were studied by DSC technic.

1. 4-methyl - 2'-hydroxy -4'-(4"-n-alkoxy benzoyloxy) azobenzenes

All the members screened by DSC exhibit prominent endothermic peaks for solid-mesogenic transitions, small peaks for smectic-nematic and mesogenic-isotropic transitions (Fig.71a, 71b)

Enthalpy and entropy data are given in Table-37. n-Decyloxy derivative did not exhibit sharp solid-nematic peak and peak for nematic - isotropic transition could not be observed.

Accept a few cases all the selected homologues having smectic phases were screened by DSC (Fig. 75a-75j). Enthalpy values of S_C and S_A phase transition agree well with the literature value. (314), which has helped in further confirmation of mesophase type

The plot of enthapies and entropies for the homologous series exhibits regular trend (Fig. 72 - 74).

Table - 37

Calorimetric data

Sr. No.	R=n-alkyl group	Wt. mg.	Transition state	Peak temp. (Microscopoic Reading)	Δ H J/G	Δ S J/g °K	Total - Δ S J/g ° K
1	Butyl	12	K - N N - I	129.1 (132.0) 250 4 (248 0)	39 171 2 655	0.09742 0 00507	0 10249
2	Pentyl	09	K - N N - I	119 5 (20.0) 246 0 (240 0)	83 380 2 288	0 21243 0 ..00441	0 21684
3.	Hexyl	13	K - N N - I	117 2 (119.0) 242.7 (238.0)	21.363 1.013	0 05475 0 00196	0 05671
4.	Heptyl	08	K - N N - I	115 2 (117.0) 226 9 (225.0)	51.633 2.354	0 13301 0 00471	0 13772
5.	Octyl	10	K - N N - I	118 6 (118 0) 219 0 (214.0)	17 948 0 801	0 04583 0.00163	0 05746
6.	Decyl	12	K - N * N - I	119.1 (111 0) -- (196.0)	7.113 ----	0 01814 ----	0 01814 ----
7	Dodecyl	07	K - N N - I	101.0 (104 0) 184 8 (182 0)	92 280 2 017	0 24674 0 00441	0 25115
8.	Tetradecyl	13	K - N N - I	106 9 (104 0) 175.9 (178 0)	42.126 1.198	0 11089 0.00267	0 11356
9.	Hexadecyl	12	K - N N - I	99 4 (103 0) 170.5 (172 0)	15.472 0.435	0 04155 0 000980	0 04253

* N - I transition was not detected by DSC.

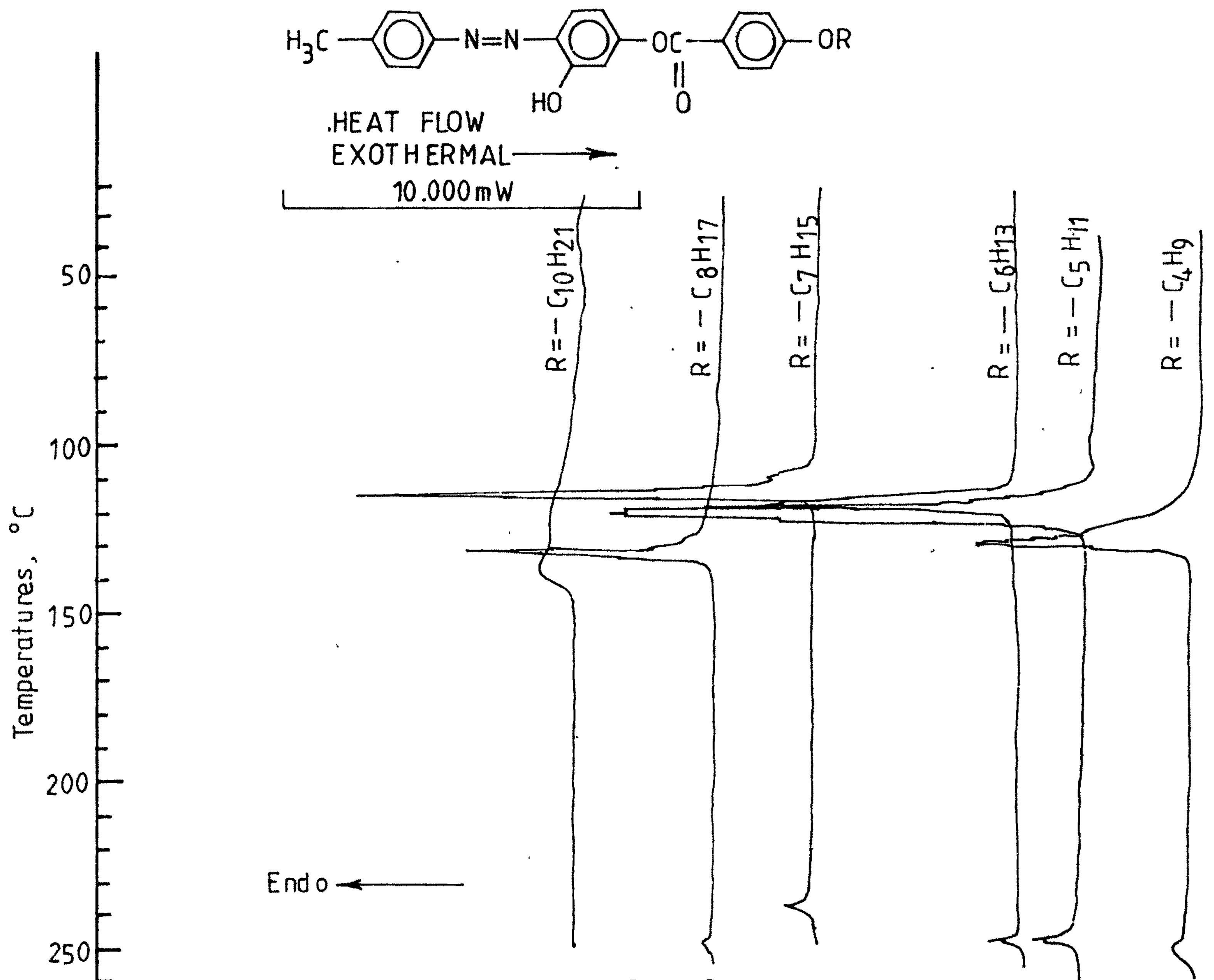
Table - 38

Calorimetric data

Sr. No.	R=n-alkyl group	Wt. mg.	Transition state	Peak temp. (Microscopoic Reading)	Δ H J/G	Δ S J/g °K
1	Hexyl Series - I	12	K - S_A S_A - I	46.7 (43 0) 53.4 (54.0)	18.485 1.722	0 05782 0 00526
2.	Octyl Series - I	14	K - S_A S_A - I	45 0 (47 0) 53 4 (58 0)	22 307 2 586	0 07015 0 00792
3.	Octyl Series - II	14	K - S_A S_A - I	40 6 (37 0) 60 3 (64 0)	52 256 4 218	0 16663 0 01265
4.	Dodecyl Series - II	14	K - S_A S_A - I	40.3 (42 0) 67.8 (71.0)	47 933 1.812	0 15300 0 00532
5.	Tetradecyl Series - III	15	K - S_A S_A - I	52 6(51 0) 66.7 (64.0)	15.377 1 928	0.04723 0 00567
6.	Hexadecyl Series - III	09	K - S_A S_A - I	59.2 (59.0) 62.9 (66 0)	{1 6594 34 819}	0.00499 0 10366
7.	Dodecyl Series -V	15	K - S_C Sc - N N - I	103 6 (106.0) 153.7 (157 0) 199 1 (198 0)	20 105 0 225 0.653	0 5338 0 00053 0 00138
8*.	Dodecyl Series - VI	10	K - N N - I	134.8 (142 0) 211.6 (215 0)	37 844 0 408	0 09280 0 00084
9	Dodecyl Series - VII	11	K - S_C S_C - I	54 6 (54 5) 58.0 (60.0)	1 029 0.147	0 003141 0 0004441
10.	Heptyl Series - XI	12	K - N N - I	175.9 (181 0) 203.6(210.0)	56 965 1.334	0 12689 0 00280
11	Decyl Series -XII	10	K - I I - S_C	82.2 (89 0) 48 5 (52.0)	70.959 0 273	0 19977 0.00085
12.	Dodecyl Series - XVI	11	K - N N - I	85.2 (87.5) 89 2 (91.0)	{0 2564 45.639}	0 00072 0 12600
13.	Diadipate Section - 4 6	07	K - I I - S_C	95 0 (101 0) 84 3 (87 0)	0 4238 22 226	0 00115 0 06220

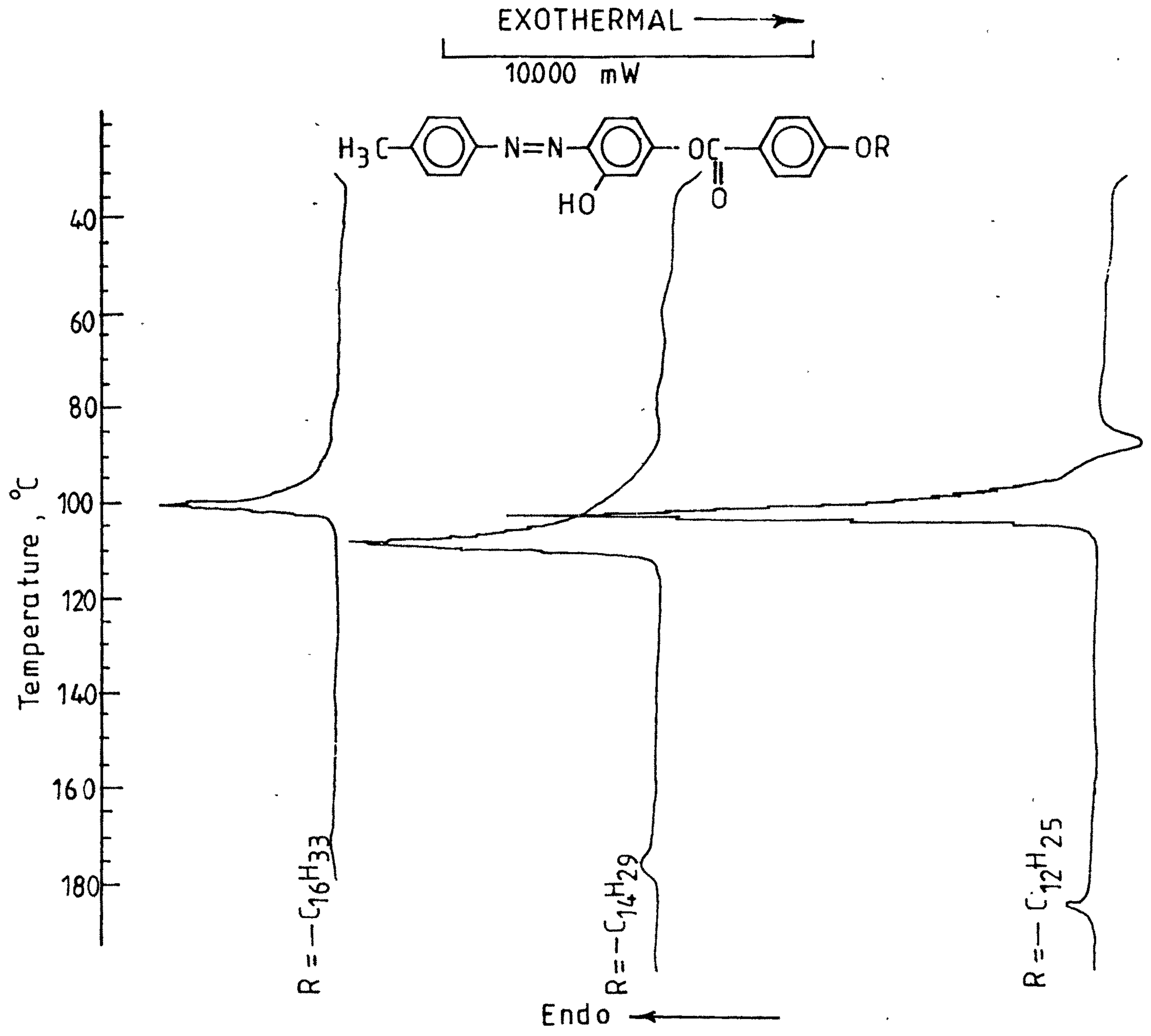
* All the enthalpies are measured on heating only.

{ } Overlapping of phase transitions



DSC THERMOGRAMS

Fig. 71(a)



DSC THERMOGRAMS

Fig. 71 (b)

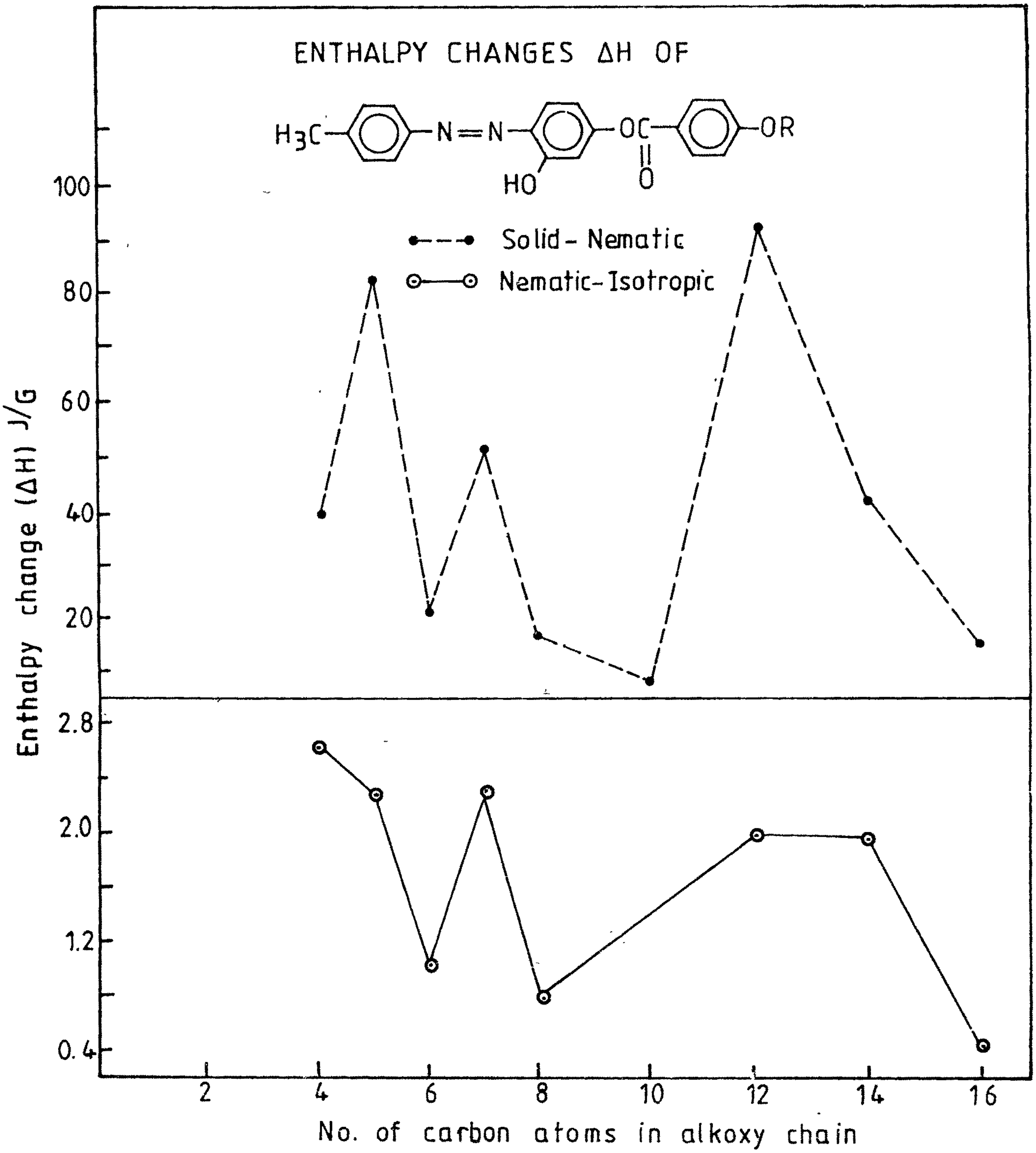

ENTHALPY CHANGES ΔH OF
H3C
N=N
HO
OC
O
OR
Solid-Nematic
Nematic-Isotropic
Enthalpy change (ΔH) J/G
100
80
60
40
20
2.8
2.0
1.2
0.4
2
4
6
8
10
12
14
16
No. of carbon atoms in alkoxy chain

Fig. 72

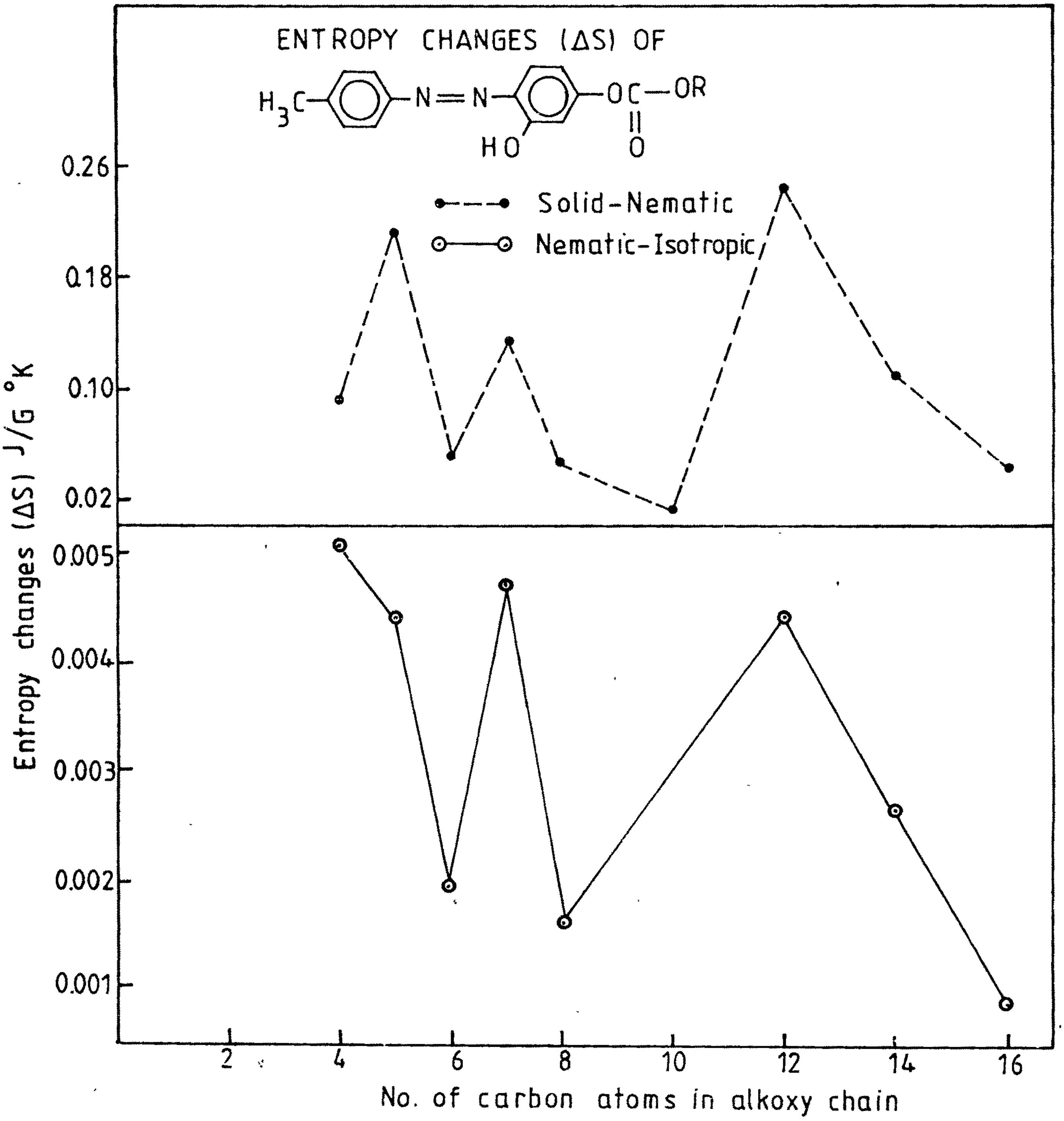

ENTROPY CHANGES (ΔS) OF
H3C — N=N — OC — OR
HO
O
Solid-Nematic
Nematic-Isotropic
Entropy changes (ΔS) J/G °K
0.26
0.18
0.10
0.02
0.005
0.004
0.003
0.002
0.001
2
4
6
8
10
12
14
16
No. of carbon atoms in alkoxy chain

Fig. 73

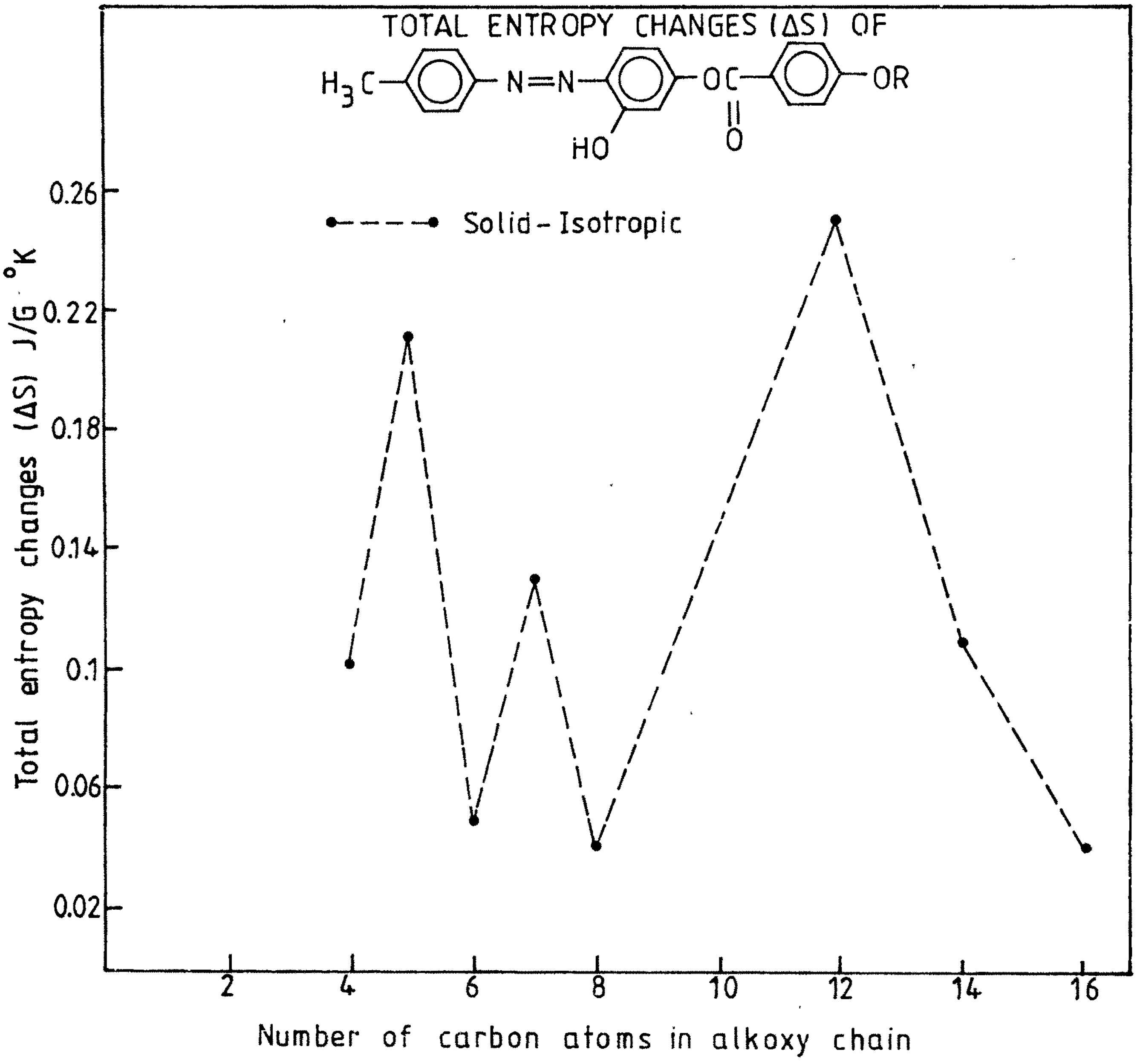
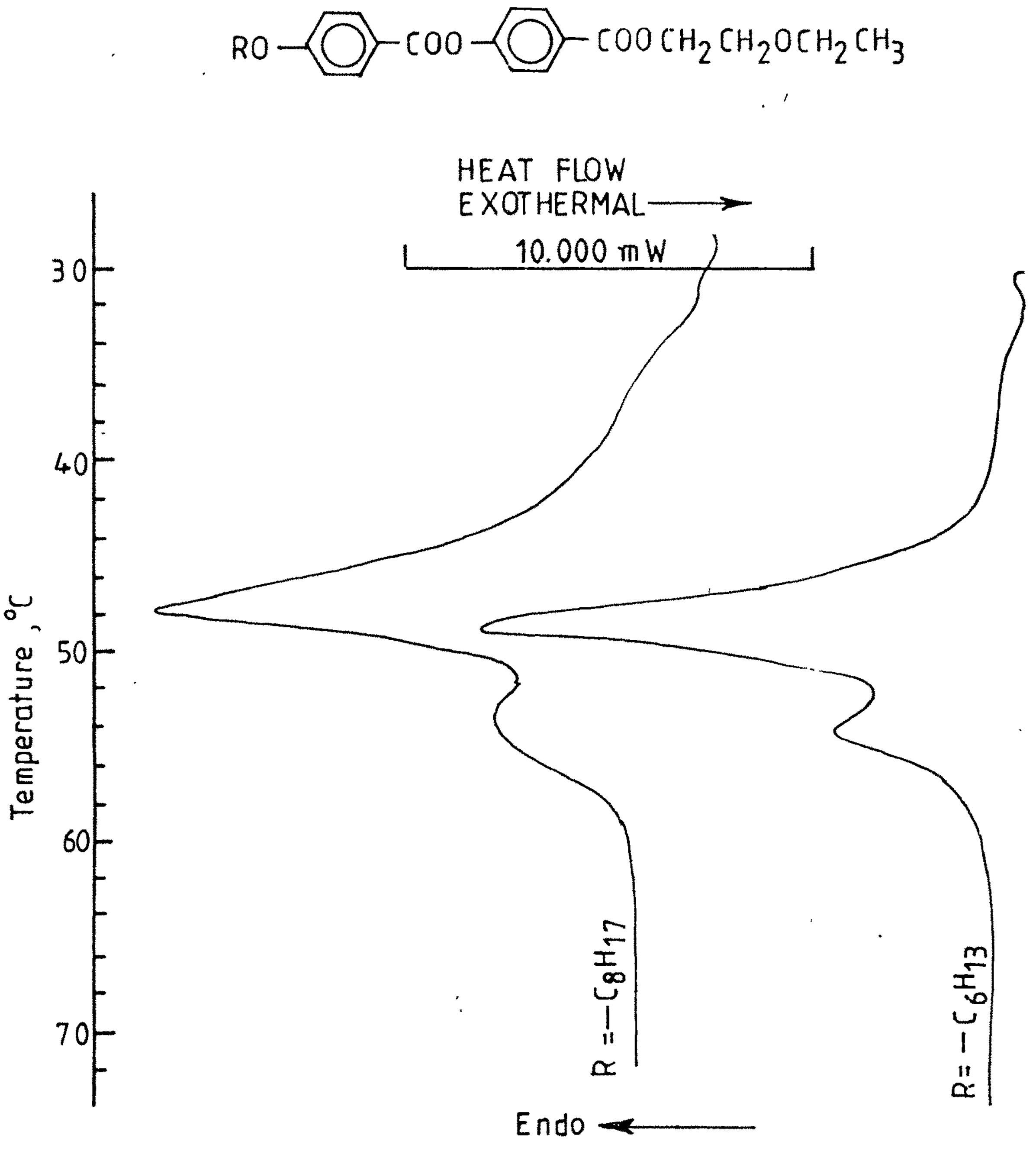
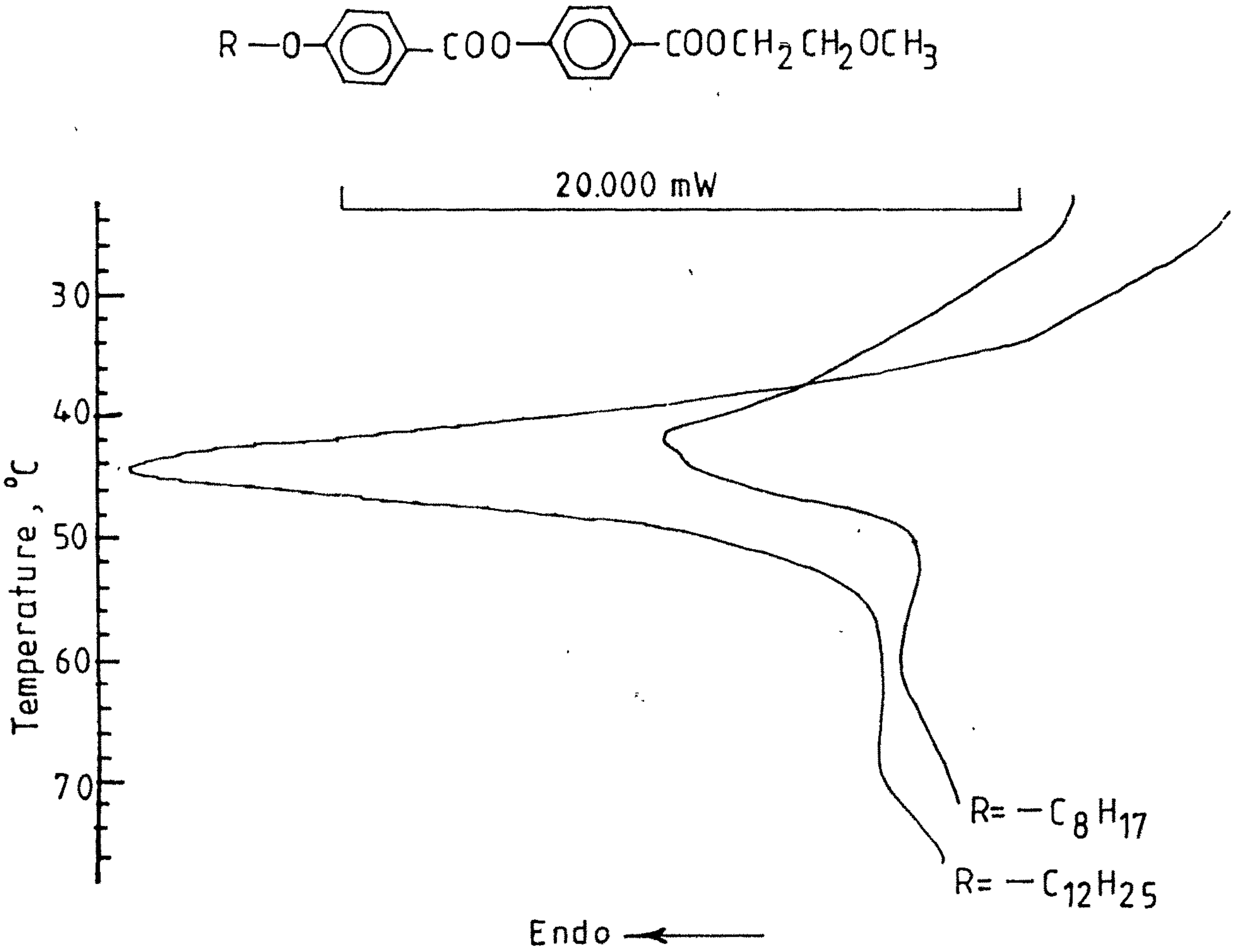

TOTAL ENTROPY CHANGES (ΔS) OF
H3C
N=N
HO
OC
O
OR
Solid - Isotropic
Total entropy changes (ΔS) J/G °K
0.26
0.22
0.18
0.14
0.1
0.06
0.02
2
4
6
8
10
12
14
16
Number of carbon atoms in alkoxy chain

Fig. 74

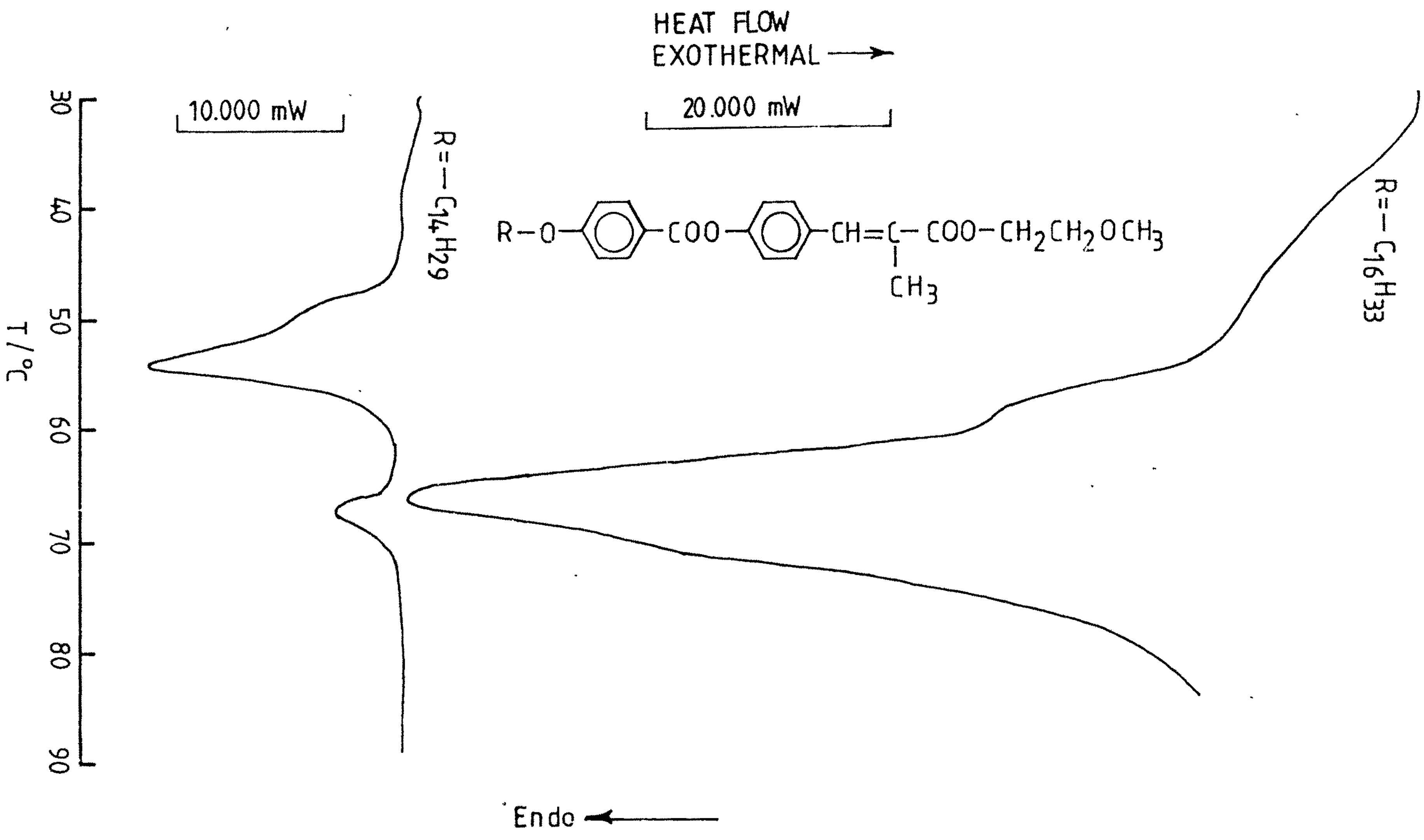


DSC THERMOGRAMS

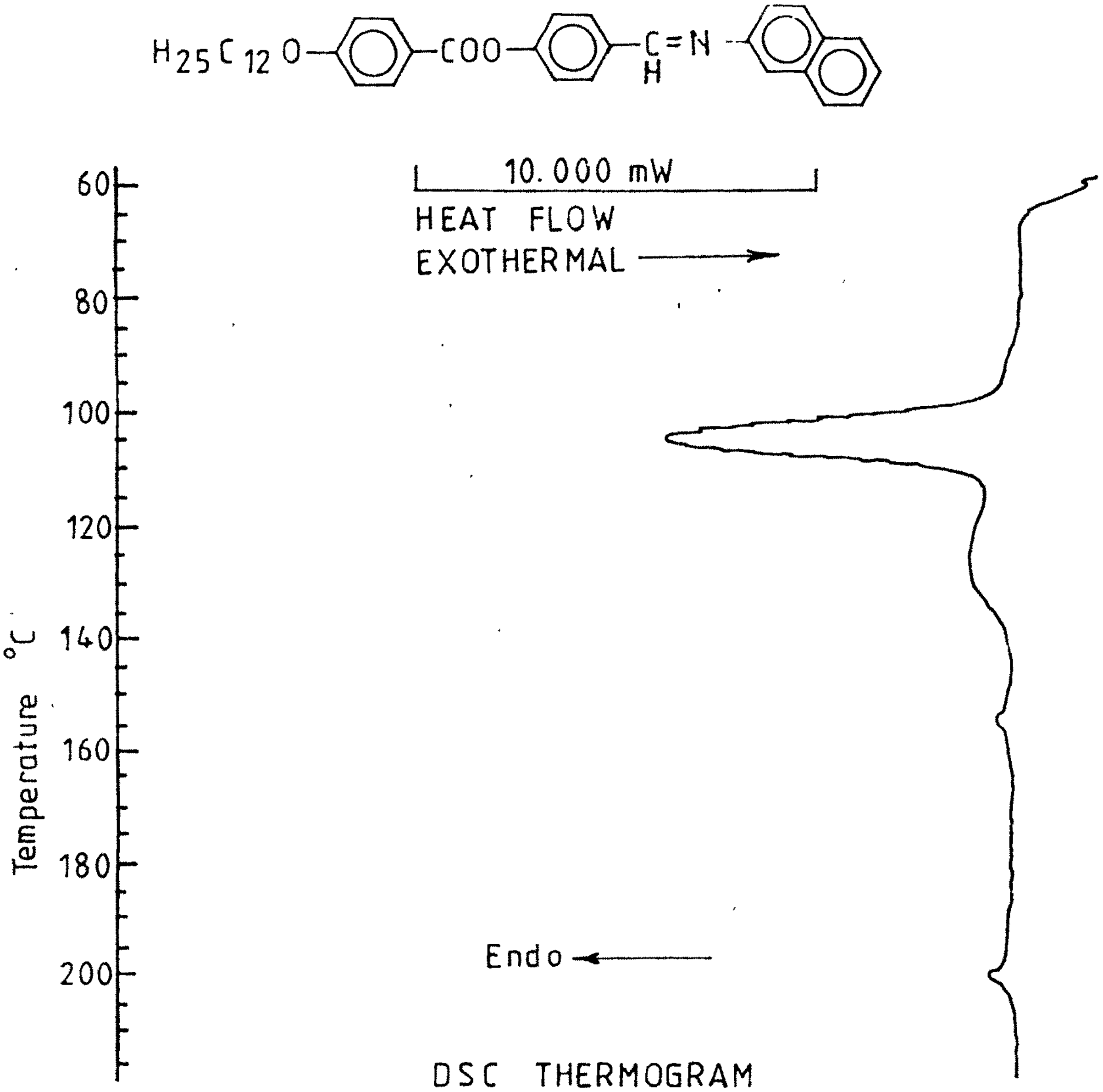
Fig.75(a)



DSC THERMOGRAMS
Fig. 75 (b)

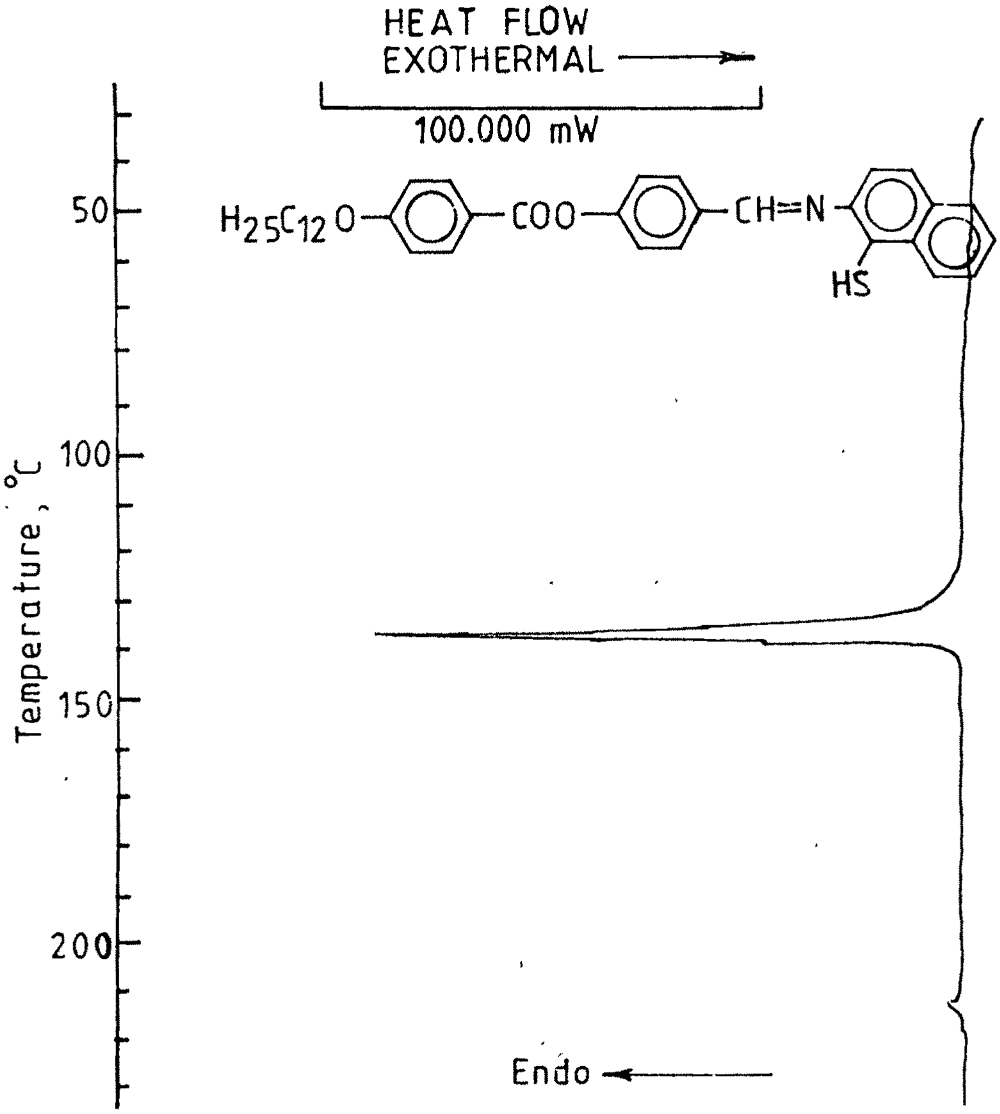


DSC THERMOGRAM
Fig.75(c)

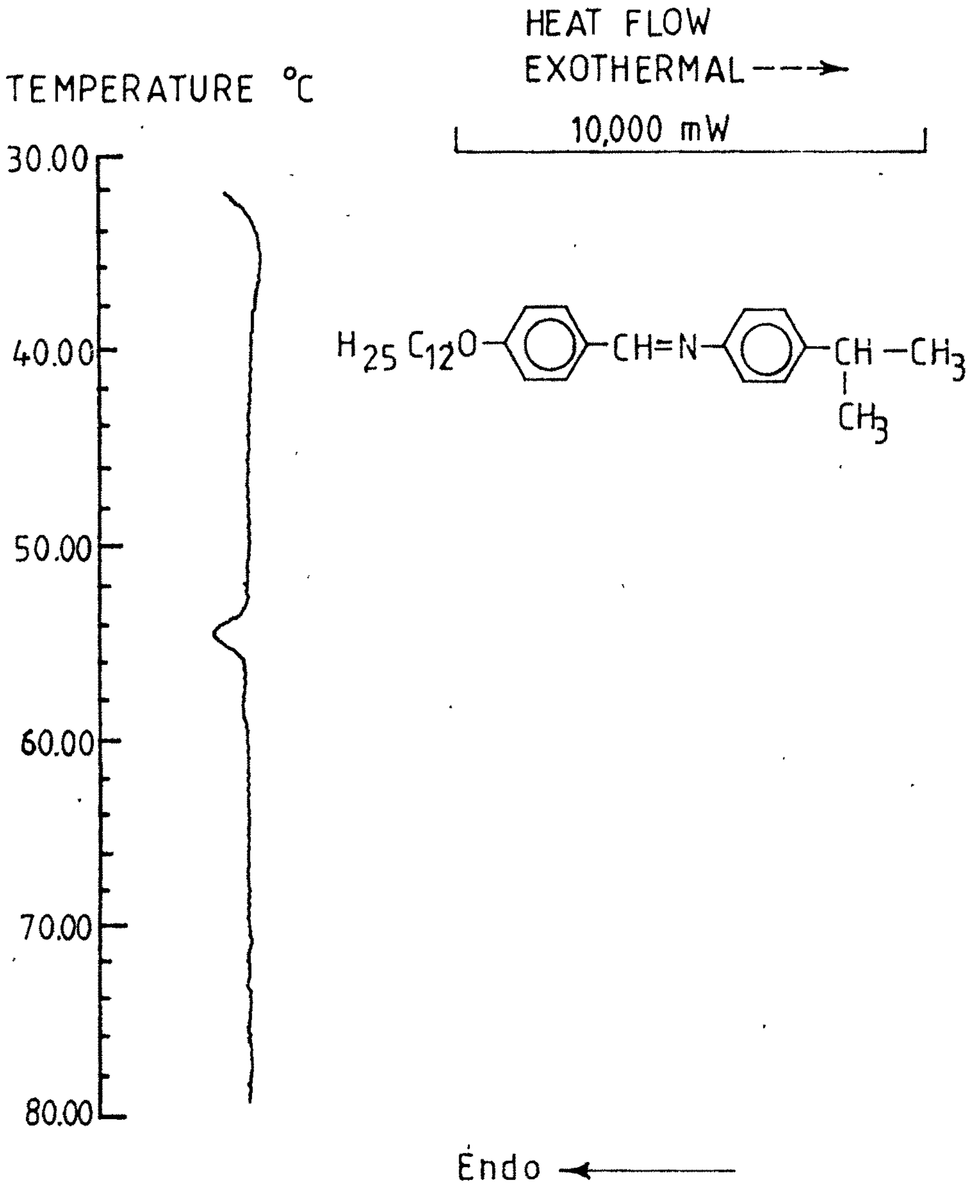


DSC THERMOGRAM

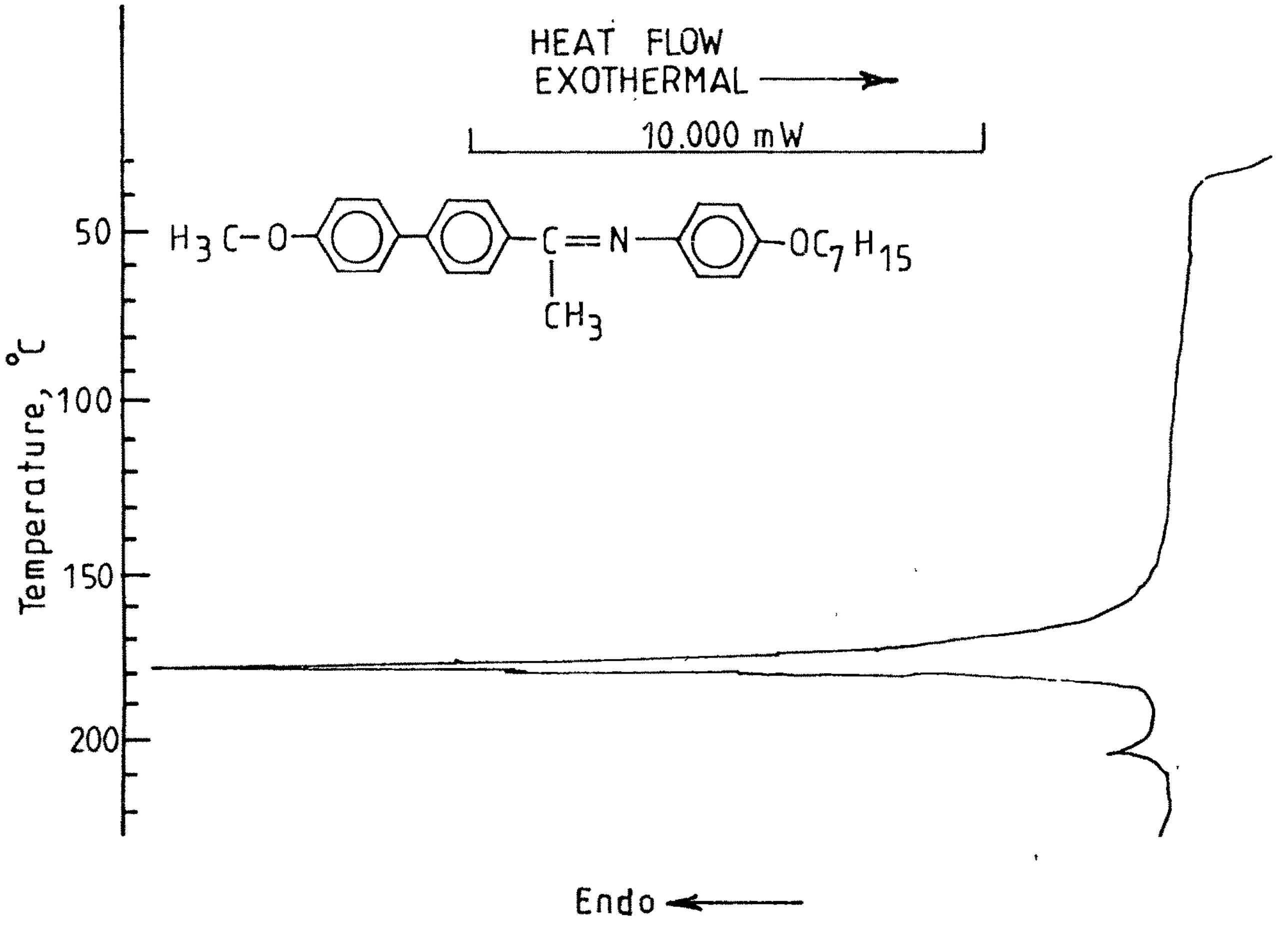
Fig.75 (d)



DSC THERMOGRAM
Fig. 75(e)

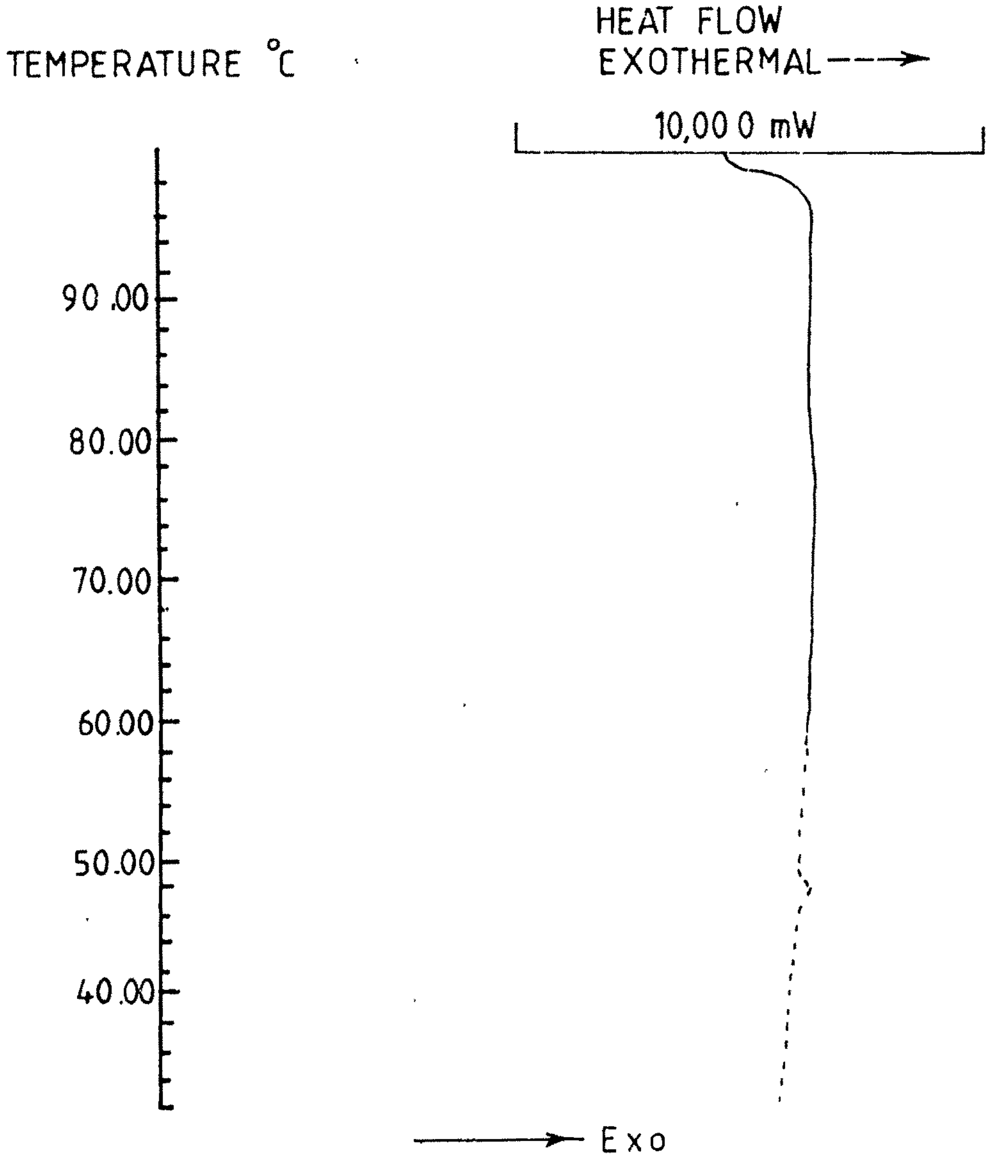


DSC THERMOGRAM
Fig. 75(f)

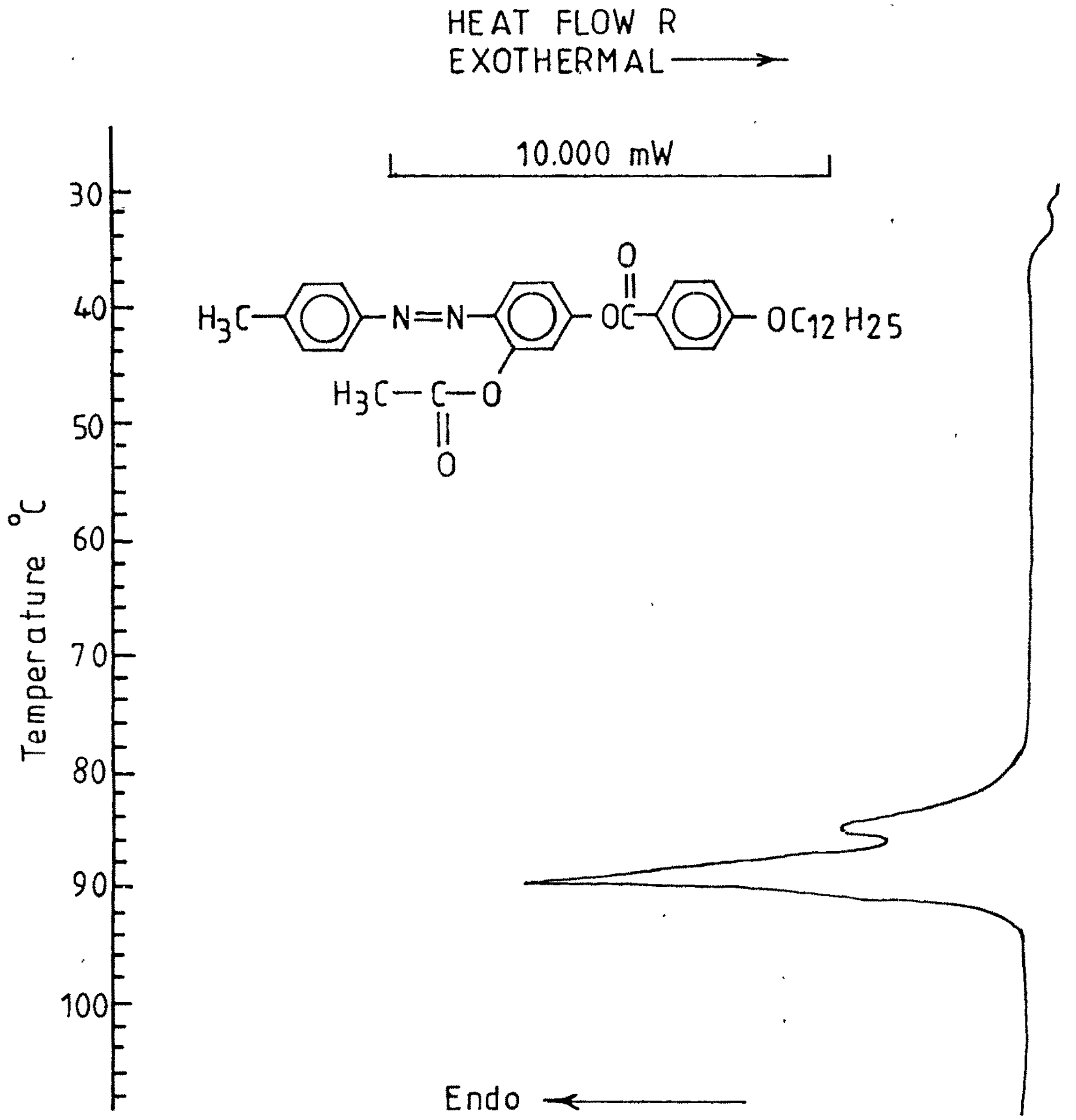


DSC THERMOGRAMS

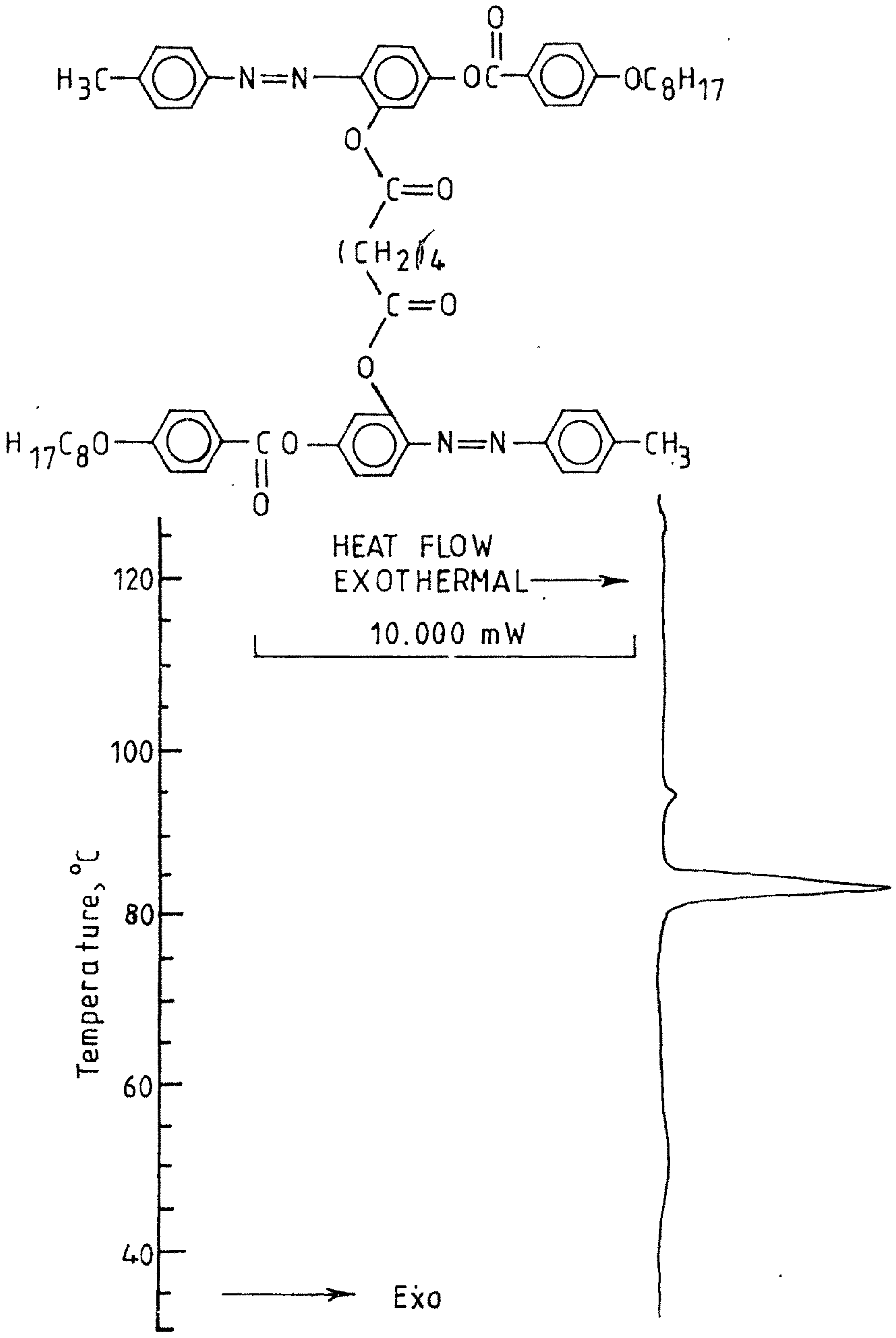
Fig. 75(g)



DSC THERMOGRAM
Fig. 75(h)



DSC THERMOGRAM
Fig. 75(I)



DSC THERMOGRAMS

Fig. 75(J)