INTRODUCTION

1. Definition and Nomenclature

Research in the field of liquid crystals has been passing through various phases of activities since it was first identified by Reinitzer (1) and O. Lehmann (2). During the last few years, interest in liquid crystals has intensified, primary as a result of its wide commercial applications.

Liquid crystals are highly associated liquids that occur over various temperature ranges in melts or solutions of certain organic molecules and some polymers. Liquid crystallinity is an intermediate state of matter existing in a peculiar twilight zone between the boundaries of the usual crystalline solids and isotropic liquids.

Friedel (3) and Friedel and Friedel (4) who studied liquid crystals in more detail proposed the term ' mesomorphism ' as this phase is neither a true liquid nor a true solid but finds place between a crystalline solid and an isotropic liquid. This term and the associated terms mesomorph, mesogens, mesoform and mesomorphism are widely used in literature. According to Rinne (5) the mesomorphic and crystalline states will belong to the class of ' eutactites ', since they possess ordered or regular structure. Brown and Shaw (6) had used the term ' mesomorphism ' for the title of their first review.

Liquid crystals are classified into two major groups on the basis of the manner in which they are obtained. One of these is identified as thermotropic liquid crystals indicating that liquid crystal phase is obtained by the application of heat. Lyotropic liquid crystals constitute the second major group where liquid crystal phase is obtained by mixing two or more components in suitable solvent. Eventhough the terms thermotropic and lyotropic are widely used Gray and Winsor (7) prefer the terms ' amphiphilic ' and ' non-amphiphilic ' for a variety of mesogens (liquid crystals). The amphiphilic mesogens are called lyotropic while the non-amphiphilic mesophases are commonly called thermotropic.

2. The Mesomorphic State

Only Vorländer (and others) prepared L.C.'s.

Soon after the discovery of liquid crystals, No Lehmann (8) and Vorlander (9) prepared hundreds of compounds which exhibited liquid crystallinity. Lehmann (10) carried out a large number of experiments to illustrate the properties and formation of liquid crystals from the isotropic liquid. Vorlander (11) believed that mesomorphic substances were truly liquid crystals and had a fixed space lattice. Further, microscopic examination of liquid crystals carried out by Mauguin (12) and Friedel and Grandjean (13) and SCHENCK ! established that the liquid crystal state is a truly physical state which is intermediate between the crystalline solid and the isotropic liquid. A.C. de Kock (14) on the basis of his work ' liquid mixed crystals ' supported the view that crystalline liquid is a homogeneous phase and not an emulsion of two liquids.

If the conditions are favourable for mesomorphism for a compound, the ordered structure breaks down in stages, and before passing to isotropic liquid, a liquid crystalline state is obtained. Further heating destroys the orientation of the molecules and the mesophase changes to the disordered isotropic liquid. The mesophase obtained is termed enantiotropic which takes place reversibly on heating and cooling though the reversal to the solid phase is usually accompanied by supercooling. However, a mesophase may be monotropic in nature. This type of metastable mesophase is obtained only during cooling of isotropic liquid which is reversible at the same temperature.

3. Thermotropic Mesophases

Friedel (15) carried out detailed optical studies of liquid crystals and conveniently divided them into three types - Smectic, Nematic and Cholesteric on the basis of molecular arrangement which gives rise to textures and other optical characteristics of the mesophase.

3.1 Smectic Liquid Crystals

The smectic mesophase is turbid viscous state, with certain properties reminiscent of those found for soaps. The term ' Smectic ' is in fact derived from the Greak word ' Smectos ' meaning soap-like. Smectic liquid crystals compounds are stratified and the melting process evidently disrupts end-to-end molecular cohesions, but the temperature at which the mesophase is stable is not sufficient to break apart lateral associations and the layers remain essentially intact. Smectic liquids therefore, retain a good deal of two dimensional order.

When smectic phase is formed on cooling the isotropic liquid, it first appears frequently in the form of non-spherical characteristic elongated birefringent particles which are known as batonnets. These increase in number as the temperature falls, coalesce and show evidence of a focal conic texture when examined in polarized light.

When focal conic texture is observed under the microscope a number of fine dark lines are seen. The shape and the arrangement of these lines are like those of ellipses and hyperbolas. The study and explanation of the focal conic texture are largely due to G. Friedel (15). Bragg (16) has given an excellent account of the focal conic texture and the geometry involved which furnish further evidence for the layer theory of the smectic texture.

Sackmann and Demus (17) have classified smectic phases according to the textures observed in the mesophases. (Table 1). They studied in detail and also reported seven smectic phases from S_A to S_G (17) which were identified by miscibility studies. De Vries and Fishel (18) have proposed the eighth possible smectic phase S_H.

Table 1

Classification of smectic liquid crystals (17)

Types of phases	Types of textures	
Smectic - A	a. Simple fan-shaped texture b. Simple polygon texture	
Smectic - C	a. broken fan-shaped texture b. broken polygon texture	Schlieren texture
Smectic - B	a. fan-shaped texture b. Polygon texture c. mosaic texture	with decreased number of lines

As suggested by Gray and Goodby (19), the thermodynamic ordering of the known smectic polymorphic forms appears to be as follow :

A, D, C, F, B, H, E, G
thermal stability decreases

However, by convention, the smectic phase occuring at highest temperature for a smectic mesogen exhibiting polymorphism, is termed S_I and subsequently S_{II}, S_{III} and so on as the temperature at which they occur decreases.

3.2 Nematic Liquid Crystals

The term nematic meaning thread like is used because of the mobile thread-like lines which are observed in nematic mesophase. Frank (20) has named these lines as disclinations.

The nematic phase is less ordered compared to the smectic as there is no layered arrangement of the molecules. The molecules lie parallel to one another but without a regular organization of their ends. Such arrangement of the molecules is referred to as an imbricated structure. The molecules in the nematic phase exist in the form of groups, each group containing about 1,00,000 parallel molecules. These groups are referred to as swarms, and the theory known as the ' Swarm Theory ' was first preposed by E. Bose (21). Considerable amount of evidence in favour of swarm theory has been provided (22-28). Zocher (29) proposed the distortion hypothesis which is now referred to as the continuum theory of liquid crystals. Brown et al. (30) in their review suggested that continuum theory is well suited to the treatment of anisotropic liquids. Luckhurst (31) applied both the swarm and distortion theories of the nematic mesophase to the study of magnetic resonance experiments and has shown that they lead to isomathematical conclusions.

A simple molecular theory of the nematic liquid crystalline state, by which it is shown that N-I transition temperatures may be determined by calculation of the free enthalpies of the phases involved at the transitions, was proposed by Maier and Saupe (32).

Disc-like and Carbonaceous Nematic Phases

Common nematogenic materials consist of rod-like molecules whose longest axes tend to be parallel in the nematic phase. Alben (33), Onsagar (34) and Dreyer (35) suggested that in addition to such positive nematics, it is reasonable to expect that there might be negative nematics with planar molecules aligned with their shortest axes parallel.

Chandrasekhar et al. (36) have reported that thermotropic mesomorphism has been observed in pure compounds consisting of simple disc like molecules viz. benzenehexa-n-alkanoates, and based on x-ray data, a structure has been proposed in which the discs are stacked

Discotics

one on the top of the other in columns that constitute a hexagonal arrangement. More references of disc-like liquid crystals are also available (37-42). Another new type of nematic mesophase obtained during the process of cocking and carbonization has been discussed by Zimmer and White (43). The distinctive feature of this carbonaceous mesophase is the plate-like molecule of nematic liquid crystal. Carbonaceous mesophase has also been reported by Sakagami and Nakamizo (44).

Nematic Reentrant Phase

The first observation about the reentrant nematic phase (the phase occuring below the smectic phase) was made by Cladis (45). Recently, there have been reports regarding this particular phase. (46 - 50).

Nematic Textures

A nematic liquid crystal on cooling from the amorphous isotropic liquid gives at first circular birefringent areas (droplets). The appearance of the textures which are formed after the completed transition often depends considerably on the layer thickness. Thicker nematic layers may show the typical threaded texture which may move and float around in the nematic liquid. In thinner layers the threaded texture changes to the Schlieren texture with point like disclinations. The appearance between crossed polaroids is characterized by dark brushes which start from points in which the direction of extinction is not defined. By suitable surface treatment it is possible to obtain films with uniform molecular alignment. With untreated surfaces, the surface may produce an irregular texture reminding one of the polished marble (the marble texture). The appearance of almost optically extinct region during microscopic observation of the slide in the nematic phase which on slight disturbance shows a spark of light indicates homeotropic texture adopted by the phase.

3.3 Cholesteric Liquid Crystals

The cholesteric mesophase is found in the melts of several compounds mainly having sterol type of skeleton. Initially they were cholesterol derivatives from which it derives the name. Friedel (15) noted a somewhat closer resemblance between the cholesteric phase and nematic phase. Nematic liquid crystal can be transformed to a cholesteric liquid crystal by dissolving an optically active compound in it. The most striking property of the cholesteric mesophase is the scattering of light to give vivid colours when illuminated by white light.

Cholesteric mesophase has fluidity like that of the nematic phase. It can be oriented by electric and magnetic fields like nematic phase (51).

and De Vries!

Friedel (15), Stumpf (52), Mathieu (53) and Gray (54) have tried to explain the optical rotatory power of the plane cholesteric texture. Oseen (55) has explained mathematically the high optical rotatory power and transmission of different colours of plane texture. Fergason (56) and Daniel Berg (57) have explained optical properties of the cholesteric phase.

Textures :

Cholesteric liquid crystals can occur in three textures (58) viz. (i) focal conic texture (ii) plane texture and (iii) isotropic texture or blue phase. The focal conic texture is obtained by cooling an isotropic liquid. It derives its name from the conic sections that are sometimes readily visible, as in the case of smectic. It changes to plane texture when the coverslip is shifted. On cooling an isotropic liquid, some cholesteric compounds exhibit a phase which is visible to the eye in reflected light, but not visible microscopically in transmitted light using crossed polarisers. The phase is known as blue phase, which changes to birefringent texture at low temperature. Bergmann and Stegemeyer (59) have reported the existence of two thermodynamically stable polymorphic forms of the so called ' blue phase ' of cholesteryl nonanoate and myristate.

4. Lyotropic Liquid Crystals

Mesomorphism formed by the effect of solvent on amphiphilic compounds is referred to as lyotropic liquid crystals. The compounds possessing two groups which differ in their solubility properties are characterized as amphiphilic.

The first lyotropic substance ammonium oleate was reported by Lehmann (60), McBain (61) has discussed the forms of mesomorphism in soap solutions. A number of cationic and non-ionic detergents when treated with water or other solvents exhibit anisotropic phases (62). Zocher and Coper (63) have reported that methylene blue, neutral red and some other dyes show lyotropic mesophases. Robinson (64) reports an interesting observation that viscous solutions of poly-γ-benzyl-L-glutamate in certain organic solvents are anisotropic. Lawson and Flautt (65) have studied NMR spectroscopy of smectic and waxy mesophases in surfactant systems such as sodium palmitate - water system.

A close relationship obviously existing between these liquid crystalline states and the truly colloidal states has been discussed by Ostwald (66). Gray and Winsor (67) have discussed constitutional analogies between thermotropic liquid crystals, plastic crystals and lyotropic liquid crystals.

5. Plastic Crystals

In contrast to liquid crystals, which are solid-like liquids ; plastic crystals are liquid-like solids. The basic difference between a liquid crystal and a plastic crystal on a molecular scale is largely one of geometry. The liquid crystal molecules are generally long and rigid whereas the plastic crystal molecules are usually compact and globular. Plastic crystals were first recognized by Timmermanns (68). X-ray diffraction studies of plastic crystals indicate that the molecules in plastic crystals have considerable mobility but they do not have literally free rotation. Both molecular rotation and self diffusion in plastic crystals have been investigated by NMR studies (69). Smith (70) has given an account relating the properties of plastic crystals and liquid crystals.

6. Mesomorphism in Biological Systems

Mesomorphic property in the form of myelin in biological systems was first shown by Virchow (71). Living sperms composed in part of protein, nucleoproteins and albumins have been shown to possess a mesomorphic state (72, 73). Chapman (74) describes the essential components of membranes of living cells and connective tissues and the significance of liquid crystals in them. Fergason and Brown (75) in their review on the liquid crystals and living systems discuss the mechanism of living systems. Ambrose (76) studied liquid crystallinity in muscle filament and reported the factor controlling liquid crystalline states and their biological interaction.

7. Chemical Constitution and Mesomorphic States

Vorlander from his study of a large number of organic compounds pointed out that close relationship exists between the symmetry of the molecule and its capacity to form liquid crystals. In general the molecules of a liquid crystalline compound are elongated, rod or lath-shaped and possess middle and terminal groups and intermolecular cohesive forces between molecules is a requirement for the formation of liquid crystals. However, the intermolecular attractions should not be so strong that the melting point of the compound is very high since at high temperature the thermal motion prevents the existence of an ordered phase. Thus the cohesive forces operating between elongated molecules must be both anisotropic and of suitable magnitude (77).

The majority of the thermotropic liquid crystals are aromatic in nature. Aromatic nuclei are polarizable, planar, rigid and can give rise to mesomorphism if the substituents are placed in proper positions, and these are p-substituted benzene rings linked together through different central linkages like $-CH=CH-$, $-(CH=CH)_n-$,

$-C\equiv C-$, $-CH=N-$, $-\underset{\displaystyle O}{\overset{}{N}}\!\!\downarrow\!=N$, $-N=N-$, $-CH=CH-\underset{\displaystyle O}{\underset{\|}{C}}-O-$, $-\underset{\displaystyle O}{\underset{\|}{C}}-O-$,

$-O-CH_2-CH_2-O-$, etc.

When more than two benzene rings are linked through more than one central group the liquid crystalline properties are enhanced. The linkage of benzene rings through o- or m-position is not favourable to the liquid crystal formation because the molecules then become non-linear.

Dewar and Goldberg (78) have shown that replacement of aromatic ring by saturated alicylic ring gives marked reduction in thermal stabilities of mesophases. It is interesting to note that Osman and Revesz (79) have reported a new class of aliphatic liquid crystals. Dewar and Riddle (80) from their studies of number of potentially mesomorphic esters and thioesters suggest that the geometry is the most important factor in determining the stabilities of the nematic mesophases. Dewar and Griffin (81) in their thermodynamic study of the role of the central group on the stability of nematic liquid crystals suggest that polarity in the central part of the linear molecule may likely reduce the N-I transition temperature through a reduction in the symmetry number, even though polarity in the terminal groups favours the nematic stability.

Destrade et al. (82) in their study of mesomorphic polymerphism in some disc-like compounds, observed that the real mesomorphic nature of the new kind of liquid crystals with physical properties very similar to red-like mesogens but with a drastically different molecular organization. Chandrasekhar et al. (36) have also noted thermotropic mesomorphism in simple disc-like molecules.

Schroeder and Schroeder (83) have reported mesogenic compounds with terminal hydroxy and amino groups. Liquid crystals with terminal and lateral hydroxy group are also known (84, 85).

Gray (77) has studied the influence of terminal substituents in pure mesogenic compounds and obtained group efficiency orders in nematic and smectic systems. Gray (54) and Dave and Vora (86) have studied the effect of the substitution in cholesteryl benzoates.

The lateral substituents may force apart the molecules and may thus reduce the intermolecular lateral cohesions but at the same time the substituent may increase the molecular polarizability which, in turn, may increase the intermolecular attractions. If the substituents occupy certain pockets in the molecule so that the breadth effect is not manifest, it is found to increase the thermal stabilities, as noted by Gray and Jones (87).

Many mesogenic derivatives of naphthalene are known (87,88-95). Liquid crystalline compounds containing phenanthrene, fluorene, fluorenone (54, 77, 96, 97) and anthracene (98) are also known. Gray and Nash (99) have discussed the liquid crystalline behaviour of heterocyclic compounds.

8. Mesomorphism in Homologous Series

The relationship between transition temperatures and increase in the alkyl chain length of mesomorphic compound is quite interesting. When the mesomorphic temperatures e.g. N-I, S-I, Ch-I, S-N, S-Ch or S-S for the homologous series are plotted against the number of carbon atoms in the alkoxy groups, smooth curves may be drawn through points for like or related transitions. The N-I, S-I and Ch-I temperatures alternate typically; these lie on two falling curves, the upper one for even and the lower one for odd number of carbon atoms in the n-alkoxy chain. For a system with n-alkyl groups attached directly to the ring, the reverse situation arises because the oxygen of the ether link in the alkoxy group is equivalent stereochemically to a methylene unit. (77).

The odd-even effect becomes less marked as the series is ascended and the two curves merge later in the series. The S-N temperatures usually do not alternate and lie on a smooth curve which rises steeply at first then levels out and merges with the falling N-I curve. However, there are cases in which the S-N transition curve does not merge with the N-I curve and last members of the series exhibit nematic mesophase along with the smectic mesophase. There are also cases in which S-N and S-Ch temperatures alternate.

This description defines usual behaviour of mesomorphic homologous series, however, homologous series

With deviations can also be found in literature.

9. Mixed Mesomorphism

Just as the melting points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals are lowered by the addition of foreign substances. When a mesomorphic compound is mixed with another mesomorphic or non-mesomorphic compound, the solid-mesomorphic or mesomorphic-isotropic transition temperatures may get depressed in the usual way following more or less the law of mixtures. De Kock (14), Bogojawlensky and Winogradow (100), Vorlander and Gahren (101), Dave and Dewar (102), Dave and coworkers (103 - 106), Sackmann and Demus (17) have contributed a lot to the study of mixed mesomorphism.

Domon and Billard (107) have shown that it is possible to predict the phase diagram of mixtures of liquid crystals. The study of mixed mesomorphism is very useful in obtaining room temperature liquid crystal mixtures. Many mixtures have been reported where a mesogen or other compound is added to the mesogen, either to decrease the melting point or to increase the mesophase range or for the change in electric conductivity and dielectric anisotropy (108 - 110).

10. Physical Properties

In recent years, a large amount of work is being done on the physical properties such as X-ray studies, spectroscopic studies, magnetic resonance studies, Mossbauer effect, viscosity, surface tension, dielectric constant, magnetic susceptibility, ultrasonic and calorimetric studies etc. of liquid crystals.

X-ray study of mesophases has helped to understand the molecular organization in the smectic and/or nematic phases (111 - 115). Guillon et al. (116) have used the small angle X-ray diffraction method for the study of the smectic polymorphism. X-ray studies of disc-like mesogens by Chandrasekhar et al. (40) indicate that the structure of the mesophase is columnar.

IR spectra of mesogens were studied and reported by L'Vova and Sushchinskii (117) that the transition of solid-liquid crystal was accompanied by sharp changes of spectra whereas the transition from liquid crystal to isotropic liquid did not cause qualitative changes of spectra.

Raman spectral study has been carried out to obtain definite data on the degree of freedom available to the molecules in various mesophases and their importance in determining the stability of a given phase. Schnur et al. (118) from their studies of the Raman spectra, concluded that S_B phase is much more solid-like in nature.

The NMR spectra of different mesophases and/or study of NMR of different substances in liquid crystals has been made by several workers (119 - 124). A number of review papers on NMR studies of liquid crystals have appeared in the literature by Luckhurst (125), Meiboom and Snyder (126) and Diehl and Khetrapal (127).

One of the most spectacular and significant of the recent investigations in liquid crystals is that of the observation of the Mossbauer effect in these phases. Uhrich et al. (128) for the first time studied this effect in Sc texture. Schenck (129), for the first time, determined the viscosity of liquid crystals and found that the viscosity of the mesophase falls off with increasing temperature, but at temperature close to mesomorphic - isotropic transition there was, in each case, a sudden break in the viscosity versus temperature curve. Several workers have also studied about surface tension (130 - 134) and dielectric constant measurements (135 - 138) of liquid crystals.

Calorimetry is a valuable method for the detection of phase transitions. Calorimetric measurements have been made using adiabetic calorimetry, differential scanning calorimetry (DSC) and differential thermal analysis (DTA). It yields quantitative results and therefore, conclusions may be drawn concerning the nature of the phases which participate in the transitions.

The most significant thermodynamic studies have been reported in an important series of papers by Arnold and coworker (139 - 142). They use the method of adiabetic calorimetric measurements for the determination of heat capacities and latent heats. Calorimetric measurements using DTA and DSC methods have been reported by Barrall et al. (143) and by Ennulat (144).

The use of liquid crystals as stationary phase in glc is a promising technique. Kelker and Von Schivizhoffen (145) have reviewed the literature on this particular subject. Dewar and Schroeder (146) could separate position isomers by using liquid crystals as stationary phase in glc.

In general, a number of books and reviews have discussed the physical properties of mesogens and their uses in different fields (147 - 151).

11. Applications of Liquid Crystals

Characteristic optical and physical properties of liquid crystals such as reflection, birefringence, circular dichroism, optical rotation and colour, temperature, pressure, presence of an electric or magnetic field or the presence of chemical vapours make the various practical uses of liquid crystals easy. Recently nematic and nematic - cholesteric mixtures of substances have stimulated progress in electronic research and industry.

Thermotropic measurement of human skin (152 - 154) using liquid crystals is helpful in early diagnosis of symptoms in gynaecology, etc. A cholesteric liquid crystal is used for the rapid detection of fever especially by oral temperature measurements. Cholesteric liquid crystals can be used for the non-destructive testing of materials in many ways (77, 154, 155) e.g. to reveal blockage in heat conducting systems. As cholesteric liquid crystals react to pressure as well as temperature by colour changes, they can be used to make temperature or pressure sensitive publicity materials and toys.

They are now common as the essential materials in many electrically controlled display devices. The numerical displays on wristwatches, pocket calculators, thermometers, games, clocks etc. and many other electrical and electronic devices depend on them. They are also on the verge of finding more uses in forming television pictures, as displays for telephones and on automobile dashboards.

Liquid crystals are used as diagnostic tool to detect carcinoma of the breast, locate the placenta of a fetus, diagnose pulmonary disease and detect carcinoma in the skin. All of these tests utilize cholesteric liquid crystals where reflected colour changes with temperature.

Materials made from liquid crystals polymer melts or solution are exceptionally strong. One such material is Du Pont's Kevlar aramid fiber. In addition, graphitic fibers which are discotic liquid crystals, are very strong and lightweight. Kevlar is used in the manufacture of many textile articles from tarpaulins to bulletproof vests because of its strength.

In addition liquid crystals are solvents for many organic compounds, which makes them useful as column packing in chromatography, for studies of reaction kinetics and in spectroscopy.

Effect of a liquid crystal matrix on the photolysis and dimerization of 2-nitroso-2-methylpropane (156) has been investigated.

A large volume of published materials is available on the applications of liquid crystals mostly in the form of patents and reviews (148, 157-159).

THEME OF THIS INVESTIGATION

Very few mesomorphic heterocyclic homologous series have been studied. Therefore, it necessitates to study more heterocyclic compounds to understand the correlation between mesomorphic properties and molecular structure of heterocyclic compounds. This helps to understand the effect of hetero atom and/or effect of heterocyclic ring, compared to carbocyclic aromatic analogs, on mesomorphism. The study of thermal stability of heterocyclic compounds is quite interesting as it includes the significance of some additional parameters such as permanent dipole due to heteroatom, electronagativity of the hetero atom etc.

With this view two homologous series containing coumarin nucleus and one series containing pyridine nucleus have been synthesized and mesomorphic properties of their members studied. The thermal stabilities of various mesophases and the appearance of the smectic phase in these series are compared with those of the other related series. The trends of the different transition curves in these series are also discussed.

The study of the effect of chemical constitution on mesogenic properties have revealed that the introduction of a lateral substituent decreases both crystal-mesomorphic and mesomorphic-isotropic transition temperatures. Keeping this in view three homologous series possessing bulky ethoxy group as a lateral substituent are synthesized and their mesomorphic properties are studied. It was expected that compounds with bulky lateral ethoxy group would exhibit low melting mesophases.

Also, the study of three binary systems has been undertaken with a view to obtaining low melting liquid crystalline mixtures as well as to observe the behaviour of components of mixtures in the admixed state.

EXPERIMENTAL

I. Synthesis of New Homologous Series

The newly synthesized mesomorphic homologous series can be broadly classfied into three distinct categories :

(i) Mesomorphic Heterocyclic Homologous Series

A1. 7-(4'-n-Alkoxybenzoyloxy)-3-phenylcoumarins

B1. 4'-Cyanophenyl 7-n-alkoxycoumarin-3-carboxylates.

C1. 2-Methyl-5-(4'-n-alkoxycinnamoyloxy)pyridines.

(ii) Mesomorphic Non-heterocyclic Homologous Series

E1. 4'-Formylphenyl 6-n-alkoxynaphthalene-2-carboxylates

F1. 6-(4'-n-Alkoxybenzoyloxy)-2-acetylnaphthalenes.

G1. 4-(4'-n-Alkoxycinnamoyloxy)toluenes.

(iii) Laterally Substituted Mesogens

H1. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-anisidines.

J1. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-toludines.

K1. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-2"-4"-dimethylanilines.

In addition, the following non-mesomorphic series was also synthesized.

I. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzaldehydes

Various steps for the synthesis of the above series are described below :

(1) 2,4-Dihydroxybenzaldehyde

Resorcinol (22 g., 0.2 mol) was dissolved in dry dimethyl formamide (16 ml) and phosphorousoxychloride (15 ml) was added dropwise, with continuous stirring and cooling the mixture externally with ice. The reaction mixture was left at room temperature for two hours. 50% sodium acetate solution (150 ml) was added to it and then heated gently to obtain clear solution. It was then extracted with ether, ethereal layer dried over sodium sulphate and allowed to evaporate. The residue was washed with water to remove unreacted resorcinol and crystallized from water to obtain colourless needles. (m.p. 135°C, reported 134°C) (160).

2. 7-Acetoxy-3-phenylcoumarin

2,4-Dihydroxybenzaldehyde (16 g), $Ph.CH_2COONa$ (25 g) and acetic anhydride (60 ml) were refluxed for 6 hr. The reaction mixture was allowed to cool and then poured onto water with stirring. The colourless product obtained was crystallized from dioxan (m.p. 182-0°C, reported 182.4°C) (161).

3. 7-Hydroxy-3-phenylcoumarin

7-Acetoxy-3-phenylcoumarin (5 g) was added in a portion to the ice-cold concentrated sulphuric acid (75 ml) with constant stirring. The reaction mixture, then, was poured into ice-containing water. The product was filtered and dissolved in 10% sodium hydroxide. The alkali solution was filtered and acidified with concentrated hydrochloric acid to afford colourless product which was crystallized from methanol.

Dey, B.B. et al. (161) prepared this compound by hydrolysing 7-acetoxy-3-phenylcoumarin with 20% KOH. (m.p. 215°C, reported 215 - 218°C).

4. 4-n-Alkoxybenzoic acids

4-Methoxybenzoic acid used was of BDH quality while the other members were prepared.

4-Hydroxybenzoic acid (0.1 mol), n-alkyl bromide or iodide (0.12 mol) and potassium hydroxide (0.23 mol) were dissolved in methanol (100 ml) and refluxed for 4 hours. 10% aqueous potassium hydroxide solution (20 ml) was added and refluxing was continued for further 2 hours to hydrolyse any ester formed. The reaction mixture was added to ice-cold dilute hydrochloric acid. The product was washed with water, crystallized from ethanol or acetic acid till they exhibited constant melting points and transition temperatures as given in Table 2. They compare quite well with those given in literature (162).

5. 7-(4'-n-Alkoxybenzoyloxy)-3-phenylcoumarins

4-n-Alkoxybenzoic acids were treated with excess of thionyl chloride and 4-n-alkoxybenzoic acid chlorides thus prepared were treated with equimolar proportions of 7-hydroxy-3-phenylcoumarin (0.005 mol) in dry pyridine and heated on water-bath for 2 hours and left overnight. The reaction mixture was then added to ice cold dilute hydrochloric acid. The product was washed with water, then with dilute sodium hydroxide (10%) and again with water. The compounds were crystallized from ethanol or ethanol - benzene mixture. Yields were approximately 60% - 70%. The analytical data for the compounds are given in Table 3.

Table 2

4-n-Alkoxybenzoic acids

n-alkyl group	Transition Temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	-	184.0
Ethyl	-	-	197.0
Propyl	-	146.0	156.0
Butyl	-	147.0	160.0
Pentyl	-	124.0	151.0
Hexyl	-	105.0	153.0
Heptyl	92.0	98.0	145.0
Octyl	100.0	107.5	146.0
Nonyl	94.0	117.0	144.0
Decyl	97.0	121.5	146.5
Dodecyl	95.0	129.0	137.0
Tetradecyl	93.0	134.5	136.0
Hexadecyl	84.0	-	131.5
Octadecyl	101.5	-	131.0

Table 3

7-(4'-n-Alkoxybenzoyloxy)-3-phenylcoumarins

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{23}H_{16}O_5$	74.20	4.30	73.74	4.37
Ethyl	$C_{24}H_{18}O_5$	74.61	4.66	74.19	4.64
Propyl	$C_{25}H_{20}O_5$	75.00	5.00	75.43	4.86
Butyl	$C_{26}H_{22}O_5$	75.37	5.31	75.30	5.18
Pentyl	$C_{27}H_{24}O_5$	75.70	5.60	75.32	5.20
Hexyl	$C_{28}H_{26}O_5$	76.02	5.88	75.63	5.65
Heptyl	$C_{29}H_{28}O_5$	76.32	6.14	75.88	6.55
Octyl	$C_{30}H_{30}O_5$	76.58	6.38	76.37	6.15
Nonyl	$C_{31}H_{32}O_5$	76.86	6.61	76.43	6.24
Decyl	$C_{32}H_{34}O_5$	77.11	6.88	76.68	6.99
Dodecyl	$C_{34}H_{38}O_5$	77.57	7.22	77.09	7.32
Tetradecyl	$C_{36}H_{42}O_5$	77.98	7.58	77.87	7.48
Hexadecyl	$C_{38}H_{46}O_5$	78.36	7.90	77.90	7.65
Octadecyl	$C_{40}H_{50}O_5$	78.68	8.19	78.27	8.03

6. Ethyl 7-hydroxycoumarin-3-carboxylate

2,4-Dihydroxybenzaldehyde (0.1 mol), diethyl malonate (0.1 mol), dry pyridine (15 ml) and a few drops of piperidine were mixed and left overnight. The reaction mixture was decomposed by dilute hydrochloric acid. The product was washed with H_2O and crystallized from ethanol (m.p. 170°C, reported 171°C) (163).

7. Ethyl 7-n-alkoxycoumarin-3-carboxylates

Ethyl 7-hydroxycoumarin-3-carboxylate (0.01 mol) n-alkyl bromide or iodide (0.012 mol), anhydrous potassium carbonate (0.07 mol) and dry dimethyl formamide (15 ml) were mixed and heated on steambath for 20 hrs. The reaction mixture was decomposed on crushed ice. The product was washed with dilute sodium hydroxide followed by water and crystallized from ethanol or acetic acid till they exhibited constant melting points as given in Table 4. They compare quite well with those given in literature. (164).

Table 4

Ethyl 7-n-alkoxycoumarin-3-carboxylates

n-Alkyl group	K-I temperature (°C)
Methyl	134.0
Ethyl	118.0
Propyl	89.0
Butyl	119.0
Pentyl	92.0
Hexyl	145.0
Heptyl	144.0
Octyl	138.5
Nonyl	136.5
Decyl	134.0
Dodecyl	132.5
Tetradecyl	129.0
Hexadecyl	128.5

8. 7-n-Alkoxycoumarin-3-carboxylic acids

Ethyl 7-n-alkoxycoumarin-3-carboxylates (0.01 mol) was dissolved in 10% alcoholic potassium hydroxide (40 ml) and left overnight. The reaction mixture was decomposed by ice-cold dilute hydrochloric acid. The product was washed with water and crystallized from ethanol or acetic acid, till they exhibited constant melting point as given in Table 5. They compare quite well with those given in literature (164).

Table 5

7-n-Alkoxycoumarin-3-carboxylic acids

n-Alkyl group	K-I temperature (°C)
Methyl	195.0
Ethyl	215.5
Propyl	199.5
Butyl	163.0
Pentyl	150.0
Hexyl	146.5
Heptyl	145.0
Octyl	139.0
Nonyl	138.0
Decyl	135.0
Dodecyl	133.5
Tetradecyl	132.0
Hexadecyl	130.0

9. 4'-Cyanophenyl 7-n-alkoxycoumarin-3-carboxylates

7-n-Alkoxycoumarin-3-carboxylic acids were treated with excess of thionyl chloride and 7-n-alkoxycoumarin-3-carboxylic acid chlorides thus prepared were treated with equimolar proportions of 4-cyanophenol (0.005 mol) in dry pyridine and heated on water bath for 2 hours and left overnight. The reaction mixture was then added to ice-cold dilute hydrochloric acid. The product was washed with water, then with dilute sodium hydroxide and again with water. The compounds were crystallized from benzene. Yield were approximately 50% - 60%. The analytical data for the compounds are given in Table - 6.

10. 4-n-Alkoxybenzaldehydes

Preparation of 4-n-alkoxybenzaldehydes has been variously described by Hildesheimer (165), Stoermer and Wodarg (166), Weygard and Gabler, (167) Gray and Jones (168). In this investigation, however, the following procedure has been adopted with better results. The first member viz. 4-methoxy benzaldehyde used was of BDH grade and purified.

Table 6

4'-Cyanophenyl 7-n-alkoxycoumarin-3-carboxylates

n-Alkyl group	Molecular formula	% Required			% Found		
		C	H	N	C	H	N
Methyl	$C_{18}H_{11}O_5N$	67.30	3.42	4.36	67.39	3.71	4.79
Ethyl	$C_{19}H_{13}O_5N$	68.06	3.88	4.17	67.74	4.02	4.50
Propyl	$C_{20}H_{15}O_5N$	68.77	4.29	4.01	68.39	4.41	4.41
Butyl	$C_{21}H_{17}O_5N$	69.42	4.68	3.85	69.91	5.07	3.86
Pentyl	$C_{22}H_{19}O_5N$	70.03	5.04	3.71	69.93	5.12	3.73
Hexyl	$C_{23}H_{21}O_5N$	70.58	5.37	3.58	70.19	5.17	3.62
Heptyl	$C_{24}H_{23}O_5N$	71.11	5.67	3.45	71.32	5.58	3.14
Octyl	$C_{25}H_{25}O_5N$	71.60	5.96	3.34	71.20	6.06	3.76
Nonyl	$C_{26}H_{27}O_5N$	72.06	6.23	3.23	72.09	6.62	3.49
Decyl	$C_{27}H_{29}O_5N$	72.78	6.48	3.13	72.30	6.21	3.13
Dodecyl	$C_{29}H_{33}O_5N$	73.26	6.94	2.94	73.52	6.85	2.95
Tetradecyl	$C_{31}H_{37}O_5N$	73.94	7.35	2.78	73.98	6.96	2.35
Hexadecyl	$C_{33}H_{41}O_5N$	74.57	7.74	2.63	74.11	7.42	3.09

0.1 Mole of 4-hydroxybenzaldehyde, 0.15 mole of anhydrous potassium carbonate and 0.15 mole of the corresponding n-alkyl bromide or iodide were added to dry acetone (60 ml). The mixture was refluxed in water-bath for three to four hours. In the case of higher members the refluxing period was extended upto six to eight hours. The whole mass was added to water and aldehyde thus separated was extracted with ether. Ether extract was washed with dilute sodium hydroxide to remove any unreacted 4-hydroxy benzaldehyde followed by water and dried. Ether was evaporated and the 4-n-alkoxybenzaldehydes thus obtained were purified by distilling under reduced pressure. Boiling points almost agreed with those reported in literature (169).

11. trans-4-n-Alkoxycinnamic acids

The appropriate 4-n-alkoxybenzaldehyde (0.02 mole), malonic acid (3.2 g, 0.04 mole), pyridine (8.0 ml) and piperidine (three drops) were mixed and heated at 100°C on a steam bath for three to four hours. In the higher members the refluxing period was extended to five to six hours. The mixture was poured in ice (25 g) containing concentrated hydrochloric acid (25 ml). The products were filtered and washed with dilute hydrochloric acid followed by water. The compound were crystallized from acetic acid. Higher homologues were crystallized twice from benzene and then from acetic acid till constant transition temperatures were obtained as given in Table 7 (168).

Table 7

Trans 4-n-alkoxycinnamic acids

n-alkyl group	Transition Temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	174.0	190.0
Ethyl	-	194.0	200.0
Propyl	-	169.0	184.0
Butyl	-	156.0	189.0
Pentyl	-	144.0	180.0
Hexyl	-	152.0	180.0
Heptyl	-	148.0	175.0
Octyl	-	145.0	172.0
Decyl	136.0	150.0	169.0
Dodecyl	132.0	157.0	164.0
Tetradecyl	127.0	-	160.0
Hexadecyl	118.0	-	159.0
Octadecyl	120.0	-	157.5

12. 2-Methyl-5-(4'-n-alkoxycinnamoyloxy)pyridines

Trans 4-n-alkoxycinnamic acids were treated with excess of thionyl chloride and 4-n-alkoxycinnamic acid chlorides (0.005 mol) thus prepared were treated with 3-hydroxy-6-methylpyridine (Aldrich Chemicals, U.S.A.) (0.005 mol) in dry pyridine (5-7 ml), was heated on a water bath for an hour and left overnight. The reaction mixture was then added to water. The products were filtered and washed with dilute sodium hydroxide followed by water. The compounds were purified by chromatography followed by crystallization from petroleum ether (Yield 40% - 45%). The analytical data for the compounds are given in Table - 8.

13. 6-Acetyl-2-methoxynaphthalene

Anhydrous aluminium chloride (20 g, 0.15 mol) was dissolved in dry nitrobenzene (100 ml) and acetyl chloride (12 g, 0.1 mol) was added to it. The mixture was cooled in ice and a solution of 2-methoxynaphthalene (19 g.) (170) in dry nitrobenzene (20 ml) was gradually added with stirring. The reaction mixture was then stirred for 2 hr. at about 10°C. The mixture is then allowed to stand for at least 12 hrs.

The reaction mixture was then poured into 600 ml water containing ice and 100 ml concentrated HCl. The nitrobenzene layer was washed with water and then steam-distilled to remove nitrobenzene. The residue was

Table 8

2-Methyl-5-(4'- n-alkoxycinnamoyloxy) pyridines

n-Alkyl group	Molecular formula	% Required			% Found		
		C	H	N	C	H	N
Methyl	$C_{16}H_{15}O_3N$	71.37	5.57	5.20	71.80	5.70	4.81
Ethyl	$C_{17}H_{17}O_3N$	72.07	6.00	4.94	72.52	6.08	4.76
Propyl	$C_{18}H_{19}O_3N$	72.73	6.39	4.71	73.18	5.95	4.46
Butyl	$C_{19}H_{21}O_3N$	73.30	6.75	4.50	73.28	6.79	4.12
Pentyl	$C_{20}H_{23}O_3N$	73.84	7.07	4.30	73.36	7.44	4.10
Hexyl	$C_{21}H_{25}O_3N$	74.33	7.37	4.13	74.50	7.45	3.77
Heptyl	$C_{22}H_{27}O_3N$	74.78	7.64	3.96	75.23	7.45	3.75
Octyl	$C_{23}H_{29}O_3N$	75.20	7.90	3.81	75.65	8.01	3.80
Nonyl	$C_{24}H_{31}O_3N$	75.60	8.13	3.67	75.68	7.71	3.42
Decyl	$C_{25}H_{33}O_3N$	75.95	8.35	3.54	75.63	8.14	4.00
Dodecyl	$C_{27}H_{37}O_3N$	76.60	8.74	3.31	76.28	8.48	3.29
Tetradecyl	$C_{29}H_{41}O_3N$	77.16	9.08	3.10	77.62	8.82	3.12
Hexadecyl	$C_{31}H_{45}O_3N$	77.66	9.39	2.92	77.57	9.43	2.89
Octadecyl	$C_{33}H_{49}O_3N$	78.11	9.66	2.76	78.05	9.30	2.61

extracted with $CHCl_3$, the chloroform layer dried over $MgSO_4$, chloroform was distilled off and residue was subjected to vacuum distillation. The yellow distillate is recrystallised from methanol. (m.p. 106°C, reported 106.5° - 108°C) (171).

14. 6-Methoxy-2-naphthoic acid

A solution of sodium hypobromite was prepared from sodium hydroxide (14.0 g), water (60 ml) and bromine (5 ml) at 0-5°C. It was added dropwise to a stirred solution of 6-acetyl-2-methoxynaphthalene (5.0 g) in dioxan (35.0 ml) during half an hour. During the addition of the hypobromite solution the temperature was kept at 35 - 40°C. The temperature was later raised to 50 - 60°C to ensure complete oxidation. Excess of hypobromite was removed by adding sodium dithionite till the colour of bromine disappeared. The mixture was diluted with water (2 : 1) and then boiled gently to remove the bromoform formed and the dioxan. The hot alkaline solution was filtered and acidified with concentrated hydrochloric acid to give pale yellow 6-methoxy-2-naphthoic acid. The product was crystallized from acetic acid and then from xylene to give pure 6-methoxy-2-naphthoic acid. Yield 70%. m.p. (206 N 219 I) (87).

15. 6-Hydroxy-2-naphthoic acid

The 6-methoxy-2-naphthoic acid (8.4 g) was heated for two and half hours with acetic acid (50 ml) and 48% hydrobromic acid solution (35 ml). The dark brown solution was then cooled and the light brown crystals obtained were washed with water and crystallized from dilute acetic acid to pale tan needles yield 65%, m.p. 249°C (87).

16. 6-n-Alkoxy-2-naphthoic acids

The 6-hydroxy-2-naphthoic acid (0.01 mol), n-alkyl halide (0.012 mol) and potassium hydroxide (0.02 mol) were dissolved in ethanol (80 ml) and refluxed for eight hours. 10% Aqueous potassium hydroxide solution (20 ml) was added and refluxing continued for two hours to hydrolyse any ester formed. The solution was cooled and acidified with hydrochloric acid to precipitate the acids. The alkoxy acids were crystallized from ethanol till they gave constant melting points and transition temperatures as given in Table 9. They agree well with those reported. Yield about 70% (87).

17. 4'-Formylphenyl 6-n-alkoxynaphthalene-2-carboxylates

6-n-Alkoxy-2-naphthoic acids were treated with excess of thionyl chloride and 6-n-alkoxy-2-naphthoic acid

Table 9

6-n-Alkoxy-2-naphthoic acids

n-Alkyl group	Transition Temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	206.0	219.0
Ethyl	-	213.0	224.0
Propyl	-	208.0	208.5
Butyl	-	198.0	208.5
Pentyl	-	179.5	199.0
Hexyl	-	147.0	198.5
Heptyl	-	163.0	192.0
Octyl	-	161.5	190.0
Nonyl	140.0	147.5	183.5
Decyl	139.0	147.0	181.0
Dodecyl	119.0	158.5	174.0
Hexadecyl	107.0	-	160.5
Octadecyl	114.0	-	159.0

chlorides thus prepared were treated with equimolar proportions of 4-hydroxy benzaldehyde (0.005 mol) in dry pyridine and heated on water-bath for two hours and left overnight. The reaction mixture was then added to ice-cold dilute hydrochloric acid. The product was washed with water, than with dilute sodium hydroxide and again with water. The compounds were crystallized from petroleum-ether. Yields were approximately 50% - 60%. The analytical data for the compounds are recorded in Table - 10.

18. 6-Hydroxy-2-acetylnaphthalene

A mixture of 5.0 g, 6-acetyl derivative of 2-methoxy naphthalene, 35 ml 70% acetic acid and 15 ml 48% hydrobromic acid was refluxed 4 hrs., It was, then, added to 350 ml ice-water, filtered and the solid extracted with 5% NaOH. The extract was acidified and the solid recrystallized from benzene to give 50% 6-hydroxy-2-acetylnaphthalene (m.p. 172-0°C, reported 173.4°C) (172).

19. 6-(4'-n-Alkoxybenzoyloxy)-2-acetylnaphthalenes

4-n-Alkoxybenzoic acids were treated with excess of thionyl chloride and 4-n-alkoxybenzoic acid chlorides thus prepared were treated with equimolar proportions of 6-hydroxy-2-acetylnaphthalene (0.005 mol) in dry

Table 10

4'-formylphenyl 6-n-alkoxynaphthalene-2-carboxylates

n-Alkyl group	Molecular formula	% Required C	% Required H	% Found C	% Found H
Methyl	$C_{19}H_{14}O_4$	74.50	3.98	74.09	4.46
Ethyl	$C_{20}H_{16}O_4$	75.01	5.00	74.66	4.96
Propyl	$C_{21}H_{18}O_4$	75.46	5.39	75.54	5.74
Butyl	$C_{22}H_{20}O_4$	75.86	5.74	76.12	5.59
Pentyl	$C_{23}H_{22}O_4$	76.25	6.07	75.83	6.10
Hexyl	$C_{24}H_{24}O_4$	76.60	6.38	76.18	6.34
Heptyl	$C_{25}H_{26}O_4$	76.91	6.66	76.68	6.24
Octyl	$C_{26}H_{28}O_4$	77.23	6.93	76.78	6.62
Nonyl	$C_{27}H_{30}O_4$	77.50	7.17	77.04	7.12
Decyl	$C_{28}H_{32}O_4$	77.76	7.40	77.36	7.31
Dodecyl	$C_{36}H_{36}O_4$	78.26	7.82	78.25	7.59
Tetradecyl	$C_{32}H_{40}O_4$	78.68	8.19	78.23	7.99
Hexadecyl	$C_{34}H_{44}O_4$	79.11	8.52	78.70	8.12
Octadecyl	$C_{36}H_{48}O_4$	79.41	8.82	78.97	8.34

pyridine and heated on waterbath for 2 hours and left overnight. The reaction mixture was then added to ice-cold dilute hydrochloric acid. The product was washed with water, then with dilute sodium hydroxide and again with water. The compounds were purified by chromatography followed by crystallization from ethanol. Yields were approximately 40% - 45%. The analytical data for the compounds are given in Table - 11.

20. 4-(4'-n-Alkoxycinnamoyloxy) toluenes

4-n-Alkoxycinnamic acids were treated with excess of thionyl chloride and 4-n-alkoxy cinnamic acid chlorides thus prepared were treated with equimolar proportions of p-cresol (0.005 mol). The reaction mixture was heated on water-bath for 30 min. The reaction mixture was left overnight and then decomposed on water, filtered and washed with 10% NaOH followed by water. The compounds were crystallized from ethanol. Yields 80% - 85%. The analytical data for the compounds are given in Table - 12.

21. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzaldehydes

A solution of equimolar amounts of 4-n-alkoxycinnamoyl chloride (0.01 mol) and 3-ethoxy-4-hydroxybenzaldehyde (0.01 mol) in dry pyridine (5-7 ml) was heated on a water-bath for 2 hours and left overnight. The reaction mixture

Table 11

6-(4'-n-Alkoxybenzoyloxy)-2-acetylnaphthalenes

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{20}H_{16}O_4$	75.01	5.00	74.94	4.64
Ethyl	$C_{21}H_{18}O_4$	75.44	5.38	75.08	5.21
Propyl	$C_{22}H_{20}O_4$	75.86	5.74	75.42	5.30
Butyl	$C_{23}H_{22}O_4$	76.25	6.07	75.80	5.84
Pentyl	$C_{24}H_{24}O_4$	76.60	6.38	76.23	5.94
Hexyl	$C_{25}H_{26}O_4$	76.91	6.66	76.55	6.40
Heptyl	$C_{26}H_{28}O_4$	77.22	6.93	76.88	6.67
Octyl	$C_{27}H_{30}O_4$	77.50	7.17	77.03	7.28
Nonyl	$C_{28}H_{32}O_4$	77.80	7.40	78.24	7.51
Decyl	$C_{29}H_{34}O_4$	78.03	7.62	77.59	7.47
Dodecyl	$C_{31}H_{38}O_4$	78.47	8.08	78.04	8.01
Tetradecyl	$C_{33}H_{42}O_4$	78.89	8.36	78.42	7.88
Hexadecyl	$C_{35}H_{46}O_4$	79.23	8.68	78.75	8.21
Octadecyl	$C_{37}H_{50}O_4$	79.58	8.96	79.14	8.48

Table 12

4-(4'-n-Alkoxycinnamoyloxy) toluenes

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{17}H_{16}O_3$	76.12	5.97	76.49	6.04
Ethyl	$C_{18}H_{18}O_3$	76.61	6.39	77.00	6.53
Propyl	$C_{19}H_{20}O_3$	77.02	6.75	77.07	6.83
Butyl	$C_{20}H_{22}O_3$	77.41	7.09	77.69	7.31
Pentyl	$C_{21}H_{24}O_3$	77.78	7.40	78.20	7.10
Hexyl	$C_{22}H_{26}O_3$	77.94	7.68	78.40	8.02
Heptyl	$C_{23}H_{28}O_3$	78.41	7.95	78.82	7.75
Octyl	$C_{24}H_{30}O_3$	78.68	8.19	79.02	8.64
Nonyl	$C_{25}H_{32}O_3$	78.94	8.42	79.32	8.59
Decyl	$C_{26}H_{34}O_3$	79.20	8.63	79.57	8.43
Dodecyl	$C_{28}H_{38}O_3$	79.62	9.00	80.04	9.10
Tetradecyl	$C_{30}H_{42}O_3$	80.00	9.33	80.28	9.27
Hexadecyl	$C_{32}H_{46}O_3$	80.34	9.62	80.11	9.59
Octadecyl	$C_{34}H_{50}O_3$	80.63	9.88	80.41	9.87

was added to ice-cold dilute hydrochloric acid. The products were filtered, washed with water and then dilute sodium hydroxide followed by water. The compounds were purified by chromatography followed by crystallization from petroleum ether. Yields were 60% - 70% The analytical data are given in Table - 13.

22. General method adopted to synthesize the Schiff bases

Equimolar proportions of a proper aldehyde and the corresponding amine were dissolved in ethanol, refluxed for one hour, allowed to cool and the product separated was coolected by filteration. The Schiff bases were crystallized from ethanol or ethanol benzene (1 : 1) mixture. The analytical data for the Schiff bases are given in Tables 14, 15 and 16.

II. Study of Transition Temperatures

The study of the mesomorphic characteristics was carried out by polarizing microscope method. The microscope used in this investigation was a Leitz Ortholux II polarizing microscope equipped with a Leitz heating stage.

Slides of the compounds were prepared by three different methods : (a) In the first method, the substance

Table 13

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzaldehydes

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{19}H_{18}O_5$	69.93	5.52	70.33	5.94
Ethyl	$C_{20}H_{20}O_5$	70.58	5.88	70.17	5.78
Propyl	$C_{21}H_{22}O_5$	71.19	6.22	71.64	6.10
Butyl	$C_{22}H_{24}O_5$	71.74	6.52	71.43	6.64
Pentyl	$C_{23}H_{26}O_5$	72.24	6.80	71.79	6.68
Hexyl	$C_{24}H_{28}O_5$	72.73	7.07	72.31	6.70
Heptyl	$C_{25}H_{30}O_5$	73.16	7.31	73.60	7.15
Octyl	$C_{26}H_{32}O_5$	73.58	7.54	74.00	7.51
Nonyl	$C_{27}H_{34}O_5$	73.96	7.76	74.40	8.19
Decyl	$C_{28}H_{36}O_5$	74.33	7.96	73.94	8.02
Dodecyl	$C_{30}H_{40}O_5$	75.01	8.33	75.41	8.65
Tetradecyl	$C_{32}H_{44}O_5$	75.58	8.65	76.00	8.30
Hexadecyl	$C_{34}H_{48}O_5$	76.12	8.95	76.37	8.88
Octadecyl	$C_{36}H_{52}O_5$	76.60	9.21	76.38	8.88

Table 14

4-(4' -n-AlKoxycinnamoyloxy)-3-ethoxybenzylidene-4"-anisidines

n-Alkyl group	Molecular formula	% Required			% Found		
		C	H	N	C	H	N
Methyl	$C_{26}H_{25}O_5N$	72.40	5.79	3.29	71.99	5.96	3.68
Ethyl	$C_{27}H_{27}O_5N$	72.80	6.06	3.14	72.75	5.72	2.96
Propyl	$C_{28}H_{29}O_5N$	73.19	6.31	3.05	73.64	6.34	3.05
Butyl	$C_{29}H_{31}O_5N$	73.57	6.55	2.95	73.14	6.19	2.80
Pentyl	$C_{30}H_{33}O_5N$	73.92	6.77	2.87	74.27	7.15	2.47
Hexyl	$C_{31}H_{35}O_5N$	74.15	7.12	2.85	73.98	7.16	2.78
Heptyl	$C_{32}H_{37}O_5N$	74.56	7.18	2.71	74.52	6.89	3.07
Octyl	$C_{33}H_{39}O_5N$	74.85	7.37	2.64	74.84	7.28	3.08
Nonyl	$C_{34}H_{41}O_5N$	75.15	7.69	2.57	75.61	7.52	2.22
Decyl	$C_{35}H_{43}O_5N$	75.37	7.91	2.52	75.10	7.54	2.18
Dodecyl	$C_{37}H_{47}O_5N$	75.88	8.03	2.39	75.98	7.89	2.65
Tetradecyl	$C_{39}H_{51}O_5N$	76.33	8.32	2.28	76.15	8.23	2.05
Hexadecyl	$C_{41}H_{55}O_5N$	76.52	8.55	2.17	76.13	8.26	1.95
Octadecyl	$C_{43}H_{59}O_5N$	76.90	8.79	2.08	76.47	8.74	2.12

Table 15

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-toludines

n-Alkyl group	Molecular formula	% Required			% Found		
		C	H	N	C	H	N
Methyl	$C_{26}H_{25}O_4N$	75.19	6.02	3.37	75.13	6.31	3.68
Ethyl	$C_{27}H_{27}O_4N$	75.51	6.29	3.26	75.02	5.90	3.06
Propyl	$C_{28}H_{29}O_4N$	75.84	6.54	3.16	75.93	6.54	3.28
Butyl	$C_{29}H_{31}O_4N$	76.15	6.78	3.06	75.95	6.86	2.69
Pentyl	$C_{30}H_{33}O_4N$	76.43	7.00	2.97	76.35	7.41	3.35
Hexyl	$C_{31}H_{35}O_4N$	76.70	7.21	2.88	76.50	7.48	2.79
Heptyl	$C_{32}H_{37}O_4N$	76.95	7.41	2.80	77.41	7.50	2.51
Octyl	$C_{33}H_{39}O_4N$	77.20	7.60	2.72	76.75	7.16	2.30
Nonyl	$C_{34}H_{41}O_4N$	77.43	7.78	2.65	76.99	7.79	2.88
Decyl	$C_{35}H_{43}O_4N$	77.62	7.94	2.58	77.21	8.15	2.75
Dodecyl	$C_{37}H_{47}O_4N$	78.03	8.26	2.46	77.56	8.17	2.29
Tetradecyl	$C_{39}H_{51}O_4N$	78.38	8.54	2.34	78.27	8.06	1.91
Hexadecyl	$C_{41}H_{55}O_4N$	78.72	8.80	2.24	78.30	8.74	1.96

Table 16

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-2",4"-dimethylanilines

n-Alkyl group	Molecular formula	% Required			% Found		
		C	H	N	C	H	N
Methyl	$C_{27}H_{27}O_4N$	75.57	6.29	3.26	75.73	6.70	2.79
Ethyl	$C_{28}H_{29}O_4N$	75.84	6.54	3.16	75.41	6.52	2.73
Propyl	$C_{29}H_{31}O_4N$	76.16	6.76	3.06	75.80	6.40	3.33
Butyl	$C_{30}H_{33}O_4N$	76.43	7.00	2.97	76.33	6.88	2.76
Pentyl	$C_{31}H_{35}O_4N$	76.70	7.21	2.88	76.33	6.88	2.90
Hexyl	$C_{32}H_{37}O_4N$	76.95	7.41	2.80	76.78	7.58	2.39
Heptyl	$C_{33}H_{39}O_4N$	77.20	7.60	2.72	77.33	7.53	2.75
Octyl	$C_{34}H_{41}O_4N$	77.43	7.78	2.65	77.81	7.55	2.89
Nonyl	$C_{35}H_{43}O_4N$	77.62	7.94	2.58	77.67	7.50	2.76
Decyl	$C_{36}H_{45}O_4N$	77.84	8.10	2.52	78.30	8.12	2.56
Dodecyl	$C_{38}H_{49}O_4N$	78.21	8.40	2.40	77.79	8.28	2.74
Tetradecyl	$C_{40}H_{53}O_4N$	78.56	8.67	2.29	78.57	8.86	2.42
Hexadecyl	$C_{42}H_{57}O_4N$	78.96	8.92	2.19	78.55	8.82	2.35

was taken on a slides and heated to a little more than the mesomorphic temperature at which stage a cover slip was placed over it and then allowed to cool. (b) In the second method, the compound was heated upto the isotropic liquid point, then a coverslip was put over it and allowed to cool. (c) In the third method, the substance was first dissolved in a suitable solvent and then a few drops of the solution was placed on a slide and a cover slip was placed over it and the solvent was allowed to evaporate.

To determine the various transition a microscope slide carrying a thin section of the material with a coverslip on it was observed under the microscope. The slide was inserted into the specimen chamber of the heating stage and the temperature was raised fairly fast ($5^{o}C$/min) to find the approximate transition temperatures. The measurements were then repeated and near the transition to be observed the rate of heating was regulated to about $1^{o}C$ per minute.

Appearance of focal conic texture with disappearance of cleavage lines of solid structure on heating is taken as solid-smectic transition. In order to confirm this change, the slide was distrubed with the help of spatula, the disturbed smectic texture can be seen indicating that it is not solid and that the transition has actually taken place. Solid-nematic change is observed, on heating, with the appearance of threaded texture sharply at a definite temperature. All enantiotropic transitions are clearly detected on cooling their isotropic liquid, the reverse transitions take place sharply at the same temperature within ± 0.2 to 0.5°C. The isotropic-nematic change is marked by separation of small droplets from isotropic liquid, which coalesce to give rise to a threaded region, an unfailing characteristic of the nematic phase.

The isotropic-smectic transition is indicated by appearance of batonnets which coalesce to form fine mosaic of focal conic pattern. Smectic-nematic changes are also clearly detected with a sharp variation in the texture from focal conic to threaded texture and exactly reverse sequence takes place on cooling, alongwith a well defined wave-front in both the cases. The homeotropic texture can easily be identified by disturbing the cover slip in almost extinct field of vision and observing the spark of light. It was easy to detect homeotropic smectic to homeotropic nematic transition because at the transition the field becomes partially birefringent for a few moments and the change is accompanied with a wave-front.

Monotropic transitions were determined by carefully observing the isotropic liquid as it cools slowly untill batonnets of smectic phase or droplets of nematic phase appear.

All the compounds under study were observed continuously under polarizing microscope from their solid state to isotropic liquid conditions on heating and from isotropic liquid to solid state on cooling ensuring confirmation of all the transitions and making it sure that no transition escapes unnoticed.

The accuracy of the heating device was checked by taking melting points and/or transition points of the known compounds such as benzoic acid, succinic acid, anthracene, p-azoxyanisole, p-methoxycinnamic acid, ethyl p-azoxybenzoate etc.

III. Mixed Mesophases

For the mixed mesomorphic study the following substance which have been synthesized in this investigation have been used for preparing the binary systems. In all, three binary systems have been studied.

Binary System No. 1

4-(4'-n-Decyloxycinnamoyloxy) toluene

4-(4'-n-Tetradecyloxycinnamoyloxy) toluene

Binary System No. 2

4-(4'-n-Decyloxycinnamoyloxy) toluene

4-(4'-n-Nonyloxycinnamoyloxy)-3-ethoxybenzaldehyde

Binary System No. 3

4-(4'-n-Tetradecyloxycinnamoyloxy) toluene
p-Azoxyanisole

Preparation of binary mixtures.

Clean sample tubes were used for the preparation of binary mixtures. Both components of the binary sys mixtures were weighed accurately in known proportions in a tube. The total weight of the mixture taken is around 0.2 g. The mixture in the tube was now heated in an oil bath to a temperature slightly higher than that at which the mixture melted. At the melting condition, the mixture was stirred thoroughly with a glass rod in order to obtain homogeneity. The tube was then cooled by quenching it in a beaker containing ice-cold water. The mixture solidified almost instantly. The tube was then taken out and again heated and shaken and allowed to solidify in a similar manner. The mixture was now taken out from the tube and then ground to fine powder with the help of agate mortar and pastle. Thus mixtures of varying proportions were prepared and then studied under microscope.

A. Mesomorphic Heterocyclic Homologous Series

In order to obtain empirical rules correlating the molecular features with properties of the mesomorphic state, usually homologous series are studied. It has been observed that liquid crystalline properties change markedly with the change in molecular structure within a group of suitable compounds. Evidently, the synthesis and investigation of the physical properties of a new homologous series of liquid crystalline compounds are important in studying the relationship between the structure of molecules and the characteristics of the mesomorphic state.

Many workers have studied the influence of molecular structure on the thermal stability of nematic and smectic liquid crystals. A number of nematogenic and smectogenic compounds and homologous series of different molecular structure has been synthesized to study the effect of chemical constitution on the mesomorphism of these compounds. It has been found that the derivatives of benzene, naphthalene and biphenyl are mostly nematic. Mesomorphic compounds containing heterocyclic nuclei are interesting because of greater possibilities in the variations of direction and magnitude of their permanent dipole moment and in consequence of that in the variation of sign and magnitude of their dielectric anisotropy-though these compounds are not still numerous.

RESULTS AND DISCUSSION

Some work has been done in the synthesis of mesomorphic heterocyclic compounds ; these are the derivatives of pyridine (99, 173-179), quinoline (180) and diazines (181-186). Some workers have done a good deal of work on pyrimidine derivatives (187-193). Derivatives of pyridazine (194), pyridone (195), pyrone (196) dioxan (197), thiophene (198) and benzoxazole (199) have also been reported. Zaschke and Hyna (200) have studied the liquid crystalline state as a criterion in structure determination of derivatives of tautomerizable heterocyclic systems. Nguyen and Pham (201) have synthesized certain liquid crystalline N-furfurylidenaniline derivatives. Pavlyuchenko et al. (202) have synthesized liquid crystalline 6-alkoxynicotinic acids as well as a series of 2,6- and 2,5-disubstituted benzazoles. Also, they studied how molecular geometry, central linkages and a heteroatom affects the mesomorphic properties of the compounds. Pavlyuchenko et al. (203) have synthesized mesomorphic series of 4-substituted phenyl 5-alkoxypicolinates and 6-alkoxynicotinates. Quite recently furan derivatives have been prepared and the thermal stabilities of these derivatives were compared with the benzene derivatives (204).

Three homologous series have been synthesized and mesomorphic properties of their members studied to ascertain the effect of heterocyclic coumarin nucleus and pyridine ring on liquid crystal thermal stability and phase type. The transition temperatures are plotted as a function of the number of carbon atoms in the alkoxy chain in each homologous series to understand the effect of molecular structure on the liquid crystalline behaviour.

The heterocyclic series studied can be classified as :

I. Derivatives of coumarin

Series A1. 7-(4'-n-Alkoxybenzoyloxy)-3-phenylcoumarins

Series B1. 4'-Cyanophenyl 7-n-alkoxycoumarin-3-carboxylates.

II. Derivatives of Pyridine

Series C1. 2-Methyl-5-(4'-n-Alkoxycinnamoyloxy) pyridines

INDIVIDUAL CHARACTERISTICS

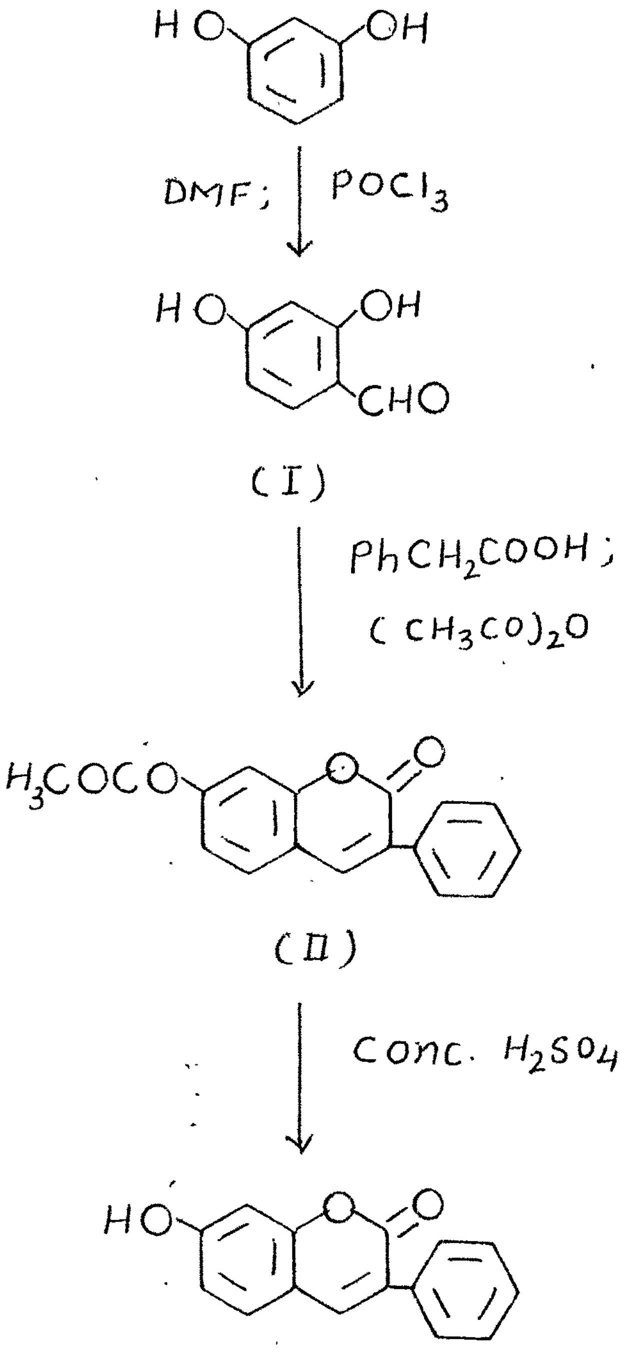
A1. 7-(4'-n-Alkoxybenzoyloxy)-3-phenylcoumarins

Recently, some ester series containing coumarin nucleus have been reported and their mesomorphic properties have been described (164, 205, 206).

A homologous series of fourteen esters in the present study was synthesized by the synthetic route shown in Scheme 1. Resorcinol was formylated using dimethyl formamide and phosphorus oxychloride at low temperature to yield compound (I), compound (I), when refluxed with phenyl acetic acid and acetic anhydride, gave compound (II) which on hydrolysis with concentrated sulphuric acid yielded compound (III). Alkylation of 4-hydroxybenzoic acid by different alkyl halides in presence of KOH and methanol yielded acids (IV) which on treatment with excess of thionyl chloride gave corresponding acid chlorides (V). The acid chlorides (V) on esterification by (III) in dry pyridine gave esters of series A1. The melting points and transition temperatures of the compounds are summarised in Table 17.

The first eight esters are enantiotropic nematic. The smectic phase commences at the nonyl derivative, the nonyl derivative is monotropic smectic and enantiotropic nematic while the decyl and dodecyl derivatives exhibit both smectic and nematic phases as enantiotropic phases. The remaining members show only enantiotropic smectic phase. The plots of transition temperatures against the number of carbon atoms in the alkoxy chain are shown in Fig. 1. The trend of the N-I transition temperature curves show a descending tendency. The S-N curve merges with the even number curbe of N-I transition. Also, S-I transition curve merges with that of N-I.

Scheme 1



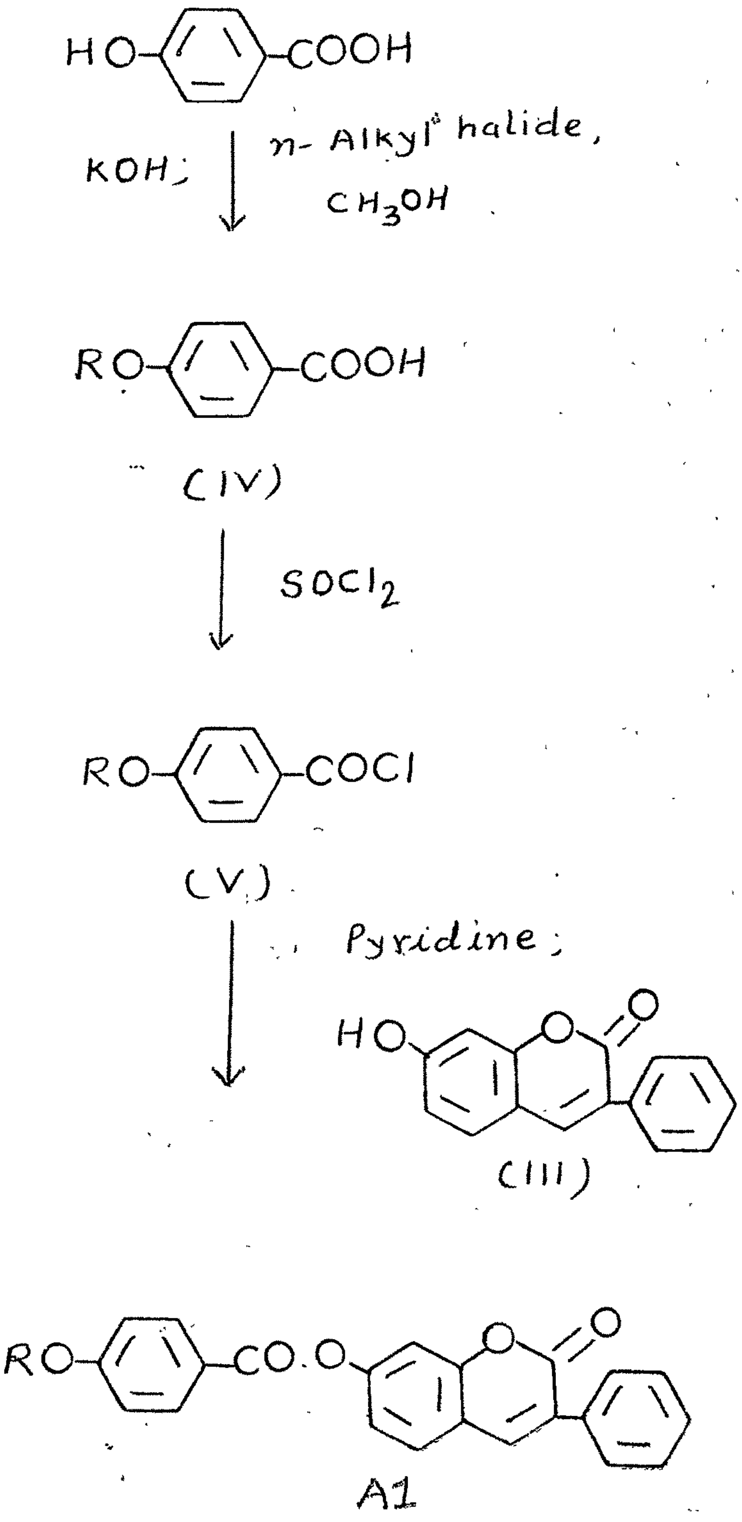
(I)

(II)

(III)

contd. ......

Scheme 1
contd. ....



R = n- alkyl group

Table 17

7-(4'-n-Alkoxybenzoyloxy)-3-phenylcoumarins

n-Alkyl group	Transition temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	199.5	207.5
Ethyl	-	201.0	208.0
Propyl	-	198.5	201.0
Butyl	-	192.0	199.0
Pentyl	-	179.5	189.0
Hexyl	-	161.0	184.0
Heptyl	-	151.5	178.5
Octyl	-	153.5	179.0
Nonyl	(146.0)	149.0	166.0
Decyl	151.5	159.0	176.0
Dodecyl	152.0	168.0	173.0
Tetradecyl	142.5	-	168.0
Hexadecyl	141.0	-	167.5
Octadecyl	139.5	-	168.5

Values in parentheses indicate monotropy

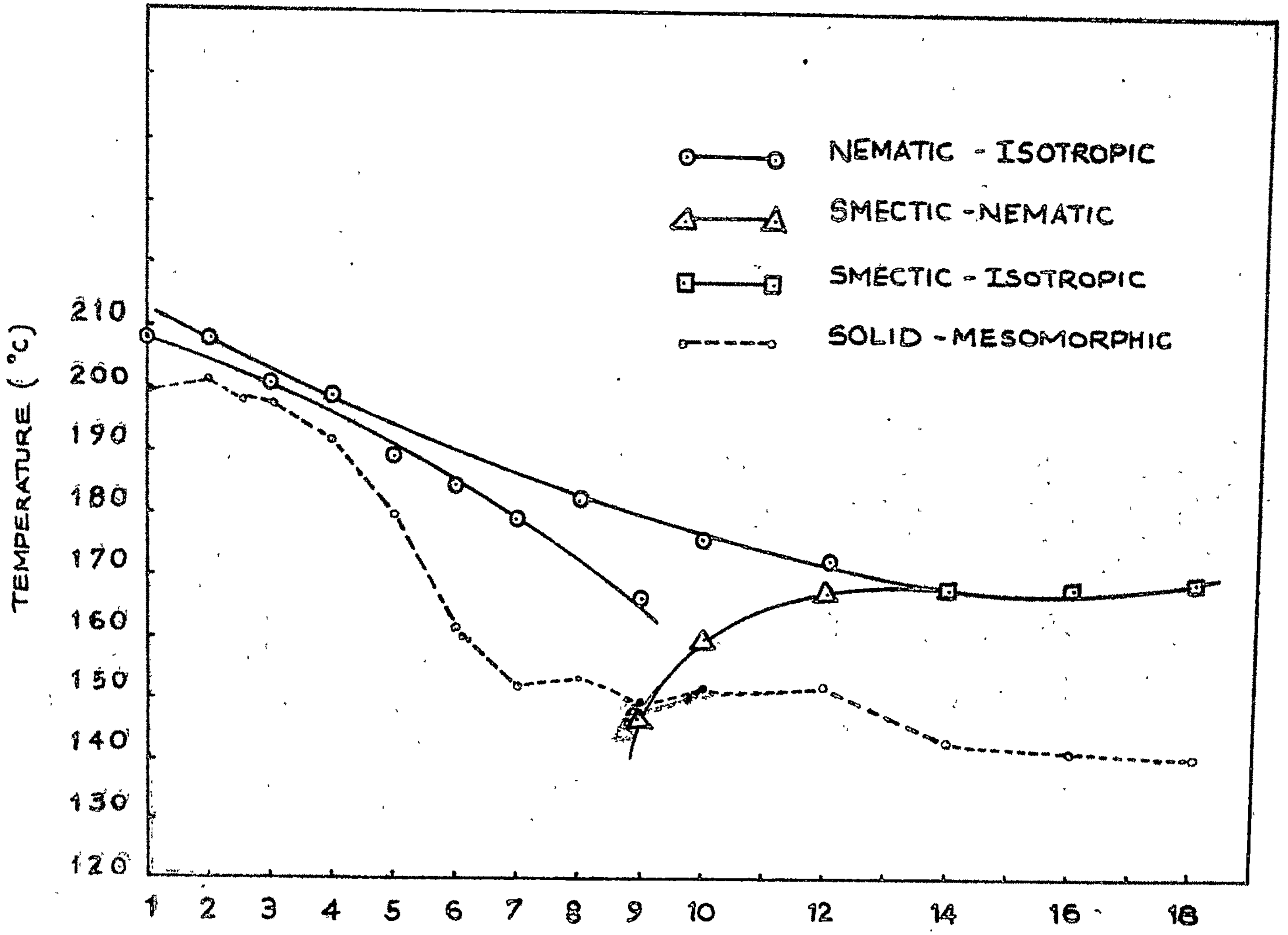


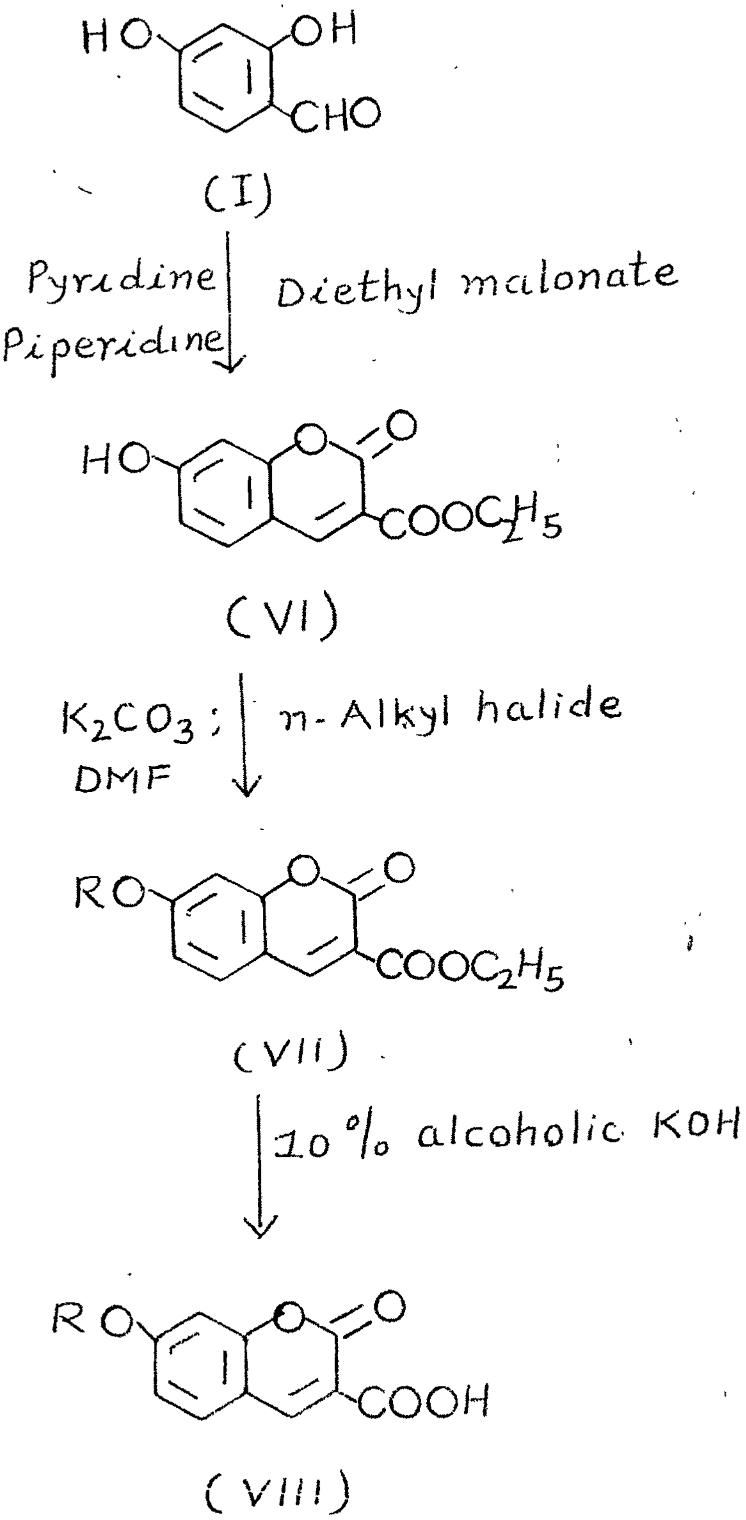
FIG.1 7-(4'-n-ALKOXYBENZOYLOXY)-3-PHENYL COUMARINS

B1. 4'-Cyanophenyl 7-n-alkoxycoumarin-3-carboxylates

A homologous series of thirteen esters was synthesized as shown in Scheme 2. 2,4-Dihydroxybenzaldehyde (I), on condensation with diethylmalonate in presence of pyridine and piperidine at room temperature gave compound (VI). Alkylation of (VI) by different alkyl halides in presence of anhydrous potassium carbonate and dry dimethyl formamide at higher temperature yielded (VII). Hydrolysis of esters (VII) by 10% alcoholic potassium hydroxide gave corresponding carboxylic acids (VIII) which on refluxing with excess of thionyl chloride yielded acid chlorides (IX). The acid chlorides (IX) were condensed with 4-cyanophenol in dry pyridine to yield cyanophenyl esters of series B1. The melting points and transition temperatures of the compounds are given in Table 18.

In this series mesomorphism does not appear until the decyl derivative. The remaining members, dodecyl, tetradecyl and hexadecyl, exhibit an enantiotropic smectic phase. Fig. 2. Shows the plot of transition temperatures versus the number of carbon atoms in the alkoxy chain. S-I transition points lie on a smooth rising curve. On cooling the isotropic liquid, batonnets separate from it and coalesce together to form quite clear fan-shaped focal conic texture in each case. In any case neither the smectic

Scheme 2



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Scheme 2
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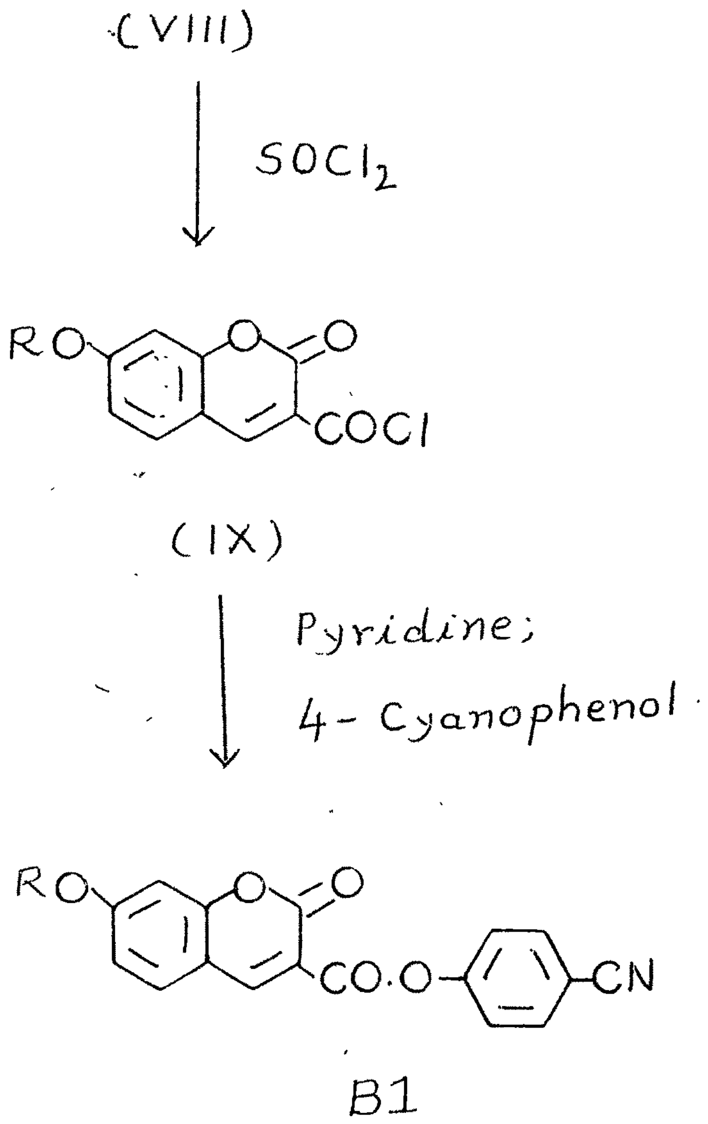


R = n-alkyl group

Table 18

4'-Cyanophenyl 7-n-alkoxycoumarin-3-carboxylates

n-Alkyl group	Transition temperatures (°C)	
	Smectic	Isotropic
Methyl	-	218.0
Ethyl	-	228.0
Propyl	-	217.0
Butyl	-	191.0
Pentyl	-	184.5
Hexyl	-	180.5
Heptyl	-	176.5
Octyl	-	172.5
Nonyl	-	171.0
Decyl	-	169.5
Dodecyl	170.5	174.5
Tetradecyl	169.5	180.5
Hexadecyl	171.0	186.0

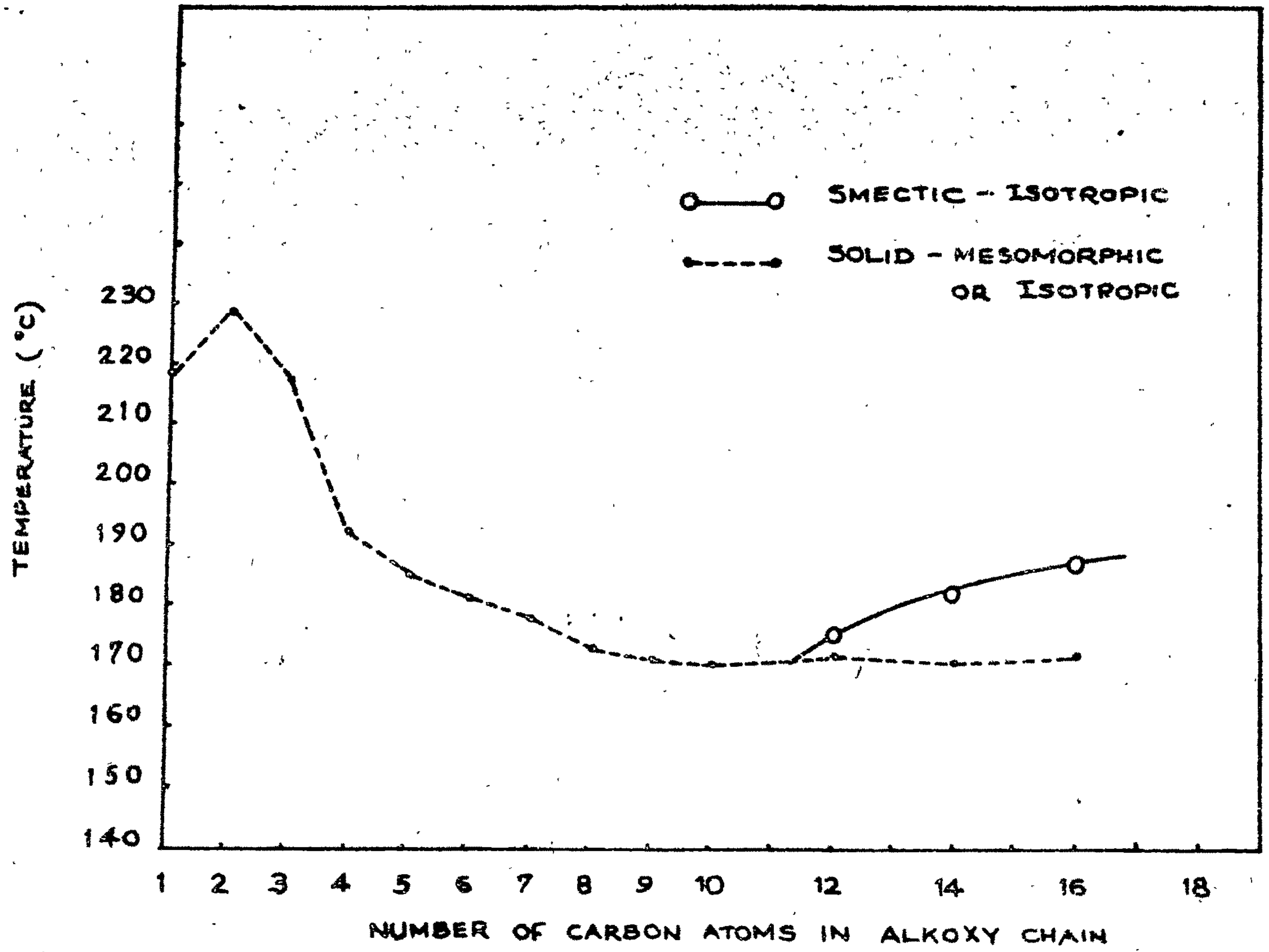


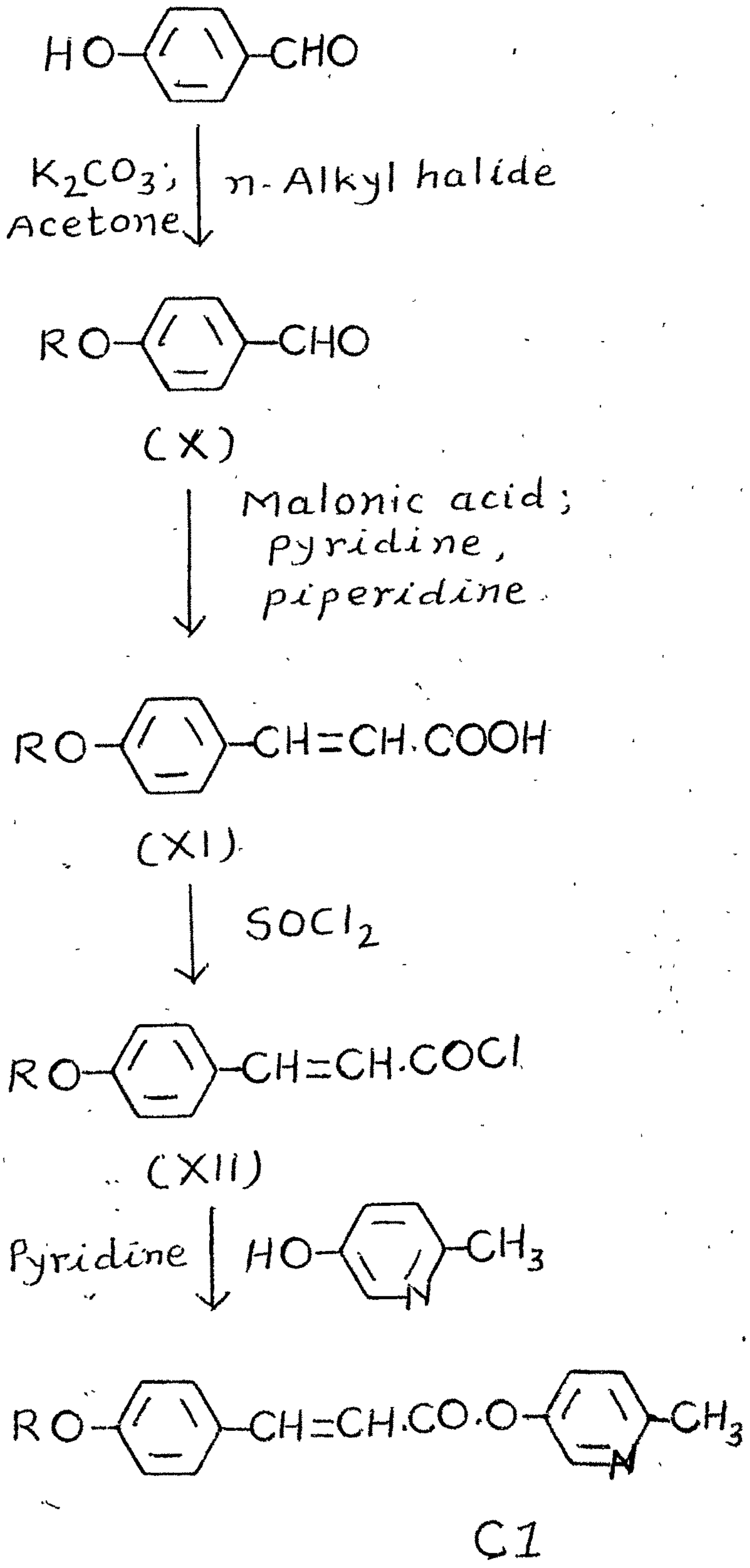
FIG. 2 4'-CYANOPHENYL 7-n-ALKOXY COUMARIN-3-CARBOXYLATES adopting a Schlieren texture has been observed nor the homeotropy.

C1. 2-Methyl-5-(4'-n-alkoxycinnamoyloxy)pyridines

A homologous series of fourteen esters was synthesized as shown in Scheme 3. 4-Hydroxybenzaldehyde was alkylated with different alkyl halides in presence of anhydrous potassium carbonate and dry acetone to give compounds (X) which were treated with malonic acid in presence of pyridine and piperidine and corresponding alkoxy cinnamic acids (XI) were obtained which on refluxing with excess of thionyl chloride yielded acid chlorides (XII). Compounds (XII) on treatment with 3-hydroxy-6-methylpyridine in presence of dry pyridine gave esters of series C1. The transition temperatures of the compounds are compiled in Table 19.

The structure of methoxy derivative was confirmed by NMR spectrum (Fig. 3). NMR ($CDCl_3$) δ 2.6 (S, 3H, methyl group at C_2), 3.85 (S, 3H, methyl group at C_4), 6,4-6.6 (d, J=18Hz, 1H, $=HC-\underset{\underset{O}{\|}}{C}-O-$ group) 6.9 - 7.0 (m, 4H, aromatic protons C'_2, C'_3, C'_5 and C'_6), 7.5 - 7.6 (d, J=9Hz, 1H, at C_4), 7.79 - 7.92 (d, J=18Hz, 1H, =CH-Ph group), 8.4 (s, 1H, at C_6).

Scheme 3



R = n- alkyl group

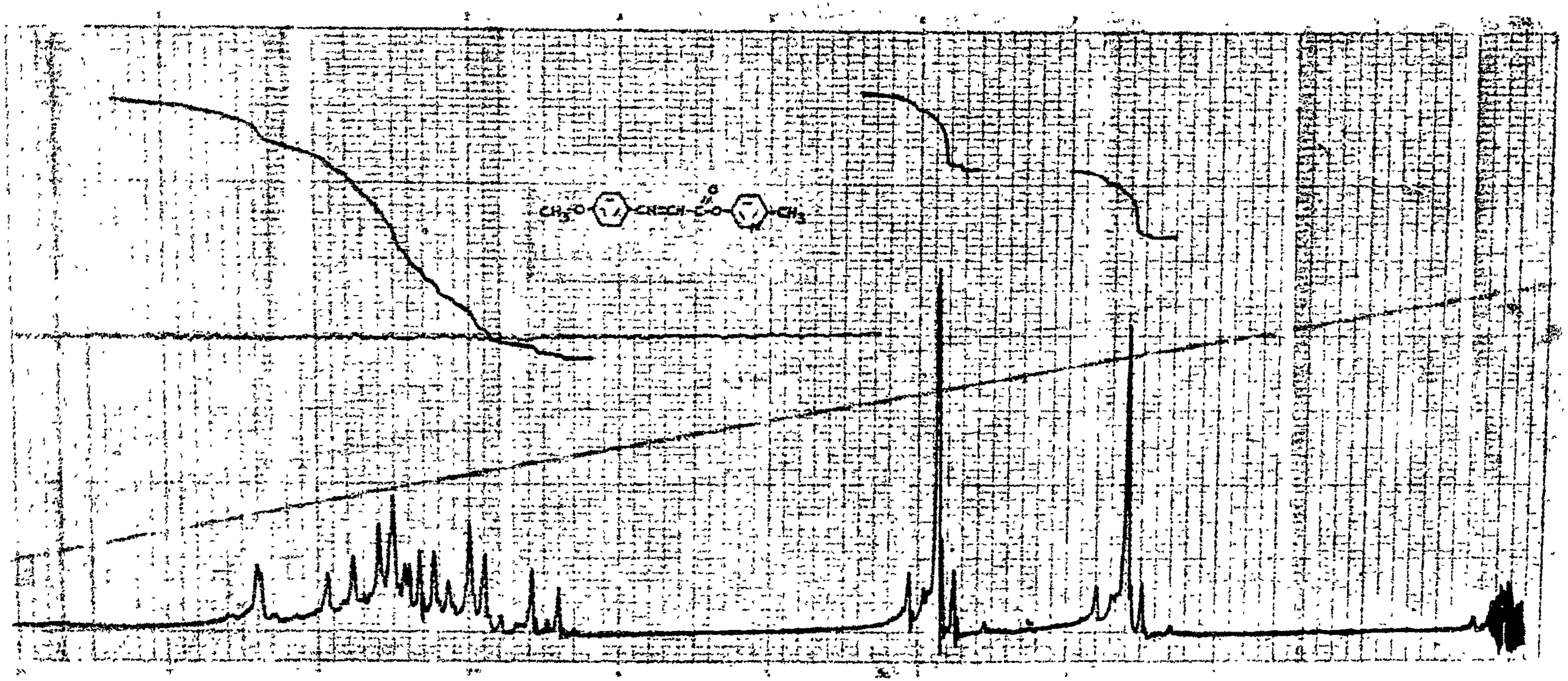


Fig. 3

Table 19

2-Methyl-5-(4'-n-Alkoxycinnamoyloxy)pyridines

n-Alkyl group	Transition temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	-	126.5
Ethyl	-	-	138.5
Propyl	-	(92.5)	105.5
Butyl	-	98.5	106.0
Pentyl	(88.5)	98.0	103.0
Hexyl	(97.0)	103.0	107.5
Heptyl	-	-	116.5
Octyl	107.0	-	108.5
Nonyl	109.5	-	110.5
Decyl	97.5	-	112.5
Dodecyl	86.0	-	113.5
Tetradecyl	91.5	-	112.0
Hexadecyl	94.5	-	110.0
Octadecyl	96.5	-	108.0

Values in parentheses indicate monotropy

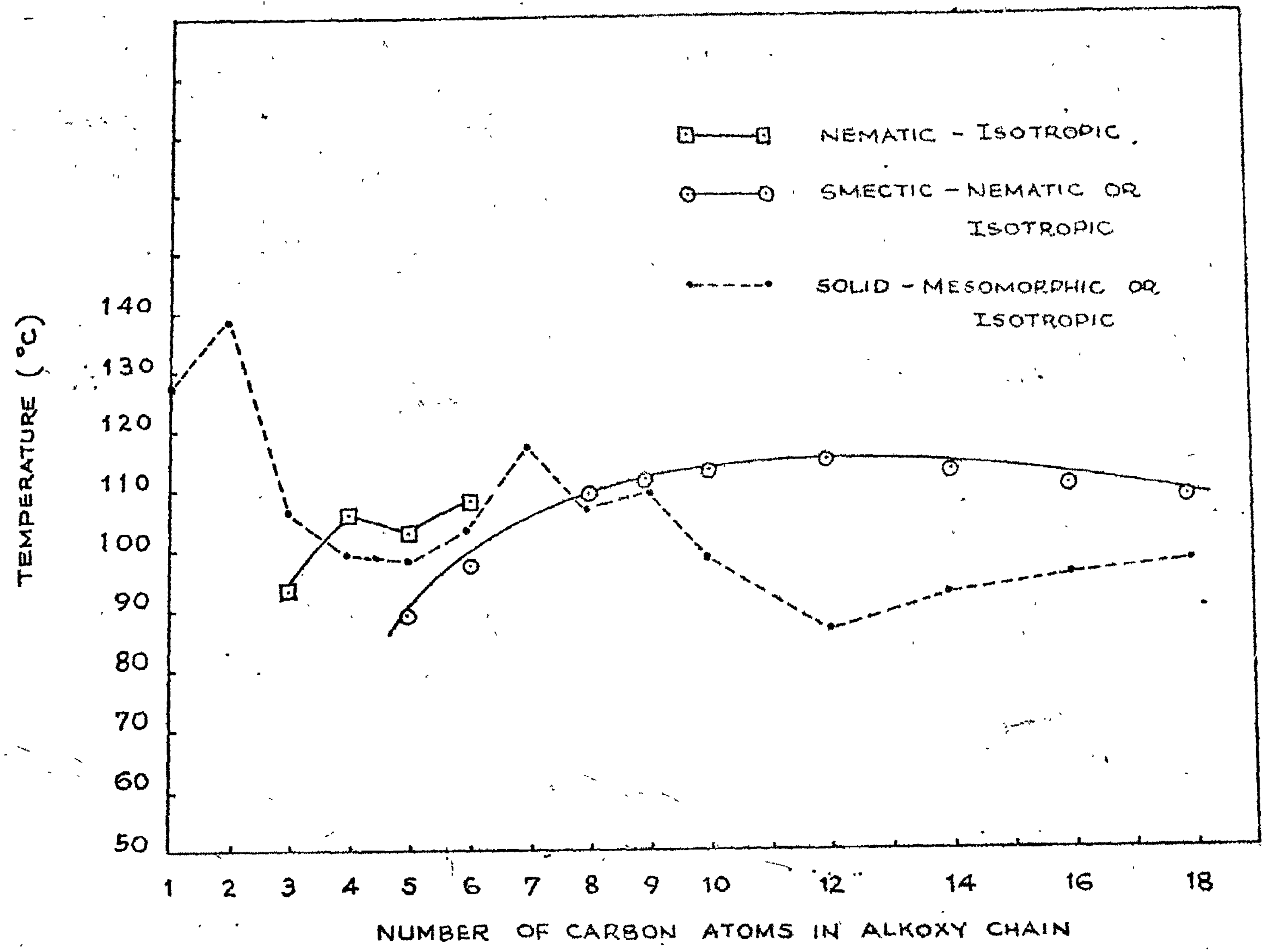


FIG. 4 2-METHYL-5-(4'-n-ALKOXY CINNAMOYLOXY) PYRIDINES

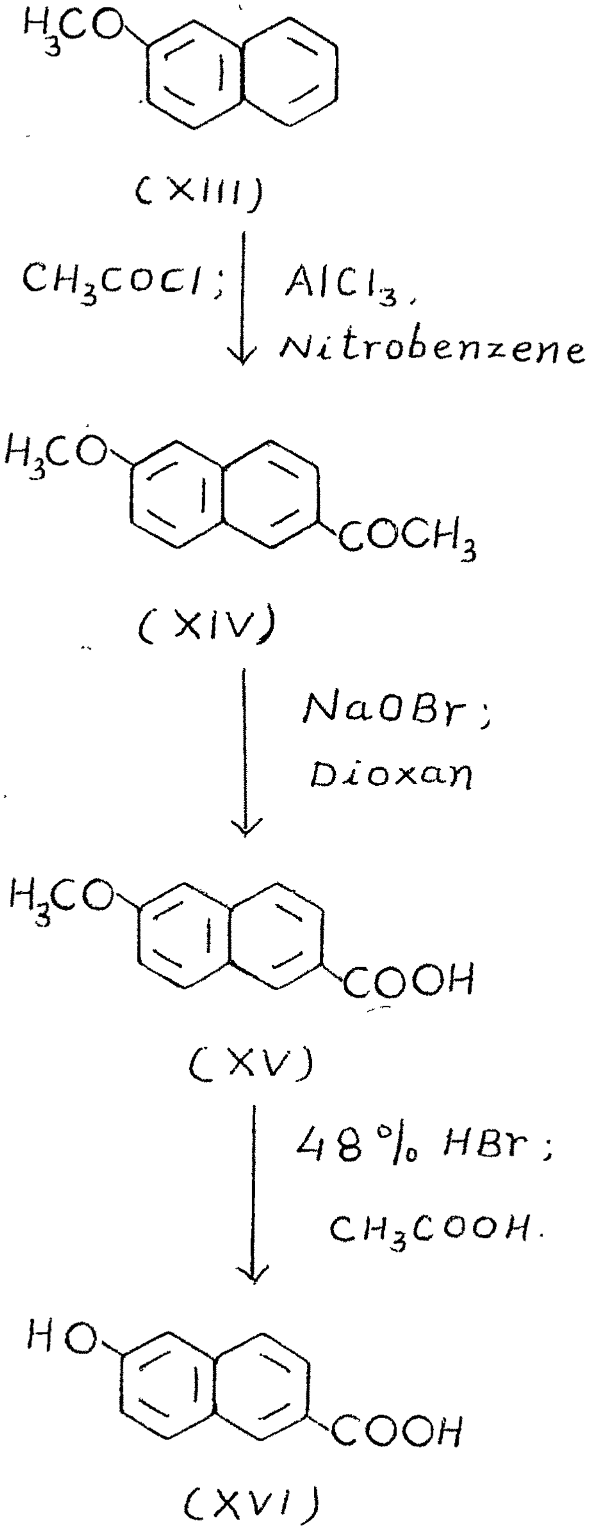
The first two esters are non-mesomorphic. The propyl derivative exhibits monotropic nematic phase while butyl derivative shows an enantiotropic phase. The smectic phase commences at the pentyl derivative. The pentyl and hexyl derivatives exhibit monotropic smectic and enantiotropic nematic phases, whereas the remaining esters show only enantiotropic smectic phase. On cooling the isotropic liquid, batonnets separate from it and coalesce together to form quite clear fan shaped focal conic texture in each case. On moving the coverslip on the slide with the sample in the smectic phase the fan shaped focal conic texture changes to exhibit minute focal conic groups but in no case, a Schlieren or a homeotropic texture has been observed. A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (Fig. 4) shows that S-N curve merges with the S-I curve. No odd-even alternation is observed in the S-I transition temperatures.

B. Mesomorphic Non-heterocyclic Homologous Series

B1. 4'-Formylphenyl 6-n-alkoxynaphthalene-2-carboxylates

A homologous series of fourteen esters was synthesized as shown in Scheme 4. Methyl ether of 2-naphthol (XIII) was acylated with acetyl chloride in presence of anhydrous aluminium chloride and dry nitrobenzene to give compounds

Scheme 4



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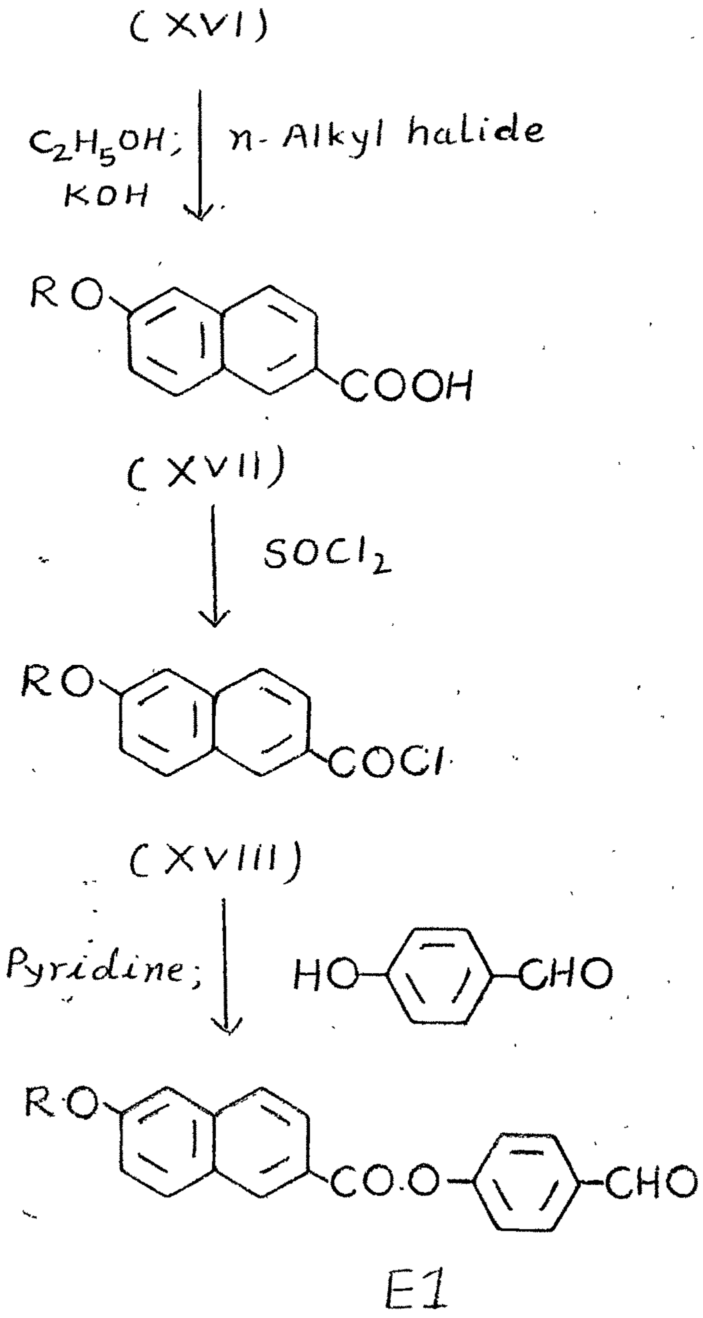
Scheme 4
contd....



R = n- alkyl group

(XIV) which was oxidized with sodium hypobromite in dioxan and compound (XV) was obtained, compound (XV), on demethylation with 48% hydrobromic acid and acetic acid, yielded compound (XVI) which on alkylated with different alkyl halides in presence of potassium hydroxide and ethanol gave compounds (XVII). Compounds (XVII), on treatment with excess of thionyl chloride gave corresponding acid chlorides (XVIII) which were condensed with 4-hydroxybenzaldehyde in dry pyridine to give esters of series E1. The transition temperatures of the compounds are compiled in Table 20.

The structure of the ethyl homolog was confirmed by NMR spectrum. (Fig. 5) NMR ($CDCl_3$) ; δ 1.5 (t, 3H, $-CH_3$ group of ethoxy chain), 4.2 (q, 2H, $-CH_2-O-$ of ethoxy chain), 7.15 - 8.2 (m, 6H, aromatic protons of naphthalene), 7.45 (d, J=9Hz, 2H, $C_{1'}$ and $C_{6'}$ protons), 7.85 (d, J=9Hz, 2H, $C_{3'}$ and $C_{5'}$ protons), 8.65 (s, 1H, $C_{4'}$ of -CHO group).

The first nine members exhibit an enantiotropic nematic phase. The smectic phase commences with the decyl derivative which exhibits both smectic and nematic as enantiotropic phases and a reentrant nematic phase. The remaining members are enantiotropic smectic. All the compounds adopt homeotropic texture when heated. When

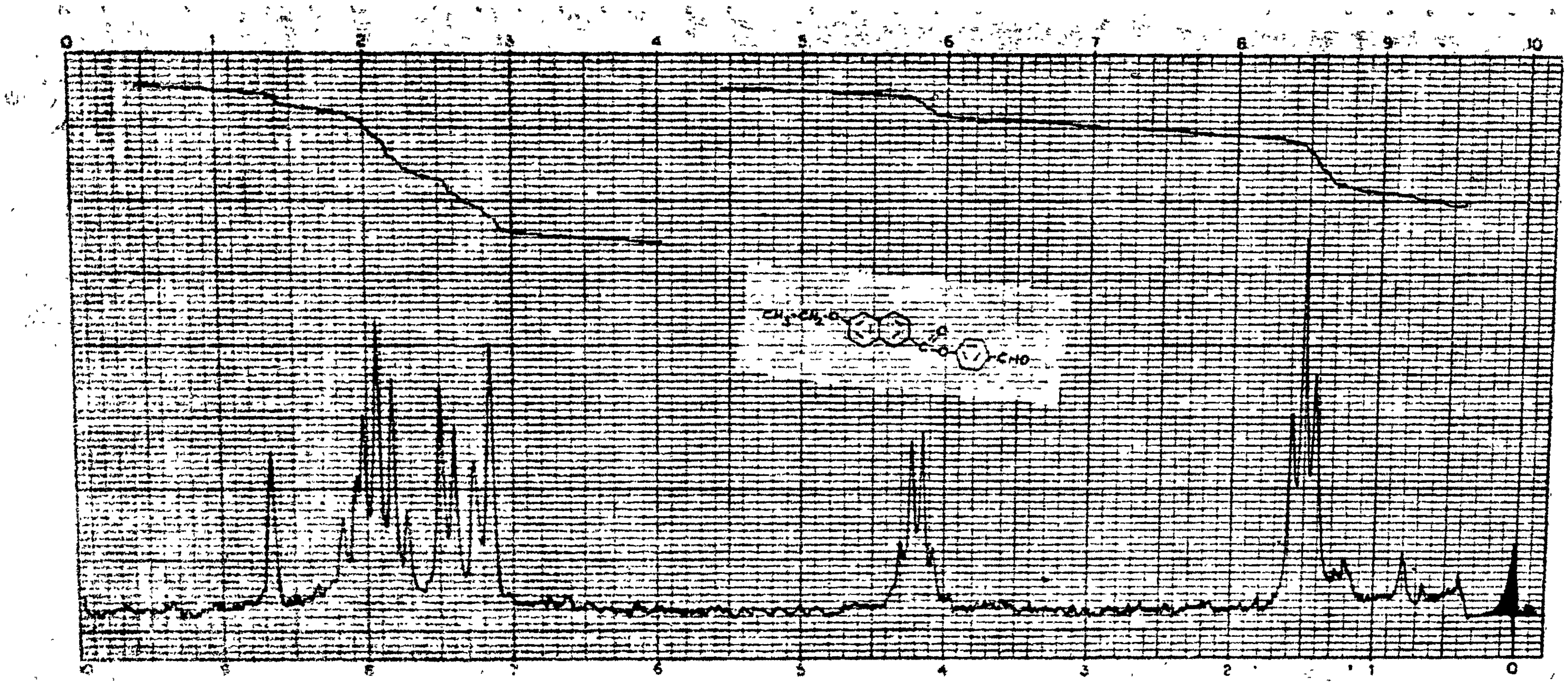


Fig. 5

Table 20

4'-Formylphenyl 6-n-alkoxynaphthalene-2-carboxylates

n-Alkyl group	Transition temperatures (°C)			
	Reentrant	Smectic	Nematic	Isotropic
Methyl	-	-	130.0	159.5
Ethyl	-	-	135.5	167.5
Propyl	-	-	101.5	137.5
Butyl	-	-	107.5	144.5
Pentyl	-	-	106.5	128.0
Hexyl	-	-	108.0	134.0
Heptyl	-	-	83.5	124.0
Octyl	-	-	75.5	125.0
Nonyl	-	-	82.0	123.5
Decyl	55.0	76.5	102.5	123.0
Dodecyl	-	89.0	121.0	123.0
Tetradecyl	-	91.5	-	125.0
Hexadecyl	-	84.5	-	125.5
Octadecyl	-	93.0	-	126.0

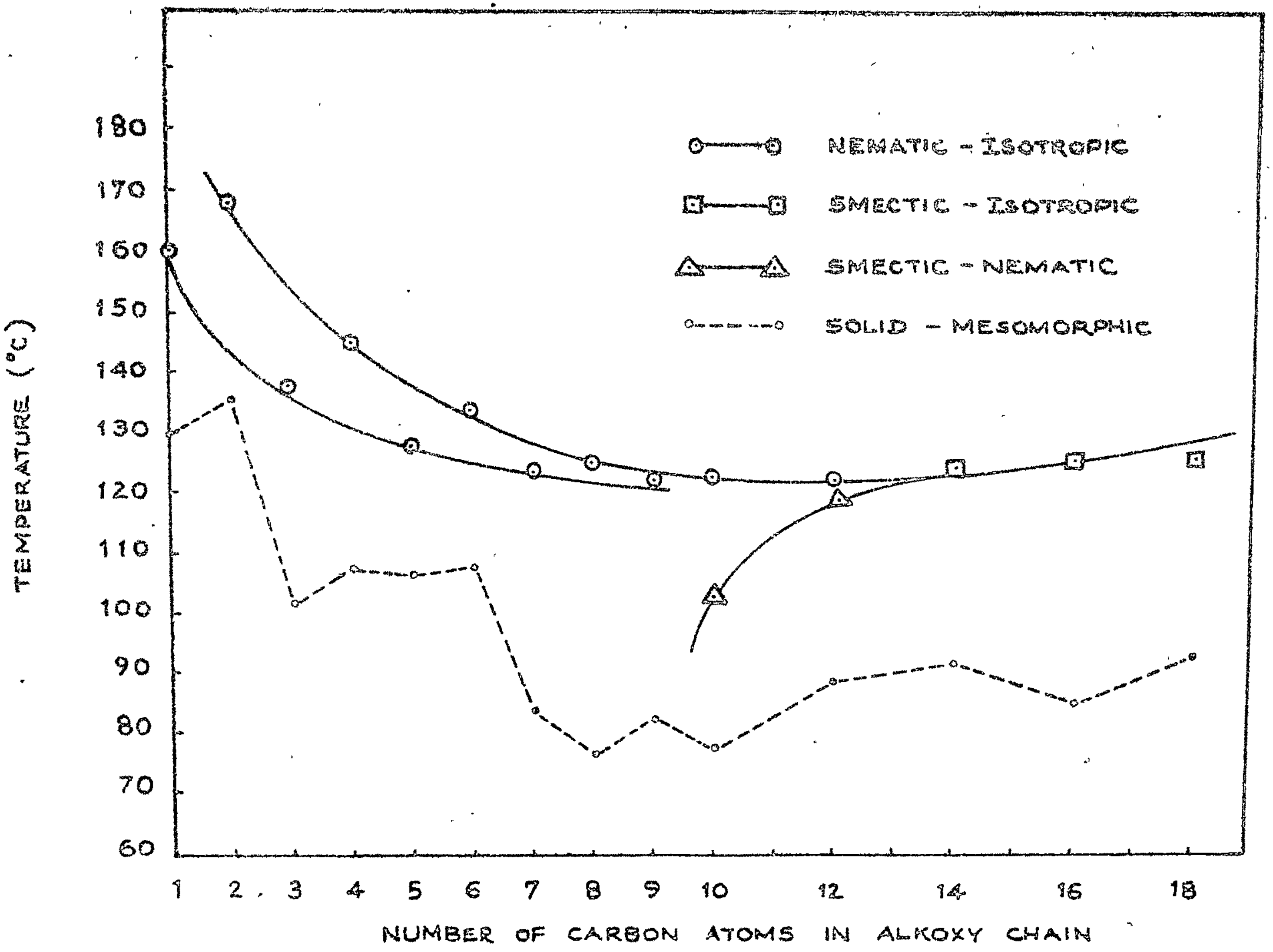


FIG. 6 4'-FORMYLPHENYL 6-n-ALKOXYNAPHTHALENE-2-CARBOXYLATES the nematic-isotropic transition points are plotted against the number of carbon atoms in the alkyl chain, they show the usual odd-even effect. The Smectic-isotropic and nematic-isotropic transition points merge with one-another (Fig. 6)

Nematic Reentrant Phase

The reentrant nematic phase (the phase occuring below the smectic phase) was first reported by Cladis (207,208). Recently there have been reports that molecules containing terminal -CHO, -CN and $-NO_2$ groups have a tendency to exhibit the reentrant nematic phase. (209-211).

The decyl derivative of the 4'-formylphenyl ester of 6-n-alkoxy-2-naphthoic acid exhibits reentrant nematic phase. On cooling the isotropic liquid of this homolog, the normal nematic phase appeared at 123.0°, the smectic phase appeared at 102.5° and before it was supercooled to the solid, the reentrant nematic phase appeared at 55.0° (Table 21). The reentrant nematic phase was identified by the typical Schlieren texture and the mobility of this phase when the coverslip is displaced.

Table 21

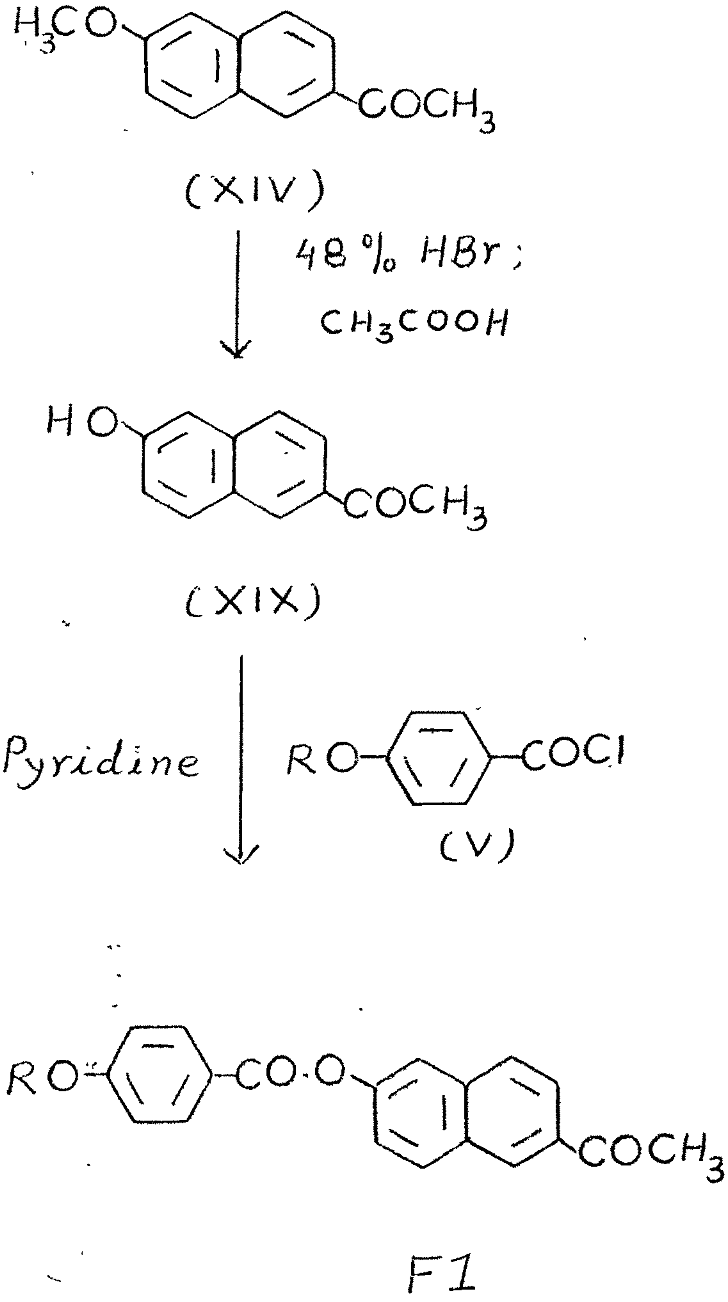
Transition Temperature of 4'-Formylphenyl 6-n-decyloxynaphthalene-2-carboxylate

Heating (°C)		Cooling (°C)	
Solid-Smectic	76.5	Isotropic-Nematic	123.0
Smectic-Nematic	102.5	Nematic-Smectic	102.5
Nematic-Isotropic	123.0	Smectic-Reentrant-Nematic	55.0
		Reentrant N-Solid	50.5

F1. 6-(4'-n-Alkoxybenzoyloxy)-2-acetylnaphthalenes

Fourteen esters of this homologous series were synthesized as shown in Scheme 5. Compound (XIV) was demethylated with 48% hydrobromic acid and acetic acid to give hydroxy derivative (XIX) which was condensed with (V) in presence of dry pyridine to yield the compounds of series F1. The transition temperatures of the compounds are given in Table 22. The structure of the decyl homolog was confirmed by NMR spectrum. (Fig. 7) NMR ($CDCl_3$) : δ 0.90 (t, 3H, terminal methyl group of decyloxy chain), 1.2 - 2.2 (m, 16H, $-(CH_2)_8-$ of the decyloxy chain), 2.7 (s, 3H, $-COCH_3$), 4.05 (t, 2H, $-CH_2-O-$ of decyloxy chain), 7.0 (d, J=9Hz, 2H, $C'_{3'}$ and $C'_{5'}$ protons), 7.32 - 8.05 (m, 5H, aromatic protons of naphthalene), 8.15 (d, J=9Hz, $C'_{2'}$ and $C'_{6'}$ protons), 8.45 (s, 1H, C_1 proton).

Scheme 5



R = n- alkyl group

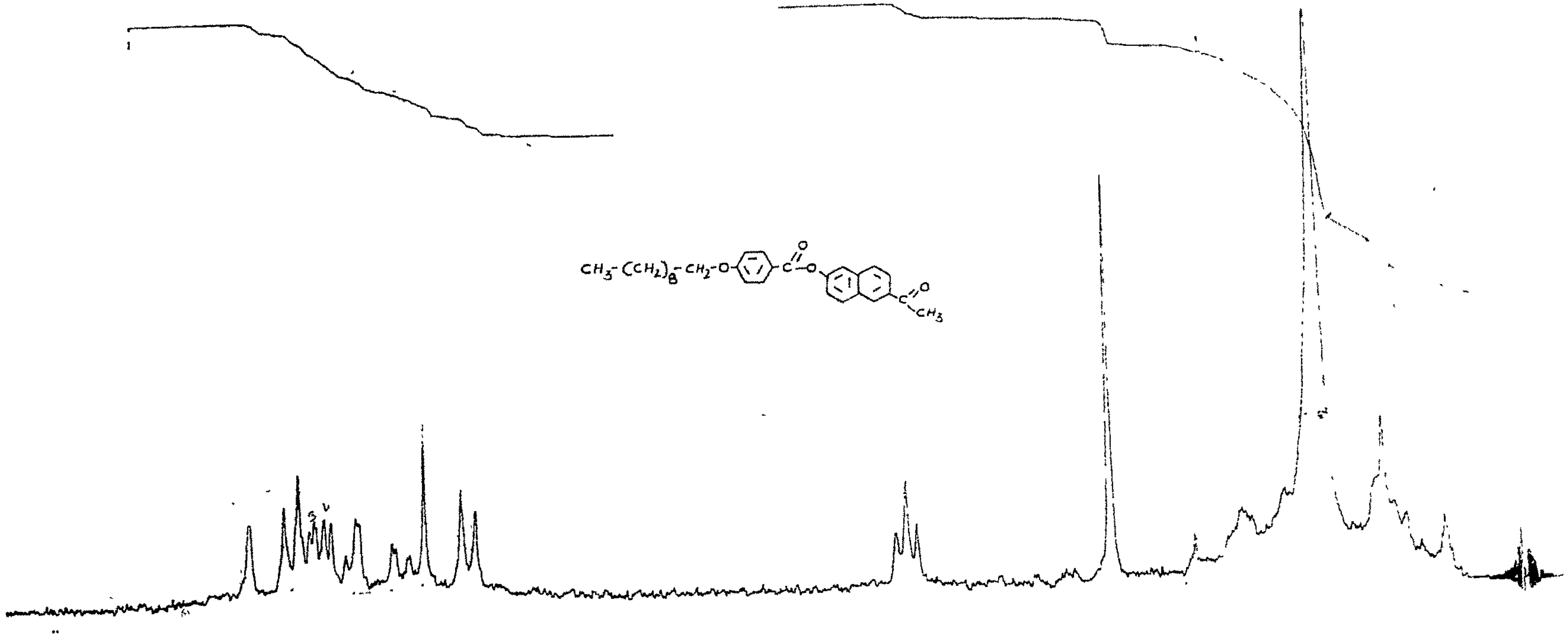


Fig. 7

Table 22

6-(4'-n-Alkoxybenzoyloxy)-2-acetylnaphthalenes

n-Alkyl group	Transition temperatures (^{o}C)		
	Smectic	Nematic	Isotropic
Methyl	-	190.0	197.5
Ethyl	-	179.0	199.5
Propyl	-	142.5	175.0
Butyl	-	140.5	173.5
Pentyl	-	118.5	163.5
Hexyl	-	117.0	163.5
Heptyl	-	113.0	156.0
Octyl	(107.5)	111.5	156.5
Nonyl	109.5	134.5	150.0
Decyl	110.5	142.0	151.5
Dodecyl	105.0	-	149.0
Tetradecyl	105.5	-	153.5
Hexadecyl	108.0	-	155.0
Octadecyl	109.5	-	156.5

Values in parentheses indicate monotropy

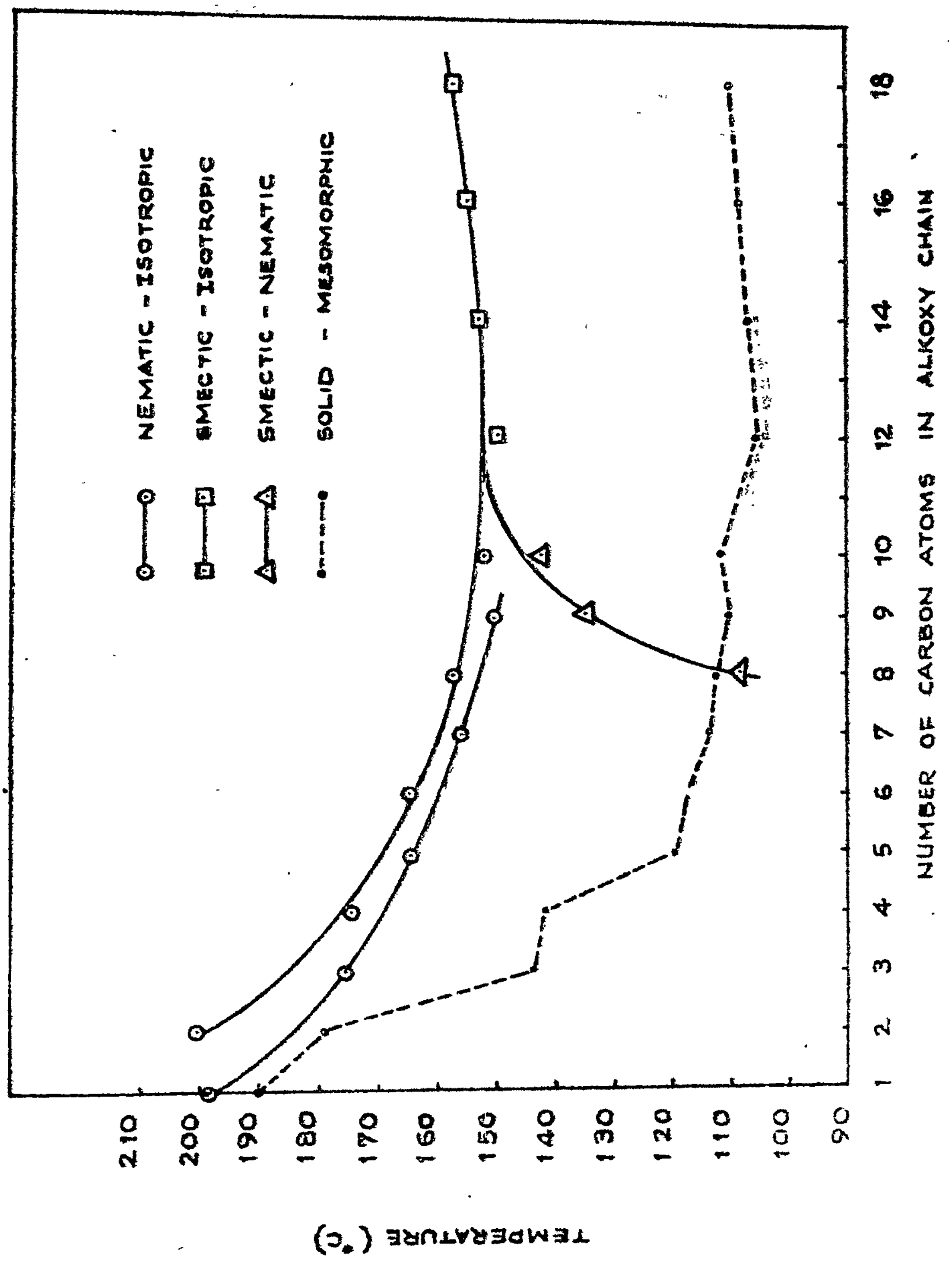


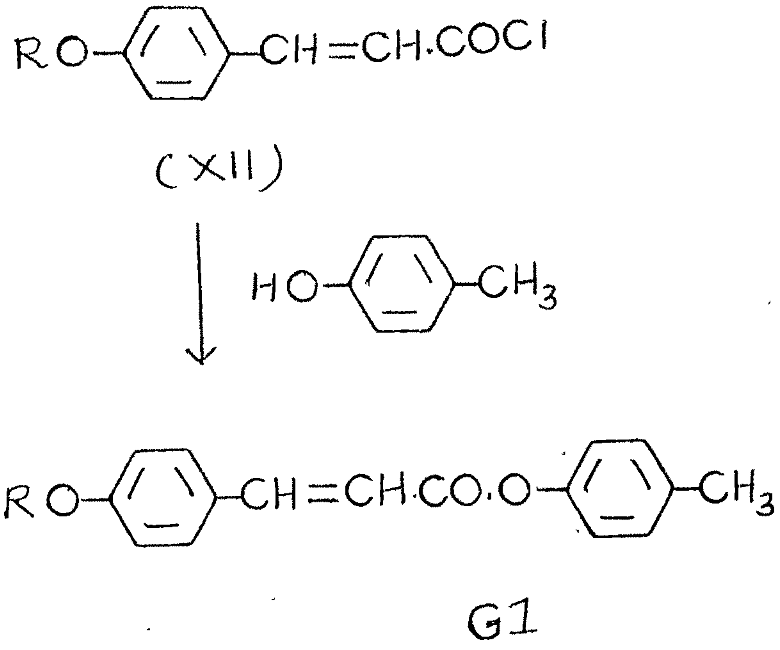
FIG.8 6-(4'-n-ALKOXYBENZOYLOXY)-2-ACETYLNAPHTHALENE

The first seven members are enantiotropic nematic. The smectic phase commences with the octyl derivative which exhibits smectic as monotropic and nematic as enantiotropic phases. The nonyl and decyl derivatives exhibit both smectic and nematic as enantiotropic phases. The remaining members are enantiotropic smectic. All the members adopt homeotropic texture when heated. The nematic-isotropic points when plotted against the number of carbon atoms in the alkyl group, show descending tendency. The smectic-isotropic and nematic-isotropic points merge with each other (Fig.8).

G1. 4-(4'-n-Alkoxycinnamoyloxy) toluenes

A homologous series of fourteen members was synthesized as shown in Scheme 6. Compounds (XII), when treated with p-cresol, yielded esters of series G1. The transition temperatures of the compounds are summarized in Table 23. The stmucture of the butyl homolog was confirmed by NMR spectrum. NMR ($CDCl_3$) δ 1.0 (t, 3H, terminal methyl group of butoxy chain), 1.4 - 1.9 (m, 4H, - $(CH_2)_2$- of butoxy chain), 2.35 (s, 3H, methyl group at C_1), 4.0 (t, 2H,- $-O-CH_2$ group of butoxy chain), 6.45 - 6.55 (d, J=18Hz, 1H, $=HC-\underset{\underset{O}{||}}{C}-O-$group), 6.8 - 7.6, (m, aromatic protons), 7.75 - 7.90 (d, J= 18Hz, 1H, $=CH-Ph$ group) (Fig. 9).

Scheme 6



R = n- alkyl group

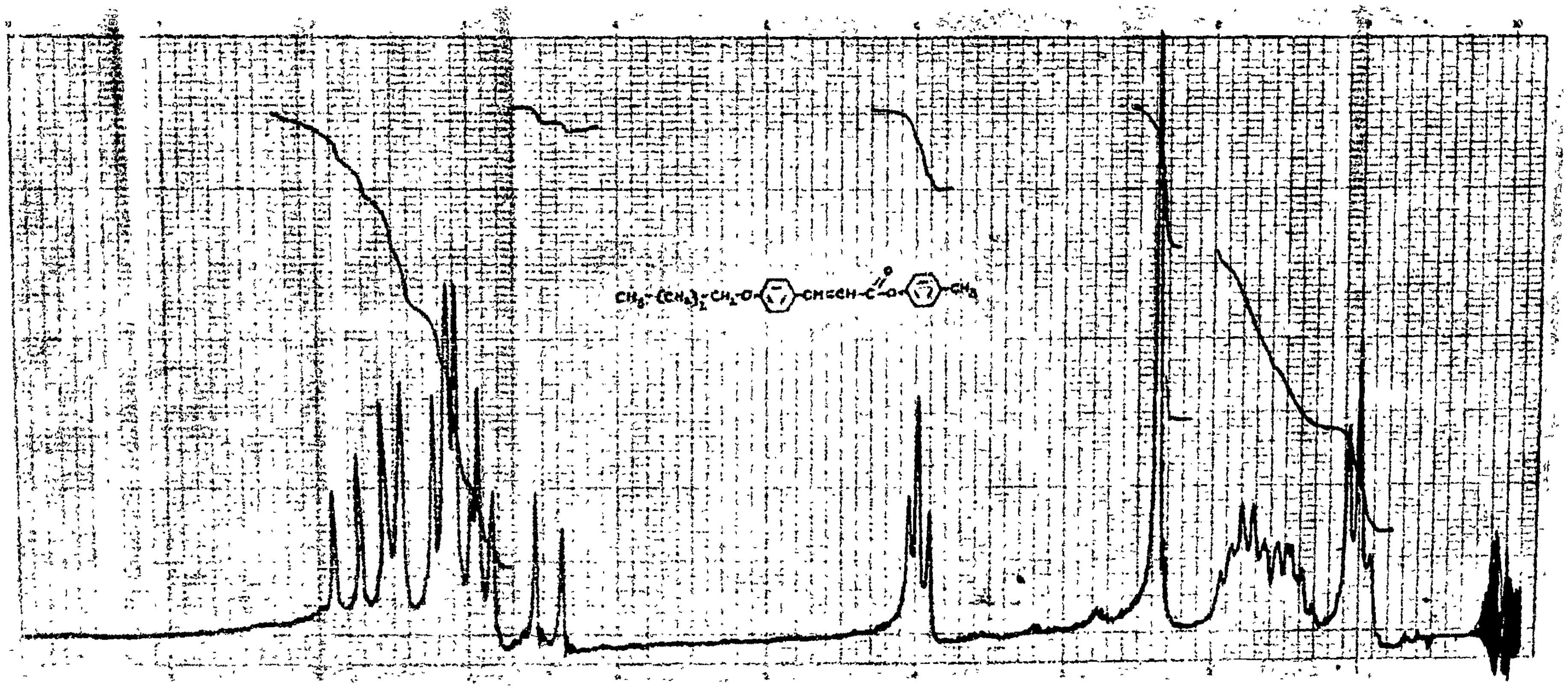


Fig. 9

Table 23

4-(4'-n-Alkoxycinnamoyloxy)toluenes

n-Alkyl group	Transition Temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	(97.5)	104.5
Ethyl	-	-	165.5
Propyl	-	(99.5)	104.5
Butyl	-	(110.0)	125.5
Pentyl	-	(102.5)	106.0
Hexyl	-	97.5	106.5
Heptyl	-	(101.0)	107.5
Octyl	82.5	101.0	104.0
Nonyl	82.0	88.0	101.0
Decyl	74.0	95.5	105.0
Dodecyl	96.0	97.0	101.0
Tetradecyl	71.0	-	100.0
Hexadecyl	73.0	-	83.5
Octadecyl	92.0	-	101.0

Values in parentheses indicate monotropy

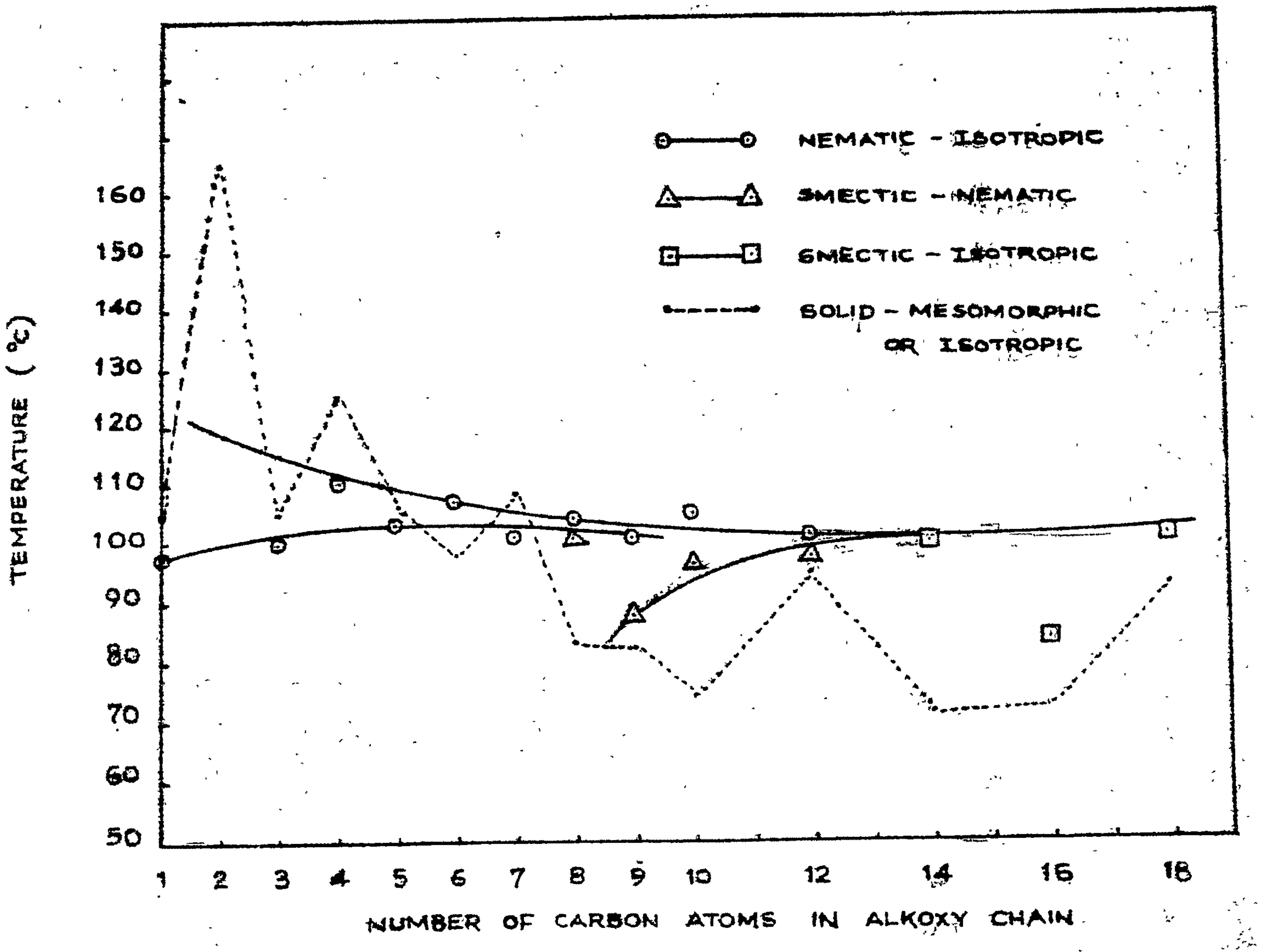


FIG.10 . 4 -(4'-n- ALKOXYCINNAMOYLOXY) TOLUENES

The first seven esters exhibit monotropic nematic phase except the hexyl derivative which shows enantiotropic nematic phase. The smectic phase commences with the octyl derivative as the enantiotropic phase. The octyl, nonyl, decyl and dodecyl derivatives exhibit both smectic and nematic as enantiotropic phases, whereas the tetradecyl, hexadecyl and octadecyl derivatives exhibit only enantiotropic smectic phase. The heptyl, octyl, nonyl, decyl, hexadecyl and octadecyl derivatives adopt homeotropic texture while heating and cooling the isotropic liquid. A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain is shown in Fig. 10.

COMPARATIVE STUDY

The transition temperatures, within a given homologous series, vary systematically with the change in molecular polarizability and molecular dimensions. The influence of certain functional groups, present in the different homologous series is manifested by the difference of transition temperatures for corresponding members. Information, about molecular arrangements and molecular interactions in the mesomorphic states, is needed to interprete such effects.

When the mesomorphic compounds are heated, the melting occurs in stages and they pass through one or more ordered intermediate stages before changing to the isotropic liquid. The molecular arrangement of nematic phase occurs in temperature regions where terminal interactions dominate while the molecular layer structure of the smectic phase occurs in temperature interval with predominant lateral attfactions. Thus the primary terminal cohesions of the molecule are overcome at the solid-smectic transition while the strong lateral intermolecular attractions are overcome at the smectic-nematic or smectic-cholesteric transitions and a nematic or cholesteric phase is formed. The residual lateral and terminal cohesions hold the molecules together in the nematic or cholesteric melt. These Van der Waals forces break down on further heating and molecules pass into a randomly arranged isotropic liquid state. The changes are represented schematically as shown in Fig. 11.

The following text deals with the comparision of various features of the series synthesized in the present investigation with different series.

I. Derivatives of Coumarin

The series A1 is compared with the following homologous series :

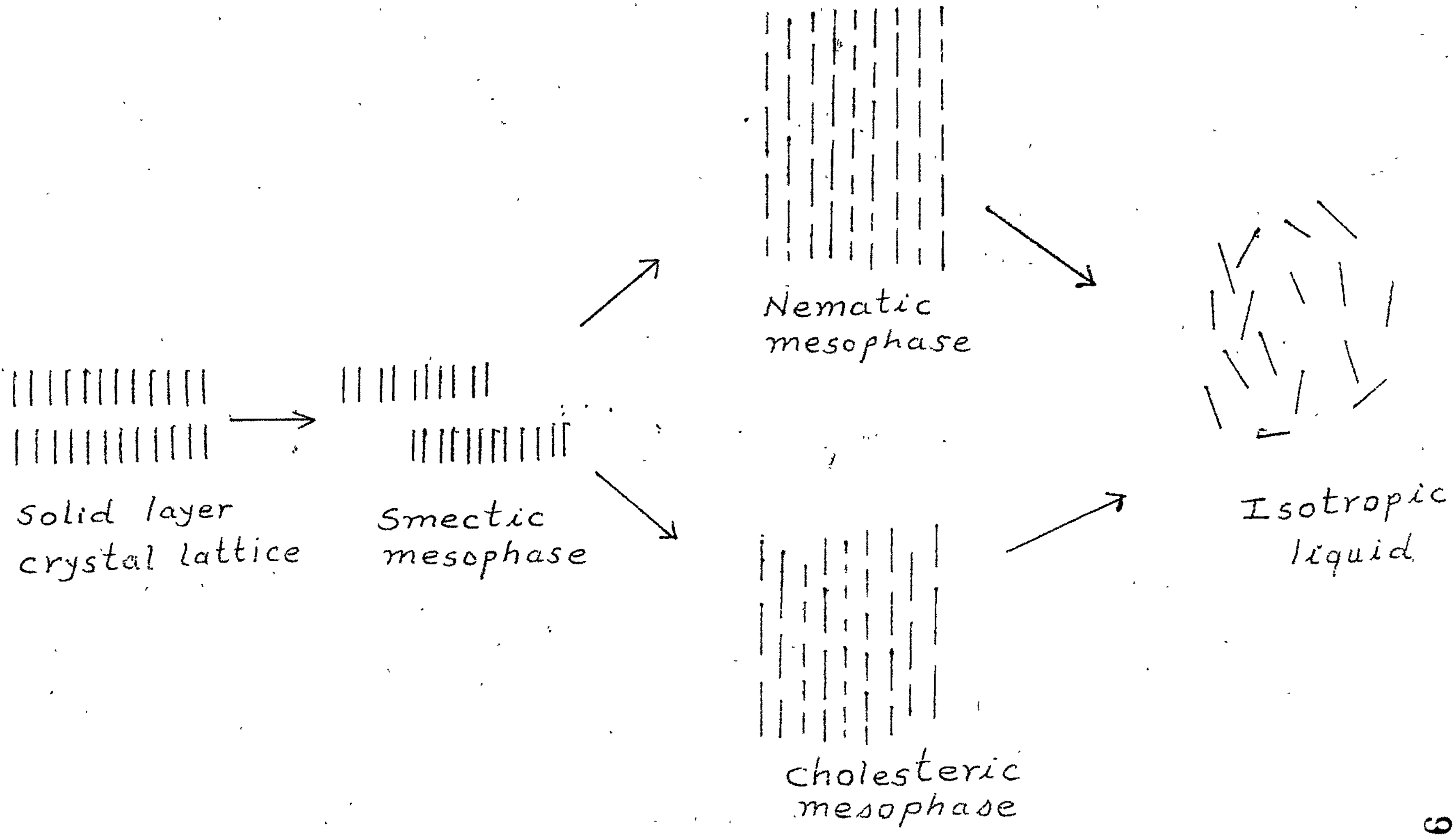

Solid layer
crystal lattice
Smectic
mesophase
Nematic
mesophase
Cholesteric
mesophase
Isotropic
liquid

Fig. 11

7-(4'-n-Alkoxybenzoyloxy)-3-acetylcoumarin (205)
.... Series A2

7-(4'-n-Alkoxybenzoyloxy)-3-benzoylcoumarins (206)
.... Series A3

Biphenyl 4-n-alkoxybenzoates (212) .... Series A4

Odd-even alternation of N-I Transition points

The odd-even alternation in N-I transition temperatures is observed in all four series A1, A2, A3 and A4 when the transitions are plotted against the number of carbon atoms in the alkoxy chain. In series A1, A2 the even members and the odd members of the alkoxy chain occupy the upper curve and lower curve respectively. Usually, the mesomorphic-isotropic transition temperatures change in a regular manner in a mesomorphic homologous series. Gray (54) tried to explain the behaviour of homologous series wherein the increment of each methylene group brings about regular changes in the transition temperatures. The separation of the aromatic centres that are highly polarizable and carrying permanent dipolar substituents is increased as the methylene chain is lengthened, consequently there should be a decrease in the strength of the terminal intermolecular cohesions. Gray (54) and Maier and Baumgartner (213) have suggested that the addition of each methylene group increases the overall polarizability of the molecules and so the lateral intermolecular attractions may also increase. With the growing chain length. The lower homologs are only purely nematic i.e. for the short chain compounds, the separation of the aromatic nuclei is at a minimum and the terminal cohesions are strongest. Smectic properties are often observed to commence from the middle members of a series, because with the increase in the alkyl chain the lateral cohesive forces also increase and the molecules maintain themselves in the layer arrangement before they give a nematic mesophase. The last few members in a series may exhibit only smectic phase. This is the general pattern for a nematogenic homologous series, involving similar rod-shaped molecules, exhibiting nematic and smectic mesophases.

Gray (214) has tried to explain the odd-even alternation for N-I transitions in terms of the conformation of the alkyl chain. Originally he explained this behaviour on the basis of a castellated conformation (cog wheel structure) (54). Later he reported that preliminary results of X-ray studies of the crystalline state of some liquid crystalline compounds make this unlikely and that the zig-zag conformation for the alkyl chain is favoured (214). Diagrammatic representation of the possible relative orientation of terminal methyl groups in end to end packing of the molecules of n-alkylarylethers, such as the p-n-alkoxybenzoic acids, is shown in Fig. 12.

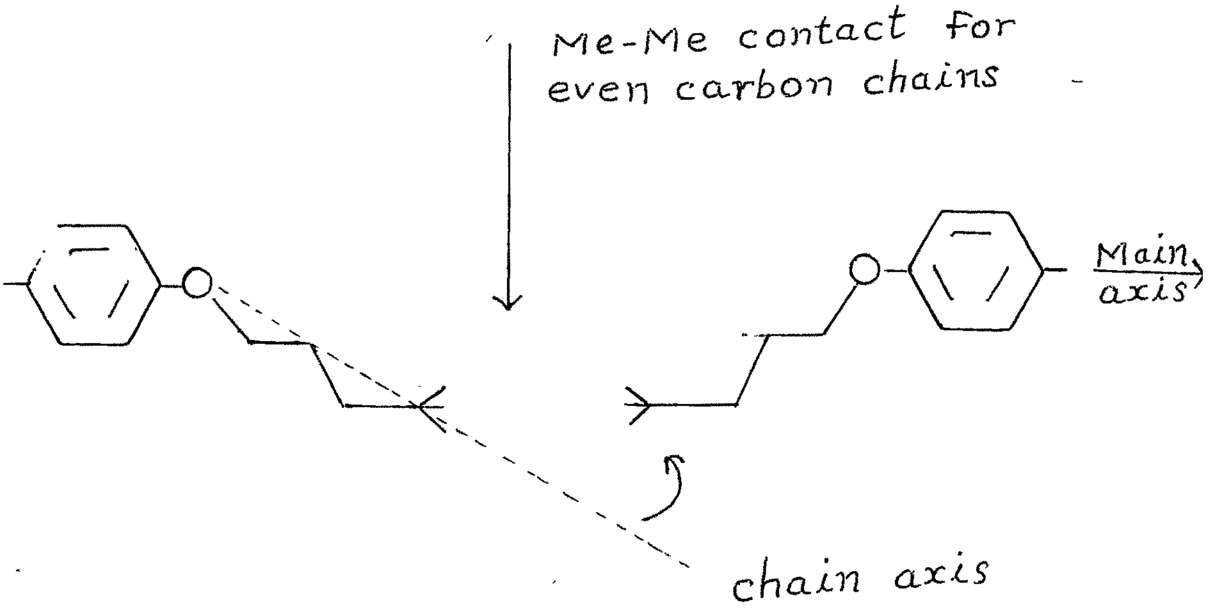


Fig. 12.

For short alkyl chains, if the chain extends strictly along its own axis (dotted line in Fig. 12) then the terminal methyl groups present different faces to one another or to other end groups in the molecule depending on whether the chain is even or odd. The different attractive forces resulting could affect the energy of the system and account for an alternation of the transition temperatures. With the higher homologs the alkyl chain may be forced (curved arrow in Fig. 12) into line with the main axis defined by the more rigid aromatic parts. Gradually, the end group contact would become the same in nature for odd and even carbon chains, and can explain the petering out of the alternation as the series is ascended.

The middle members of a potentially nematogenic homologous series exhibit smectic and nematic mesophases. The lateral intermolecular attractions for such homologs must be considerably strong. The residual lateral attractions increase as the alkyl chain is lengthened and the weaker residual terminal attractions which are responsible for the nematic-isotropic transition temperatures are disrupted. The increase in the residual lateral attractions reduces the rate of decrease in the nematic-isotropic transition temperatures as the series is ascended, causing ultimate levelling of the nematic-isotropic curve for the longer chain homologs for which residual lateral attractions may be the strongest.

Maier (215) and Maier and Baumgartner (213) in their study of the dipole moment and dielectric anisotropies of the series 4,4'-di-n-alkoxyazoxybenzenes have tried to explain the alternation in N-I transition temperatures of the lower homologs. They concluded that it is the difference in the polarization effects between the sides of the molecules containing even and odd number of carbon atoms in the alkyl chains that explains the alternation effect.

Marcelja (216) has shown, on the basis of the total energy consideration, that the calculated alternations in N-I transitions are in good agreement with the observed values for a number of homologous series and states that the addition of even numbered carbon atoms in the preferred trans conformation is along the major molecular axes, while the opposite is true for odd-numbered carbon atoms. This presentation resembles that of Gray's (217) zig-zag conformation and should explain the odd-even effect obtained in the homologous series synthesized in this investigation.

Rising tendency of S-N transition temperatures curve:

The S-N transition temperatures curve rises smoothly in case of series A1, A2 and A4. In series A3, S-N transition does not occur. It merges with the N-I curve to give pure smectic mesophases.

The initial increase in the S-N transition temperatures can be explained by the overall increase in the polarizability of the molecules as the alkyl chain is lengthened. This effect enhances the cohesive forces operating between the sides of the molecules which lie parallel to one another with their ends in the line forming the smectic layers. The increase in molecular weight tends to make it more difficult for the thermal vibrations to cause a sliding of the molecules out of layers to give imbricated orientation of a nematic melt.

Although the intermolecular forces operating between the ends of the molecules, across the smectic strata are relatively weak since the layers may slide over one another, these residual attractions may tend to locate the ends of the molecules near to one another across the strata when slipping is not taking place. Therefore, the forces having tendency to resist the sliding of a molecule in the direction of its long axis, from one stratum to another must be the lateral cohesive forces between the molecules and the residual terminal cohesive forces operating across the strata. If the polarizable aromatic rings are represented by the rectangles and the two end alkoxy groups are represented by small lines , the molecular arrangement in the smectic melt may be as shown in Fig. 13.

The residual terminal attractions tend to become weaker and offer less resistance to interpenetration

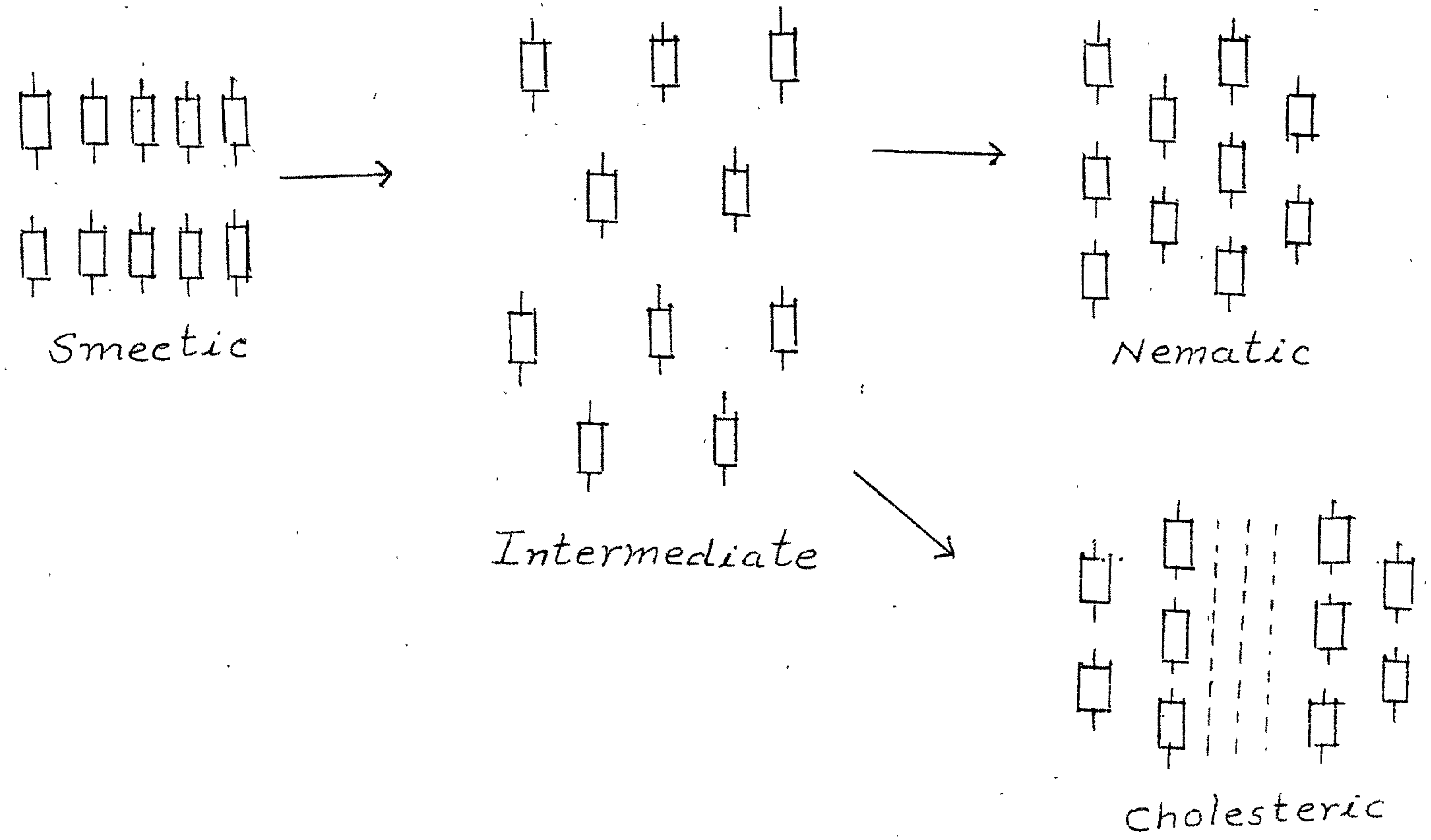


Fig. 13

with the increase in chain length. Therefore an intermediate state, as shown in Fig. 13, is formed where the ends of the molecules are still in line. As the temperature rises, the tendency for interpenetration of the chains grows, thus forcing apart the aromatic centres giving an imbricated nematic orientation to the melt as shown in Fig. 13. The dislocated residual terminal intermolecular cohesions at the S-N transitions are probably temporary. As the interpenetration of the layers becomes great and the normal imbricated arrangement of the molecules of the nematic melt is reached, the ends of the molecules may once again become associated, consequently the terminal interactions can again start to influence the thermal stability of nematic melt as they do in purely nematic liquid crystals. The increasing molecular mass and polarizability tend to increase the resistance to the sliding of the molecules from one stratum to another and also increase the tendency for interpenetration of the layers, thus causing the terminal attractions between them to become weaker. The role of these effects explains the shape of S-N transitions curve.

In the series A1, A2 and A4, no odd-even alternation in S-N transitions is observed. This is the general behaviour for the S-N transitions in the normal nematogenic systems.

Thermal Stabilities and Commencement of Smectic phase

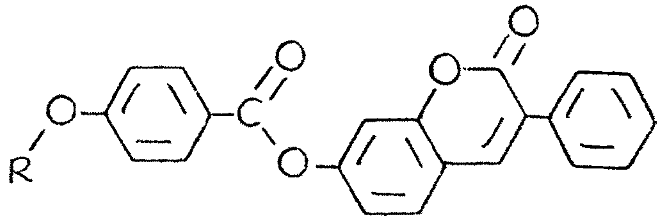
There is a close relationship between mesomorphism and molecular constitution of organic compounds. Therefore, the thermal stability which is a measure of mesomorphism can be correlated with the molecular constitution of the compounds. The average thermal stabilities of the nematic and smectic mesophases and the point of commencement of the smectic mesophase in the series A1, A2, A3 and A4 are summarized in Table 24.

Table 24

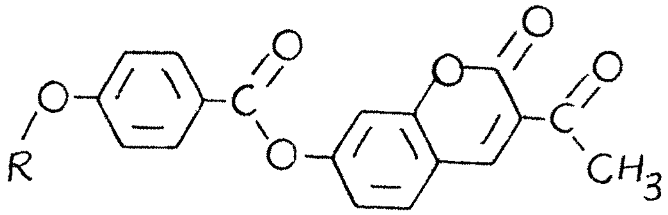
Average thermal stabilities (°C)

Series	A1	A2	A3	A4
N-I (C_1-C_{13})	187.3	143.3 (C_4 - C_6)	90.0 (C_{10})	130.5
S-N or I C_{14} - C_{18}	168.0	151.2 (C_5 - C_{18})	112.6 C_{12} - C_{18}	109.6 (C_{10} - C_{12})
Commencement of smectic phase	C_9	C_5	C_{12}	C_{10}

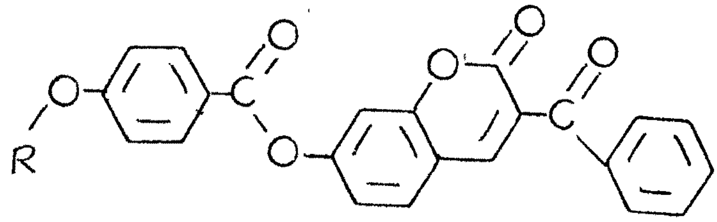
The geometry of these series is given in Fig. 14.



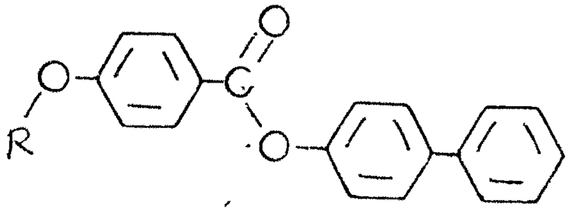
A1



A2



A3



A4

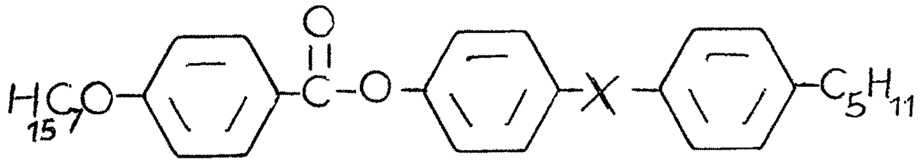
Fig. 14

Reference to Table 24 indicates that both nematic and smectic thermal stabilities of series A1 are higher than those of series A2, A3 and A4. The difference in the molecules of the first two series is that the molecules of series A1 have a more polarizable benzene ring at 3-position whereas the molecules of series A2 have $-\underset{\underset{O}{\|}}{C}-CH_3$ gr o up at 3- position.

The molecules of series A3 have $-\underset{\underset{O}{\|}}{C}-C_6H_5$ group at the 3-position in place of benzene ring in the molecules of series A1. The higher values of nematic and smectic thermal stabilities of series A1 compared to series A2 can be attributed to the higher molecular length of series A1 which will increase intermolecular cohesions of all types. The earlier commencement of the smectic phase in series A2 can be attributed to the more favourable close packing of the molecules.

Both the nematic and smectic thermal stabilities of A1 are higher than those of series A3. This can be attributed to the $-COC_6H_5$ end group in series A3. The molecules of series A3 have two central linkages viz. $-\underset{\underset{O}{\|}}{C}-O-$ and $-\underset{\underset{O}{\|}}{C}-$ whereas the molecules of series A1 have only $-\underset{\underset{O}{\|}}{C}-O-$ central linkage.

The compounds possessing $\overset{O}{\overset{\|}{-C-}}$ as one of the central linkages and exhibiting mesomorphic properties are rare as this group destroys linearity of the molecules and hence length : breadth ratio of the molecules is decreased much. Nguyen Huu Tinh et al. (218) have reported several compounds having the following general structure :



Where X = $-CH{=}N-$, $-N{=}N-$, $-CH{=}CH-$, $-CH_2-CH_2-$, and $\underset{O}{\underset{\|}{-C-}}$, $-CH_2-\underset{O}{\underset{\|}{C}}-$

The compounds having the central linkages other than $\underset{O}{\underset{\|}{-C-}}$ are all mesomorphic whereas the only compound having $\underset{O}{\underset{\|}{-C-}}$ central linkage fails to exhibit mesomorphism.

The difference between the series A1 and the series A4 is that the former possesses coumarin nucleus with benzene ring as terminal group, whereas the latter possesses only a biphenyl nucleus at the corresponding position and no end group attached to it. From the molecular geometry it seems that the molecules in the case of series A1 are lengthier than those of series A4. The higher nematic thermal stability of series A1 may be due to the terminal benzene ring.

The smectic phase of series A1 is thermally more stable than that of series A4. In series A1, the molecules are rather broad due to the presence of a ketonic group in coumarin moiety and there is an additional permanent dipole across the major axis of the molecules due to the presence of lactone moiety as shown in Fig. 15.

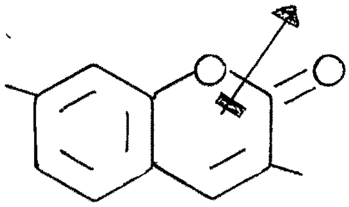


Fig. 15

This seems to become the conclusive factor while comparing their smectic thermal stabilities. Due to increase in lateral intermolecular attractions arising from dipole-dipole interactions in the molecules of series A1, the higher values of smectic thermal stability is observed.

Having explained the thermal stabilities of the series discussed, it should be interesting to discuss the point of commencement of the smectic mesophase in these homologous series. The appearance of the smectic properties in a series is influenced by the melting points of the compounds and/or by the supercooling tendencies of the melts. Both these factors are related to the crystal structures of the compounds, which ultimately are dependent on the geometry, dipole moment and overall polarizability of the molecules. Knowledge about the appearance of the smectic mesophase may help in the search for certain series where the appearance of smectic mesophase might be delayed so that purely nematic or cholesteric substances could be obtained.

A survey of the homologous series and the point of commencement of the smectic mesophase indicates that the appearance of the smectic mesophase is influenced by the geometry of the molecules. If the molecules of the series are long, straight, rod-shaped and polarizable, the smectic phase commences early in the series. If the molecules are short and linear, the smectic phase appears at the middle members of the series but in homologous series where breadth is increased, the commencement of the smectic phase is always delayed ; sometimes it appears very late in the series, i.e. at the C_{16} or C_{18} derivative.

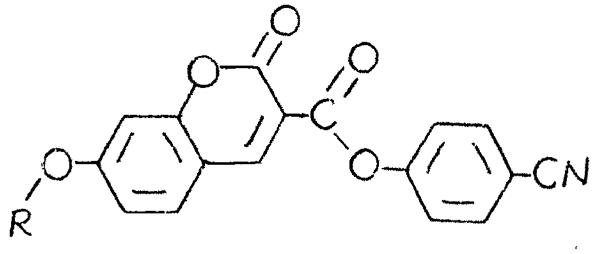
As can be seen from Table 24, the smectic phase in series A1, commences late as compared to series A2 and it is earlier as compared to series A3 and A4. The increased lateral intermolecular attraction in series A1 compared to series A3 explains the early commencement of the smectic phase in series A1. In series A4, the smectic phase, commences late by one member compared to series A1. The molecules of series A4 are shorter compared to series A1, but in the former series the breadth of the molecules is not more as well as the close packing of the molecules is not difficult. So the commencement of smectic phase is not delayed much. The molecules of series A1 are longer but the close packing of molecules is difficult and so, the commencement of smectic phase is not much earlier.

Thermal stability of series B1 is compared with that of the following series :

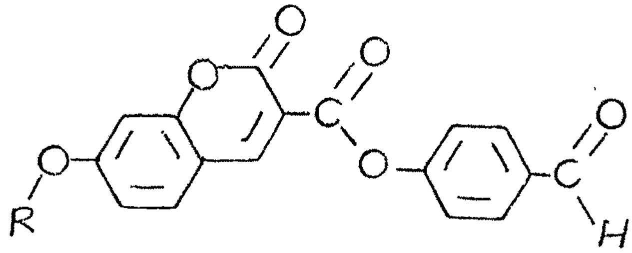
4-Formylphenyl 7-n-alkoxycoumarin-3-carboxylates (205) .... Series B2

4-(4'-n-Alkoxycinnamoyloxy)nitrobenzenes (219) ... sereis B3

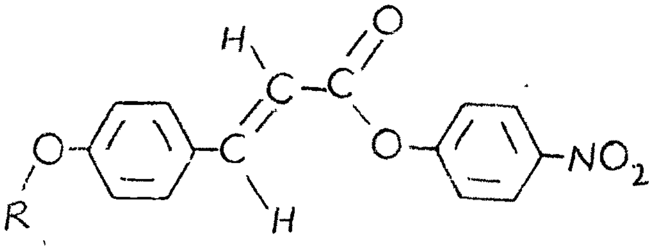
The thermal stabilities of these series are given in Table 25. The molecular geometry of the series is given in Fig. 16.



B1



B2



B3

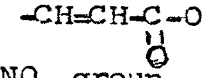
Fig. 16

Table 25

Average thermal stabilities (°C)

Series	B1	B2	B3
S - N or I	180.3	152.4	131.0
(C_{12} - C_{16})		(C_8 - C_{16})	(C_8 - C_{18})
Commencement of smectic phase	C_{12}	C_8	C_7

Reference to Table 25 indicates that the smectic thermal stability of series B1 is higher than that of series B2 and B3. The molecules of series B1 have a terminal -CN group whereas the molecules of series B2 have -CHO group at the corresponding position. The difference between the molecules of series B1 and those of series B3 is that the former series possesses a coumarin moiety and a terminal -CN group, whereas the latter has a $-CH{=}CH-\underset{\underset{O}{\|}}{C}-O$ group as the central linkage and a terminal $-NO_2$ group.



There are certain end groups which are known to impart smectogenic tendencies to the system. An ester group whose dipole is acting across the major molecular axis generally imparts smectogenic tendencies, i.e. the system becomes purely smectic. Patel (220) observed in his study of some Schiff base ester that the presence of $-CN$ and $-NO_2$ as the end groups change the system from nematogenic to smectogenic. The higher smectic thermal stability of the molecules of series B1 than those of series B2 can be attributed to the presence of strong dipolar terminal $-CN$ group in the series B1.

The smectic thermal stability of the molecules of series B3 is lower than those of series B1. Series B3 exhibits both smectic and nematic phases whereas the series B1 is pure smectogenic. In discussing the smectic group efficiency order for the low efficiency of $-CN$ and $-NO_2$, Gray attempted to relate it to the strong dipoles of nitro and cyano groups acting along the long molecular axis. Such dipoles can certainly be envisaged (214) as giving repulsions between molecules which lie parallel to one another i.e. side by side, and perpendicular to the layer planes of smectic liquid crystals. A number of homologous series are reported having a $-CN$ or $-NO_2$ end group but most of them are nematogenic in nature (221, 222). The molecules of series B1 contain coumarin moiety and in it the presence of lactone unit make the molecules of series B1 broad. While the molecules of series B3 contain a central linkage $-CH=CH-COO$ which not only increases the length but polarizability of the molecules. The increase in breadth of the molecules of series B1 and increase in length and polarizability of the molecules of series B3 can explain the higher thermal stability of series B1 and occurence of nematic phase in the series B3.

II. Derivatives of Pyridines

C1. 2-Methyl-5-(4'-n-alkoxycinnamoyloxy)pyridines

The thermal stability of this series will be discussed alongwith the comparision with the following series :

2-Methyl-5-(4'-n-alkoxybenzoyloxy)pyridines (223)	.....	Series C2
4-(4'-n-Alkoxybenzoyloxy)toluenes (224)	.....	Series C3
4-(4'-n-Alkoxycinnamoyloxy) toluenes	.....	Series G1

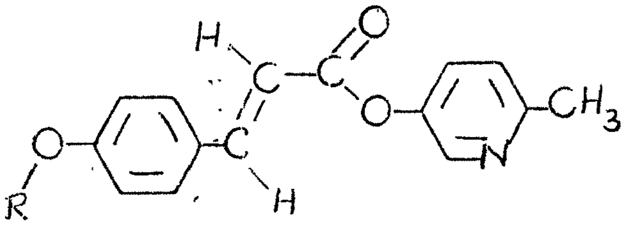
Table 26 compares the average thermal stabilities of series C1, C2, C3 and G1.

Table 26

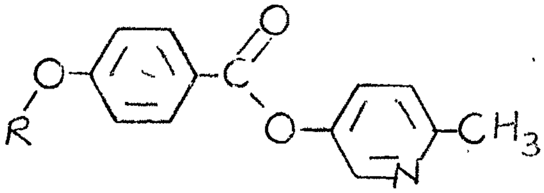
Average thermal stabilities (°C)

Series	C1	C2	C3	G1
S-N or I	110.7	65.4	52.8	94.9
(C_8 - C_{18})		(C_9 - C_{14})		(C_8 - C_{12})
Commencement of smectic phase	C_5	C_7	C_9	C_8

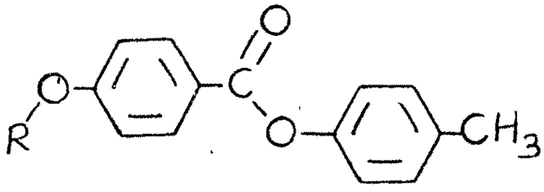
The geometry of these series is given in Fig. 17.



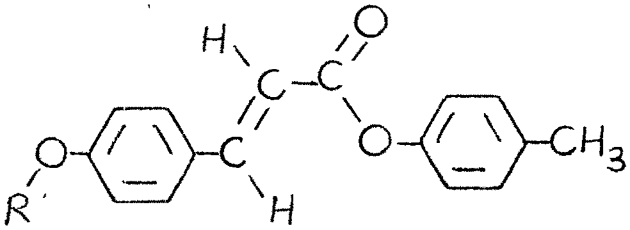
C1



C2



C3



G1

Fig. 17

The difference between the molecules of Series C1 and series C2 is that the former contain a vinylene unit. Due to the presence of vinylene group, the molecules of series C1 are longer than those of series C2. Generally an increase in the length of a molecule in a mesomorphic compound increases the overall thermal stability provided that it also increases the polarizability of the molecule. Thus by the addition of a unit such as a benzene ring or vinylene group to the molecule of a mesomorphic compound the thermal stability of smectic mesophase will increase as along as the molecule is not broadened. Thus the presence of the vinylene unit increases the length and the polarizability of the molecules of series C1 without any apparent change in the breadth of the molecules. The thermal stability of series C1, should therefore be increased as can be seen from the Table 26.

The thermal stability of series C1 is higher than that of series C3 and G1. The molecules of series C1 contain a vinylene group and a pyridine nucleus whereas the molecules of series C3 have a benzene ring in place of the heterocycle. The molecules of series C1 and those of series G1 do not differ in length. They have identical terminal groups and central linkages. The molecules of series C1 possess a heterocyclic pyridine nucleus whereas those of G1 possess a benzene ring.

In the case of pyridine derivatives (Series C1), the lateral dipole is added with little perturbation in molecular geometry as compared to benzene analogs (series C3 and G1). This is expected to lead to increased intermolecular forces of attraction (dipole - dipole and dipole - induced dipole). As suggested by Dewar et al. (125) in the case of pyridine ring, there exists a permanent dipole in the ring as shown in the following figure (Fig. 18).

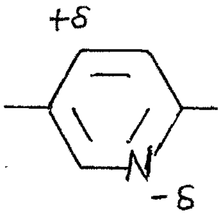


Fig. 18

This will have an attractive influence which will order molecules above and below it such that their dipoles will orient themselves to maximize ring dipole-dipole attractive forces. This mesophase strengthening effects lead to a greater thermal stability for this mono aza-aromatic system than the parent system.

The more pronounced smectogenic tendencies of the compounds of series C1 can be attributed to the presence of heterocyclic nitrogen atom. Oh (226) has suggested that the presence of the nitrogen atom in heterocyclic liquid crystalline Schiff bases is credited with enhancing smectogenic properties.

The smectic phase in series C1 commences at the pentyl derivative whereas in the series C2, C3 and G1, the smectic phase begins with the higher homologs. Konstantinov et al., (227) in their study of p-acylphenyl esters of p-n-alkoxybenzoic acids, have proposed that conjugation between the chain carbonyl group and the unshared electron pair of the ether oxygen atom via the π benzene ring system can enhance the primary formation of a smectic mesophase so that a smectic phase will occur at a lower homolog. According to them, such conjugation leads to an increase in polarizability of this particular part of the molecule and to an increase in the dipole moment of the carbonyl due to the growth of a partial negative charge on its oxygen. As a result there is increase in the energy of the intermolecular interactions of the dipole-dipole and dispersion types. This additional contribution to the energy of interaction between molecules predominates in the lateral direction and favours formation of a smectic mesophase starting with a lower homolog. A similar conjugation between the carbonyl group and the unshared electron pair of the heterocyclic nitrogen atom in the present series C1 as represented in Fig. 19 can explain the early commencement of smectic phase.

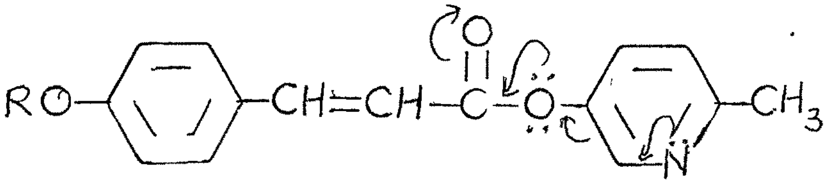


Fig. 19

Thus it can be said that the higher thermal stability of smectic mesophase in the case of series C1 than that in series C3 is due to the presence of the vinylene group which increases the length and polarizability of molecules of series C1 and the presence of pyridine nucleus whereas the higher thermal stability of smectic mesophase in series C1 than that in series G1 can be explained on the basis of difference in pyridine nucleus and benzene ring as discussed above.

The series E1 is compared with following homologous series.

4'-Formylphenyl 7-n-alkoxycoumarin-3-carboxylates (205) .... Series E2

4-(4'-n-Alkoxybenzoyloxy)benzaldehydes (228).... Series E3

4-(4'-n-Alkoxycinnamoyloxy)benzaldehydes (229).. Series E4

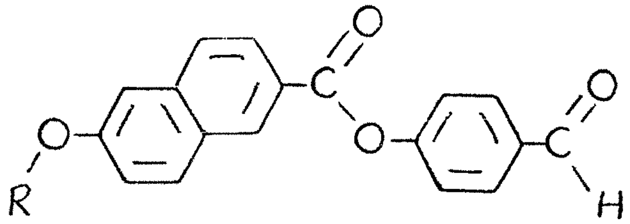
Thermal stabilities of these series are given in Table 27.

The molecular geometry of these series is given in Fig. 20.

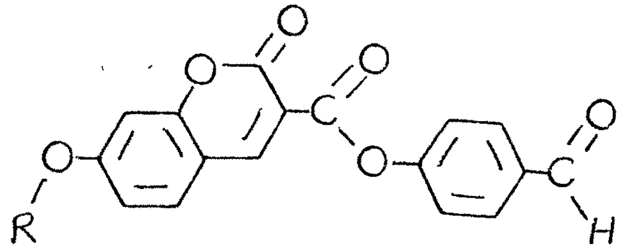
Table 27

Average thermal stabilities (°C)

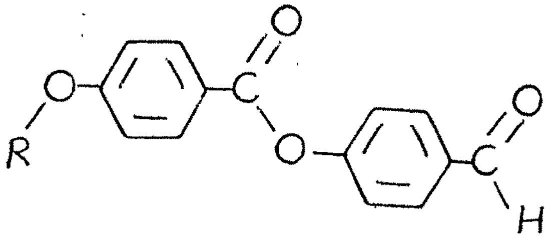
Series	E1	E2	E3	E4
N - I (C_1 - C_{12})	144.5	-	65.0	115.0 (C_1 - C_{10})
S - N or I (C_{14} - C_{16})	125.5	152.4 (C_8 - C_{16})	75.1	109.1
Commencement of smectic phase	C_{10}	C_8	C_{10}	C_8



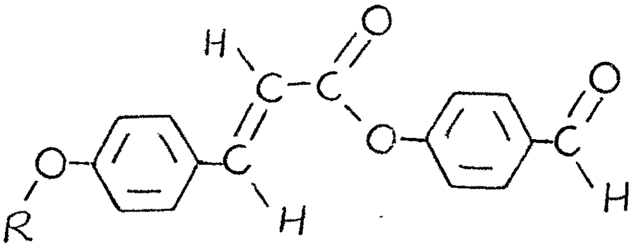
E1



E2



E3



E4

Fig. 20

Reference to Table 27 indicates that smectic thermal stability of series E1 is less than that of series E2. The only difference in the molecules of these two series is that the molecules of series E1 contain naphthalene nucleus whereas the molecules of series E2 containing coumarin nucleus . In naphthalene nucleus, both the rings are coplanar. In coumarin nucleus, also both the rings are almost coplanar. Now the difference between naphthalene and coumarin moiety is as follows :

In the series E1, the breadth of the molecules increases due to the presence of naphthalene nucleus, but the breadth increase will be less than that in series E2 because (i) the molecules of latter series are rather broad due to the presence of a ketonic group in coumarin moiety and (ii) there is an additional permanent dipole across the major axis of the molecules due to the presence of lactone moiety as shown in Fig. 16.

According to factor (i), the close packing of the molecules is rendered difficult in series E2. Hence intermolecular forces of attraction are weaker, giving rise to mesophases having less thermal stabilities. It *is* interesting to note that the smectic thermal stability is affected. The increase in the breadth of the molecules usually reduces the smectic thermal stability more compared to nematic thermal stability as the increase in the breadth reduces lateral intermolecular cohesions. But this is not observed in the case of series E2 as the reduction in the lateral intermolecular cohesions due to increase in breadth are compensated by the presence of the additional permanent dipole in coumarin moiety which exerts its attractive effect in the lateral direction. (factor (ii)).

The molecules of series E1 and series E2 are almost similar in length, but due to the presence of coumarin moiety in the molecules of series E2, the molecules of series E1 are comparatively longer than those of series E2. The relative increase in length of the molecules of series E1, explains the appearance of nematic phase upto dodecyl derivative. It is interesting to note that nematic phase is absent in series E2. Had the initial homolog been mesomorphic, the appearance of the nematic phase would have been expected as the molecules of series E2 are also long.

The molecules of series E1 are thermally more stable than those of series E3, both the smectic and nematic thermal stabilities are increased. The two series are similar, except that the series E1 possesses a naphthalene nucleus in place of benzene ring in series E3. Thus the molecules of series E1 are longer and more polarized than those of series E3 due to the presence of one more polarizable benzene ring. Generally, an increase in the length of a molecule in a mesomorphic compound increases the overall thermal stability, provided that it also increases the polarizability of the molecules. Thus by the addition of a unit such as a benzene ring to the molecules of the mesomorphic compound, the thermal stabilities of the mesophases will increase as long as the molecule is not broadened. Thus the length and the polarizability of the molecules of series E1 will be increased without any apparent change in the breadth of the molecules. Both the thermal stabilities of series E1 should, therefore, be increased as can be seen from the Table 27.

The mesophases of series E1 are thermally more stable than those of series E4. The only difference between the two series is that the former contains naphthalene nucleus in place of vinylbenzene nucleus at the corresponding position in series E4. Gray and Jones (230) have reported that 6-n-alkoxy-2-naphthoic acids and trans-p-n-alkoxycinnamic acids are similar in shape and size. The molecules of series E1 should, therefore, be similar in shape and size to those of series E4 ; the effect should thus be similar on the two mesophases. But the presence of one more aromatic ring in series E1 compared with the vinylene bond in series E4, make the molecules of series E1 more polarized and consequently more mesomorphic. The presence of vinylene bond in the 4'-formylphenyl trans-p-n-alkoxycinnamates makes the close packing of the molecules more difficult. Thus the lateral attractions will be reduced more, which in turn will reduce the thermal stability of the smectic phase in series E4.

The thermal stability of series F1 will now be compared with that of the following series :

7-(4'-n-Alkoxybenzoyloxy)-3-acetylcoumarins (205)
.... Series F2

4-(4'-n-Alkoxybenzoyloxy)acetophenones (228)
.... Series F3

4-(4'-n-Alkoxycinnamoyloxy)acetophenones (231)
.... Series F4

4- (4'-n-Alkoxybenzylidene)amino) acetophenones (232)
.... Series F5

The thermal stabilities of these series are given in Table 28.

Table 28

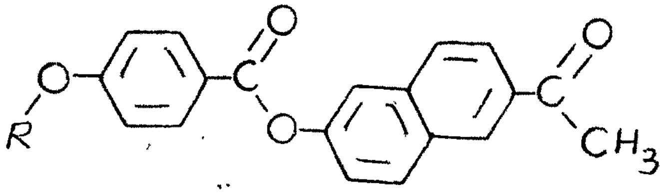
Average thermal stabilities (°C)

Series	F1	F2	F3	F4	F5
N - I (C_1 - C_{10})	168.5	143.3 (C_4 - C_6)	86.8	136.8	109.4
S - N or I (C_{12} - C_{18})	153.5	151.2 (C_5 - C_{18})	93.9	134.4	109.7
Commencement of smectic phase	C_8	C_5	C_5	C_5	C_3*

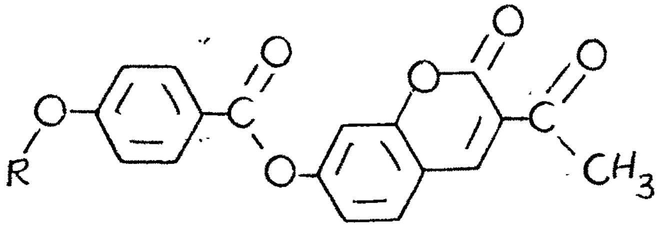
* Haller and Cox have not reported first two homologs but Arora et al. (233) have reported and they are non-mesomorphic.

The molecular geometry of the series is given in Fig. 21.

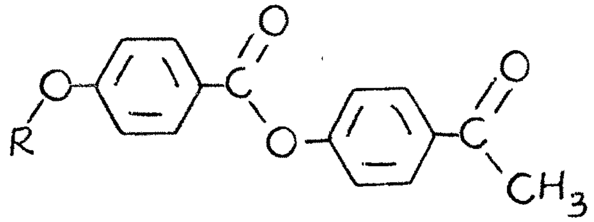
Compared with series F1, the thermal stability of the nematic phase in series F2 is less, while the smectic thermal stability of the series F1 is almost the same as that of series F2. Both the series have identical corresponding



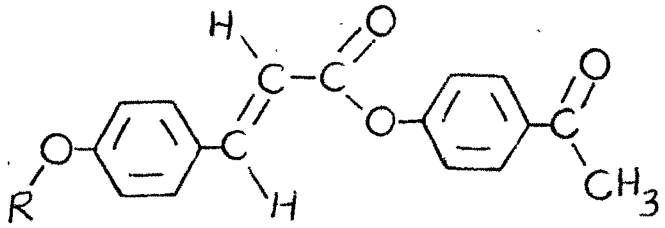
F1



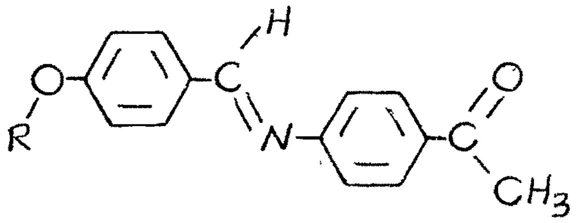
F2



F3



F4.



F5

Fig. 21

end groups and the central linkages. The difference between the two series is that the former possesses naphthalene nucleus whereas the latter possesses the coumarin nucleus. The presence of a ketonic group and an additional permanent dipole across the major axis of the molecules in series F2 makes them shorter than those of series F1. The increase in length and polarizability due to benzene nucleus makes the nematic mesophase of series F1 thermally more stable than that of series F2. The smectic thermal stability of series F1 and F2 is almost equal because the lateral attractions due to the C=O group of lactone ring in series F2 is less effective as it operates almost at the end of the molecules and renders the close packing of molecules rather difficult. The lateral intermolecular attractions are weaker.

Both the thermal stabilities, smectic and nematic of series F1 are higher than that of series F3. The difference in the thermal stabilities of the two series lies in the fact that the series F1 contains a naphthalene nucleus in place of a benzene ring in the series F3. As discussed earlier, presence of one more benzene ring not only increases the length but also the polarizability of the molecules of series F1.

The mesophases of series F1 are thermally more stable than series F4. The difference between the two series is that the former possesses a naphthalene ring whereas the latter possesses a benzene ring and secondly, the central linkage in the former is $-\underset{\underset{O}{\|}}{C}-O-$ unit while that in the latter is $-CH=CH-\underset{\underset{O}{\|}}{C}-O$ unit. The presence of benzene ring makes the molecules of series F1 longer and more polarizable compared to series F4. But the thermal stability of series F4 is not as much decreased as compared to series F3, because the molecules of series F4 have one more polarizable unit in the form of vinylene bond than those of series F3.

The higher values of nematic and smectic thermal stabilities of series F1 compared to series F5 can be attributed to the higher molecular length of series F1 which will increase intermolecular cohesions of all types. The molecules of series F5 will be less non-coplanar due to $-CH=N-$ central linkage compared to those of series F1 which possess $-C-O-$central linkage (233). The earlier commencement of the smectic phase in series F5 compared to series F1 can be attributed to the more favourable close packing of the molecules and to the low melting points of the compounds.

C. Laterally Substituted Mesogens

Generally the introduction of a lateral substituent is deterrent to all types of mesophases. Literature survey reveals several classes of liquid crystals with lateral substitution (214, 234-244). Several systems are known (245-249) wherein a lateral substituent either in a phenyl ring or in the α -position of a central linkage has reduced the melting as well as the clearing temperatures, the latter, however being more marked. The liquid crystals exhibiting mesophases near room temperatures are thus possible if a lateral substituent is placed at a proper position in suitable system. In quest of obtaining low melting liquid crystals with broad mesophase range, it was noted that a lateral substituent like chloro or methyl is quite effective in reducing crystal - mesophase temperature to give low melting liquid crystals. In light of this it seemed of interest to introduce a bulky ethoxy group as a lateral substituent in a p-phenylene system. It should decrease the crystal - mesomorphic and mesomorphic - isotropic liquid transition temperatures. The mesogenic compounds with lateral ethoxy group are rare.

In the present study the three homologous series (one with lateral methyl and a bulky ethoxy substituents and two with bulky ethoxy substituent) were synthesized and mesomorphic properties of their members studied.

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-anisidines .... Series H1

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-toludines .... Series J1

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-2"-4"-dimethylanilines ..... Series K1.

INDIVIDUAL CHARACTERISTICS

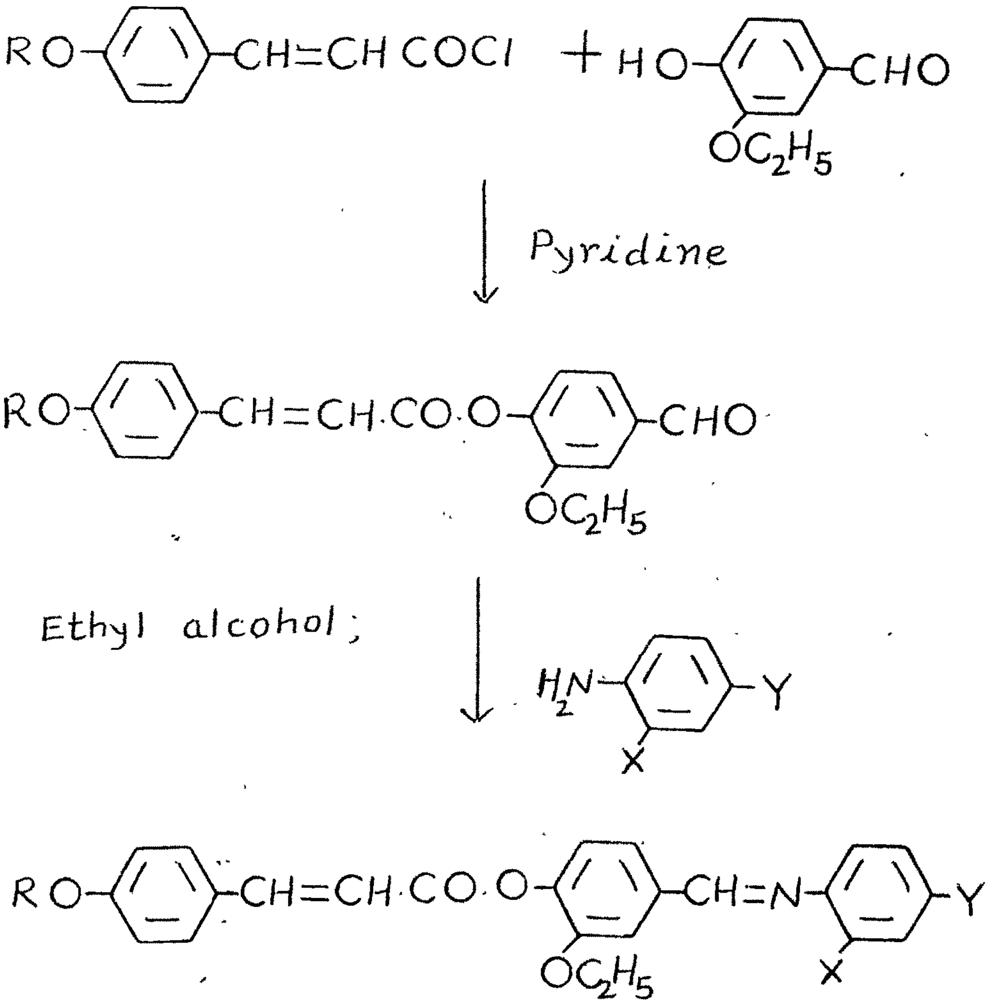
H1. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-anisidines

A homologous series of fourteen Schiff base esters was synthesized by the synthetic route shown in Scheme 7. The melting points and transition temperatures of the compounds are summarized in Table 29. The structure of hexyl homolog was confirmed by NMR spectrum.

NMR ($CDCl_3$) : δ 0.9 (t, 3H, $-CH_3$ of hexyloxy chain), 1.3 - 1.8 (m, 11H, $-CH_3$ of lateral ethoxy group and $-(CH_2)_4-$ of hexyloxy chain), 3.8 (s, 3H, $-CH_3$ of methoxy gr. at $C_{4''}$), 3.9 - 4.3 (m, 4H, two $-O-CH_2-$ of hexyloxy at C_4, and lateral ethoxy gr.) 6.4 - 6.6 (d, 1H, J=18Hz), of =CH-COO gr.) 6.8 - 7.6 (m, 11H, aromatic protons), 7.7 - 7.9, (d, 1H, (J=18Hz), =CH-Ph gr), 8.4 (s, 1H, -CH=N gr) (Fig. 22).

All the Schiff base esters are enantiotropic nematic exhibiting beautiful nematic threaded texture. No member adopts homeotropic textures. Smectic phase is absent

Scheme 7



where $X = H$; $Y = OCH_3$ ------- series H1
$X = H$, $Y = CH_3$ ------ series J1
$X = Y = CH_3$ ---------- series K1

Table 29

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-anisidines

n-Alkyl group	Transition temperatures (°C)	
	Nematic	Isotropic
Methyl	146.5	201.5
Ethyl	154.0	220.0
Propyl	136.5	197.5
Butyl	134.0	196.0
Pentyl	119.0	182.0
Hexyl	92.5	176.5
Heptyl	101.0	174.5
Octyl	104.0	163.5
Nonyl	96.5	161.5
Decyl	91.0	158.4
Dodecyl	95.5	153.0
Tetradecyl	95.0	146.5
Hexadecyl	95.0	136.5
Octadecyl	96.5	127.5

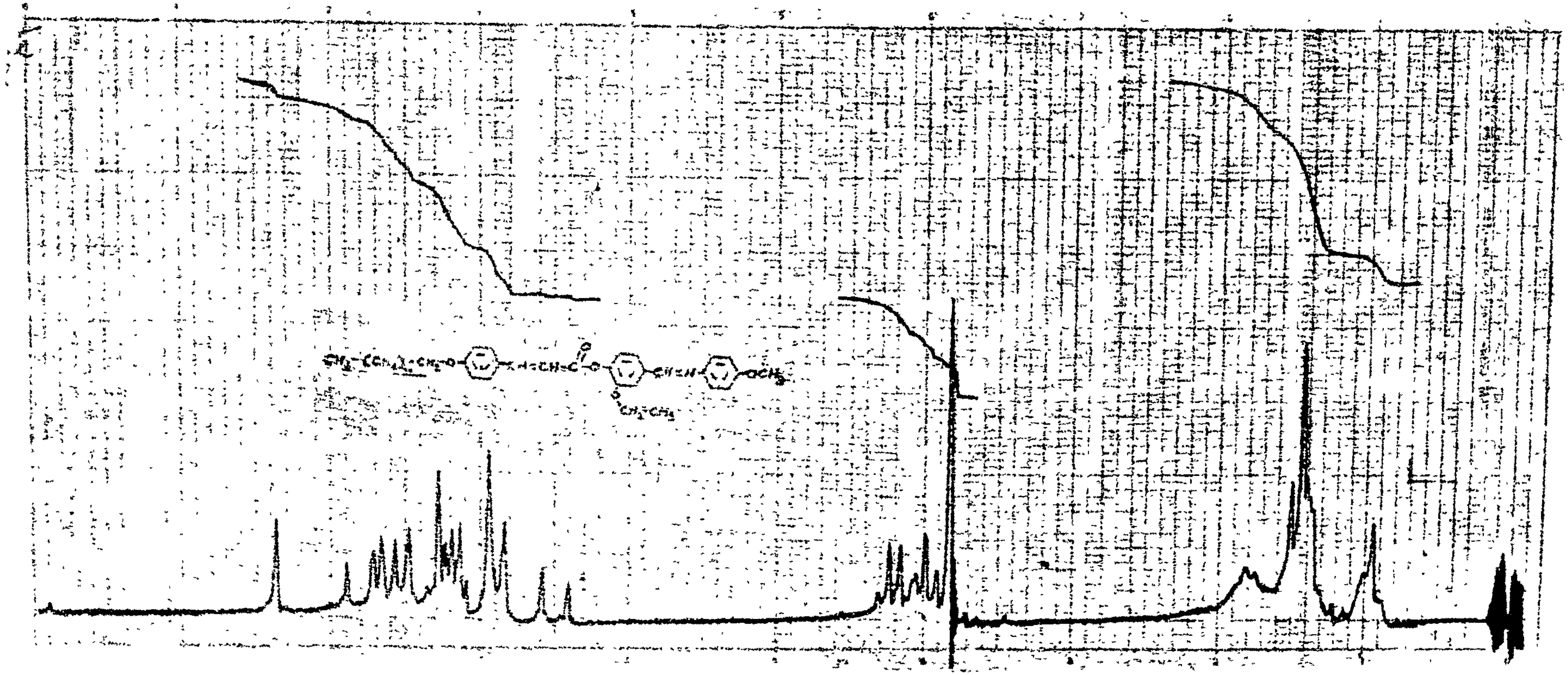


Fig. 22

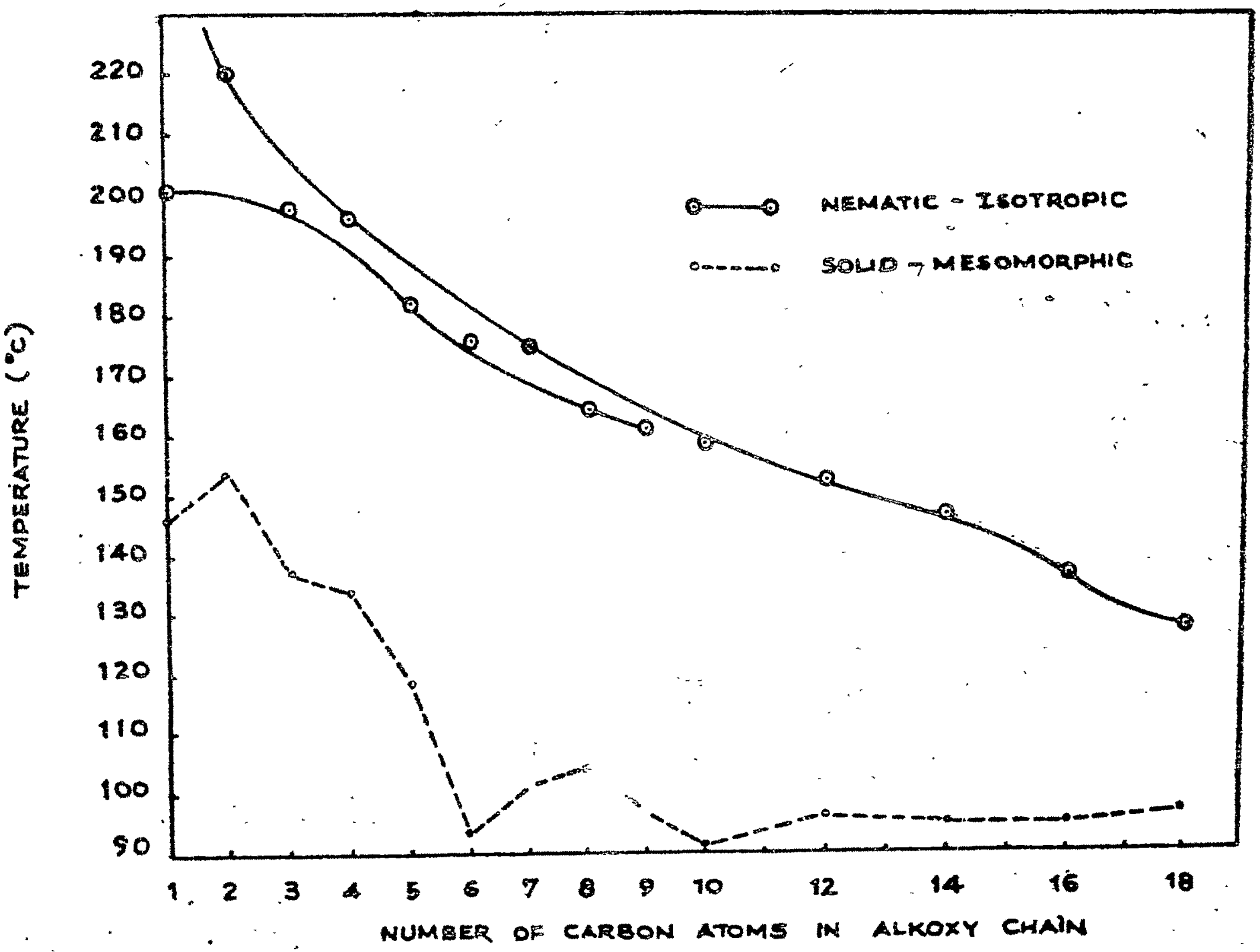


FIG.23 4-(4'-n-ALKOXYCINNAMOYLOXY)-3-ETHOXYBENZYLIDENE-4''-ANISIDINES in the series. When the N-I transitions are plotted against the number of carbon atoms in the alkoxy chain (Fig. 23), they exhibit odd-even effect. The even members occupy upper curve as usual.

J1. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-toludines

A homologous series of thirteen Schiff base esters was synthesized as shown in Scheme 7. The transition temperatures of the compounds are compiled in Table 30. The structure of the pentyl derivative was confirmed by NMR spectrum. NMR ($CDCl_3$) : δ 1.0 (t, 3H, CH_3 of pentyloxy chain), 1.4 - 2.0 (m, 9H, CH_3 of lateral ethoxy group and $-(CH_2)_3-$ of pentyloxy chain), 2.5 (s, 3H, CH_3 group at $C_{4''}$). 4.05 - 4.4 (m, 4H, two $-O-CH_2-$ of pentyloxy at $C_{4'}$ and lateral ethoxy group), 6.55 - 6.75 (d, 1H, J = 9Hz, of = CH.COO gr.), 7.00 - 7.85 (m, 11H, aromatic protons), 7.9 - 8.1 (d, 1H, J = 9Hz, of CH = Ph gr.), 8.5 (s, 1H, -CH=N gr.). (Fig. 24).

All the Schiff base esters are enantiotropic nematic except the hexadecyl derivative which exhibits monotropic nematic phase. No member adopts a homeotropic texture. Smectic phase is absent in the series. Fig. 25 shows the relationship of transition temperatures to carbon numbers

Table 30

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-4"-toludines

n-Alkyl group	Transition temperatures (°C)	
	Nematic	Isotropic
Methyl	153.0	173.5
Ethyl	170.5	182.5
Propyl	137.5	177.0
Butyl	123.5	167.0
Pentyl	135.5	156.5
Hexyl	122.5	153.5
Heptyl	107.0	142.5
Octyl	111.5	134.0
Nonyl	97.0	130.5
Decyl	98.5	126.5
Dodecyl	105.0	126.0
Tetradecyl	89.5	115.5
Hexadecyl	(65.0)	96.0

Values in parentheses indicate monotropy

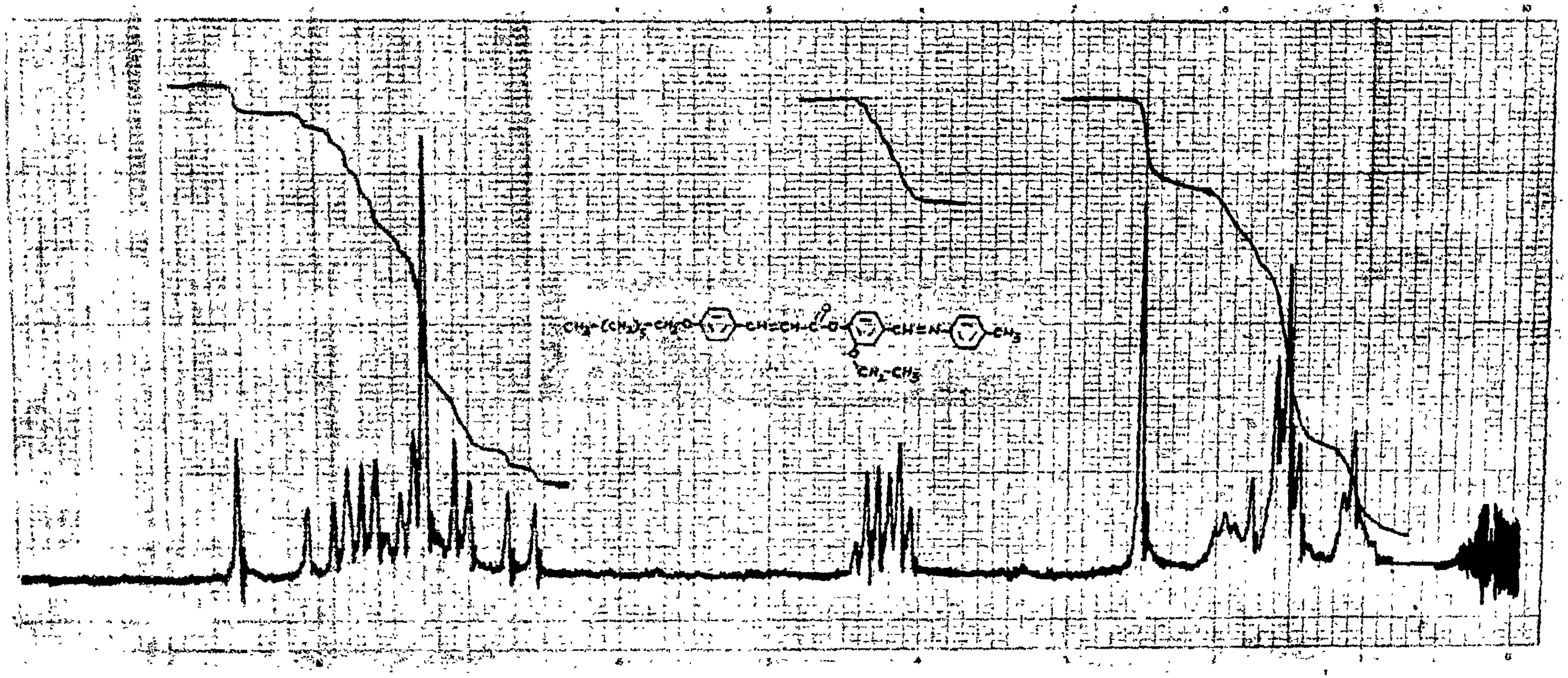


Fig. 24

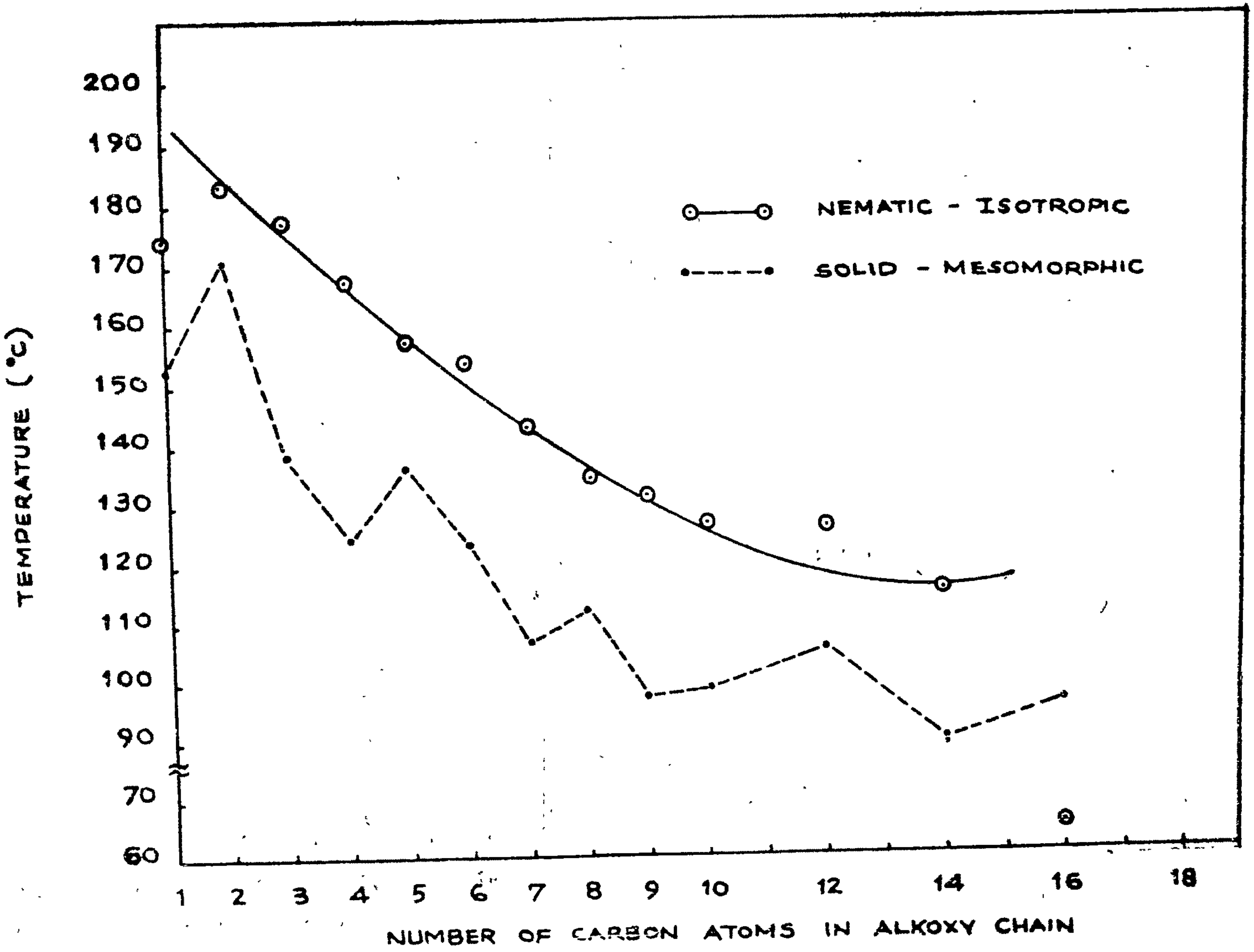


FIG 25 4-(4'-n-ALKOXYCINNAMOYLOXY)-3-ETHOXYBENZYLIDENE-4''-TOLUIDINES in the alkoxy chain. The N-I transitions lie on the one falling curve and do not exhibit odd-even effect.

K1. 4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-2",4"-dimethylanilines

A homologous series of thirteen Schiff base esters was synthesized by the synthetic route shown in Scheme 7. The melting points and transition temperatures of the compounds are summarized in Table 31. The structure of the hexyl homolog was confirmed by NMR spectrum. NMR ($CDCl_3$) δ 0.9 (t, 3H, CH_3 of hexyloxy chain), 1.3 - 1.6 (m, 11H, CH_3 of lateral ethoxy group and $-(CH_2)_4-$ of hexyloxy chain). 2.3 (s, 6H, two CH_3 groups at $C_{2''}$ and $C_{4''}$), 4.05 - 4.4 (m, 4H, two $-CH_2-O-$ of lateral ethoxy gr. and hexyloxy chain), 6.55 - 6.75 (d, 1H, J = 9Hz, of $=CH.COO$ gr.), 6.95 - 7.8 (m, 10H, aromatic protons), 7.85 - 8.05 (d, J = 9Hz, 1H of = CH-Ph gr.), 8.4 (s, 1H, of $-CH=N-$gr). (Fig. 26)

All the Schiff base esters are enantiotropic nematic. The smectic phase commences at the tetradecyl derivative as monotropic form and continues upto the last member, hexadecyl derivative. The nematic and smectic phases observed in this series have nematic threaded and focal conic smectic textures respectively. Only one member,

Table 31

4-(4''-n-Alkoxycinnamoyloxy)-3-ethoxybenzylidene-2",4"-dimethylanilines

n-Alkyl group	Transition temperatures (°C)		
	Smectic	Nematic	Isotropic
Methyl	-	138.5	151.5
Ethyl	-	140.5	153.5
Propyl	-	121.5	143.5
Butyl	-	97.5	147.0
Pentyl	-	98.5	143.0
Hexyl	-	87.5	134.0
Heptyl	-	88.5	124.5
Octyl	-	106.5	125.5
Nonyl	-	94.0	123.5
Decyl	-	94.5	114.5
Dodecyl	-	92.0	112.5
Tetradecyl	(42.5)	95.0	109.5
Hexadecyl	(61.5)	96.0	102.5

Values in parentheses indicate monotropy

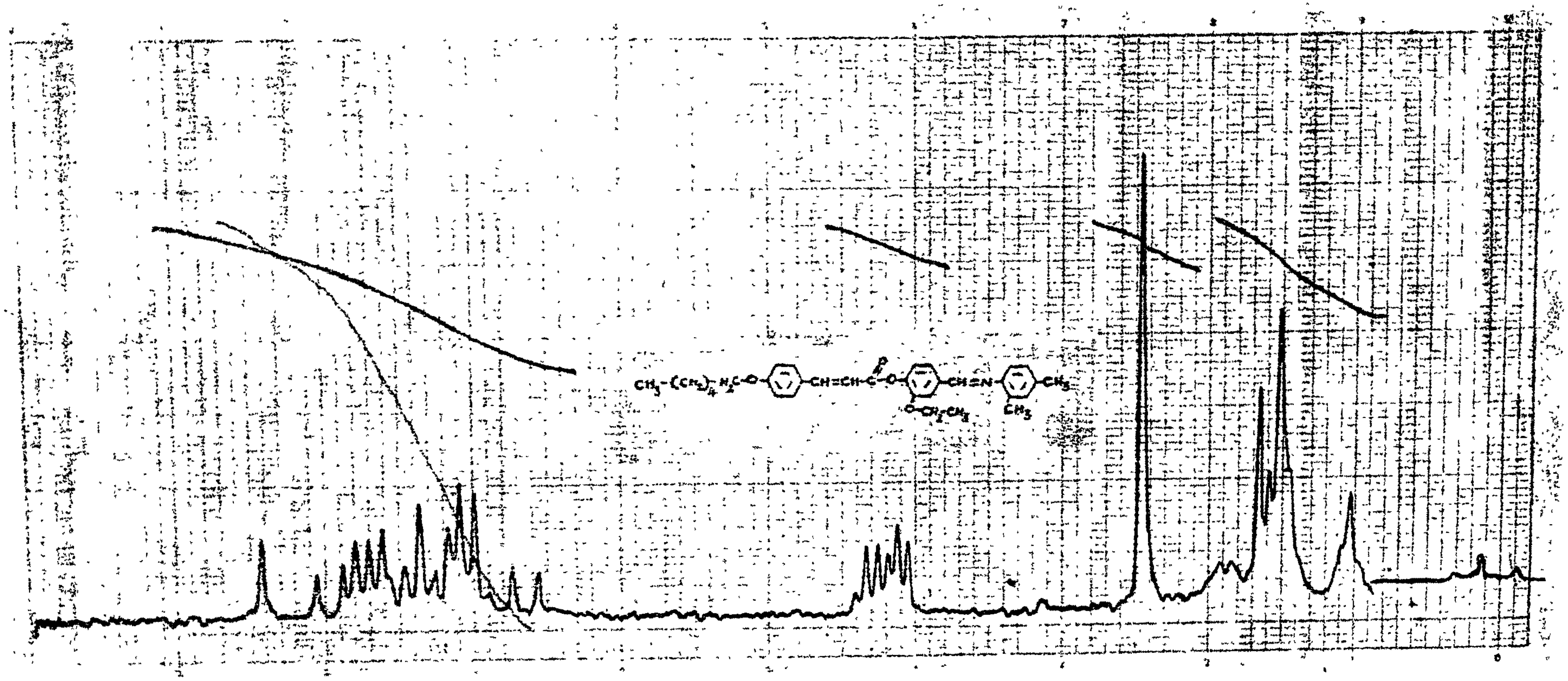


Fig. 26

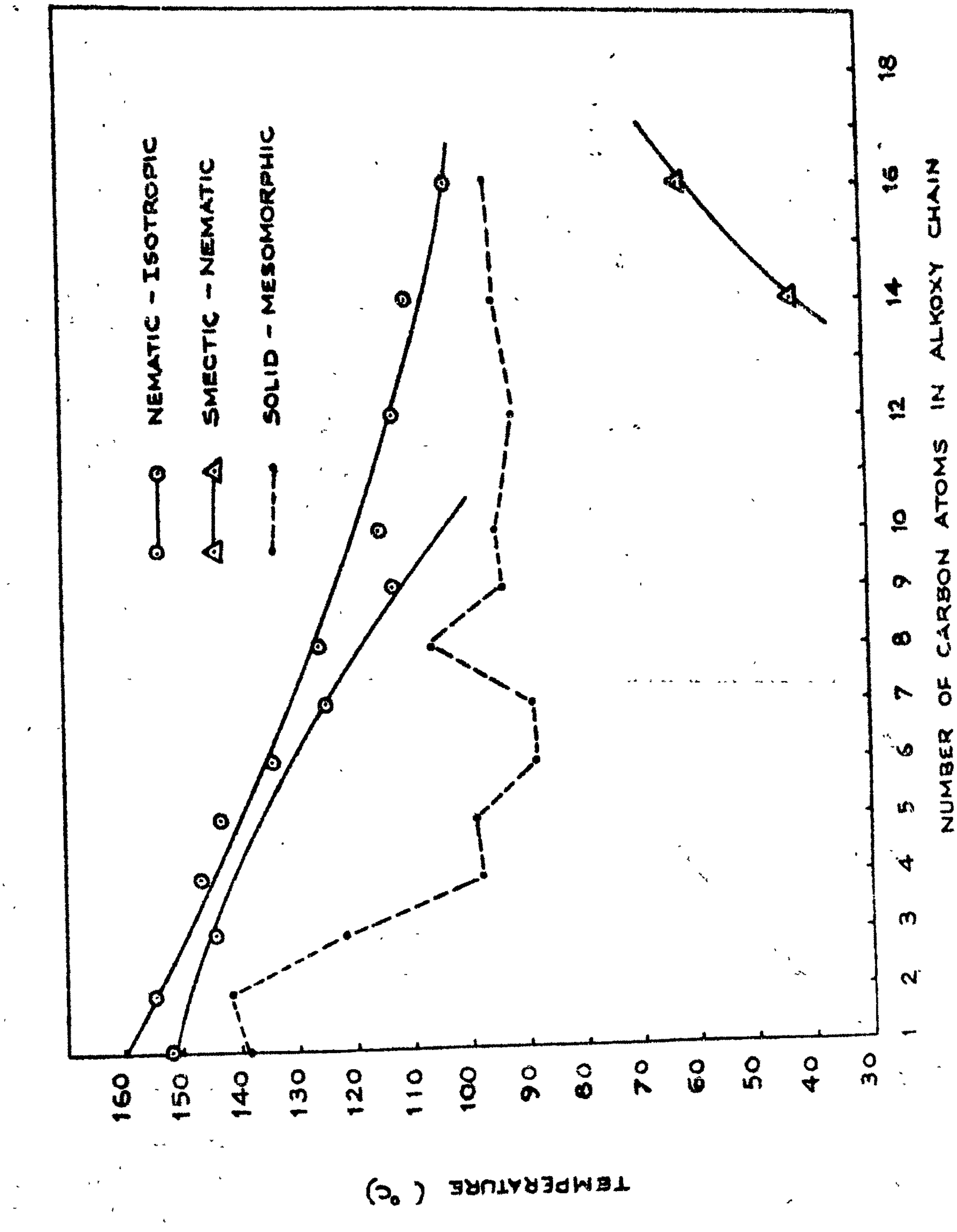


FIG 27 4-(4'-n-ALKOXYCINNAMOYLOXY)-3-ETHOXYBENZYLIDENE -2'',4''-DIMETHYLANILINES the propyl derivative, adopts a homeotropic texture during cooling. Fig. (27) shows the relationship of transition temperatures to carbon numbers in the alkoxy chain The N-I transitions lie on two falling curves exhibiting normal odd- even effect, the even members occupying the upper curve as usual. The S-N transition curve rises smoothly but does not merge with the descending N-I transition curve.

COMPARATIVE STUDY

The thermal stabilities of the mesophases of the series H1 will be compared with those of the following series :

4-(4'-n-Alkoxybenzoyloxy)-3-ethoxybenzylidene-4"-anisidines (206) ...... Series H2

4-(4'-n-Alkoxybenzoyloxy)-3-methoxybenzylidene-4"-anisidines (250) ...... Series H3

4-(4'-n-Alkoxycinnamoyloxy)benzylidene-4"-anisidines (251) ...... Series H4

Table 32

Average thermal stabilities (°C)

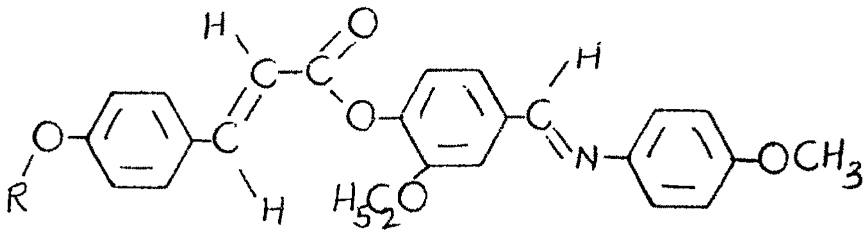
Series	H1	H2	H3	H4
N-I	171.0	128.0	160.3	249.2
(C_1 - C_{18})		(C_1 - C_{16})		(C_7 - C_{18})
Commencement of smectic phase	*	*	*	C_8

* Smectic phase is absent

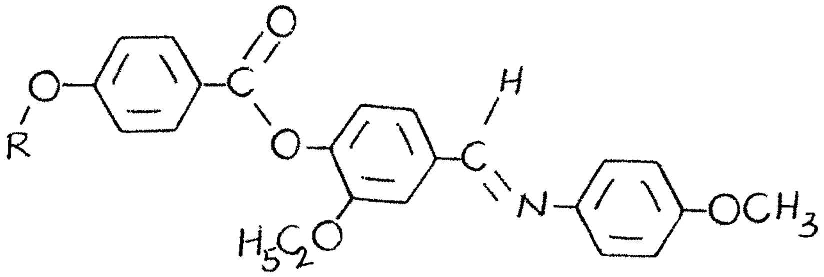
The geometry of these series is given in Fig. 28

The thermal stabilities of the molecules of series H1 are higher than those of series H2. The molecules of series H1 contain an extra vinylene bond as the central linkage. The higher nematic thermal stability of series H1 must be resulting from the increases in length and polarizability of its molecules due to the presence of the vinylene bond.

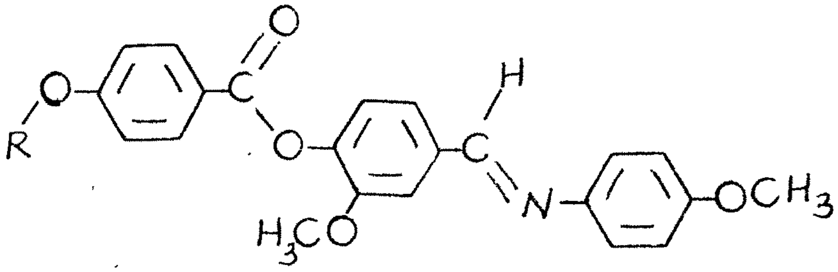
The melting points of the compounds of series H1 range from 91.0°C to 154.0°C ; for the series H2 from 83.0°C to 151.0°C ; for the series H3 from 81.0°C to 149.0°C and the range in the case of series H4 is from 96.5°C to 162.0°C.



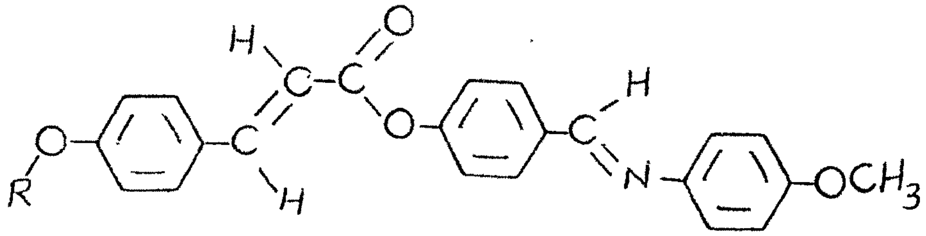
H1



H2



H3



H4

Fig. 28.

The series H4 does not have any lateral group (other than H atom) and the series H3 has lateral methoxy group on the central benzene ring and ortho- to the CO-O linkage. Now the series H1 and series H2 have lateral ethoxy group in the said position, even than not much difference in melting point is observed compared to series H3. It is indicated that the melting points are not much affected furthermore by making the lateral group bulkier ; but the nematic - isotropic transition temperatures are definitely affected. The comparision of melting point range of series H1, series H2 and series H3 suggests that in the solid state, the molecules of these series arrange in such a way that the ethoxy group as well as the methoxy group fit in some sort of pockets and hence the crystal mesomorphic transition temperatures are not much affected. The detail about the overall moleculer arrangement in the crystal lattices of these compounds can only be revealed by X-ray studies. The higher nematic thermal stability of series H1 than that of series H3 can be attributed to greater molecular length and polarizability of the molecules of series H1, as they have an extra vinylene unit in the centre. Thermal stability of series H1 is less than that of series H4. The difference between the two series is that the former has a lateral substituent ethoxy group, whereas the latter has a hydrogen atom at the corresponding position. Introduction of a lateral substituent into the side position of the molecule of a mesomorphic compound has two opposing effects (214).

(i) The substituent will decrease both smectic and nematic thermal stabilities by increasing the separation of the long axes of the molecules and

(ii) The substituent will increase both smectic and nematic thermal stabilities because of its polarization effects which will enhance intermolecular cohesions.

Of the two opposing effects, the first always predominates unless the substituent does not exert its full breadth increasing effect.

As suggested by Arora et al., (252) when a substituent is on central benzene ring, its position being ortho to the ester linkage, the twisting around C_4-O bond in the compounds of series H1 will be more due to the steric factor of the ethoxy group. This may result in twisting in these molecules and this further reduce the coplanarity of the molecules. This in turn, will decrease the polarizability of the laterally substituted compounds compared to unsubstituted ones, there will also be a change in resultant moments. Thus we could expect a decrease in the thermal stabilities of the liquid crystals phases in the laterally substituted derivatives.

Molecules of series H1 have a bulky ethoxy group ortho- to the ester linkage which has two fold effects.

(i) of increasing the breadth of molecules and

(ii) of reducing the coplanarity of the molecules

Therefore, the lower nematic thermal stability of series H1 compared to series H4 can be understood.

The next point is the absence of smectic phase in series H1, H2 and H3. In the case of series 4-n-Alkoxy benzylideneamino fluorenones and 4-n-Alkoxybenzylidene aminobiphenyls having substituent in 2- or 3-positions (96) and 2-methyl-1,4-phenylene bis (4'-n-alkoxybenzoates) (252) the last members of the series do not exhibit only smectic phase. In these series, the steric effect due to lateral substituent increases the thickness of the molecules which, in turn, makes the close packing of the molecules difficult in a parallel alignment and results in a weakening of intermolecular cohesions. The last members of the naphthylidene Schiff bases synthesized by Dave et al.

(90, 91) also do not show only smectic phase i.e. they are not purely smectogenic. However, there are a number of homologous series exhibiting pure nematic mesophase upto the last member of the series and without commencement of smectic mesophase (220, 253). This indicates that irrespective of mesophase type, if the molecule is broad and the length to breadth ratio is changed considerably, the normal behaviour of the homologous series is changed. This can be explained as the increase in breadth reduces lateral cohesive forces and for a compound to exhibit only smectic phase, the lateral cohesive forces should be much higher than the terminal cohesive forces. In such systems, even in the last members, the molecules are arranged in such a manner that, on heating, the molecular layers get disrupted directly to the nematic or isotropic state. The absence of smectic phase in series H1 can thus be understood.

Now the thermal stability of series J1 will be compared with the following series.

4-(4'-n-Alkoxycinnamoyloxy)benzylidene-4"-toludines (254) ..... Series J2

4-(4'-n-Alkoxybenzoyloxy)-3-ethoxybenzylidene-4"-toludines (36) ..... Series J3

4-(4'-n-Alkoxybenzoyloxy)-3-methoxybenzylidene-4"-toludines (253) ...... Series J4.

Table 33 summarizes the average thermal stability of these series.

Table 33

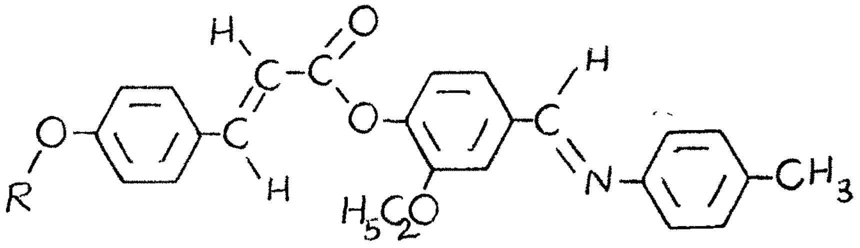
Average thermal stabilities (^{o}C)

Series	J1	J2	J3	J4
N-I (C_1 - C_{16})	144.7	234.7	93.7	130.2
Commencement of smectic phase	*	C_7	*	*

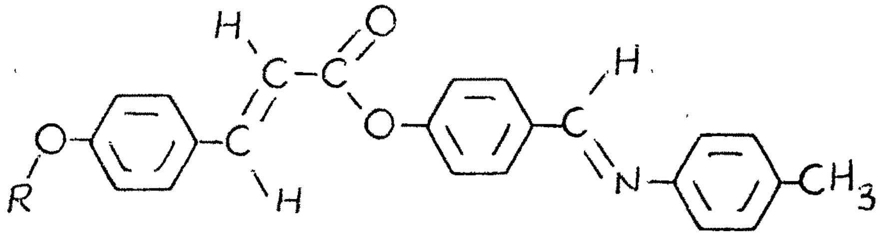
* Smectic phase absent

The geometry of these series is given in Fig. 29.

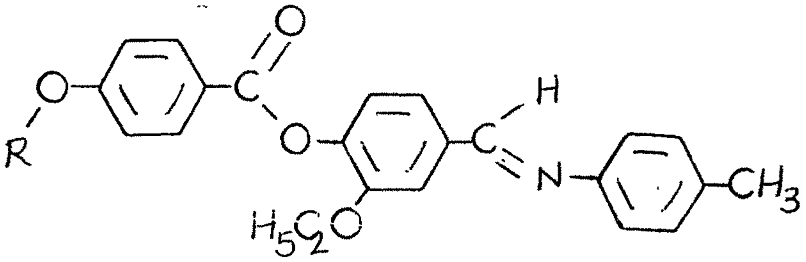
The higher thermal stabilities of nematic phase in series J1 than that of series J3 and J4 and the lower thermal stability of series J1 than series J2 can well be explained by the similar arguments, as mentioned in the comparision of thermal stabilities of series H1, series H2, series H3 and series H4. Also, the absence of smectic phase in the series J1, series J3 and series J4 can be understood.



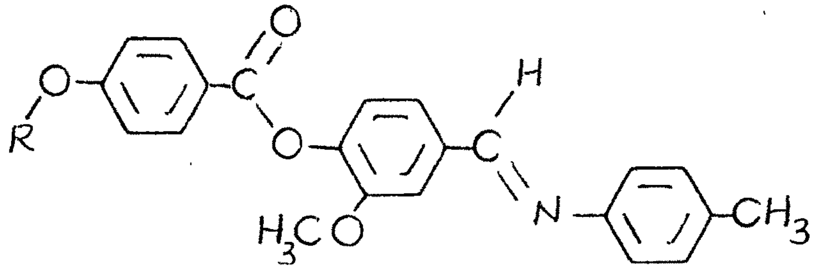
J1



J2



J3



J4

Fig. 29

Now, the nematic thermal stability of series H1 is higher than that of series J1. The molecular geometry of the two series is similar, the only difference being in the terminal substituents ; series H1 has a methoxy group at one end of the molecule and series J1 has a methyl group at the corresponding end of the molecule. It has been observed that in a homologous series a terminal methoxy group enhances the nematic thermal stability. The thermal stability orders of terminal groups for smectic and nematic mesophases in mesomorphic compounds have been deduced by Gray (54) in which MeO > Me for the nematic order.

Table 34 summarizes the difference in average nematic thermal stabilities among the series.

Table 34

Difference in average nematic thermal stabilities (°C)

Series No.	Difference (°C)
H4 - H1	78.2
J2 - J1	90.0

Reference to Table 34 indicates that introduction of lateral ethoxy group lowers the nematic thermal stability very much in the case of series H1 and J1 when compared with the unsubstituted one. It is interesting to note that the introduction of lateral ethoxy group in the non-substituted series H4 causes the lowering in nematic thermal stability by 78.2°C and the introduction of lateral ethoxy group in series J2 causes the lowering in nematic thermal stability by 90.0°C that is almost similar. Thus the lowering in nematic thermal stability due to lateral ethoxy group is independent of the nature of the terminal group, series H1 and J1 have different terminal groups at the right end.

The thermal stabilities of the mesophases of the series K1 will be compared with those of the following series :

4-(4'-n-Alkoxycinnamoyloxy)benzylidene-4"-toludines (254) .... Series J2

4-(4'-n-Alkoxycinnamoyloxy)benzylidene-2"-toludines (219) ..... Series K2

4-(4'-n-Alkoxybenzoyloxy)benzylidene--2",4"-dimethylanilines (248) ..... Series K3

Table 35 summarizes the average thermal stabilities and the commencement of the smectic mesophase in these series.

Table 35

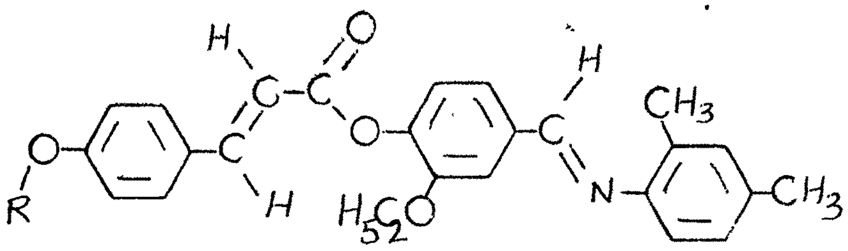
Average thermal stabilities (°C)

Series	K1	J2	K2	K3
N - I (C_1 - C_{16})	128.0	234.0	167.7 (C_1 - C_{12})	173.7 (C_1 - C_{18})
S - N or I (C_{14} - C_{16})	52.0	167.6 (C_7 - C_{18})	102.1	103.6 (C_{10} - C_{18})
Commencement of smectic phase	C_{14}	C_7	C_4	C_{10}

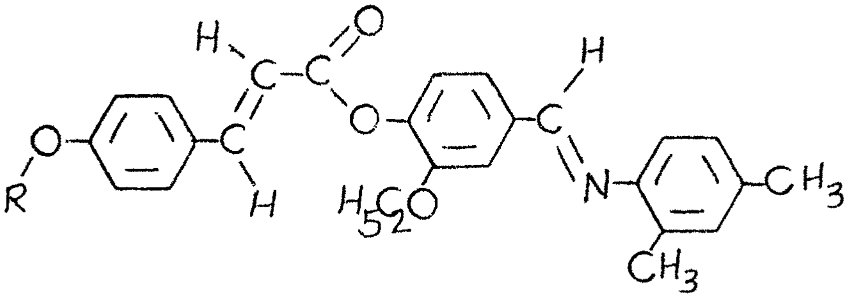
The molecular geometry of these series is given in Fig. 30.

The homologous series K1 and J2 differ in lateral substitution i.e. there is only H atom ortho- to the -CH=N- unit and at the 3-position in series J2 whereas there is a methyl group and a bulky ethoxy group at the said positions.

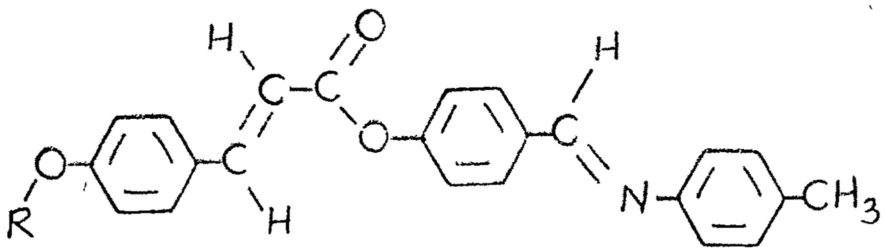
While series K1 is compared with the series J2, the average decreases, Δ t (H-Me, Eto) nematic = 106.0°C and Δ t (H-Me, Eto) smectic = 115.6°C in mesomorphic thermal



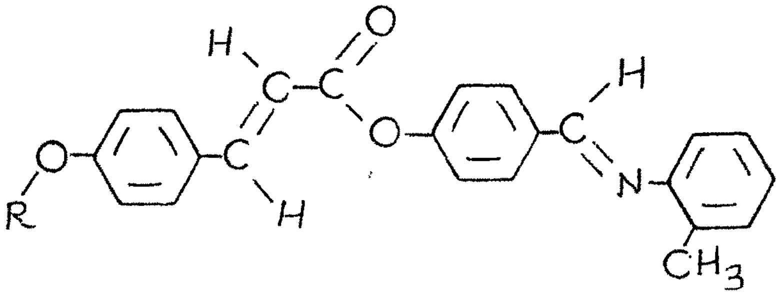
cis-K1



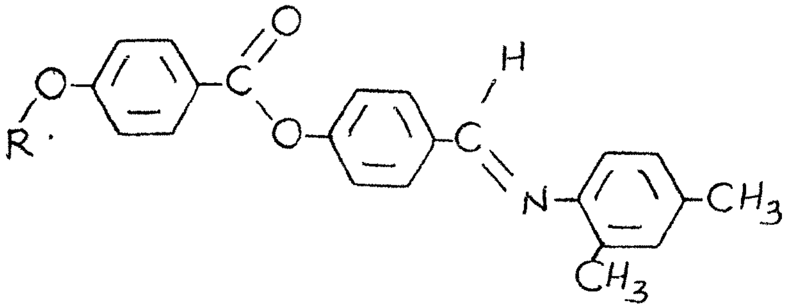
trans-K1



J2



K2



K3

Fig. 30

stability resulting from the introduction of methyl and ethoxy substituents are large.

The reason for the average decrease in the nematic and smectic thermal stabilities can be explained in two different ways :

(i) If the lateral methyl group and the -N=CH- linkage lie cis to one another (Fig. 30), the steric effect between the substituent and the hydrogen of the -N=CH- unit will prevent the molecule from being coplanar and rotation of parts of the molecules out of the plane has severe repercussions on the close packing giving rise to marked difference in thermal stability.

(ii) If the lateral methyl group and the -N=CH- linkage lie trans to one another the molecular breadth is considerable and the nematic, in particular smectic thermal stability should be low.

From the above discussion the decrease in smectic thermal stability is expected to be more than the decrease in nematic thermal stability.

The commencement of smectic phase is late in series K1 as compared to series J2. The arguments made for the less mesophase thermal stabilities can well explain the late commencement of smectic too. Due to increased breadth of the molecules, the lateral intermolecular forces of attraction are decreased in series K1 compared to the corresponding members of series J2. Hence, it requires longer alkoxy group in series K1 to observe smectic phase.

It is noteworthy that Gardlund et al. (255) and Gray (256) did not observe smectic phase in their studies on laterally substituted mesomorphic series. Gardlund et al. (255) synthesized shorter molecules compared to those of series K1 and they concluded that small increase in molecular breadth destroys smectic behaviour regardless of alkoxy or alkyl group chain length. The 3-substituted biphenyl monoanils of Gray (256) and the Schiff base esters of present series K1, both have three benzene rings. The biphenyl monoanils have substitution on central benzene ring, whereas the molecules of series K1 have substitution on central as well as terminal benzene ring. Moreover, there is no methyl group at the end of the biphenyl ring and there is methyl group at the right end in series K1. Due to combined effect of these two factors, the monoanils of Gray do not exhibit smectic phase.

The thermal stabilities of both the smectic and nematic mesophases in the case of series K1 are lower than those in the series K2 and K3. The difference between the molecules of series K1 and those of series K2 is that the former has one more lateral substituent ethoxy group and a terminal methyl group at 4"-position whereas the latter has hydrogen atoms at the corresponding positions. The increase in breadth to length ratio in the molecules of series K1 explains the lower thermal stability than series K2.

The difference between the molecules of series K1 and K3 is that the former possesses a vinylene unit in the centre and a lateral ethoxy group. The length of the molecules of series K1 is increased due to the presence of vinylene unit. The nematic thermal stability of series K1 should, be higher than series K3 since increase in length and polarizability of molecules increases the nematic thermal stability, but series K1 is thermally less stable than series K3. The presence of lateral ethoxy group in the molecule of series K1 must be increasing breadth to such an extent that the length and the polarizability of the molecules due to vinylene unit is not that effective. This should explain the higher smectic thermal stability and early commencement of smectic phase in the case of series K2 and K3.

D. Non-mesomorphic Homologous Series

Fourteen laterally substituted aldehydes of this series were synthesized. The crystal-Isotropic temperatures of the compounds are compiled in Table 36.

All the members of this series are non-mesomorphic. This is quite an interesting phenomenon as the related and laterally, non-substituted homologous series 4-(4'-n-Alkoxycinnamoyloxy)benzaldehydes (Series E4) is mesomorphic. The non-mesomorphism in the present series can be attributed to the fact that length to breadth ratio is considerably reduced. The molecules of the series 4-(4'-n-Alkoxycinnamoyloxy)benzaldehyde and the present series will be less coplanar due to the presence of central ester group (252). In addition, the latter series possesses a lateral bulky ethoxy group which will make the molecules broad and thick as well. So, the possibility of mesomorphism is eliminated in the present series. It was then proposed to increase the length of the molecules by a benzene ring having p-substituents. This was achieved by simple Schiff base formation with different p-substituted anilines that yielded the series H1, J1 and K1. All the compounds of the three series are mesogenic and are already discussed.

Table 36

4-(4'-n-Alkoxycinnamoyloxy)-3-ethoxybenzaldehydes

n-Alkyl group	K - I temperatures (°C)
Methyl	103.0
Ethyl	118.5
Propyl	114.0
Butyl	107.0
Pentyl	106.0
Hexyl	107.5
Heptyl	94.0
Octyl	94.5
Nonyl	83.5
Decyl	86.0
Dodecyl	96.5
Tetradecyl	100.5
Hexadecyl	104.0
Octadecyl	105.5

E. Mixed Mesomorphism

Binary mixtures where both the components are mesomorphic have now been largely studied. Bogojawlensky and Winogradow (257) and Dave and Lohar (103) have discussed the molecular forces operating and their effects on the binary phase diagrams where both components are mesogenic in nature. Hirata et al. (258) and Szabo et al. (259) have studied the binary nematic mesophase systems and obtained phase diagrams. They have indicated the advantage of such mixtures over the pure individual component in the field of applications. Hsu and Johnson (260) have also reported some binary nematic mesophase systems. In the present study the low melting toluene mesogens prompted us to study some mixtures and observed the effect of melting points, mesogenic - isotropic transitions and the chemical constitution on mixed mesomorphism. With this view three binary systems are studied. The binary systems are given in Table 37 with the transition temperatures against their constituent homolog.

The first binary system consists of the homologs of the same homologous series G1. The transition temperatures for this binary systems are given in Table 38. The component X exhibits both smectic and nematic phases

Table 37

Binary System No.		Homolog	Transition (°C)
1	X	4-(4'-n-Decyloxycinnamoyloxy)toluene	K $\underset{46.5}{\overset{74.0}{\rightleftarrows}}$ S $\underset{95.5}{\overset{95.5}{\rightleftarrows}}$ N $\underset{104.5}{\overset{105.0}{\rightleftarrows}}$ I
	Y	4-(4'-n-Tetradecyloxycinnamoyloxy)toluene	K $\underset{42.5}{\overset{71.0}{\rightleftarrows}}$ S $\underset{99.5}{\overset{100.0}{\rightleftarrows}}$ I
2	X	4-(4'-n-Decyloxycinnamoyloxy)toluene	K $\underset{46.5}{\overset{74.0}{\rightleftarrows}}$ S $\underset{95.5}{\overset{95.5}{\rightleftarrows}}$ N $\underset{104.5}{\overset{105.0}{\rightleftarrows}}$ I
	Y	4-(4'-n-Nonyloxycinnamoyloxy)-3-ethoxy-benzaldehyde.	K $\underset{46.0}{\overset{83.5}{\rightleftarrows}}$ I
3	X	4-(4'-n-Tetradecyloxycinnamoyloxy) toluene	K $\underset{42.5}{\overset{71.0}{\rightleftarrows}}$ S $\underset{99.5}{\overset{100.0}{\rightleftarrows}}$ I
	Y	p-Azoxyanisole	K $\underset{83.0}{\overset{119.5}{\rightleftarrows}}$ N $\underset{138.5}{\overset{138.5}{\rightleftarrows}}$ I

Table 38

Binary System 1 :

4-(4'-n-Decyloxycinnamoyloxy) toluene (Component X)

4-(4'-n-Tetradecyloxycinnamoyloxy) toluene (Component Y)

Mole % of component Y	Transitions (°C)		
	Smectic	Nematic	Isotropic
100.00	71.0	-	100.00
88.77	69.0	98.5	101.0
77.97	62.5	97.5	100.5
67.09	58.5	98.0	101.0
56.83	51.5	96.0	101.0
46.63	50.5	96.5	102.5
36.88	53.5	96.0	102.9
27.34	59.0	96.5	104.0
17.96	64.0	96.5	104.0
08.84	67.5	95.0	103.5
00.00	74.0	95.5	105.0

(enantiotropic) and the other component Y is a pure smectogen. The phase diagram for this system is given in Fig. (31). The phase diagram shows that the solid-smectic transition is the lowest at about 47 mole % of component Y. The temperature at this composition of the mixture is 50.5°C which is the eutectic point of the system. The components X and Y have solid-smectic transitions, 74°C and 71°C respectively. Thus the depression in solid-smectic transition is about 20°C as compared to component Y. The mesomorphic range of smectic mesophase at this eutectic point is 46.5°C which is quite good as compared to the mesomorphic range of the pure components particularly thet of component X. The S-N or I transition curve and the N-I transition curve more or less remain parallel to the abscissa with minor deviations. Both the smectic and nematic mesophases are exhibited by the binary system. This is expected as the series G1 to which the two compponents belong, is a nematogenic and also the components have long alkyl chain at one end, thereby providing more lateral attractions for the exhibition of smectic phase. This observation is supplemented by the fact that the smectic mesophase in the series G1 appears from octyl homolog, and the higher members of the series G1 are pure smectogens.

The second binary system consists of the components from two different homologous series ; series G1 and the

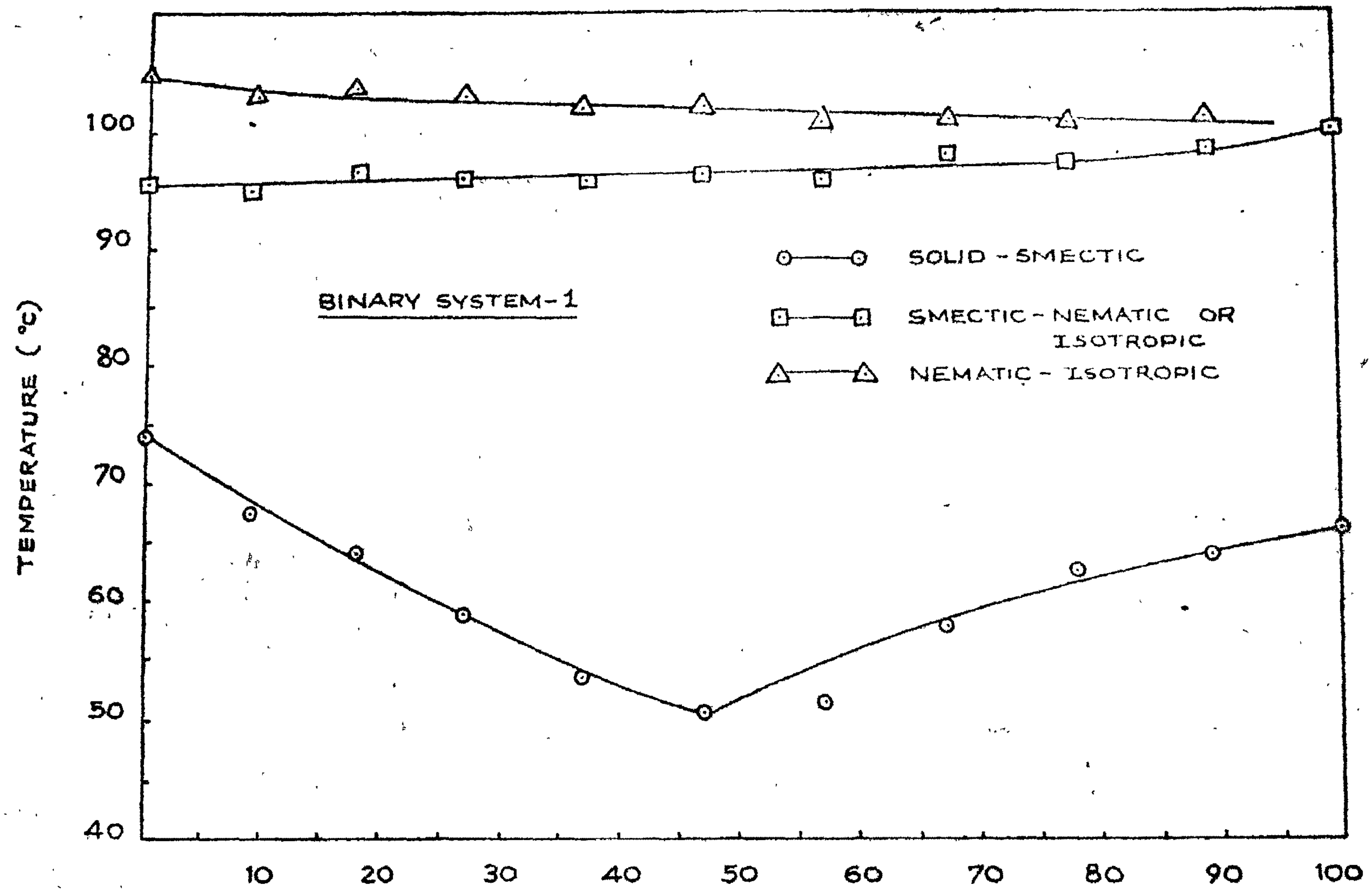


FIG. 31 MOLE % OF 4-(4'-n-TETRADECYLOXYCINNAMOYLOXY) TOLUENE

non-mesomorphic series synthesized under this investigation. The transition temperatures for this system are given in Table 39. The component X of this system is one of the components of binary system 1. Both the components of this system differ very much in their molecular geometry. Components X and Y have decyloxy and nonyloxy alkoxy chains at one of the ends respectively. At the other end, both the components have different nuclei. The component X exhibits both smectic and nematic phases, whereas the component Y is a non-mesomorph with solid-isotropic value of 83.5°C. Reference to the phase diagram (Fig. 32) will indicate that both the smectic and nematic transitions of mesomorphic component X are lowered by gradual addition of non-mesomorphic component Y. The smectic and nematic transition curves intercept the solidus curve at about 28 mole % (65.0°C) and 52 mole % (68.0°C) addition of component Y respectively. Below this point both the curves continue as monotropic phases for some distance. Thus by the addition of the non-mesomorphic component the low melting mesomorphic mixture compared to the pure component can be obtained. The maximum lowering in the case of smectic and nematic transitions compared to pure mesogen X is about 37.0° and 30.0°C respectively. The effect is expected as the two components differ in the composition and so there will be difficulty in the close packing of the molecules.

Table 39

Binary system 2

4-(4'-n-Decyloxycinnamoyloxy) toluene (Component X) :
4-(4'-n-Nonyloxycinnamoyloxy)-3-ethoxybenzaldedhyde
(Component Y)

Mole % of Component Y	Transitions (°C)		
	Smectic	Nematic	Isotropic
100.00	-	-	83.5
89.13	-	-	81.5
78.20	-	-	79.5
67.79	-	(51.0)	77.0
57.32	-	(62.5)	73.0
47.30	-	62.5	72.5
37.43	(50.0)	63.0	76.0
27.84	(64.0)	62.5	85.5
18.35	67.0	76.0	92.5
09.08	70.5	85.0	97.5
00.00	74.0	95.5	105.0

Values in parentheses indicate monotropy

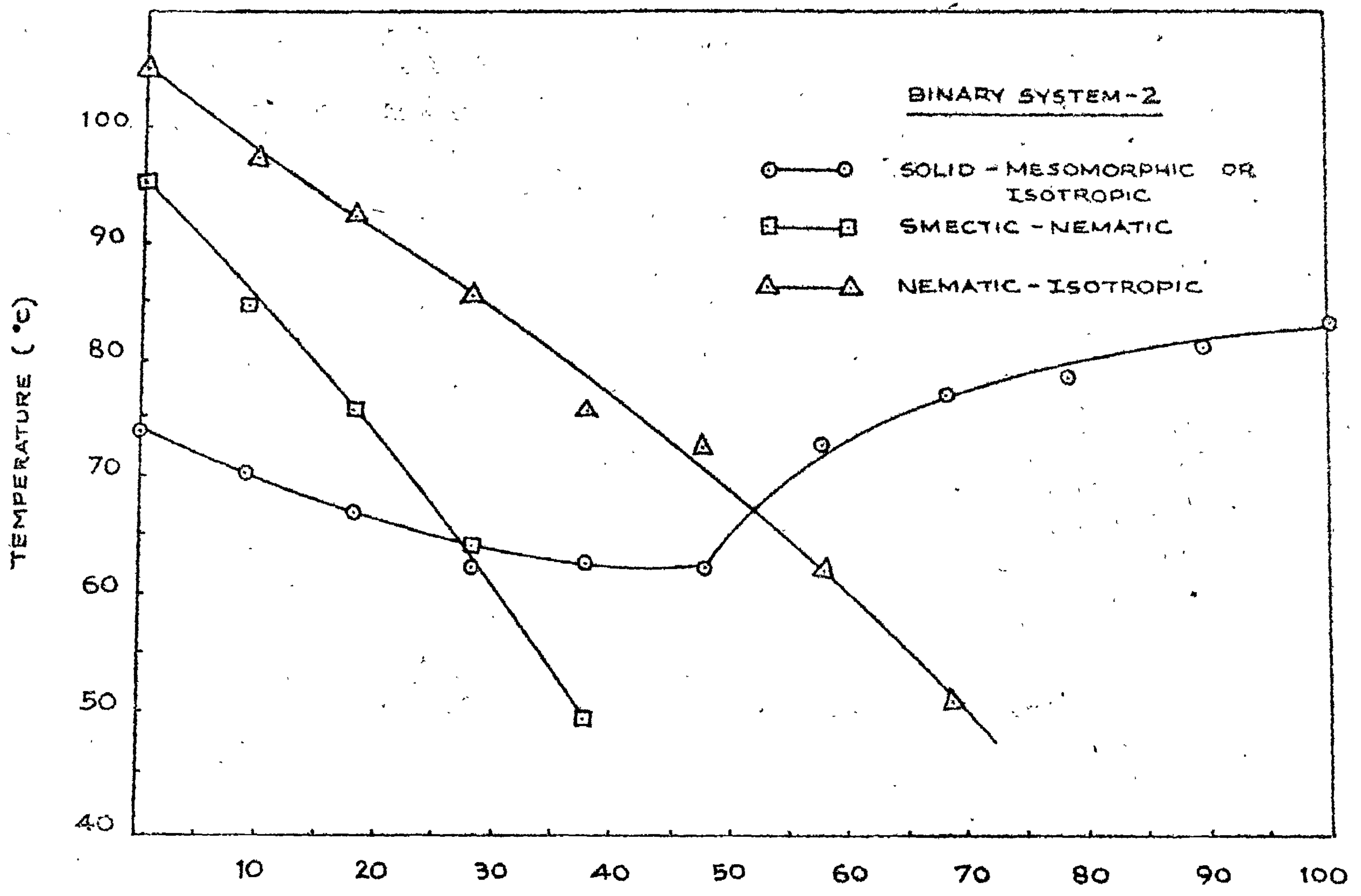


FIG. 32 MOLE % OF 4-(4'-NONYLOXYCINNAMOYLOXY)-3-ETHOXY BENZALDEHYDE

The third binary system includes a pure smectogen from the series G1 and p-azoxyanisole. The transition temperatures for this system are given in Table 40. Fig. 33 shows phase diagram for this system. The component X (of series G1) is an enantiotropic smectogen with a smectic mesophase range of 29°C ; whereas component Y (p-azoxyanisole) is enantiotropic nematogen with nematic range of 19°C. The reference to the phase diagram shows that by gradual addition of p-azoxyanisole (Y) to smectic mesogen (X), the smectic transition points are lowered and the smectic transition curve cuts the solidus curve at 28 mole % addition of component Y (82.0°C). Similarly the N-I transition point of component Y is lowered by gradual addition of component X. The eutectic point occurs at 55 mole % addition of component Y (82.5°C). The effects are as expected as the two components differ in their molecular structure.

Table 40

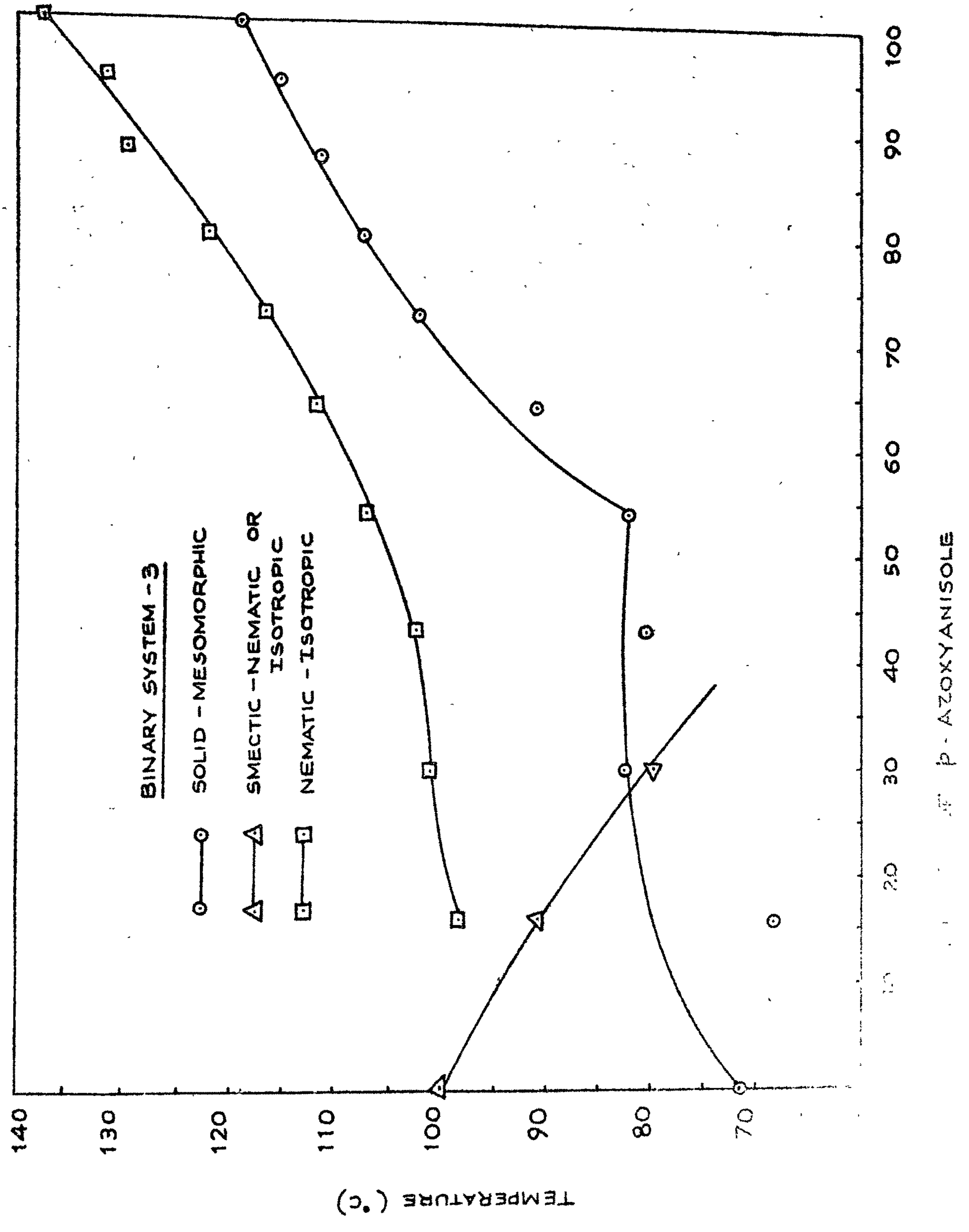
Binary System 3

4-(4'-n-Tetradecyloxycinnamoyloxy)toluene (Component X) :

p-Azoxyanisole (Component Y)

Mole % of Component Y	Transitions (°C)		
	Smectic	Nematic	Isotropic
100.00	-	119.5	138.0
94.07	-	115.5	132.0
87.57	-	112.0	130.0
80.17	-	107.5	122.5
72.36	-	103.0	116.5
63.60	-	91.5	112.0
53.81	-	82.0	107.5
42.64	-	80.5	102.5
30.39	(80.0)	82.5	101.0
16.23	68.0	91.0	98.5
00.00	71.0	-	100.0

Values in parentheses indicate monotropy


BINARY SYSTEM -3
SOLID - MESOMORPHIC
SMECTIC - NEMATIC OR ISOTROPIC
NEMATIC - ISOTROPIC
TEMPERATURE (°C)
140
130
120
110
100
90
80
70
% p - AZOXYANISOLE
10
20
30
40
50
60
70
80
90
100