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STUDY OF THE EFFECT OF STRUCTURAL VARIATION ON MESOMORPHIC CHARACTERISTICS IN THERMOTROPIC MESOGENES

Thesis Submitted to
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For the degree of
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In
Chemistry
Faculty of Science
By

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March-2011

Statement under O. Ph. D. 7 of Saurashtra University

The work included in the thesis is my own work under the supervision of Dr. A, V. Doshi, M.Sc., Ph.D., F.I.C., and leads to some contribution in chemistry subsidized by enough number of references.

Date: - 03 -2011

Place: RAJKOT (R. B. Patel)

This is to certify that the present work submitted for the Ph.D. degree of Saurashtra University by **Mr. R. B. Patel,** M.Sc. is his own work and leads to the advancement of chemistry. The thesis has been built up under my supervision.

Date: -03 -2011

Place: RAJKOT

Dr. A. V. DOSHI
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-Roshan B. Patel.

INDEX

INTRODUCTION

There are three well-known states of matter. Viz; solid, liquid and gases or vapours. However there exists a fourth, physically distinct state of matter between crystalline solid and a true liquid. It has flow property like liquid and its optical properties like birefringence resemble to crystalline solid. The interstate transition from solid to true liquid is known as melting point and from liquid to gas or vapour is known as boiling point of liquid at constant pressure. Some times a solid substance may pass directly from solid to gas or vapour without passing through true liquid state or vice versa inter state transition is called sublimation. The existence of an additional intermediate state between crystalline solid and true isotropic liquid is not exhibited by all substances but it is exhibited by some substances having intermolecular anisotropic forces of adhesions of suitable magnitude occurred as a consequence of molecular rigidity or core structure and molecular flexibility of lateral and terminal substitution with the suitable geometrical shape of a molecule. The stability of a thermodynamically stable substance depend upon the amount of energy released from system (substance under study) to surrounding[a part of universe other than a system] during its birth and acquiring crystalline state in layered or unlayered form. Thus, stability of a substance depend upon the intermolecular adhesion which depend upon amount of energy (ΔH) released by a substance from a system to surrounding. When a substance under study is heated i.e. heat supplied from surrounding to a system, the molecules of a substance start absorbing energy and undergo dancing or say, the molecules start to play from translational motion to rotational motion and from rotational motion to vibrational motion. Thus, as temperature rises, the molecular motion varies from translational motion to vibrational motion through rotational motion. Thus, as temperature increase, molecules of substance under investigation (system) tend to move from thermodynamically, the most stabilized state to a less stabilized state of higher entropy (ΔS) or higher magnitude of randomness or to a high order of disorder. Hence molecules are disorderly orient at higher temperature than before at room temperature. Thus, as temperature increases, entropy of a system increases and at a particular temperature t^{0C}, a system is transformed in to higher state of existence from crystalline state to anisotropic liquid or a isotropic true liquid corresponding to energy (ΔH). Hence, entropy $\Delta S= \Delta H / T$ where $T= t^{0C} + 273$ = Absolute temperature in degree Kelvin (or ^{0}K) and t= temperature in degree centigrade. If a substance under investigating acquires a state of existence, intermediate to crystalline solid and isotropic liquid called anisotropic liquid, it starts to appear at temperature t_1^{0C} under hot stage polarizing microscope and continue to appear till higher or lowers temperature t_2^{0C}, for enantiotropic (reversible) or monotropic (irreversible) anisotropic mesophase. The $t_2 - t_1 = t_R$ is called a range of temperature, t_R^{0C} between which anisotropic floating liquid appeares. For enantiotropic liquid $t_2 > t_1$ and for monotropic liquid $t_2 < t_1$. If $t_2 – t_1 = 0 = t_R$ i.e. $t_2 = t_1$, then a liquid is called isotropic liquid or a true liquid which flows on the surface with high magnitude of randomness or disordered fluid. Such substance for which $T_R=0$ is called a nonmesomorphic substance which passes directly from solid state to isotropic liquid state without passing through an intermediate state of existence called anisotropic liquid or mesomorphic state or liquid crystal state or non amphiphilic state or mesogenic state. Anisotropic liquid is more viscous and turbid than isotropic liquid.

Reinitzer [1] observed first an abnormally behaved viscous and turbid fluid in 1888. A carefully purified sample of cholesteryl benzoate observed to be melted at 145.5 ^{0C} giving cloudy fluid and on continuing the heating, the substance was clarified at 178.5 ^{0C}, subsequent cooling gave colour effects similar to those observed with cholesteryl acetate. Then Lehmann [2] using the polarizing microscope, confirmed Reinitser`s observation. Later [3] he observed similar phenomena on cooling the amorphous melt of cholesteryl esters of fatty acids. Lehmann proposed the name “liquid crystal” or “crystalline liquid” to a new intermediate state between crystalline solid and isotropic amorphous true liquid.

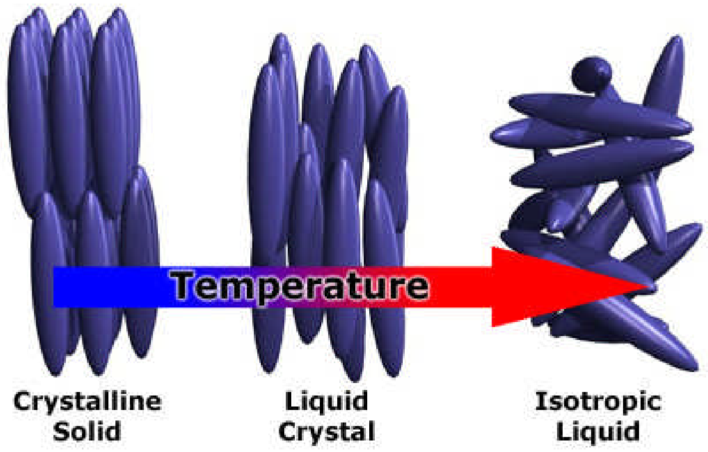


Figure-1(a)

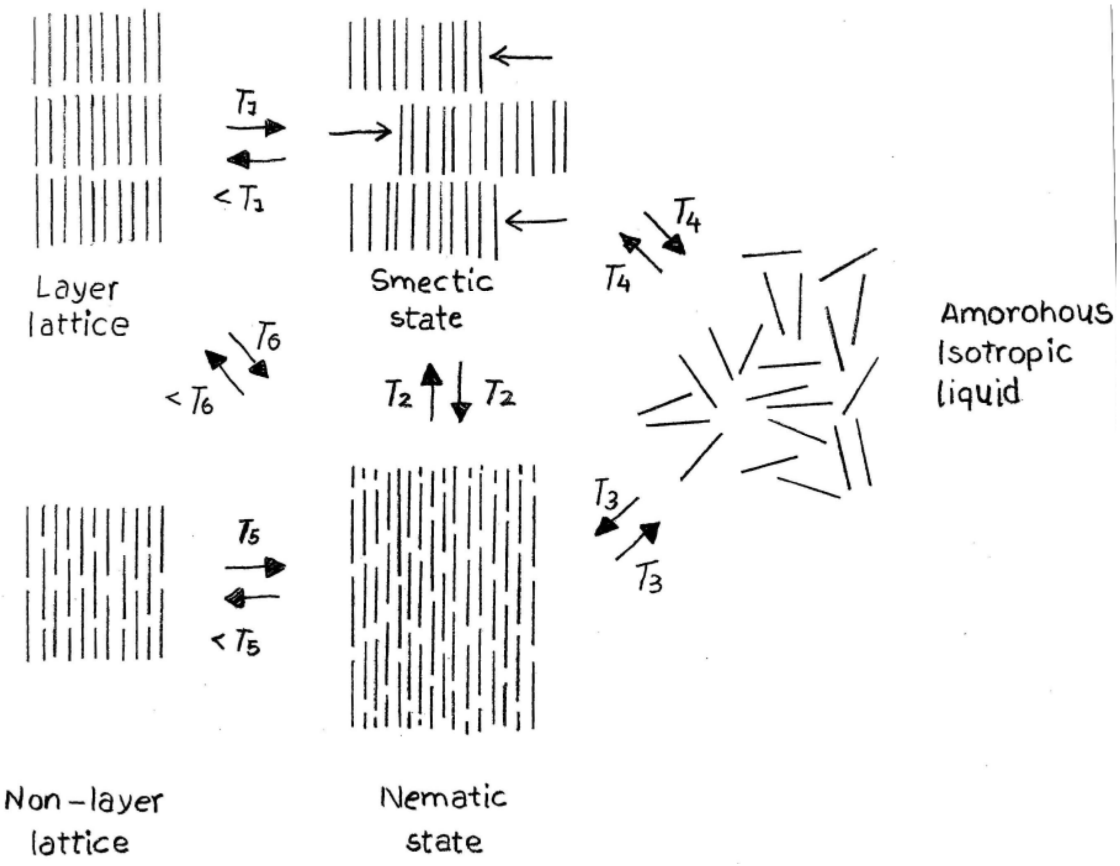


Figure-1(b)

Nomenclature:

Friedel (1922) termed ‘les etats mesomorphs’ to avoid the ambiguities and controversies. [4]. Friedel and Friedel led to the conclusion that, intermediate phase is neither truly liquidous nor truly crystalline and suggested ‘mesomorphic state’ with specific meaning (Greek-meso means intermediate and morphs means form) and derived the terms ‘mesomorphism’, ‘mesomorphs’, ‘mesoforms’, mesophase’ and ‘mesogen’etc. Thus, a term ‘MESOMORPHIC STATE’ between the perfectly ordered periodic structure of solid crystals and the perfectly disordered structure of the isotropic amorphous liquid.

Rinne [5] did not agree or satisfy by the word ‘Mesomorphic state’ assigned to intermediate state between crystalline solid and amorphous isotropic liquid. According to Rinne’s views, anisotropic liquid may be classified the matter either as ‘ataxy’ means irregular or amorphous structure and ‘eutaxy’ means regular or ordered structure. The substance belonging to ataxy class category are called ‘atactites’ and eutaxy class category are called eutactites. He proposed the name ‘paracrystals’.

Brown and Shaw [6] preferred the term ‘mesomorphism’. However, the popular term ‘liquid crystal’ is frequently used through out the literature till the date. Using the nomenclature of Friedel [7], Lawrence and Jelly [8], a ward “Thermotropic mesomorphism” is applied to the mesomorphs acquiring mesomorphic state by the application of heat and a word “Lyotropic mesomorphism” is applied to the mesomorphs acquiring mesomorphic state by solvation. The solvent being used generally water.

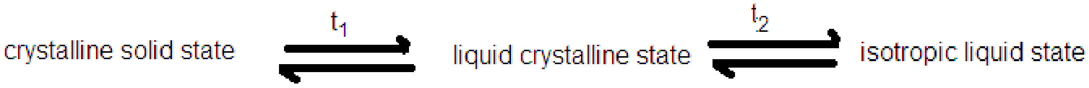
Mesomorphic substances are classified as smectic means soap like material [10] and nematic, means thread like material on account of their linear discontinuities twisted like threads. The smectic structure is stratified, the molecules are being arranged in layers with their long axis approximately normal to the plane of the layers. The molecules preserve a parallel or nearly parallel orientations in the nematic type of mesomorphs. A further distinction between nematic and cholesteric as clarified by Friedel that the cholesteric form is a modified form of nematic mesophase but it is not a distict phase than smectic and nematic. It is called cholesteric because this phase is mainly shown by cholesteryl derivatives which are optically active compounds.

The mesomorphic state:

Gattermann and Ritschcke [9] in 1990 observed a similar phenomenon in p-azoxyanisol and p-azoxyphenetol after the first discovery of the phenomenon observed by Reinitzer [1]. Vorlander [10] and others prepared members of new compounds of like behavior. It was genralised that, a compounds with straight elongated molecular shape is expected to exhibit mesomorphic state or mesophase. Tamman, Nernst and Quiacke [11] considered mesophase as heterogeneous, as an emulsion of two components. Scheucks and Vorlander [12] disagreed to consider liquid crystal state as heterogeneous phase and considered as a homogeneous independent state of existence. de Koch [13] supported the Scheucks and Vorlander's views, that a liquid crystal phase is a homogeneous.

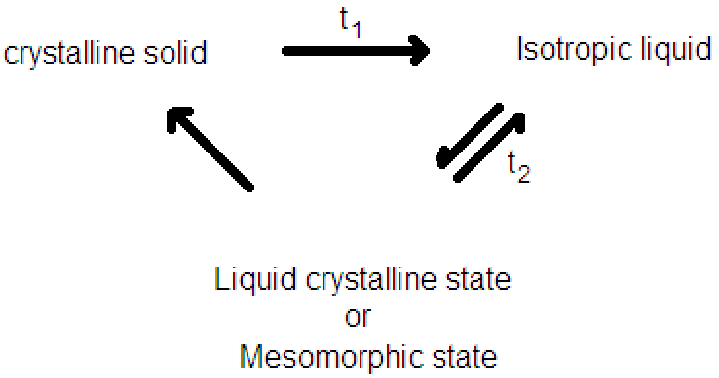
Pawloff and walff and Voigt [14] tried to discuss the nature of mesophase. According to Lehmman [15], the phenomenon observed under polarizing microscope is due to the formation of crystals in liquid condition. Vorlander [16] and others said that, liquid crystals had a fixed space lattices without any basis for this idea. However liquid crystal state was accepted as an independent state of existence other than solid, liquid and gas between crystalline solid and amorphous isotropic liquid.

E. Bose [17] proposed a theory, known as Swarm theory, which provided the most rational explanation about phenomenon of liquid crystals. Experiments on X-Ray analysis , influence of an electromagnetic field and measurement of viscosity at different temperatures [18] supported Swarm theory. In absence of space lattice structure, the shape of molecules favors the parallel alignment as a consequence of intermolecular forces arising from molecular rigidity and flexibility was considered as the connecting link for mesophase formation between solid crystals and true isotropic liquids. Presence of polar terminal groups and their varying polarity and induced polarizability was considered as connecting link for degree of liquid crystallinity. Thus, when a crystalline solid is heated, the gradual thermal break down may be represented as under.



[Enantiotropic mesophase]

If a specimen of a substance is heated and simultaneously observed under polarizing microscope with heating stage, it remains birefringent when it reaches to fluid condition. Some times mesophase appeares below melting point irreversibily, i,e. a specimen substance under examination may directly pass from solid to isotropic liquid but on cooling the same, it display liquid crystal behavior at a temperature t_2 below melting point. Such liquid crystals are called monotropic liquid crystals and a transition is called monotropic transition which acts irreversibly. Such irreversible change is represented as under.



(monotropic mesophase)

Thermotropic liquid crystals: Non-amphiphilic mesogens:

Temperature induced liquid crystal materials are called a thermotropic liquid crystals or non-amphiphilic liquid crystals [19] Gray and Winsor [20] used a word non-amphiphilic liquid crystals or non-amphiphiles. Fridel [1] classified thermotropic liquid crystals on the basis of molecular arrangement in to three main types viz. Smectic, Nematic or Cholesteric. He referred birefringent patterns of masophases as ‘texture’.

Smectic mesophase:

Smectic means soap like appearance and behavior. The molecules are arranged in layers with their long axes approximately normal to the planes of the layers. The spacing of the molecules within each layer is not uniform. It is allowed to spread over a flat surface, it tends to form a series of strata or terraces called as Grandjean planes [21]. The fluidity of the phase is due to sliding of layers, stepped drops observed under polarizing microscope when smectic mesophase start to occur. The layered structure of the mesophase provides regular periodicity, normal to the layers and hence X–ray diffraction pattern is obtained. The layers are homogeneous. The distance between the layers is approximately equal to the length of the molecule [Figure-2] and if the molecules in the layer are tilted, deviation can arise [Fgure-3]. If the layers are observed through ordinary light, it looks like isotropic liquid. But the layers are appeared as homogeneous birefringent patches under polarized light. The interstate transformation is as under.

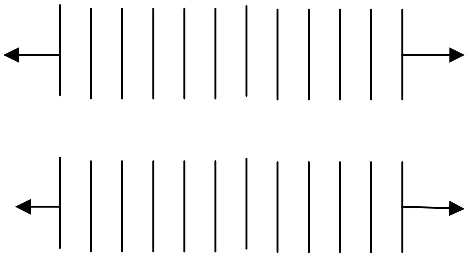


Figure-2

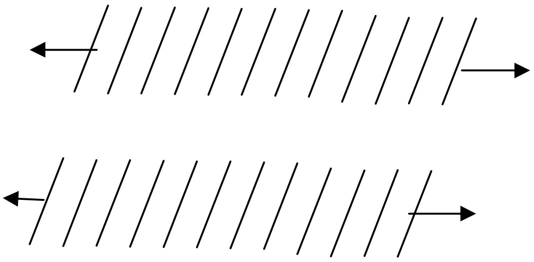


Figure-3

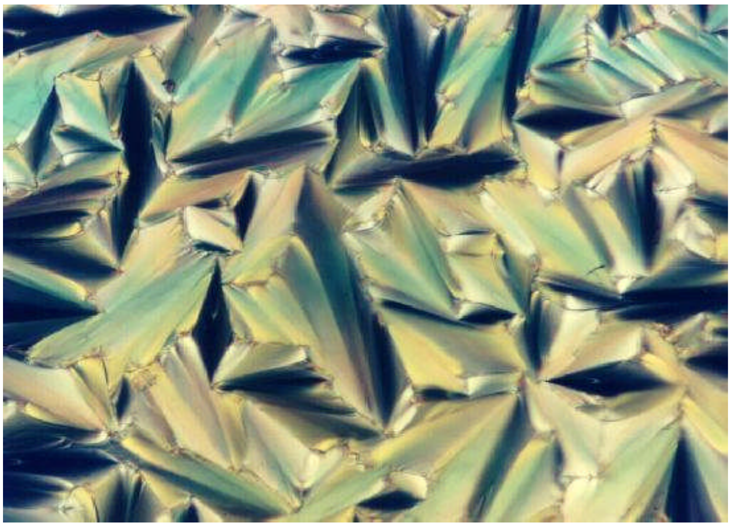


Fig. 9(a) Texture of the Smectic liquid crystal phase

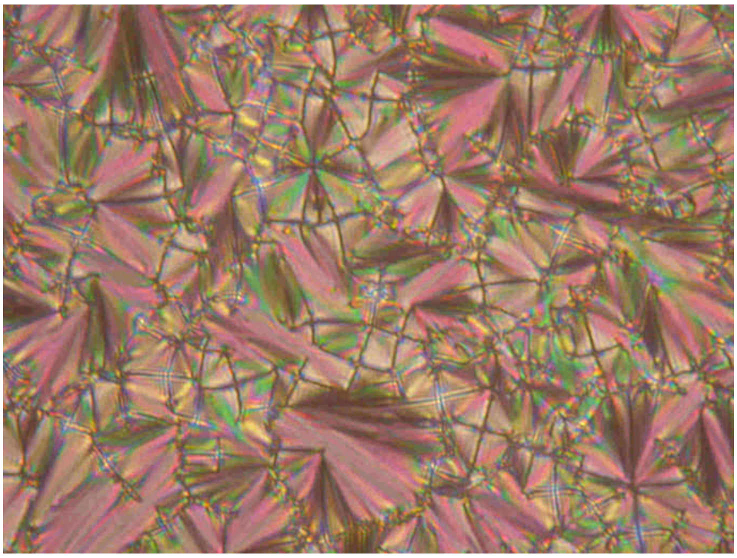


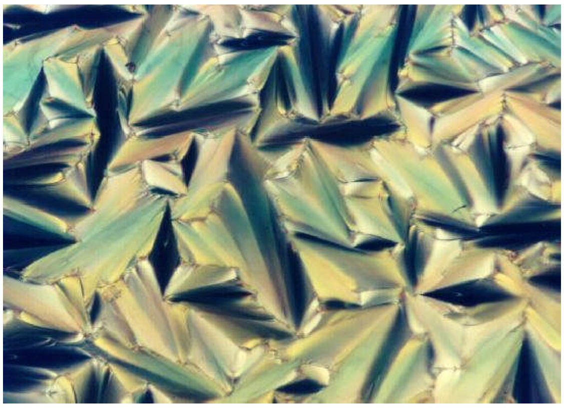
Fig. 9(b) Texture of the Smectic liquid crystal phase

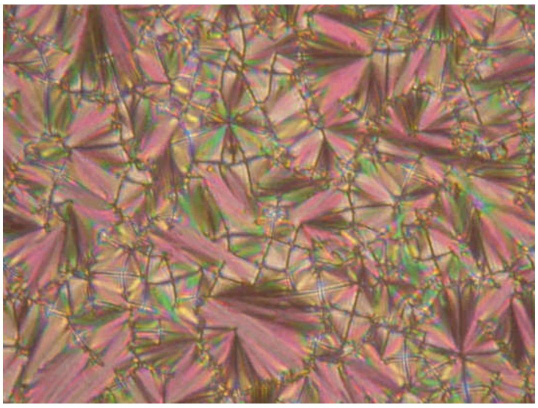
Crystalline solid $\overset{t_1}{\rightleftharpoons}$ Smectic liquid crystal $\overset{t_2}{\rightleftharpoons}$ Isotropic liquid.
('A'——> 'C'——> 'B')

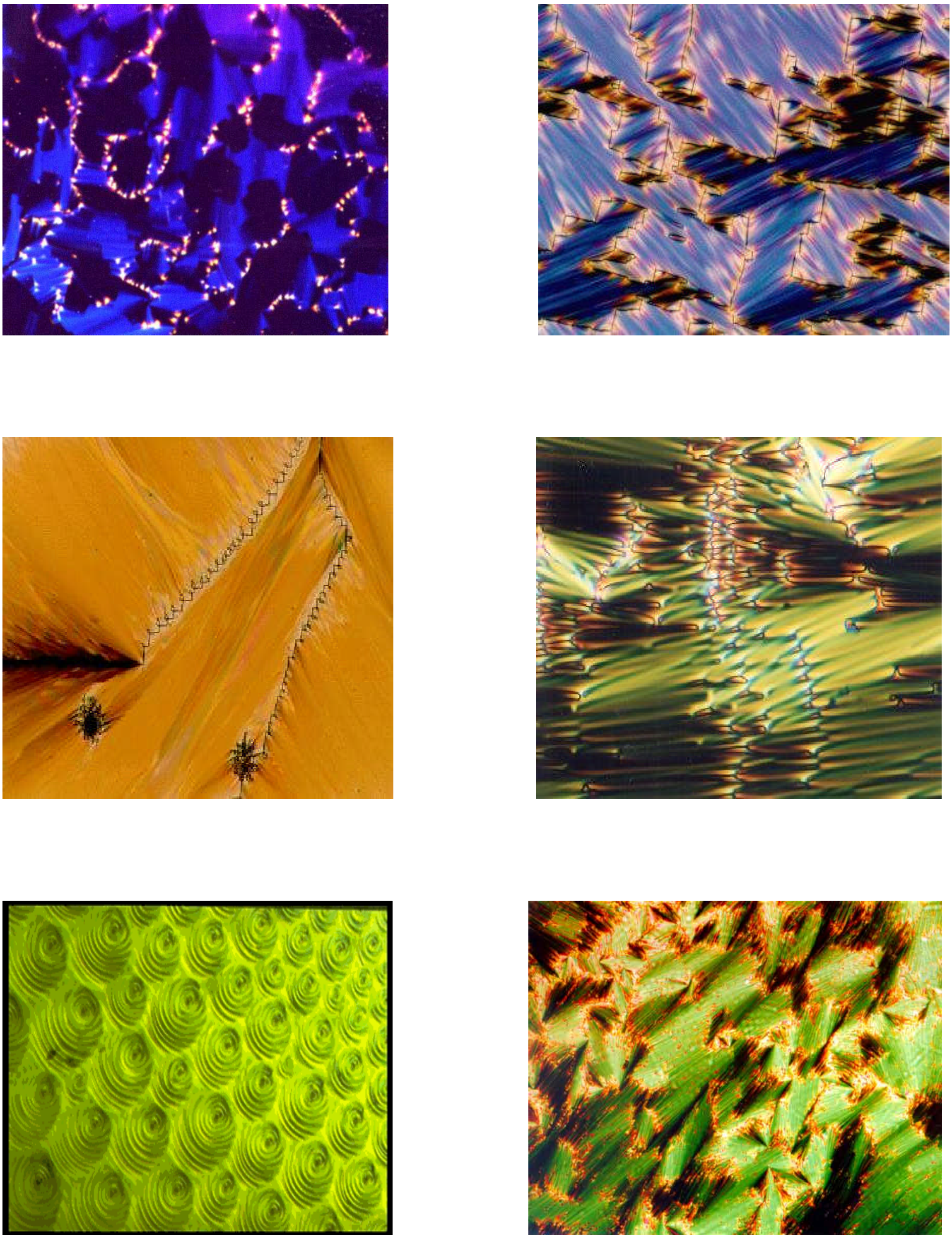
For polymesomorphic mesomorphs,

Crystalline solid $\overset{t_1}{\rightleftharpoons}$ Smectic mesophases $\overset{t_2}{\rightleftharpoons}$ Nematic or Cholesteric $\overset{t_3}{\rightleftharpoons}$ Isotropic liquid
A,B,C,D,E,F,G,H---

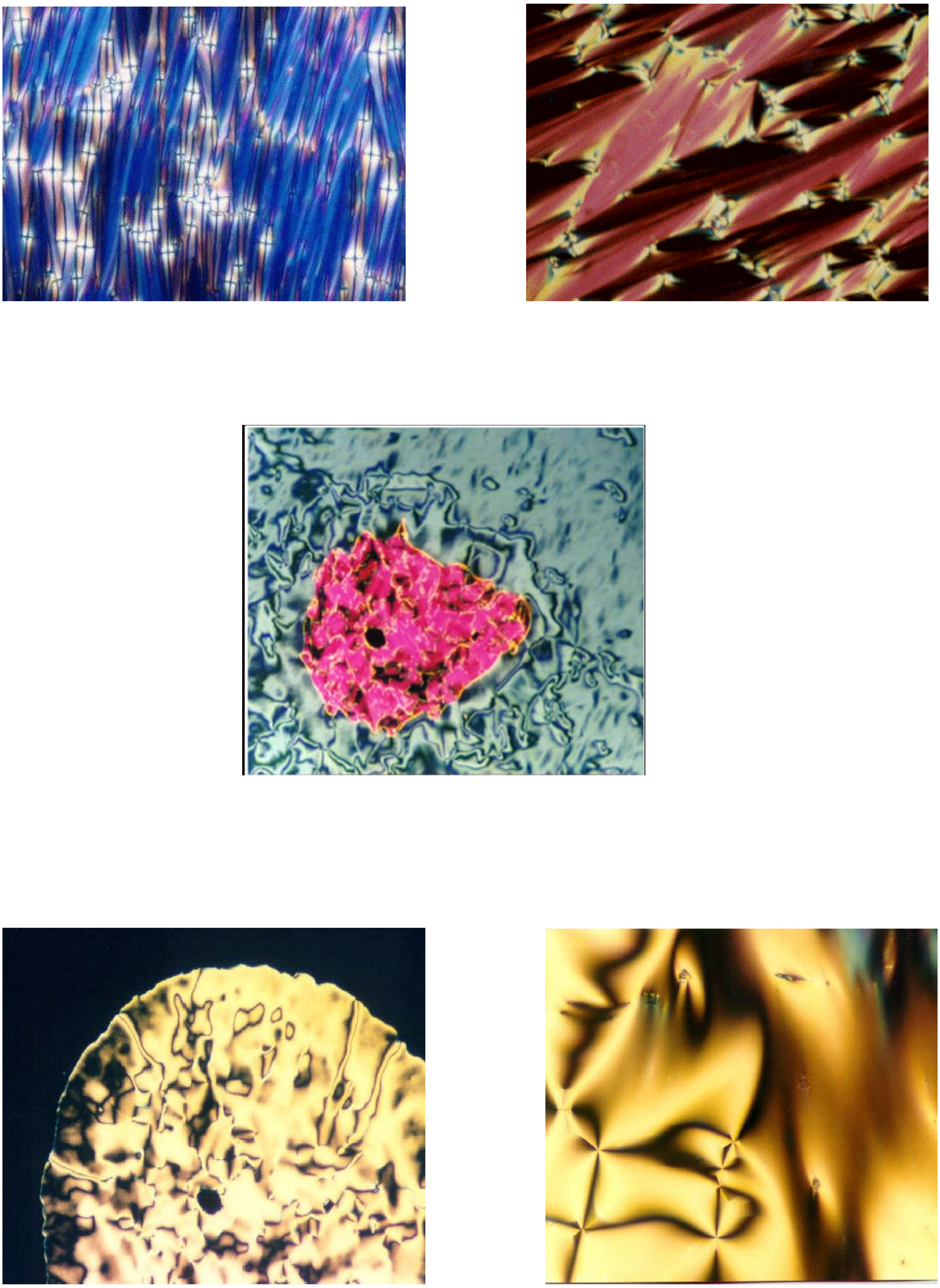
The smectic mesophase behaves as positive uniaxial crystal and remains unaffected by electric and magnetic field. Herrmann [22] proposed to divide smectic into two groups as unstructured and structured layers. Smectic-‘A’ and ‘C’ belong to unstructured layers while smectic-B belong to second group i.e. structured layers. Sackmann and Demus [23] reported smectic A, B, C, D, F, G as identified by miscibility method. de Vries [24] classified smectic as α, β, γ on the basis of X-ray study according to increasing order of molecular packing. α class involve smectic A, C, F and D while, β involve smectic-B and γ involve smectic E, G and H variety. de Vries [25] classifies smectic-H as a separate phase. The most common smectic phases identified and designated as S_A, S_B, S_C- - - etc. according to their order of discovery. S_B and S_C phases are reported by Gray etal [26] and others. Reentrant smectic phases are also reported by Nguyen et al [27].



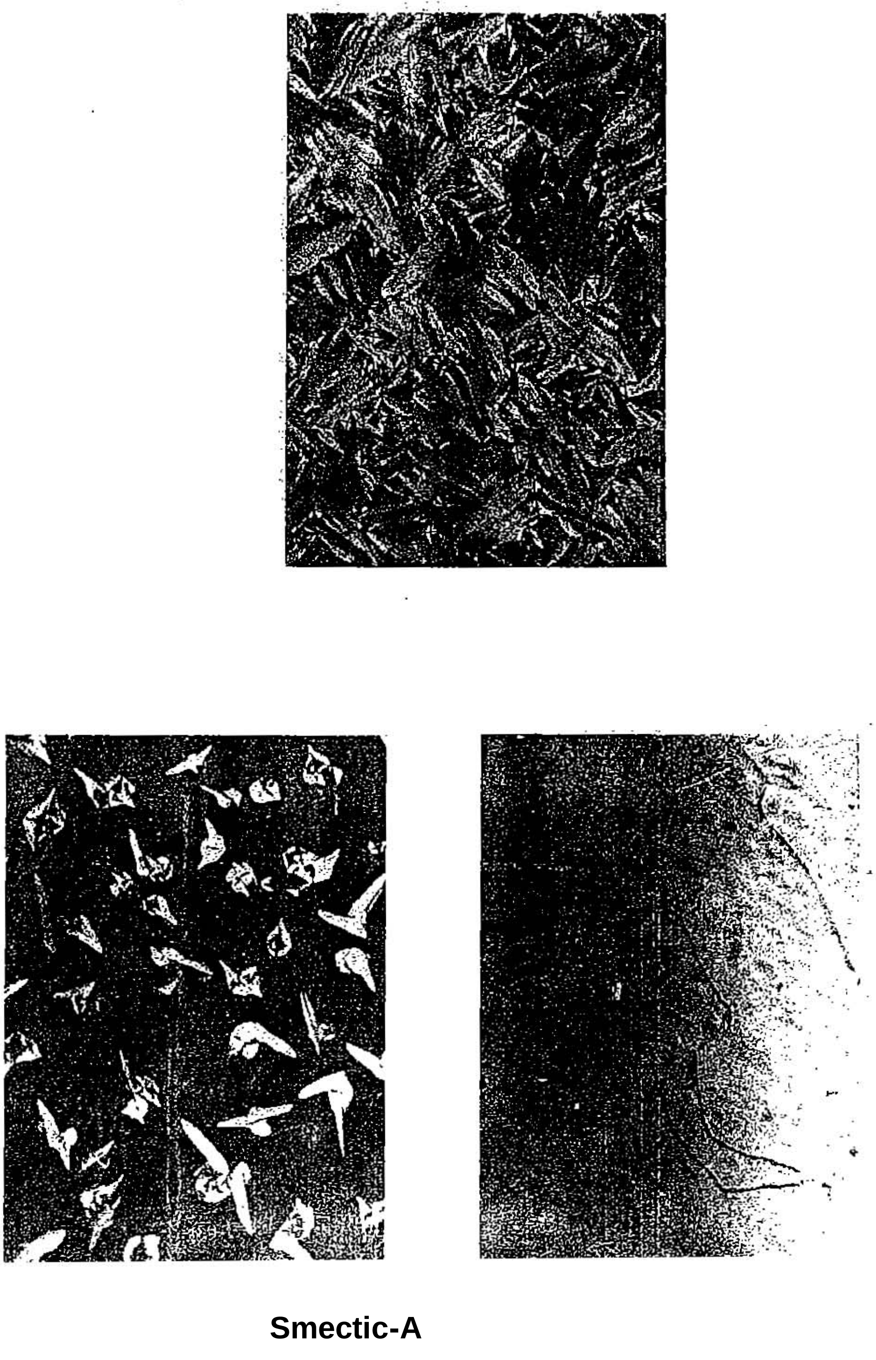




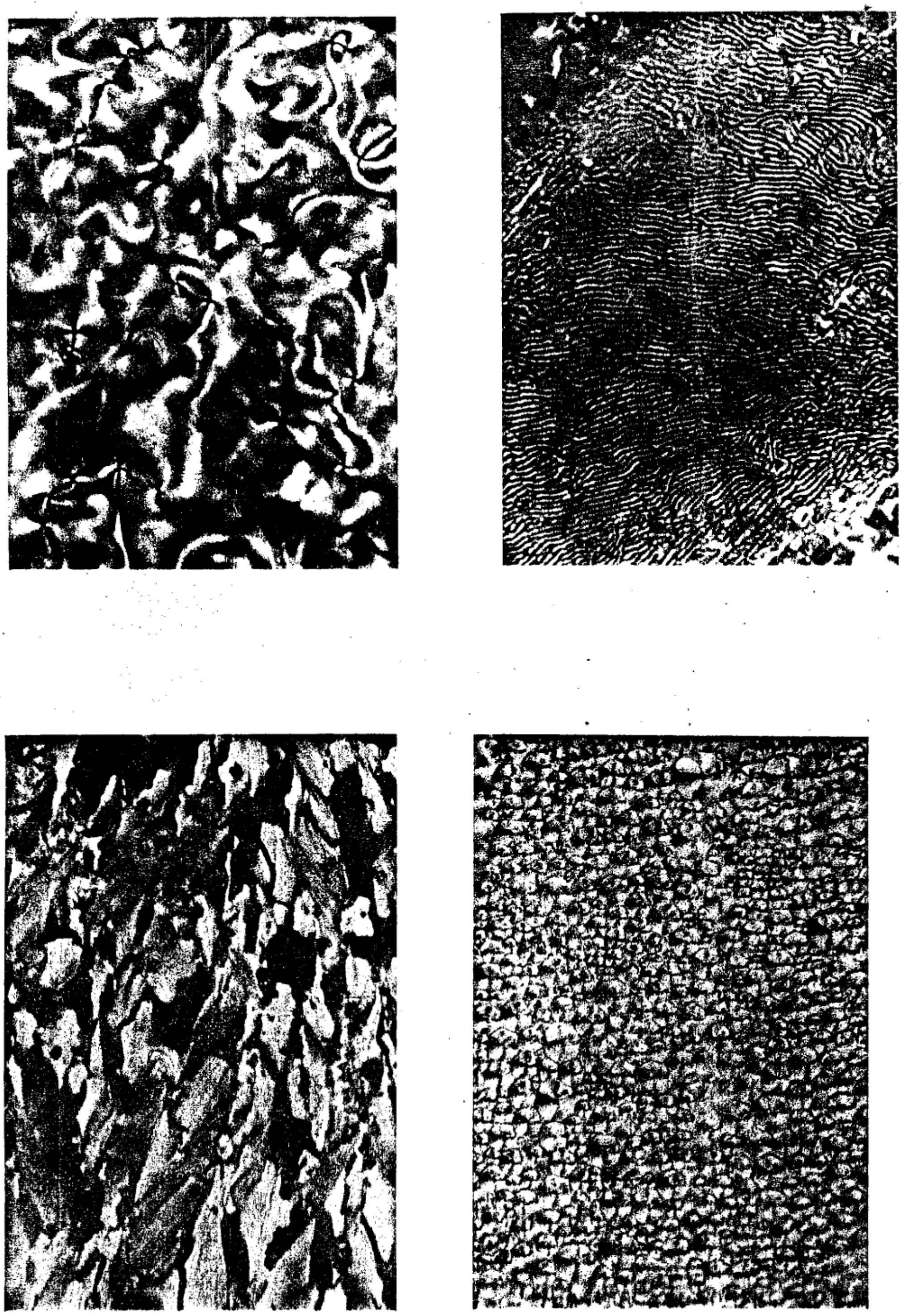
Smectic Phase



Smectic Phase



Smectic-A



Smectic-c

Nematic mesophase :

Nematic means a thread like texture or structure. The molecules arrange themselves parallel or approximately parallel orientations to each other without any layered arrangement or a regular organization of the ends of the molecules. The molecules are drawn past one another in the direction of their long axis and hence nematic mesophase is more fluid and less viscous than smectic mesophase. There exist strong end to end molecular attractions. Nematic mesoforms are oriented by electric and magnetic fields. The molecules set themselves with their axis at right angle to the line of force under the influence of an electric field, while, they lie with their long axis parallel to the lines of force under the influence of magnetic field. The nematogenic mesophase separate as spherical golden like drops from their melts or solution on cooling. The texture appeared depend upon the thickness of specimen substance under microscopic examination. Relatively thicker specimen appears typical threaded texture. In thinner layered specimen a threaded texture transforms to the 'Schlieren texture' with point like disclinations. The appearance of schlieren forms are characterized by dark brushes which originates from the points, usually points with two or four dark brushes are observed. Some times with untreated surfaces, an irregular texture resembling appearance of polished marble can be obtained due to surface effect, the texture being known as 'marble texture'. The molecules in nematic mesophase are interlocked or imbricated in floating condition as under.[figure-4]

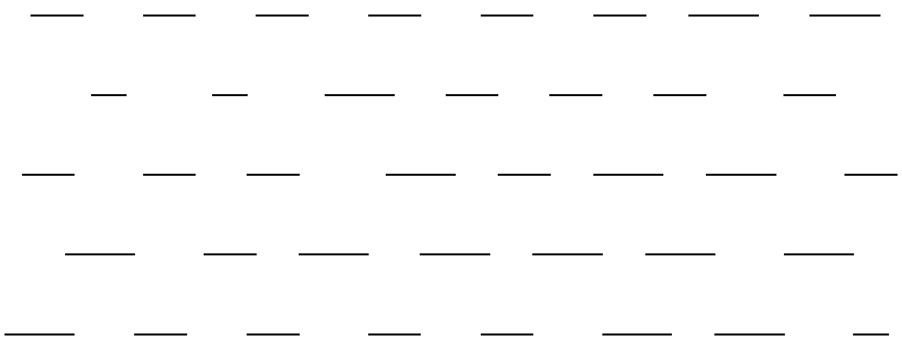
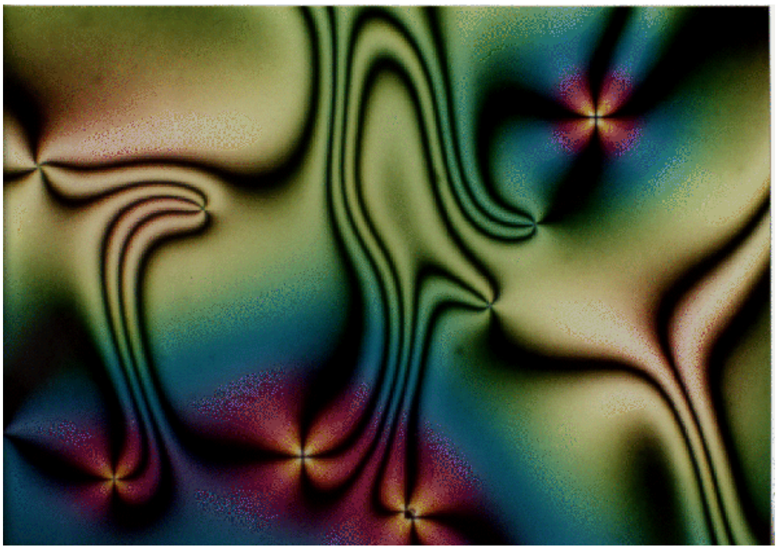
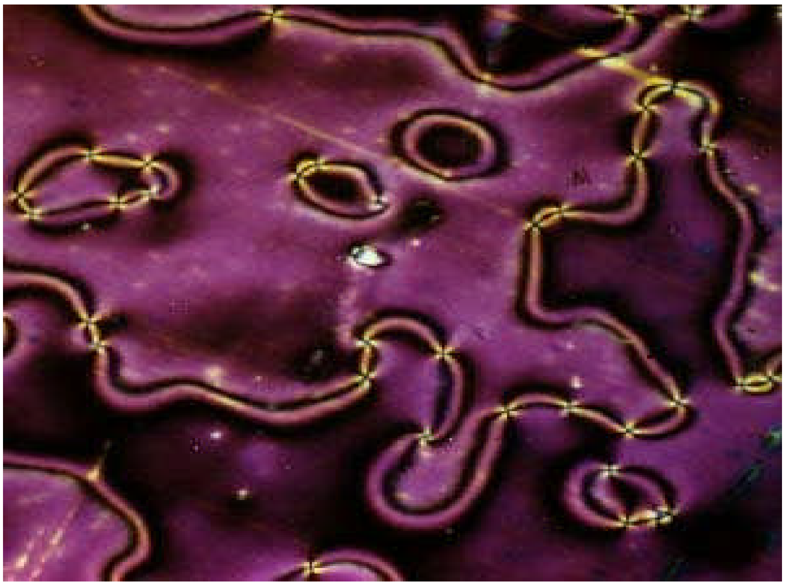
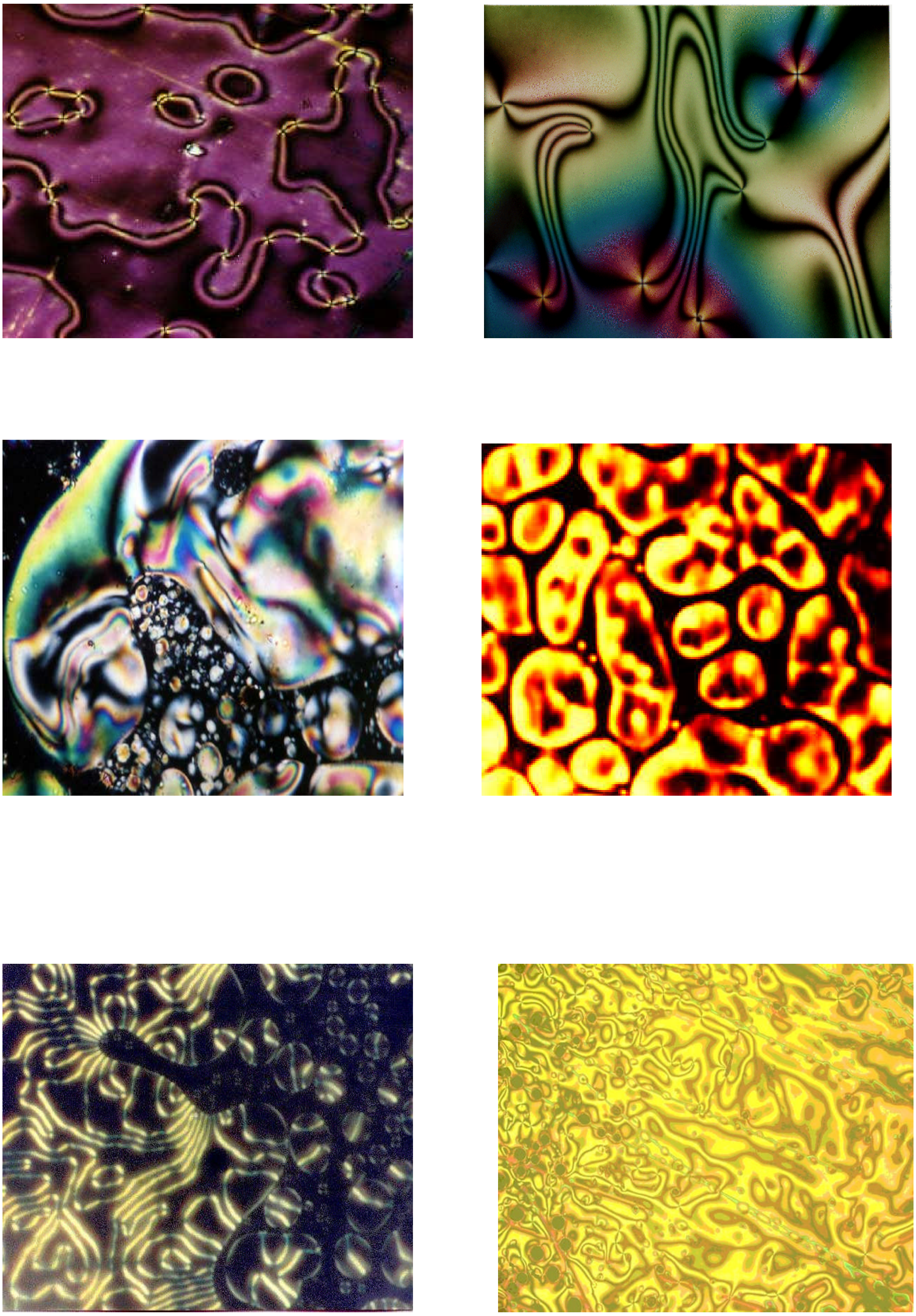


Figure -4 Molecular organization in nematic mesophase.

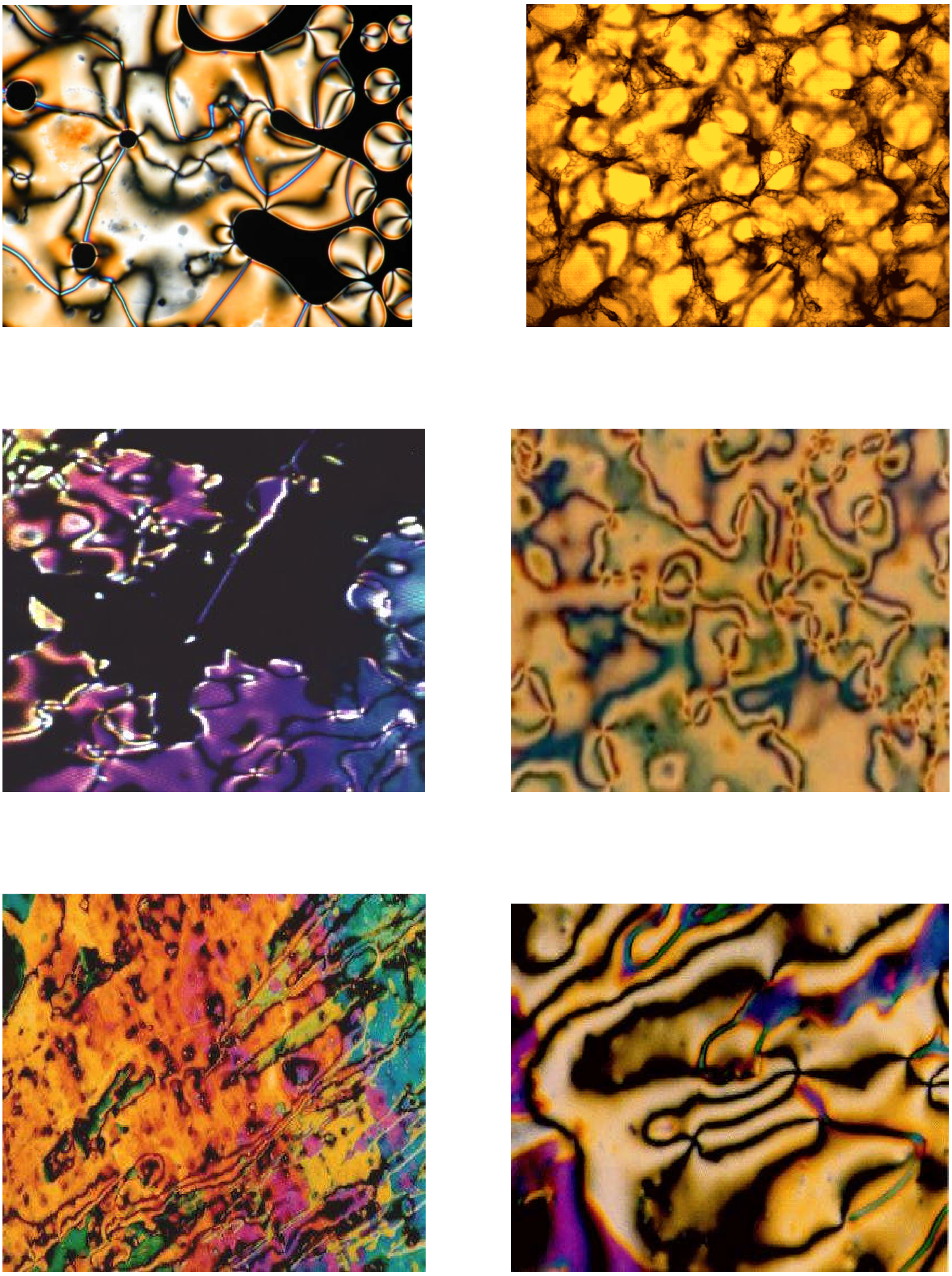




Textures of the nematic liquid crystal.

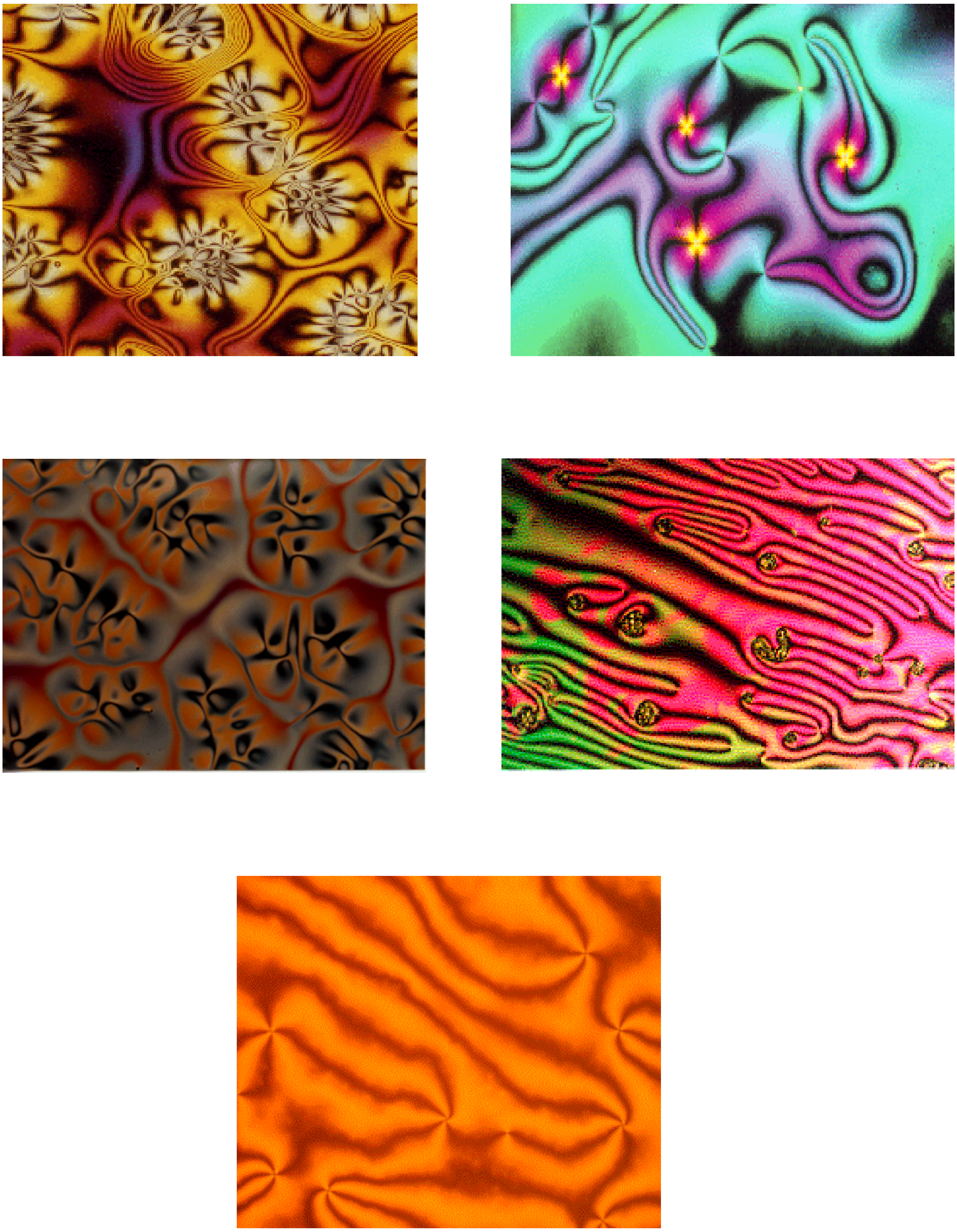


Nematic textures



Nematic textures

Nematic textures



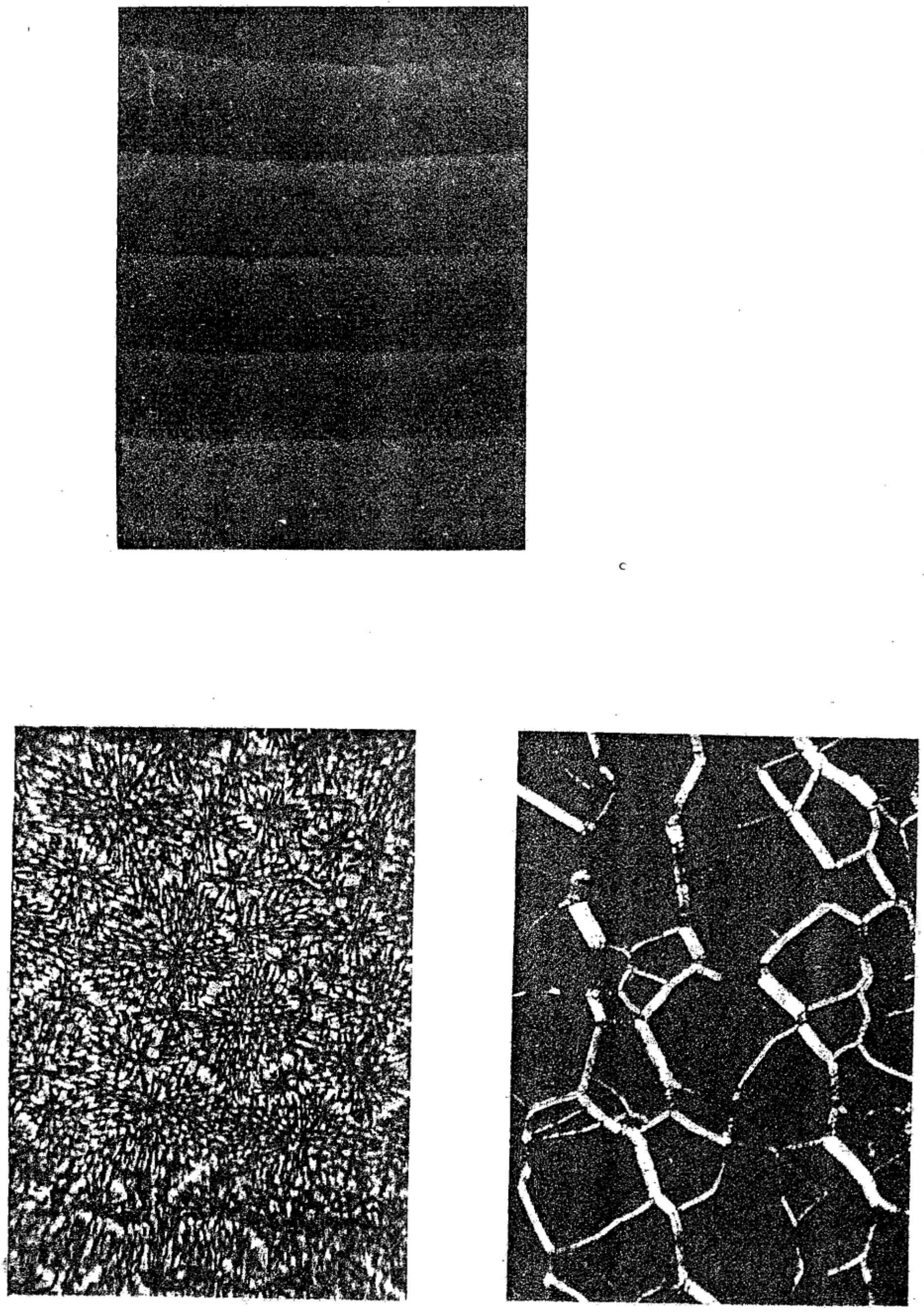
Nematic textures

Bernal and Crowfoot [28] used a word imbricated meaning overlapping like scale of a fish to describe the arrangement of the molecules. The Swarm theory accounts satishfactorily for terbidity of nematic mesophase, the light scattering properties of swarms (aggregated molecules). Properties such as transparency [29], refractive index [30], magnetic and electric properties [31] supported Swarm theory. In spite of criticizing some points of Swarm theory, no better explanation was given by any other theory. Apart from threaded and Schlieren texture of nematic phase, a ‘homeotropic’ or ‘pseudomesophase’ mesophase is also emerge in which the uniformly aligned films get their optic axes normal to the surface. de Vries [32] proposed three types of nematic phases based on X-ray diffraction as (i) skewed cybotactic (ii) normal cybotactic and (iii) the classical nematic.

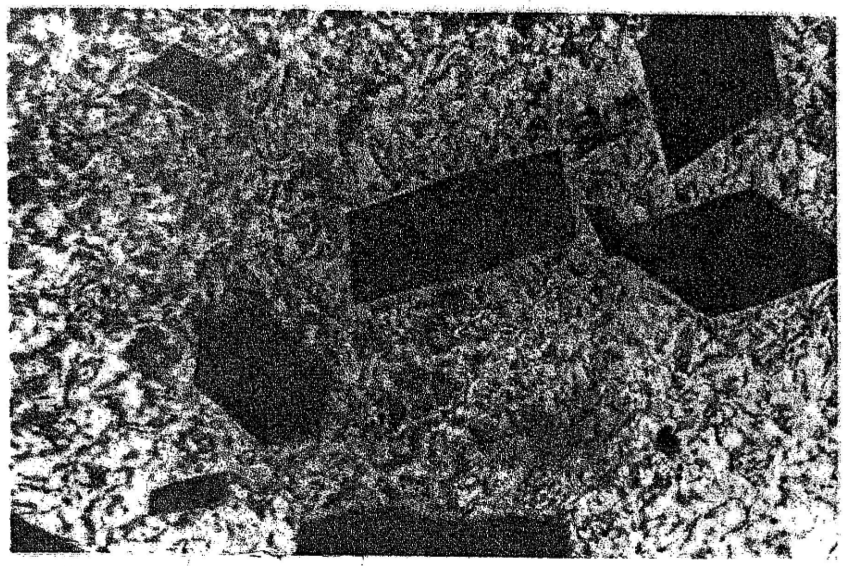
Nematic liquid crystal are optically positive and can be formed by optically inactive or by racemic modification. Alben, Onsagar and Dreyer[33] suggested that, there might be negative nematic with planer molecules aligned with their shortest axis parallel to each other. Zimer and White [34] obtained new nematic mesophase called carbonaceous mesophase as observed from the process of carbonization. Nitro or cyno compounds with positive dielectric anisotropy show re-enterant nematic phase below smectic phase [34].

Cholesteric Liquid Crystals :

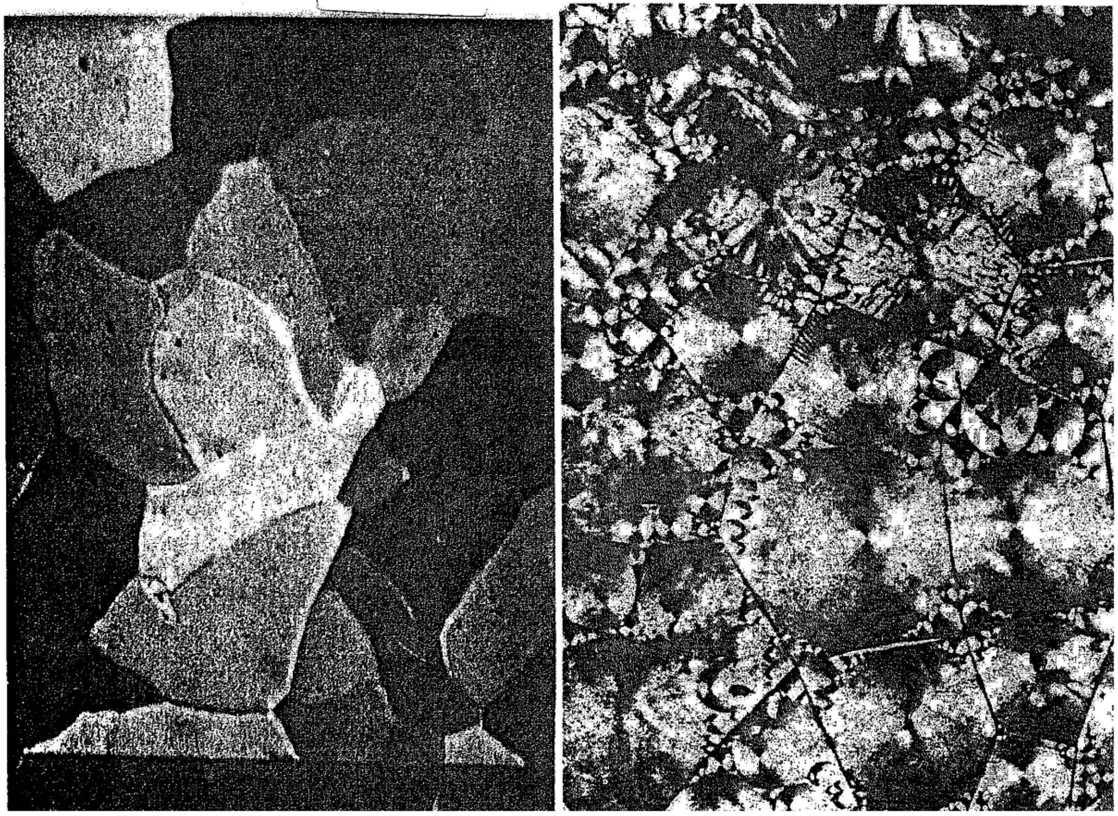
The cholesteric liquid crystals are cholesterol derivatives of an optically active compound with helical structure. Cholesteric liquid crystals are named as chiral nematic also. [35]. Gray, Dave and Vora [36] studied cholestryl esters. A texture in which a specimen is uniformly aligned with the twist axis perpendicular to the plane of the film is called plane texture. The alignment discontinuities can show reflected colures. For perpendicular incidence, the wavelength of the light at the center of reflection band is equal to the wavelength of pitch, multiply by reflective index. Some cholesteric mesomorphic substances on cooling from isotropic liquid phase show a phase visible to the eyes in reflected light over a small range of temperature are called **blue phase**. Blue phase is a cubic structured or amorphous ‘fog’phase. Goodby et al [37] has discovered a frustrated smectic liquid crystal



Cholesteric



Smectic-B



phase, which, occurs at the temperature above the normal smectic phase in some chiral materials and is called the TGBA phase has a double helix structure which resemble to blue phases.

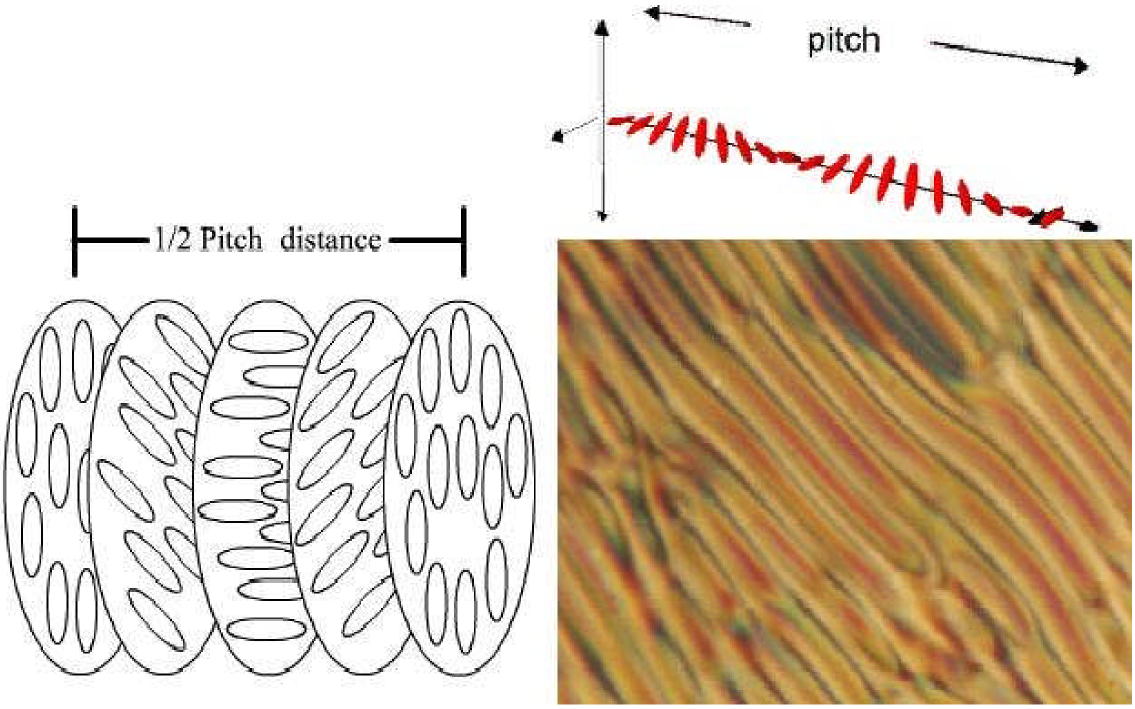


Figure-5(a): The cholesteric liquid crystal: Schematic representation of the helical structure.

Ferroelectric, Antiferroelectric Liquid Crystals:

When a mesophase has permanent polarization in absence of electric field, the mesogenic phase is solid to be a ferroelectric phase as discovered by Robert Meyer [38]. A chiral smectic C* or ferroelectric liquid crystal is a modification of smectic C phase having twist axes normal to the layers. The director of smectic C* mesophase is neither parallel nor perpendicular to layers but it rotates from one layer to the next. Figure-6 represent the twist of the director in each layer.

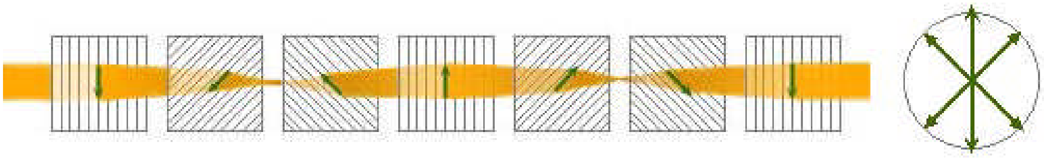
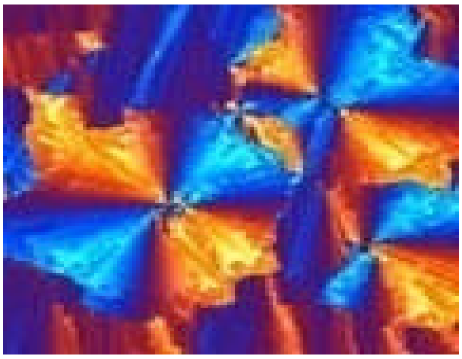
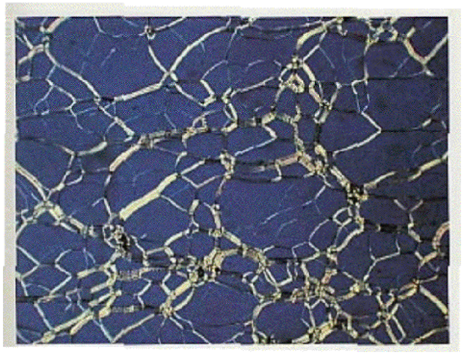


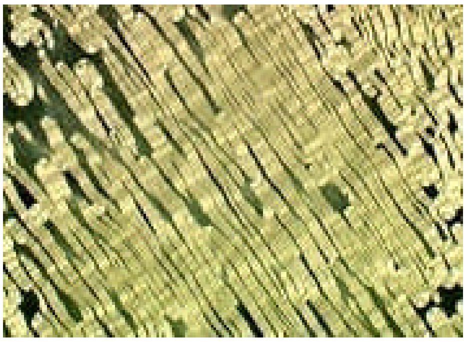
Figure. -5(b):- A schematic representation of a smectic C* phase (left), and a view of the same phase, but along the axis (right).



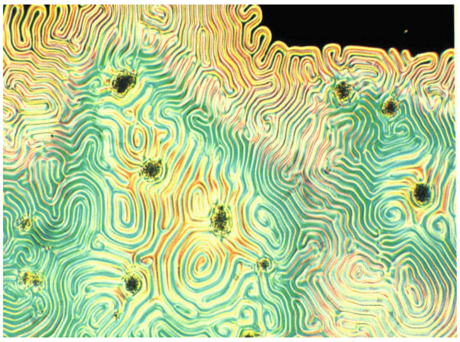
Anti FLC



Chiral Nm



Chiral Sm-C

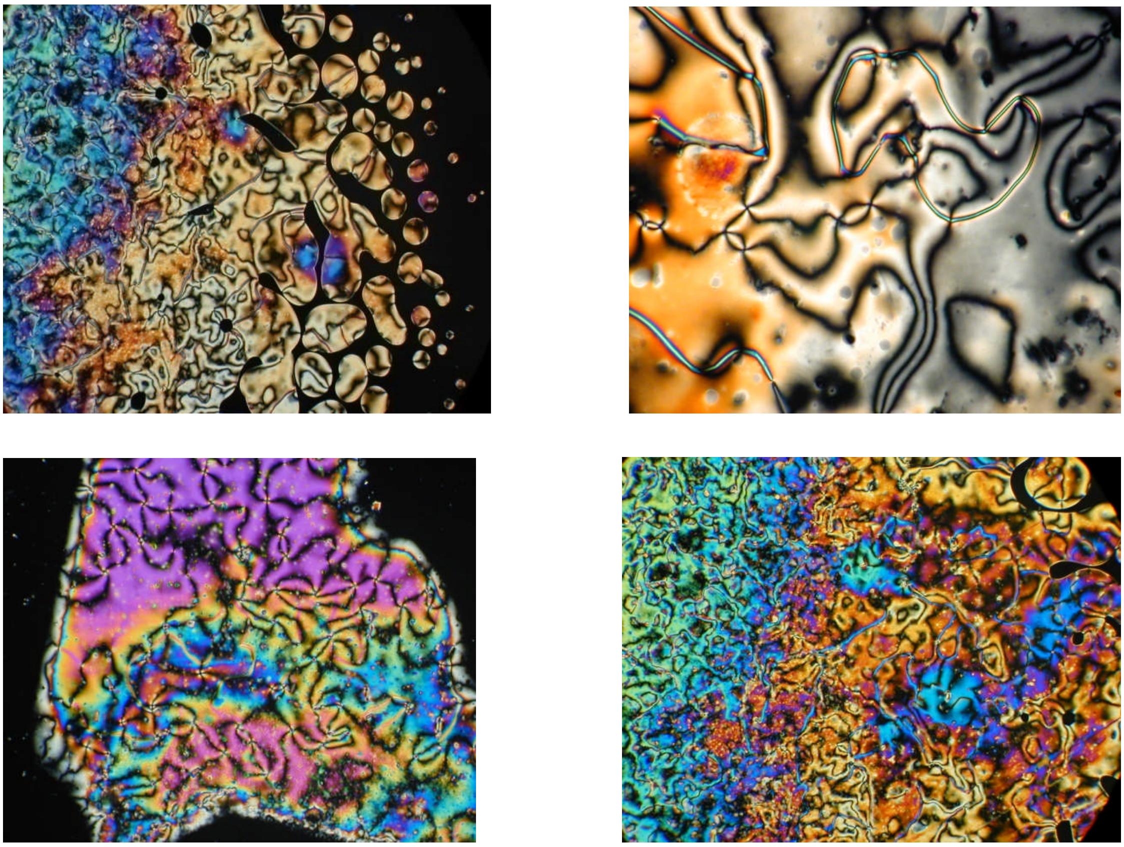


Cholestric

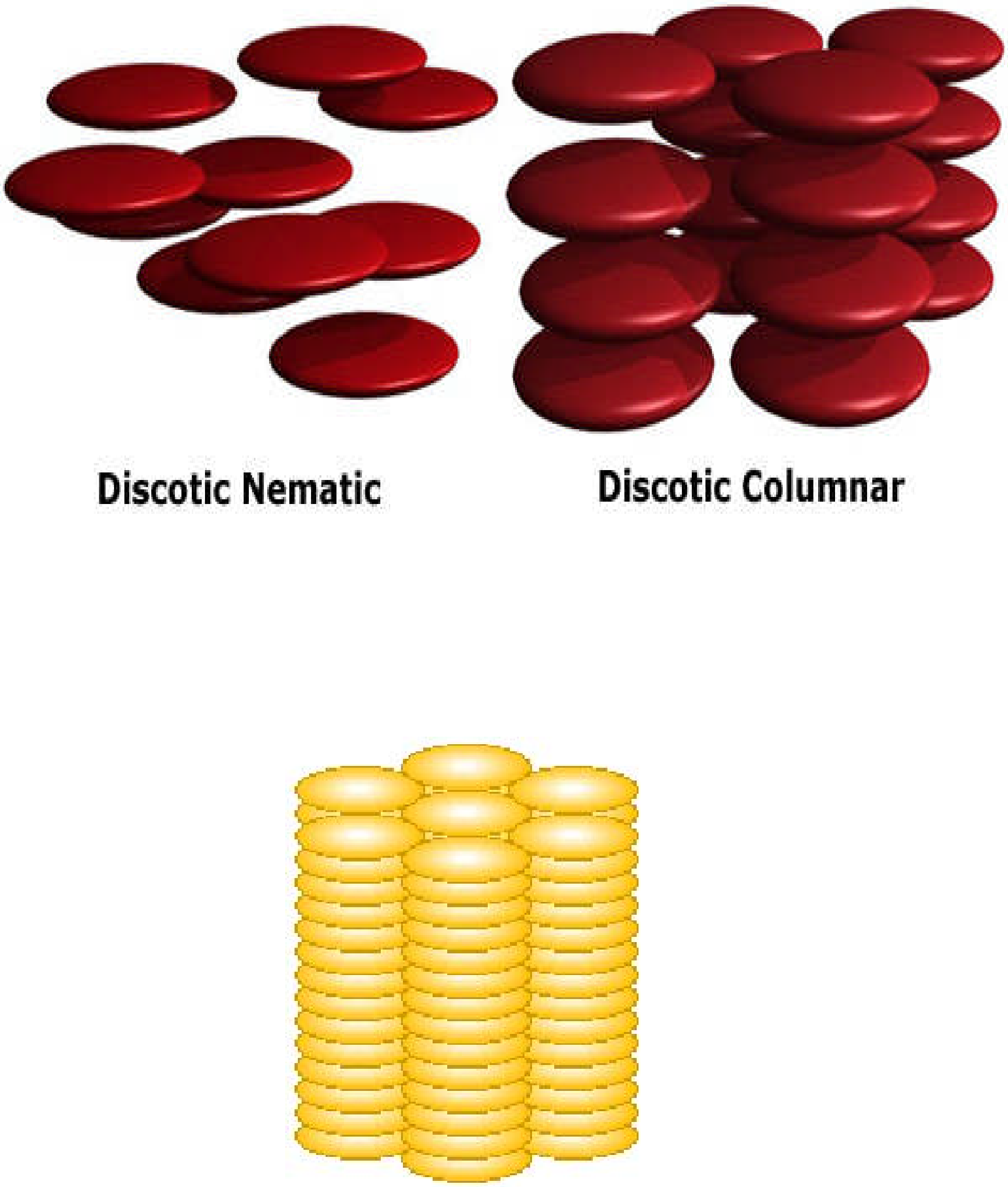
If the director is tilted in opposite direction in alternate layers, a liquid crystal phase is termed as an antiferroelectric liquid crystal. These materials are like ferroelectric liquid crystals are chiral and possess a spontaneous polarization. The different arrangement of molecules in layer plane exists in case of antiferroelectric liquid crystals. A member of new materials possessing anti ferroelectric liquid crystal SC^*_A has been synthesized [39(a),(b),(c),(d),(e)]and reported [40].

Discotic Liquid Crystal:

A mesogenic substance with a disc like shape is called a discotic liquid crystal. Discotic type mesophase was first time reported by S. Chandrasekhar et al in 1977 [41] . discotic mesophase forming materials are formed from molecules with nearly flat aromatic cores, possessing four or six lateral substituents with at least five carbon atoms. Generally such compounds exhibit nematic or number of variants columnar phases [42]. A room temperature electron deficient new discotic system of branched chain tricyclo quinazoline as reported by Sandeep kumar et al [43]. Swen Mahlstedt et al reported novel donor-accepter mesogens, composed of disc like triphenylene donor group to a flat trinitrofluorene accepter via a rod shaped azobenzene moity [44]. Reentrant phenomenon in discotic molecules is reported by Destrade et al [45].



Discotic Mesophases



Colunar

Figure-6: Schematic representation of discotic liquid crystal

Sanidic Liquid Crystals:

The term sanidic liquid crystals is derived from Greek word meaning board like in which a mesomorphic substance has its exhibition between rod like and disc like molecules i.e. a polymeric liquid crystals by Ringsdorf et al in 1986 [46].

Cubic Mesophases:

A term cubic mesophase is applied to optically isotropic matter, the structure of which is derived from X-ray investigation. Three dimensional long range order with respect to the position of the lattice unit exist in such mesophase [47]. With very high viscosity exhibited by the molecules of liquid like structured molten alkyl chains and lyotropic liquid crystals.

Plastic Crystals: Amphiphilic and nonamphiphilic mesophases

Plastic crystals are accepted as an integral part of wide mesomorphic range. On heating liquid crystals, fluidity comes first, but in case of plastic crystals isotropy comes first. Plastic crystals are comparable with nematic and cholesteric mesophases on account of X-ray diffraction patterns. Plastic crystals possesses long range posinal order while, liquid crystal has orientational order and zero (or reduced) positional order. Liquid crystal molecules are long and rigid while, plastic crystals molecules are usually compact and globular. Liquid crystals are solid like liquids whereas plastic crystals are liquid like solids. Thus, plastic crystals are regarded as liquid crystals in type [48] based upon above facts. e.g. tetramethyl methane, cyclohexane, carbontetra chloride, hexamethyl ethan, 2,2 dimethylbutan, camphor, cyclobutan. Plastic crystals are generally globular molecules but all globular molecules are not necessarily give rise to plastic crystals. e.g. methane, silane, german and carbon tetrachloride form plastic crystals while, silicon tetra chloride does not. This may be due to the longer Si-Cl bonds, producing greater molecular inter locking which can hinder rotator displacements.

Quasi Liquid Crystals:

Organic compounds with novel form of organization are called quasi liquid crystals [QLCs] [49]. Mesomorphic inorganic complexes [50] are reported with novel form of molecular organization. Spyro pyrans containing mesogenic groups exhibit some features of liquid crystals like birefringence, orientation in an electric field but their structures are differed than conventional liquid crystals.

Metallomesogens:

Metal containing liquid crystals are called metallomesogens as reported by Volander [51] in 1910. Alkali metal carboxylates, R-($CH_2)_n$-COONa forms classical lamellar phase on heating. Since then number of new reported e.g. d-block elements metallomesogens with monodentate ligands cynobiphenyl, n-alkoxy stibazole, monostibazole, distibazole 4-substituted pyridine, ferrocenes [52]. T-Shaped dimesogenes are reported by Surendranath V. from kent state university [53].

Banana Shaped or Bent core Liquid Crystals:

Liquid crystal phase formed by bent molecules are known as banana shaped liquid crystals, reported in 1994 by Matsunaga et al [58] for the very first time. Polar order within smectic layers can deduced as a consequence of bent shape which results into exhibition of ferro or antiferro electric properties in spite of molecular nonchirality. The general structure of banana shaped molecule is as under [59].

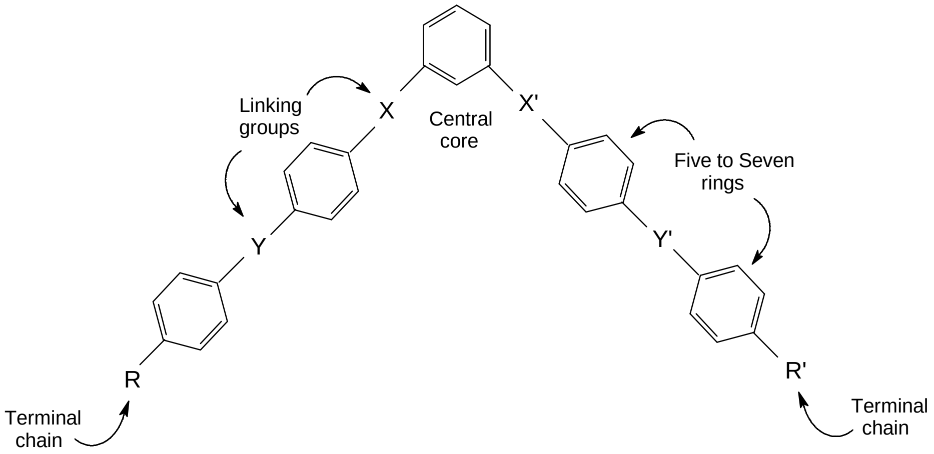


Figure-7

Antiferroelectric properties find useful applications in display technology. The banana shaped molecules are exteremly sensitive to structural modifications in repect of mesophase attainment. Flexibility, bond angle, nature of central core, molecular length, nature of lateral, terminal, central groups and substitution to them, dipole and direction of linking are varying parameters which relates to structural properties with mesophase formation.[60]

Modern Research trend:

New chiral liquid crystals possessing ferro, antiferro and ferrielectric properties. Distinct ferroelectric smectic liquid crystals, new homologous series of racemic symmetric and non symmetric, liquid crystal dimmers with branched alkyl chain, α-halogenated triphenylene based discotic liquid crystals to prepare attractive devices application. Anisotropic networks, elastomers and gels applied to passive optical and nonlinear optic film, supramolecular mesogenic material, halographic gratings and holographic image storage via photochemical phase transition of polymeric azobenzene liquid film, synthesis and evalution of mesomorphic properties of trimesogen consisting of three non-identical calamitic mesogenic entities [61], synthesis of chalcones [62], Nanoscal electric conductivity of discotic LC azo dye.[64], Effect of lateral substitution on mesophase through mesomorphic azodyes [65], synthesis of supramolecules [66], linear hydrogen bonded liquid crystals [67], bent shaped nitro oxadiazoles and thiadiazoles [68] and many other types of researches going in, synthesis, study of their properties and exploitation of their properties in various fields of applications.

Lyotropic Liquid Crystals:

The solvent induced liquid crystal formation is called lyotropic liquid crystals. solute molecules are solvated in suitable solven (generally water) or a solute gives rise to a mesophase by the process of solvation in which solution of a solute molecules are allowed to evapourate at a particular temperature, (or solvent is added to solute.) a mesophase formation occure at particular concentration of solute in a given solvent. The solute molecules are called amphiphilic molecules or amphiphiles. Generally hydrophilic groups –COOH, $-SO_3K$, COONa, -OH, $-O-(-CH_2-CH_2-O-)n-H,-N(Me)_3Br$ are water soluble and insoluble in hydrocarbon are typically amphiphilic in nature. Gradual break down of liquid crystal lattices may take place by addition of solvent or by removal of solvent by evaporation is as under.

$$\substack{\text{crystalline}\\ \text{substance}} \underset{\text{dehydration}}{\overset{\substack{\text{Solvent}\\ (H_2O)}}{\longleftrightarrow}} \text{Liquid crystal} \underset{\substack{(H_2O)\\ \text{Evaporation}}}{\overset{\substack{\text{Excess of}\\ \text{solvent } H_2O}}{\longleftrightarrow}} \substack{\text{True solution}\\ \text{or}\\ \text{colidal solution}}$$

Multimolecular units called as ‘aggregates’ or ‘micelles’ which are commonly ‘liquid’ or fused in character. The sequence of appearance with increasing concentration of amphiphilic compounds are as under.

$$\underset{\substack{\text{Isotropic}\\ \text{phase}}}{S_1C} \longrightarrow \underset{\substack{\text{The middel}\\ \text{phase}}}{M_1} \longrightarrow \underset{\substack{\text{The viscous}\\ \text{isotropic}\\ \text{phase}}}{V_1} \longrightarrow \underset{\substack{\text{The neat}\\ \text{phase}}}{G} \longrightarrow \underset{\substack{\text{The inverse}\\ \text{phase}}}{V_2} \longrightarrow \underset{\substack{\text{The inverse}\\ \text{phase}}}{M_2}$$

This classification of mesophases in binary systems consisted of water and amphiphile [69]. Viscous solution of poly-p-benzal-L-glutamate is anisotropic in certain organic solvents [70]. Certain dyes, soaps, salt of naphonic and resin acids, cationic and nonionic detergents exhibit lyotropic mesomorophesm [71].

Mesomorphasm in Biological systems:

The biological mesomorphism was first observed by Virchow in 1854, in myelin forms [72], much earlier than the first discovery of a mesomorphic substance by Reinitzer in 1888(1). Myelin dodies play an important role in microbiological reaction in which dissolving power of myelin bodies in mesomorphic state to various mesomorphic or nonmesomorphic substances is important. Diffused myelin or myelins of lacithin like nature are probably essential constituents of the cells of the most tissues. The lacithin present in significant amount in the red corpuscles probably fits these bodies to be the common carriers of the organism [73]. Slight variation in composition and in physical or chemical properties can naturally affect the formation, continuation or cessation of the mesomorphic state, a delicate balance characteristic also of many biological processes. The structure of the mesomorphic state may provide a favourable environment for the catalytic biological processes. Biological systems are multicomponent and contain numerous types of macromolecules, inorganic ions etc.

Mesomorphic phenomenon in biological systems was studied and experimented by number of scientists, as under.

(1)A solution of tobacco mosoic virus by X-ray diffraction, birefringence in case of muscles tissues were noted [74].

(2)Nervous tissues shows the presence of two components in optical opposition in the concentric multilayers of lipid or lypoproteins forming the myelin sheath [75].

(3)Structure of hemoglobin study, assum a liquid crystal form in red blood cells [76].

(4) Polypeptide-poly- benzene-L-glutamate existed in organic solvents as a cholesteric liquid crystal spiral [77].

(5)Thus, structure of living cells and tissues contain liquid crystal structured matters [78]. e.g.
Complex lipids present in adrenal cortex, overies, myelin and in a thermomatous arteries existed at body temperature in a cholesteric mesophase.
The cause of mesomorphism (liquid crystallinity) in biological systems was explained by Stewart[79].

(6)Mesomorphism in muscle filament and factors controlling mesomorphicity and their biological interaction was studied by Ambrose[80].

(7)The isolation of tetracyclic triterpenes esters exhibiting smectic and cholesteric . masophases from banana peels and seeds of strychnine producing plants was reported [81].

(8)A mesomorphic state of nucleic acids proved by Evdokimov et al [82].

(9)Properties of cholesteric proteins present in biological systems as cholesteric liquid crystals reported by Neville [83].

(10)Effect of drugs on liquid crystallinity of model biological membranes and role of mesomorphic property in biological processes was studied [84].

Physical Properties of Liquid Crystals:

The study of physical properties is significant as it decides the applicability of liquid crystals, so that,they can be used for practical advantages.

Large volume of work has been carried out by scientists in early days of liquid crystals to study the various physical properties of liquid crystals. X-ray studies were carried out by Vander Lingen [85], hukel [86], deBrogli and Friedel [87], Cladis et al [88] and Brown et al.[89]. NMR studies were carried out by Spence et al. [90,91], lippmann et al. [92] and Saupe and Englert [93]. A number of researchers like Maier et al. and L’vova et al. carried out ultra violet and inffra-red spectroscopy studies [94, 95]. Viscosity studies were carried out by Schenk [96] and Porter and Johnson [97] .

In chromatography, Dewar et al. [98] and Kelker [99] initiated the use of liquid crystal as stationary phases. Vora et al. [100] and others [101,102,103] exploited few liquid crystalline compounds as stationary phase in gas chromatography. Number of reviews and books are published where detailed study of physical properties are discussed [104,105,106].

Mixed Mesomorphism:

When a mesomorphic compound is mixed with another mesomorphic or a non-mesomorphic component, the solid-mesomorphic and mesomorphic isotropic transition temperatures may be depressed and the degree of depression will depend upon the nature and the concentration of the added component in the binary mixture.

Binary systems have been studied by a number of workers [107,108,109]

showing the depression of melting points and transition points in the phase diagrams of the mixtures showing liquid crystal properties. The extent of mixed mesophase and the effect of terminal substituents in the exhibition of mixed mesomorphism have been studied in great detail by Dave and Dewar [110]. Dave and Lohar[111], Dave and Vasanath [112], Lohar and Shah [113],LOhar and Patel[114], Lohar and Doshi [115],Doshi, Odedara and Joshi [116], Doshi and Vyas [117] and Vora et al.[118], Padmini et al.[119] reported induced nematic phase in a binary systems consisting of a polymorphic smectogen and non mesogenic Schiff's bases. Arora et al.[120] and Neutbert et al.[121] have reported creation of nematic phase in smectogen by addition of the second mesogenic component. Chiral smectic liquid crystal mixture containing 1,3-difluloro naphthalene derivatives and compounds with fluorinated side chain have been studied by Wolfgang et al.[122].

Sackmann and Demus [123] identified smectic mesophases on the basis of miscibility, criteria and texture phenomenon.

Bogowlensky and Winnogrodow [124] deduced the latent transition temperatures by extrapolation method from the study of mixed mesomorphism. Dave and Dewar [125] initially did not agree with the extrapolation method but later, agree with consistant results for same substance Dave and Lohar [126] Lohar and Doshi [127] and Doshi et al.[128-134] also studied number of binary systems and determined LTTs of nonmoesomorphic components and found better evidence in favour of the accuracy and credibility of extrapolation method.

Mesomorphism in Homologous Series:

For a homologous series, when the mesomorphic transition temperatures e.g. nematic isotropic, smectic-isotropic, smectic-nematic, or smectic-smectic are plotted against the number of carbon atoms in the n-alkyl chain of alkoxy group, smooth curves may be drawn for like of related transitions. Usually the crystal mesomorphic transitions do not exhibit regular trends.The mesomorphic isotropic temperature lie on two falling curves, the upper one for even and lower one for odd number of carbon atoms in the n-alkoxy chain. The odd-even effect usually becomes less marked as the series ascended and the two curves merge for later homologues of the series. The smectic-nematic transition temperature usually do not altermate and lie on a smooth curves, which rises steeply at first, then levels off and may or may not merge with the falling nematic-isotropic, smectic-isotropic curves. However, nematic-isotropic transition temperatures should always show descending tendency as series is ascended is not an universal law. It may rise or fall depending upon anisotropic intermolecular forces of attractions arising as a consequence of molecular rigidity and flexibility. Nematic-isotropic transition curve initially may rise or fall and may fall or rise after passing through maxima or minima and may fall or rise depending upon the geometrical shape, size, type, of central and/or terminal or laterally, substituted flexible planer or non-planer groups contributing to overall rigidity and flexibility of a molecule. A maxima or minima in nematic isotropic transition curve may appear from early or late homologue or may not appear till the last homologue, provided homologues are absolutely pure and of true structure. Thus, there is no specific rule which govern the trend of the curve. One should represent his or her experimental results without keeping any rigid conclusions in mind or the conclusions made earlier.

Polymer Liquid Crystals:

Polymers are substances with long chain structure and high molecular weight. Polymers have been extensively used in almost every necessity of life. New polymers with better properties are developed for new application.

After the initial discovery of liquid crystallinity in polymeric solutions by Oster [135] and Robinson [136], number of liquid crystalline polymers have been reported. Polymer liquid crystals [PLCs] interlink properties of polymers with those of liquid crystals.

These “hybrids” show the same mesophase characteristics as that of ordinary liquid crystals,yet retain many of the useful and versatile properties of polymers. In order for normally, flexible polymers to display liquid crystalline characteristics, rod-like or disc-like elements must be incorporated into their chain.The placement of the main chain liquid crystalline polymers are formed when the mesogens themselves are the part of main chain of a polymer. Conversely, side-chain liquid crystal polymers are formed when the mesogens are connected as side-chain to the polymer by a flexible “bridge” which is called the Spacer.

The molecular structure and mesomorphic character of liquid crystal polymers are discussed in detail by Finklemann [137] and Ober [138].

Liquid crystalline polymers can be classified into main-chain liquid crystalline polymers and side-chain liquid crystalline polymers.[**figure** -8]

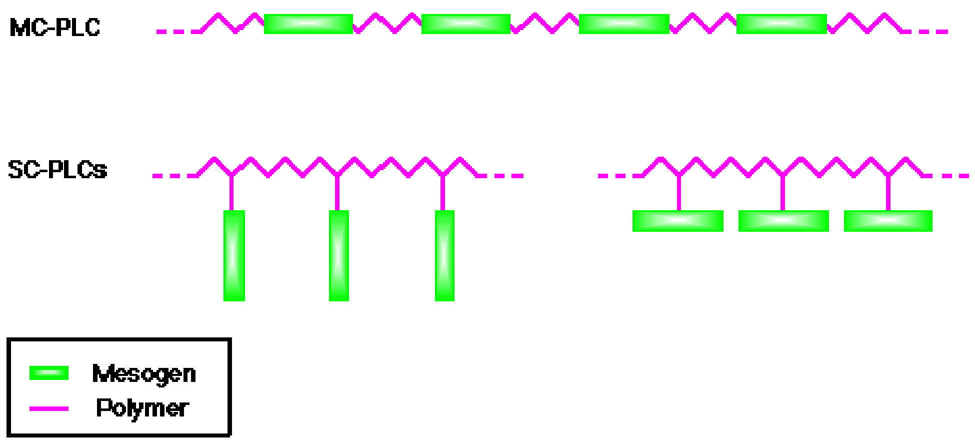


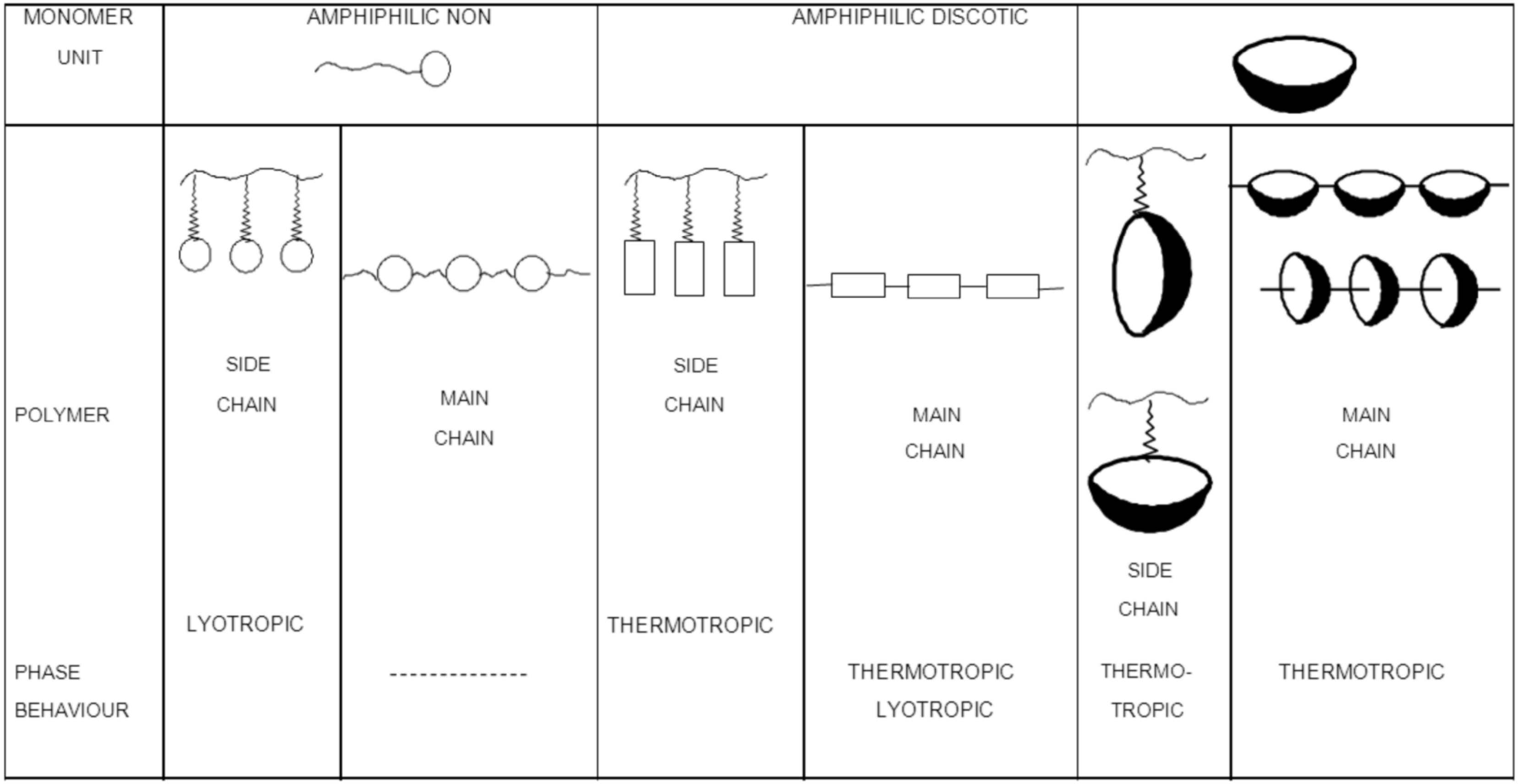
Figure-8

The mesogenic polymers can be subdivided into the scheme given in **Table-** . For both polymers, the original mesogenic moieties of the low molecular weight compound has been presented which suggests the idea that the ability of forming a liquid crystal phase can be preserved. Liquid crystal main-chain polymer exhibit outstanding mechanical properties, while, liquid crystal side-chain polymers offer field effects and optical properties.

The liquid crystal states in polymers have been characterized by optical and electron microscopy, X-ray, thermal studies, DSC and TGA, Spectroscopic methods like IR and NMR, solution or viscosity behaviors, light scattering methods based on visible light and study on the effects of electric and magnetic field.

Polymerization of non-mesogenic monomers having mesophase conducive side-chain may result in polymers with thermotropic liquid crystalline

CHART-I : CLASSIFICATION OF LIQUID CRYSTALLINE POLYMERS



MONOMER UNIT	AMPHIPHILIC NON		AMPHIPHILIC DISCOTIC			
POLYMER	SIDE CHAIN	MAIN CHAIN	SIDE CHAIN	MAIN CHAIN	SIDE CHAIN	MAIN CHAIN
PHASE BEHAVIOUR	LYOTROPIC	--------------	THERMOTROPIC	THERMOTROPIC LYOTROPIC	THERMO-TROPIC	THERMOTROPIC

Figure – 9

properties [139,140]. Number of patents and reports claiming the production of fibres (Kevlar fibres) from polymer solutions, existing in liquid crystalline state are known.[141-143]

The fibres have been reported to have tenacities which are greater in magnitude than those reported for steel on a weight basis, Kevlar fibre has been shown to be useful as a tire cord; as a replacement for glass and steel belts in bias belted and belted tires. A bulletproof jacket woven from Kevlar fibers is used as an armour, which saves the life of a victim attacked by a bullet.

Vora and Patel [144] reported mesogenic polymers incorporating a monomer having symmetrically substituted triazine heterocyclic moiety and evaluated the effects of chemical structure on mesomorphism.

Liquid crystal polymers having mesogenic side chains on the rigid backbone and with flexible spacers have been reported by Reck and Ringsdorf [145].

Applications of Liquid Crystals:

Liquid crystal technology has had a major effect in many areas of science and engineering, as well as devices technology. Applications to this special kind of materials are still being discovered and continue to provide effective solutions to many different problems.

The technology benefit of the developments in the field of liquid crystals is evident by existence of a variety of consumer products that use these materials in displays ranging from simple indicators to sophisticated colour laptop computers and in various non display applications.

General applications:

Liquid crystal paintings have been used on fabrics like T-shirts etc. Certain cosmetics containing liquid crystals are also now available.

The change of colour depending on body temperature and atmospheric temperature.Mood jewellery also contain liquid crystals. the body temperature varies according to the mood of a person. Thus, the change of the colour of the jewellery [146] or LC BINDIA is useful to decide the temperament or mood of a lady or a person concern. Electronic LC screens are also available to maintain privacy of dealing in the business office or house. LC cloths are available with different colours which are changing their colours with changing intensity of light. Thus same cloth ware show different colours in morning, noon, evening and night. In such case the LC dyes used to colour original cloth which are photo sensitive.

Non –Display Applications of Liquid Crystals:

There are many non-display applications of liquid crystals. some of the most developed application that currently being researched is in optical correlators, optical interconnections, wavelength, filters and optoelectronic neutral networks.

Liquid crystal lenses:

The ability to control the refractive index of a liquid crystal allows the implementation of liquid crystal lenses. The refractive index profile in these devices act as a curved surface of a glass and hence act as a lens. [147].

A novel form of liquid crystal “lens” is the switchable hologram [148]. The exact functionality of the device depends on the design of the pattem.

Three dimensional Video:

This application of liquid crystal technology may not seen to fit into the category of non-display applications, but the actual use of the liquid crystal is not in the display of images, rather it is used to perform the angular multiplexing which grows to make up the three dimensional image [149]. The display itself is autostereoscopic, with no external optics, such as 3-D glasses, required. The viewer can see the 3-D image over a viewing angle of 40^{0C} with the naked eye.

Medical themography:

The thermochromic liquid crystal have found extensive uses in medical applications. The use of liquid crystals in evaluating deep vein thermbosis is described by several authors [150-156]. Sandler and Martin, for example [157] consider liquid crystals thermography as a screening test for deep-vein thrombosis. The prediction of fast ulceration in diabetic patients through thermal mapping using liquid crystal technology is described by Benbow et al.[158].

Subcutaneous and intracutaneous malignant tumours are typically 0.9-3.3^{0C} warmer than the surrounding tissue [159]. The use of liquid crystal thermography has also been reported for the determination of the extent of basal cell carcinomas [160] and cancer in other parts of the body.[161-165].

Indeed liquid crystal thermography has found use in areas as diverse as core body temperature measerments in anesthetic recovery [166], headache clinic setting [167], investigation of spinal root syndromes [168-172], chronic [173] and low [174] back pain, scrotal temperature in cases of spinal cord injury [175], knee joint stress[176], evaluation of the diabatic foot [177], the thyroid [178], as a diagnostic test in acute [179] and destructive [180] lactation mastitis and carpal tunnel syndrome[181,182].

High strength fibers:

An application of polymer liquid crystal that has been successfully developed for industry is the area of high strength fibers, e.g. Kevlar fibers, which are used to make such things as helmets and bulletproof vests, is just one example of the use of polymer liquid crystals in application calling for strong light weight materials[183].

Radiation Detection:

The technical details of the construction and operation of the detectors are readily available in the patent literature [184-188]. Membrance devices including a thin layer of carbon back, are often used for infra-red radiation detection and visualization [189,190] and such detectors are particularly useful in the observation of the modes and emission parameters of infra-red lasers [191-196].

A thermal imaging devices that offers the possibility of night vision had also been described [197]. There have been suggestions that thermochromic liquid crystals may be used for the detection of elementary particles[198].

Liquid crystals as solvents in spectroscopy:

Liquid crystalline media, particularly nematic, provide the bulk molecular orientation necessary for observation of spectroscopic details analogous to those obtained in solid state experiments. These media have been widely used as solvents in NMR, EPR and optical spectroscopic studies on oriented molecules. A few general reviews in this area of applications have appeared [199,200].

Liquid crystals as solvents in chemical reactions:

Thermotropic liquid crystals have been used as solvents to alter course or rates of uni- and bi- molecular thermal and photochemical reactions.The unique anisotropic properties of liquid crystals are utilized to control the efficiency and specificity in micro synthesis, elucidation of reaction mechanism etc. Factors important in defining the ability of liquid crystals to control solute reactivity have been reviewed to be able to choose the liquid crystals of proper morphology as a solvent [201-204].

Liquid crystals in gas liquid chromatography [GLC].

The sensitive dependence of the activity co-efficients on the molecular geometry provide the basis for the applicability of liquid crystals stationary phase in gas liquid chromatography [GLC].

A number of models have been developed to describe more quantitatively the enhancement in selectivity that is obtained from the anisotropic orientational ordering of liquid crystals [205-215]. Earlier use of liquid crystals as stationary phases in gas chromatography are available [216-221]. Stationary phases can be prepared from either monomeric or side chain polymeric liquid crystals.

Display Applications of Liquid Crystals:

The most common application of liquid crystals is in display devices (LCDs). Liquid crystal displays (LCDs) had a humble beginning with wrist watches in the seventies. Continued research and development in this multidisciplinary field have resulted in displays with increasing size and complexity. After three decades of development in performance, LCDs now offer a formidable challenge and replacement to cathode ray tube (CRT).

This field has grown into a multi-billion dollar industry and many significant and engineering discoveries have been made. From the ubiquitous wrist-watchres and pocket calculators to an advanced VGA (video graphics Array), computer screen, the types of displays have evolved into an important and versatile interface. A liquid crystal display consists of an array of tiny segments (pixels) that, can be manipulated to present information. This basic idea is common to all displays, ranging from simple calculators to a full colour LCD television and mobile telephone screens. The most widely used electro optic effects in display are the twist, super twist and guest host modes.

Active matrix LCD and STN (Super twisted nematic) LCDs are leading display technologies for portable application such as notebook computers. New LCD device configuration and new LCD operation mode have been introduced. The existing technologies and the new LCD operation modes require improved liquid crystalmaterials. Advanced liquid crystalline material had to be developed in order to fulfill the requirements of higher resolution and large size LCDs. The most common LCD that is used for everyday items like watches and calculators is called the twisted nematc (TN) display.

Thirty years ago G.W.Gray [222,223] invented TN mixtures based on cyanobiphenyls. Broad range TN mixtures with improved viewing angle using phenyl cyclohexanes [224,225] were then used for automotive applications.

The introductionof STN displys require materials with large dielectric anisotropy, e.g. cynoesters with lateral fluoro substitution [226]. Thin film technology (TFT) displays require liquid crystalline materials with stability like fluorinated liquid crystals [227-229].

A major contribution to the growth of LCD technology has come from the development in addressing techniques used for driving matrix LCDs. There are several approaches, like passive matrix addressing, active matrix addressing and plasma addressing to drive a matrix display, passive matrix LCD has a simple construction and used the intrinsic non-linear characteristic of the LCD for driving.

A review on the use of liquid crystals in laser optics [230,231] has also appeared in the literature. Owsik et al. [232] have reported design, synthesis and physical properties of new liquid crystalline materials containing saturated and aromatic ring systems, for active matrix LCD. The physical properties of new crystalline materials and mixture designed for active matrix LCD are reported by Iwashita et al.[233]. Liquid crystalline polymers have been intensively investigated with respect to their non-linear optical properties. Chiral polymers [234] are used for photo-optical and optoelectronic applications.

The polymers possessing coumarin side chain being used for liquid crystal photo alignment layers which are reported by Kelly et al. [235]. Main chain liquid crystalline polymers are used essentially as high performance materials.

Thermal mapping and Non-destructive testing.

A film of cholesteric liquid crystals may be applied to large, uneven area. This makes it an ideal tool for thermal mapping and non-destructive testing. The great deal of flexibility in the colour play range allows for a great diversity in potential applications ranging from food processing to electronics and space application e.g. thermocromic paints have been used on printed circuit boards to examine overheating of components. The area in which liquid crystal thermography is of use in nondestructive testing continues to grow due to the development on few chiral nematic materials which offer improved performance over the cholesteryl esters used in early application.

Structural characteristics of the thermotropic liquid crystals:

Liquid crystal property of a substance is strongly related to its molecular structure. Therefore, it is necessary to find out the correlation between liquid crystal properties and molecular structure. Thermo tropic liquid crystals are varied widely in their chemical constitution. However, some common features based on molecular shape, size, geometry, aromaticity lateral substitution affect the anisotropy. Thus there are two important parameter viz;(I) Molecular geomentry (ii) Intermolecular anisotropic forces of attractions of suitable magnitude which influence the liquid crystal properties as a consequence of molecular rigidity and flexibility. The liquid crystal formed under the influence of heat or by solvation are classified broadly as smectic,nematic or cholesteric as discussed earlier in this thesis. Cholesteric mesophase is a modified form of nematic type liquid crystal. Mesophase which is exhibited by cholesteric or a helical twist undergoing substances which are optically active and contain asymmetric carbon.

(A)Rod-like elongated molecule tend to pack in a regular manner giving rise to a parallel arrangement in crystalline state along their major axis. The presence of, polar terminal group, middle or lateral groups and polarisable unit in p-p'-positions along with phenyl ring in elongated molecule play an important role in imparting liquid crystalline property. Thus, only elongated nature of the molecules is not resulting into the display of mesomorphism but, the molecules of laterally substituted groups are also show, mesomorphic behavior. (130, 274) (125, 62(a)) (128) (65(a),(b)) (117, 134)(65(c)) (129).

(B)There are three types of the intermolecular forces.

(1)Dipole-dipole attraction and interactions the direct interaction between already present dipoles in the molecules.

(2)Induced dipole attractions arising from the mutual polarization of the molecules by their permanent dipole moment.

(3)Dispersion forces- the interaction between instantaneous dipoles produce by spontaneous oscillations of the electron clouds of the molecule.

The non-polar molecules of the n-parafins do not possess attractions of the type (1) and (2) and the polarizability of an alkyl chain is not sufficiently high for the dispersion force i.e. factor (3) is also weak. Therefore, low molecular attractions which are incapable of resisting the thermal break down on heating and hence mesomorphic property is absent. The monomeric molecule of a carboxylic acid possessa dipole moment but the effective packing unit in the lattices is a dimer, hence resultant dipole is zero and attractions of the type (1) and (2) are of little significance.

Therefore, a long narrow molecule containing groups of atoms associated with permanent dipolemoment and with its high polarizability can exhibit potentially high degree of mesomorphism. The polarizability of an atom increases with increasing atomic radius and in case of a bond between two atoms. Its polarizability increases with increasing bond order. Addition of polarizable atomic rings and unsaturated linkages ensure high polarizability of the rod-like molecules. Maintaining linearity, the essential criterion, a vast majority of organiccompounds which exhibit mesomorphism are aromatic in nature and frequently contain additional double or triple bonds. Para-para disubstituted benzene derivarives exhibit mesomorphism due to the maintainance of linearity in shape. Similarly 4-4'' disubstituted p- terphenyls are frequently mesomorphic e.g. p-n-alkoxy benzoic acids [236] are linear dimmers with two aromatic rings and dipolar ether groups and polarizable >C=O bond, trans –p-n-alkoxy cinnamic acids [237] are also linear dimmers with two aromatic rings, dipolar ether groups and polarizable >C=O and >C=C< bonds. The cis –p-n-alkoxy cinnamic acids are non mesomorphic as they do not form linear dimmers. Trans –p-n-alkoxy cinnamic acids exhibit thermally more stable mesophases compared to corresponding p-n-alkoxy benzoic acid due to the greater polarizability which is conferred on the dimeric molecule by the double bond and not due to the greater molecular length resulting from –CH=CH- units.

2,4 –nonadienoic acid [238,239] is mesomorphic in nature due to the existence of molecular polarizability. Thus, CH_3-CH_2-CH_2-CH_2-CH=CH-CH=CH--COOH unsaturared system show enhancing intermolecular attraction due to the polarizability of the double bond to a level favoring mesophase formation. Introduction of large atoms or groups is necessary for obtaining or enhancing polarizability. Increase in the polarizability results into the exhibition of mesomorphism or enhance the thermal stability of originally mesomorphic compounds. Introduction of a bulky atom or group in a position other than at the end of the molecules, appreciably broaden the rod-likemolecule and hence intermolecular attraction decreases or the distance between the attracting centres increases which results into the decrease in the thermal stabilities of the mesophases of the parent molecule.

Aromaticity of the Compound:

This need for rigidity explains the fact that a majority of thermotropic mesogens are aromatic in nature. The aromatic rings are polarizable, planar and rigid and by suitable positioning of substituents and linking units. Stiff lath-shaped molecules are easily built up. It can be represented as

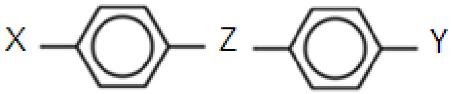
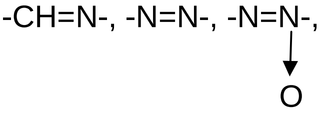


Figure 10

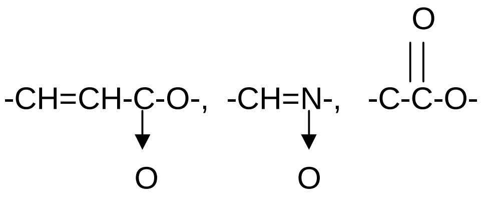
Z=central linkage, X and Y =terminal substituents.

The wel known central linkages are as follows:

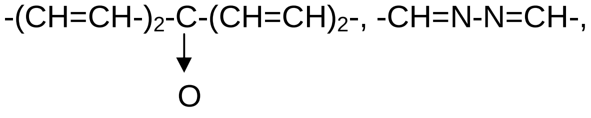
-CH=CH-, - $(CH=CH-)_{2-3}$, -C≡C-



$-CH=N-,\ -N=N-,\ -N=\underset{\underset{\displaystyle O}{\downarrow}}{N}-,$

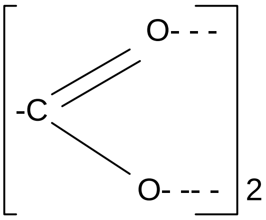


$-CH{=}CH-\underset{\substack{\downarrow\\ O}}{C}-O-,\ -CH{=}\underset{\substack{\downarrow\\ O}}{N}-,\ -C-\overset{\substack{O\\ \|}}{C}-O-$



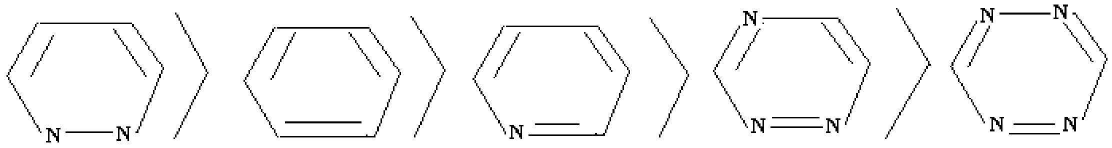
$-(CH{=}CH-)_2-\underset{\substack{\downarrow\\ O}}{C}-(CH{=}CH)_2-,\ -CH{=}N-N{=}CH-,$

$-CH_2-CH_2-$, $-O-CH_2-CH_2-O-$, $-CH{=}CH-CO-$



Extended conjugation in central linkage enhance liquid crystalalline, character [237,236] e.g. benzoic acids and cinnamic acids,when more than two phenyl rings are linked through more than one central linkages, the liquid crystalline properties are enhanced.

Certain cyclohexanes derivatives have been reported [239] to exhibit mesomorphism. Heterocyclic ring system have also been reported to show mesomorphism [238,240]. Their mesomorphic behavior is discussed by Gray and Nash[241]. Schubert et al. [242,243(a)] examined a range of related compounds containg different heterocyclic rings ‘X’ as the central ring and having either two alkyl or alkoxy groups in the internal positions. From this data they have given the order of efficiency for the smectic phase. certain results quoted by Dewar et al. [243(a)] are also relevant in this context.



The effect of terminal substituents:

This terminal groups contributes greatly in display of mesomorphism by a particular substance. The polarity of terminal groups is an important feature in this phenomenon.

Alicyclic rings if subjected to certain constraints to diminish its flexibility, give rise to mesomorphs [244].

By study of mixtures of mesomorphic and nonmesomorphic compounds [245] as well as by examining a range of pure mesomorphs [20]. It was clear that the substituents selected at the para position were more efficient than a terminal hydrogen in promoting nematic mesogenic property. Gray [20] has given an average terminal group efficiency order as

-Ph > $-NHCOCH_3$ > -CN > $-OCH_3$ > $-NO_2$ > -Cl > -Br > $-N(CH_3)_2$ > $-CH_3$ > -F > -H

- OCH_3, 2,5 dichloro, 2,4dichloro,-CH=CH-COOR, where R= 1,2,3,4- - - -

Some order of efficiency is maintained for cholesteric systems [245]. The situation for smectic terminal group efficiency is less clear. Terminally substituted hydroxyl and amino groups disfavor liquid crystalline phase formation due to their capacity to give polymeric hydrogen bonding which raises melting point and may disfavor parallel arrangement.[246,248]

Some series of compounds with phenolic end substituents have been found to be mesomorphic [245]. Branching of the terminal alkyl group decreases the thermal stability of the nematic mesophase more, than of smectic mesophase [244-251]. Branching at first carbon atom of the chain reduce thermal stability the most. Movement of the point of branching away from the first carbon atom of the chain towards the end of the chain, causes the transition temperature to rise again [251].

Alternation of nematic-isotropic transition or its absence in the case of smectic-nematic transitions, with odd or even number of carbon atoms of the alkyl chain of the terminal substituent has been explained on the basis of zigzag conformation [252] or on the basis of the considerations advanced by Flory [253] Marce;ja [254].

The effect of lateral substituents:

Lateral substituents incorporate two oppositely operating forces viz;(I) the force apart the molecules and reduce intermolecular lateral cohesions, but at the same time (ii) they may increase the molecular polarisability which in turn increases the intermolecular attractions. When the first force predominates; the lateral substituents have three pronounced effects on liquid crystallinity.

(1) Lower the temperature at which mesophase appears.

(2) Decrease the stability of mesophase.

(3) Destroy any smectogenic property regardless of alkoxy or alkyl grou[p chain length.

But, when second force predominets, the thermal stabilities of laterally substituted compounds are increased [256]. o-Hydroxy substituted mesogens are exceptions to the above general rule, due to intermolecular hydrogen bonding which increase the overall polarizability of the molecule. Gray has given [20] the order of the substituent effect for the lateral substituents.

Smectic order: $-H < -F < -Cl < -Br < -NO_2 < -Me < -I \quad -OCH_3$

Nematic order: $-H < -I < -Me < -Cl < -Br < -F < -NO_2$

Garland et al. [237] have studied the effect of lateral methyl group on benzylidine anilines. Griffin et al. [257] investigated the effect of lateral trifluoromethyl group on mesomorphism and correlated it with a lateral methyl group. Arora and co-workers [258] have synthesized a series of phenylene esters in which the effect of a lateral methyl group on the transition temperaters was investigated. The introduction of the lateral methyl group results in a decrease of the transition temperature of all phase due to change in molecular conformation as well as broadening of the molecule. The increased dissymmetry resulting from methyl group leads to less effective packing in crystal lattaces and lowering the transition temperatures. Gray and Jones [256], Wiegannd [259] and Dave et al. [260,261] have studied mesomorphic properties of 2:5, 1:5 and 1:4 substituted naphthalene derivatives giving the order of stability of compound as,

$$2:5 > 1:5 > 1:4$$

The effects of lateral substitution of the type, which in addition to broadening the molecule, increases its thickness by imposing its steric effect on the system i.e. by causing a twisting about one of the bonds, so that part of the molecule is rotared out of plane[262,263]. A combination of breadth and steric effect greatly reduce the thermal stabilities of the ordered arrangement of molecules in the liquid crystal and as expected smectic thermal stability is affected more than nematic thermal stability.

OBJECTS

The applications of liquid crystal [LC] materials in various fields like display devices, thermographic measurements, chromatography, drugs and chemical analysis, medical science, defense gadgets, architectural purpose non destructive testing, biological processes etc. Liquid crystals are currently having an important phase of matter, both scientifically and technologically. Therefore many scientists and technologists are trying to study unique properties of liquid crystals which has flow property like liquid and optical properties like crystal from all possible angles like physical, chemical, analytical, biological etc. The most important areas of liquid crystal chemistry are the relationship between molecular structure and the properties of various liquid crystalline phases. The LC phases are possible in a wide range of structures with varying textures.

The existing literature with advancing frontiers are responsible to carry out synthesis of newer mesogens and study of the varying characteristics in accordance with the changing molecular geometry or moiety. Several mesogenic homologous series with varying molecular geometry have been synthesized by various research workers, many of them exhibit liquid crystallinity. A critical review supports the idea that, certain specific changes if brought out in the moieties without disturbing core structure, may modify mesogenic properties in a varying manner.

The present investigation is visualized with a view to carry out synthesis of new liquid crystalline materials, to avail in manufacture of various articles at economical cost, in a variety of applications.

The present investigation has been also motivated with similar objectives, i.e.

Synthesis of homologous series of new mesogens and study of their mesomorphic characteristics.

This study may help to understand the subject as well as find new objects for further research. Thus, following points are the prominent features of the object in view.

(1)To synthesize new homologous series of mesogens by changing the alkyl chain length of n-alkoxy left terminal keeping rest of the molecular part common. Thus, the aim is fixed as to synthesise number of new homologous series with a potential of mesogenic exhibition.

(2)The study aimed at discerning the unobserved transitions if any, by investigating the homologous series under analytical observations such as DSC or DTA of representative.

(3)Decrease of thermal stabilities, raising or lowering of transition temperatures, changes in the extent of mesomorphism and textures in relation with the changing molecular geometry.

(4)The results of study of mesomorphic substances may support or provide negative evidences or help in generalizing the current views. All these are to be discussed after experimental work. An exercise in any of these aspects would be quite interesting and fruitful.

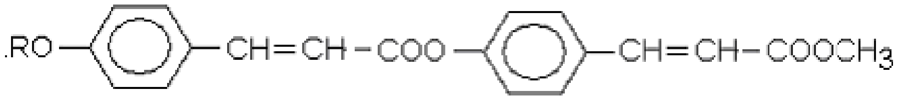
(5)Finally, it is aimed to explore on the ‘probability’ basis whether the current work under investigation finds applications and hence becomes productive. However, such an objective is very difficult to realize keeping in mind the limited resources available at the laboratory of the proposed work.

A balancive approach will be adopted for the fulfillment of the objects under consideration. Due to inadequate facilities at the working laboratory, the investigation is dependent for need help of outside agencies and other universities or institutes fo completion.

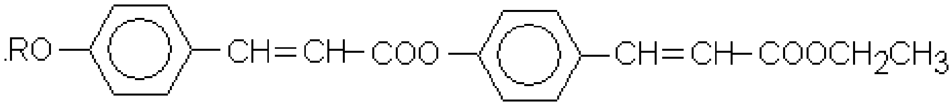
EXPERIMENTAL

Synthesis of the following new homologous series of esters is carried out. All the homologous series are mesomorphic or liquid crystals or mesogenic in character, except one.

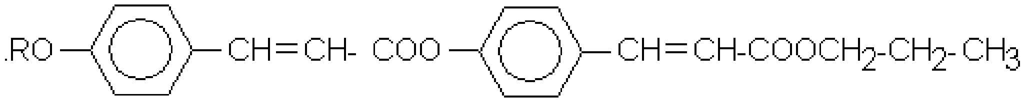
Series-1: Cis Methyl-p-(p’-n-alkoxy cinnamoyloxy) cinnamates



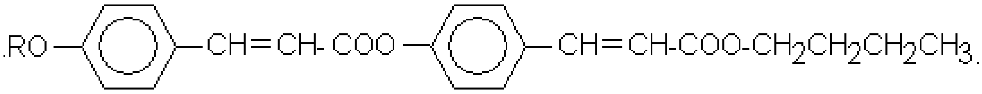
Series-2: Cis Ethyl-p-(p’-n-alkoxy cinnamoyloxy) cinnamates



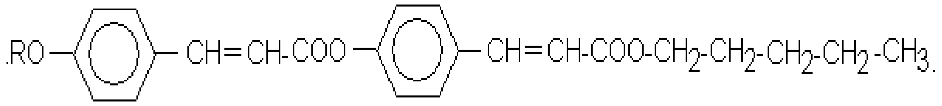
Series-3 : Cis n-Propyl-p(p’-n-alkoxycinnamoyloxy) cinnamates



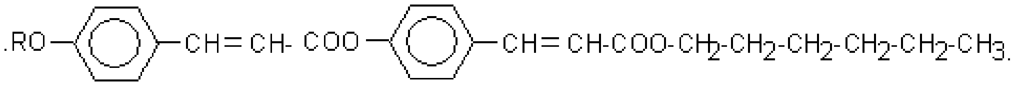
Series-4 : Cis n-Butyl-p-(p’-n-alkoxy cinnamoyloxy) cinnamates



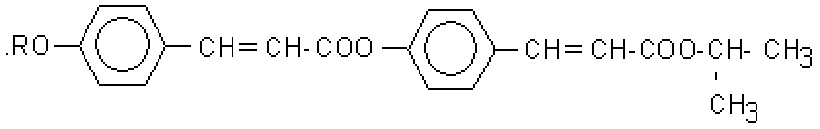
Series-5 : Cis n-Pentyl-p-(p’-n-alkoxy cinnamoyloxy) cinnamates



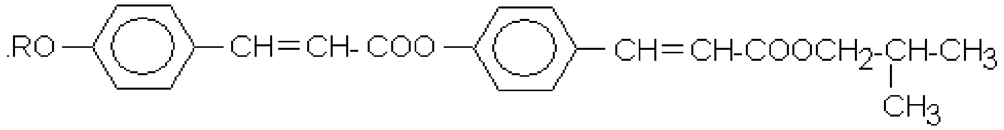
Series-6: Cisn-hexyl-p-(p’-n-alkoxy cinnamoyloxy)cinnamates



Series-7: Cis Isopropyl-p-(p’-n-alkoxy cinnamoyloxy) iso-propyl cinnamates



Series-8 : Cis Isobutyl-p-(p’-n-alkoxy cinnamoyloxy)cinnamates



Series-9: p-(p’-n-alkoxy cinnamoyloxy) β-benzoyl styrene.

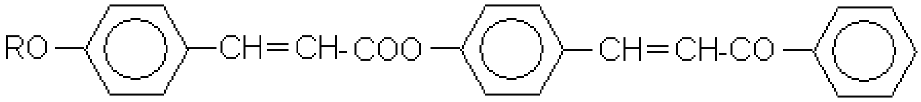


Figure-11

Scheme of synthesis for series-1 to -8.

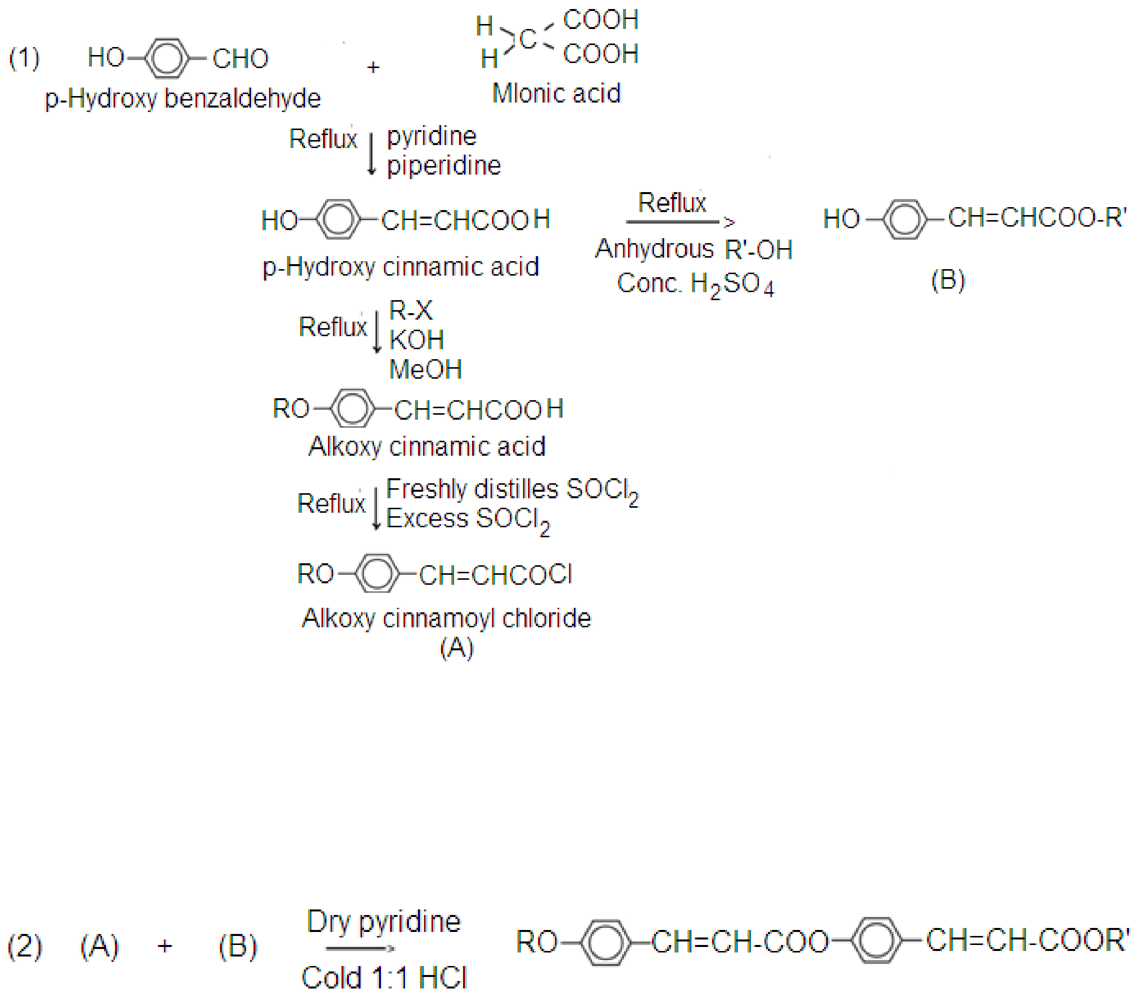


Figure-12

Scheme of synthesis for series-9.

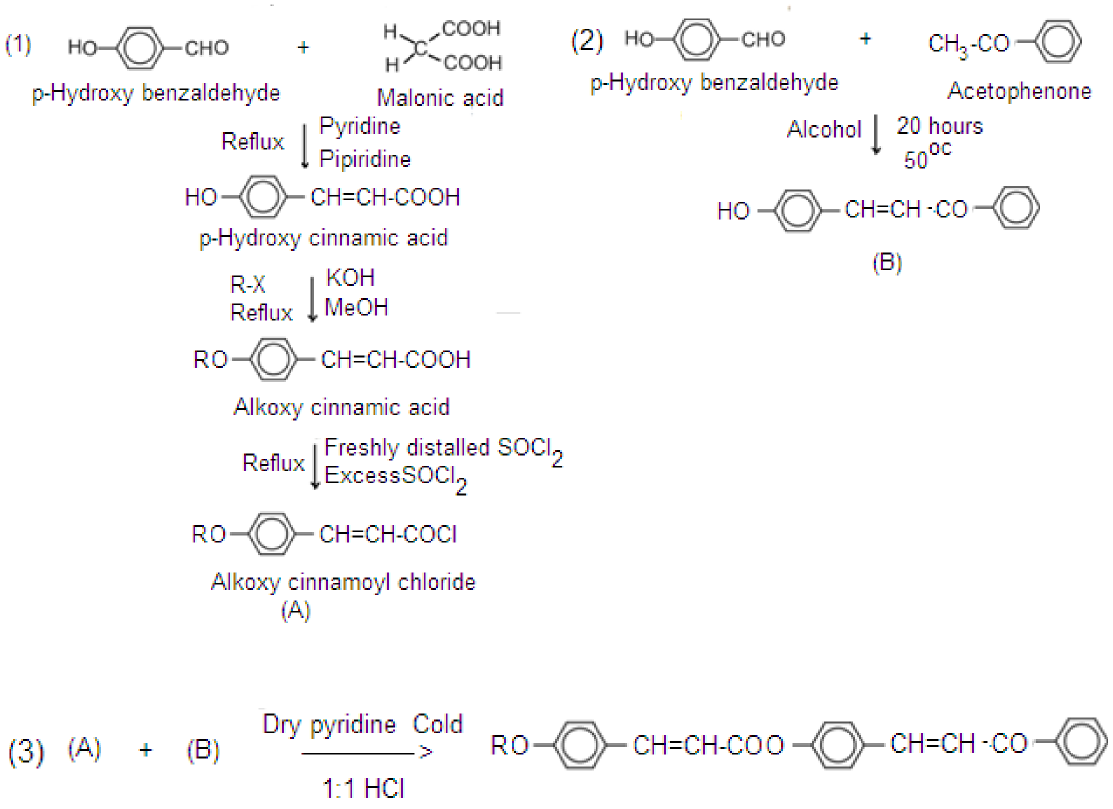


Figure-13

The above homologous series of new mesogens have been synthesized by adopting following different steps.

(A) Preparation of Compounds :

Synthesis of methyl- p-(p’-n-alkoxy cinnamoyloxy) cinnamates.

(a) Synthesis of n-alkyl halides :

Corresponding purified alcohols were used to synthesis of n-alkyl halides by standard methods[272] and pure products were obtained, from ethyl to hexyl halide. Transition points are satisfactorily agreed with the reported literature. Higher alkyl halides viz heptyl, octyl, decyl, dodecyl, tetradecyl,hexadecyl, were directly purchased from market and used as received. .

(b) Synthesis of Cis p-n-alkoxy cinnamic acids :

Number of methods (276) are known for alkylation of p-hydroxy benzoic acid and p-hydroxy cinnamic acid. P-Hydroxy cinnamic acid were alkylated by the treatment of corresponding alkyl halide with p-hydroxy acid by the modified method of Dave and Vora [276]

p-Hydroxy cinnamic acid (0.1 mole), corresponding alkyl halide (0.12 mole) and potassium hydroxide (0.25 mole) were dissolved in 100 ml methanol and reaction mixture was refluxed for 3 to 4 hours, 10% aqueous potassium hydroxide solution (20 ml) was added and refluxing continued for further two hours to hydrolyse any ester formed. The solution was cooled and acidified with 1:1 hydrochloric acid to precipitate the corresponding alkoxy cinnamic acids. Time period for refluxing of reaction mixture was extended with increasing alkyl chain length. Cinnamic acids were crystallized from ethanol or acetic acid till constant melting points were obtained.

(c) Synthesis of p-n-alkoxy cinnamoyl chlorides :

p-n-alkoxy cinnamoyl chlorides were prepared by reacting the corresponding p-n-alkoxy cinnamic acids with excess of freshly distilled thionyl chloride and heating on a water bath till the evolution of hydrogen chloride and SO_2 ceased. Excess of thionyl chloride was distilled off under reduced pressure using water pump and the acid chloride left behind preserved in flask in moisture free atmosphere and directly treated for next reaction without further purification.

(a) Synthesis of p-hydroxy cinnamic acid :

p-Hydroxy cinnamic acid was prepared by dissolving p-hydroxy benzaldehyde (0.15 mole) and malonic acid (0.375 mole) in pyridine (50.0 ml) to which few drops of piperidine added and then heated for a rapid evolution of CO_2 take place. The reaction completed by boiling the solution for five minutes. It was cooled and poured into excess of water containing enough hydrochloric acid to remove excess of pyridine. The p-hydroxy cinnamic acid was separated and filtered off, washed with water and recrystallized from alcohol several times as white shining crystals. The fine crystals obtained were melted sharply at their reported melting point 214^{0C} yield is 69.9 %.

(b) Synthesis of p-hydroxy methyl cinnamte:

p-Hydroxy methyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute methyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 69.0% & M. P. is $117^{o}C$.

Synthesisof methyl- p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy methyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 62.9%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of Ethyl - p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

n-Alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described above respectively.

p-Hydroxy cinnamic acid was synthesized as describedabove.

(b) Synthesis of p-hydroxy ethyl cinnamte :

p-Hydroxy ethyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute ethyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 63.68% & M. P. is 80^{o}C.

Synthesisof Ethyl- p-(p’-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy ethyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 60.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of n-propyl - p-(p’-n-alkoxy cinnamoyloxy) cinnamates:

n-alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described as above.

(a) Synthesis of p-hydroxy cinnamic acid was synthesized by the proceduure described as above.

(b) Synthesis of p-hydroxy n-propyl cinnamte :

p-Hydroxy n-propyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute n-propyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 62.58% & M. P. is 240.0^{o}C.

Synthesisof n-propyl- p-(p’-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy n-propyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 55-60.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of n-butyl - p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

n-alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described as above.

p-hydroxy cinnamic acid was synthesized by the procedure as described above.

(b) Synthesis of p-hydroxy n-butyl cinnamte :

p-Hydroxy n-butyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute n-butyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 62.6% & M. P. is 126.0^{o}C.

Synthesisof n-butyl- p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy n-butyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10%

aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 61.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of n-pentyl - p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

n-alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described as above.

p-hydroxy cinnamic acid was synthesized as described above.

(b) Synthesis of p-hydroxy n-pentyl cinnamte:

p-Hydroxy n-pentyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute n-pentyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 62.6% & M. P. is 122.0^{o}C.

Synthesisof n-pentyl- p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy n-pentyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 64.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of n-hexyl - p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

n-alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described as above.

p-hydroxy cinnamic acid was synthesized as describedabove.

(b) Synthesis of p-hydroxy n-hexyl cinnamte :

p-Hydroxy n-hexyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute n-hexyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 61.68% & M. P. is 160.0^{o}C.

Synthesisof n-hexyl- p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy n-hexyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 64.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of iso-propyl - p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

n-Alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described above.

p- Hydroxy cinnamic acid was synthesized as described above.

Synthesis of p-hydroxy iso-propyl cinnamte:

p-Hydroxy iso-propyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute iso-propyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 60.50% & M. P. is 130.0^{o}C.

Synthesisof iso-propyl- p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy iso-propyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 62.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of iso-butyl - p-(p'-n-alkoxy cinnamoyloxy) cinnamates:

n-Alkyl halides, p-n-alkoxy cinnamic acids and p-n-alkoxy cinnamoyl chlorides were synthesized as described above.

p-Hydroxy cinnamic acid was synthesized as described above.

Synthesis of p-hydroxy iso-butyl cinnamate :

p-Hydroxy iso-butyl cinnamate prepared by adding p-hydroxy cinnamic acid (1 mole) to absolute iso-butyl alcohol (1 mole) and concentrated (98%) sulphuric acid (2 ml). The reaction mixture involving methyl alcohol refluxed in water bath for 4 to 5 hours. The white mass then cooled and poured into excess of ice cooled water (1 liter or more). The solid product so obtained filtered after some days, washed with (4N) aqueous sodium carbonate solution and then with water. The product was crystallized from 98% ethanol till constant melting point obtained. The yield is 63.70% & M. P. is 122.0^{o}C.

Synthesisof iso-butyl- p-(p’-n-alkoxy cinnamoyloxy) cinnamates:

p -Hydroxy iso-butyl cinnamate (0.01 mole) was dissolved in dry pyridine (10 ml) and cooled, then added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from ethanol 80% and 20% benzene. The yield was 64.0%.

The transition temperatures, elemental analysis and spectral data of some selected homologues are recorded separately.

Synthesis of p-(p’-n-alkoxy cinnamoyloxy) β-bezoyl styrene:

n-Alkyl halides, p-n-alkoxy cinnamic acids and p-n- alkoxy cinnamoyl chlorides were synthesized as described above.

Synthesis of p-hydroxy β-bezoyl styrene:

p-Hydroxy benzaldehyde (0.1mole) and acetophenone (0.1mole) were dissolved in minimum amount of ethanol 50% potassium hydroxide solution was added to the above solution. The flask was heated at 500C for twenty hours or room temperature overnight. The solution was acidified by cold 1:1 hydrochloric acid. Crystalline solid product with light yellow colour was filtered and washed with water. The p-hydroxy βbezoyl styrene was recrystallized from ethanol M.P. is 1650C and yield is 60%.

Synthesis of p-(p’-n-alkoxy cinnamoyloxy) β-bezoyl styrenes:

p-Hydroxy βbezoyl styrene (0.1mole) was dissolved in dry pyridine (10 ml) and was added dropwise with constant stirring to the corresponding p-n-alkoxy cinnamoyl chloride (0.015 mole). The reaction mixture was warmed on water bath for about an hour and allowed to stand overnight. It was decomposed in cold 1:1 hydrochloric acid. The precipitates were filtered, washed with water, 10% aqueous sodium bicarbonate solution and again with water. The solid esters were crystallized from 80% and 20% benzene. The yield was approximately 69.0%.

the transition temperatures, elemental analysis and spectral data are recorded seperately

Polarizing microscopy:

A polarizing microscope equipped with hot stage comes handy for detecting a mesomorphic and polymesomorphic compound. A polarizing microscope with heating stage has been used for present investigation largely.

A sample under investigation on polarizing microscope required to be mounted on a slide. Therefore, each sample under microscopic examination should be mounted separately on different slides. The slides are prepared by following methods:

(a) A substance is taken on a slide and heated to a temperature, little above the mesomorphic temperature and a coverslip with minor pressure is placed on it and then cooled.

(b) A substance is heated upto the isotropic liquid point or preferably mesomorphic liquid point and then a coverslip is to be put on it and allowed to cool.

(c) A substance is first dissolved in a suitable solvent and then a few drops of the solution are placed on a slide and the solvent is allowed to evaporate and a coverslip is put on it, till dry.

(d) A small portion of a substance under investigation is taken on the previously dried and cleaned surface of a slide and heated upto the temperature at which it melts or anisotropic state achieved. Then a coverslip is pushed in a direction of the melted substance in such a way that an end of it touch to the melted mass and heating continued for a while, fluid mass of a sample spreads uniformly between the surface of the slide and coverslip forming an uniform thin layer of a substance on cooling. Substance may be pure mesomorphs or a homogeneous mixture containing two or more components.

Thus, well prepared slide of a sample is placed on the heating stage of the polarizing microscope. The switch is put on and sample gets heated gradually. Slow rate of heating say 1^{0C} per minute is maintained. The changing texture over the temperature ranges carefully observed and characteristics of the phase are noted.

The accuracy of a heating device is checked by taking melting points and / or transition points of very pure known substance like benzoic acid, succinic acid, p-azoxyanisole, p-azoxyphenetole etc.

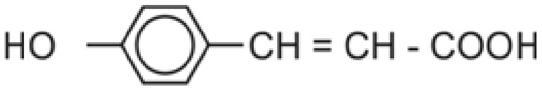
Initially a slide of a sample is heated with pretty fast rate, say about 5^{0C} per minute, till interstate transition temperatures approximately determined. At this stage heating is stopped and cooling is permitted to take place until stable solid reappears. Once again the temperature is raised at highly regulated rate of 1^{0C} per minute from about 5^{0C} to 10^{0C} below the expected transition points in order to measure the transition points accurately. A meticulous observance of this system for measurement of the transitions ensures a great deal of accuracy. The transitions and phases are clearly observed and recorded as the appearance of focal conic, plane, homeotropic and threaded structures of smectic as well as nematic phases emerge under polarized light. Formation of isotropic liquid is clearly marked by the field of vision becoming extinct in polarized light.

Appearance of focal conic structure and disappearance of cleavage lines of solid structure on heating is taken as solid-smectic transition. In order to confirm this change, the slide be disturbed with the help of a spatula, the disturbed smectic phase 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 the isotropic liquid, the reverse transitions take place sharply at the same temperature or within ± 0.2 to ± 0.5^{0C}. Isotropic-nematic change is marked by separation of small droplet from the isotropic liquid, which coalesces to give rise to a threaded region – an unfailing characteristics of the nematic phase. Isotropic-smectic transition is indicated by appearance of battonets which coalesces 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 structure while heating and exactly the reversed sequence on cooling under the microscope.

Monotropic transitions are determined by carefully observing the isotropic liquid as, it cools slowly until battonets of smectic phase or droplets of nematic phase appear.

In case of monotropic mesomorphism, it was possible to raise the temperature before crystalisation occurs, which caused disappearance of the mesophase at the same temperature at which it had appeared on super cooling. This mode of observation confirmed the monotropic change as well as the temperature at which the change occurred. All the compounds under investigation were observed continuously under the polarizing microscope from their solid state to isotropic liquid condition on heating and from isotropic liquid condition to solid state on cooling ensuring confirmation of all the transitions and making it pretty sure that, no transition gets escaped unnoticed.

All observations were repeated several times. In case of any doubt, the compounds were purified again and then were subjected to the study under microscope afresh. Homeotropic texture were observed very carefully.



[272]

p-Hydroxy cinnamic acid

M.P. 214^{0C}

IR: in cm^{-1}

1000, 1230, 1700, →Confirms –COO- of carboxylic group

840.0 →Confirms p-sub. Phenyl ring

1150. 0 →Confirms aromatic –OH group

698.2 →Confirms cis –CH=CH- group

3300.0 →Confirms -OH group

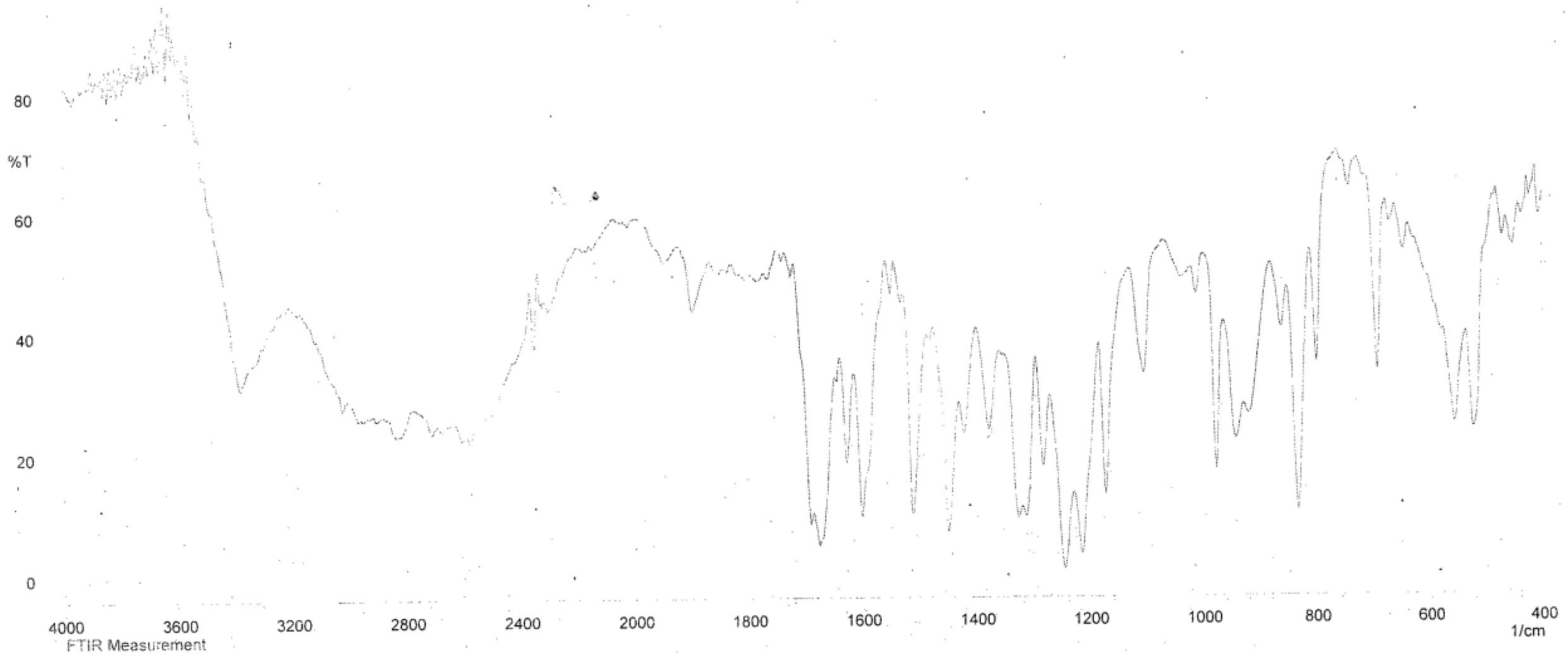
I R confirms the structure.

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 26/11/2010

SAMPLE NAME : a

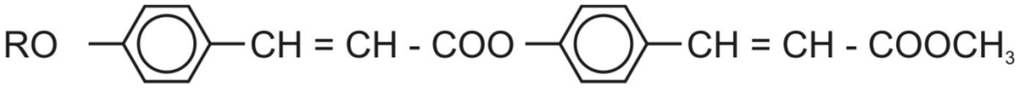


ANALYST : H.P.

No. of Scans; 16

Resolution; 4

VAIBHAV ANALYTICAL SERVICES



Cis Methyl –p-(-p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

Table- 2 : Transition temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	178.0
2	Ethyl	-	-	170.0
3	Propyl	-	124.0	140.0
4	Butyl	-	115.0	128.0
5	Pentyl	-	118.0	125.0
6	Hexyl	-	112.0	128.0
7	Octyl	-	125.0	150.0
8	Decyl	-	120.0	166.0
9	Dodecyl	-	135.0	175.0
10	Tetradecyl	-	132.0	163.0
11	Hexadecyl	-	130.0	138.0

(Page 75 to 78) transferred back as 167 (a, b, c, upto k)

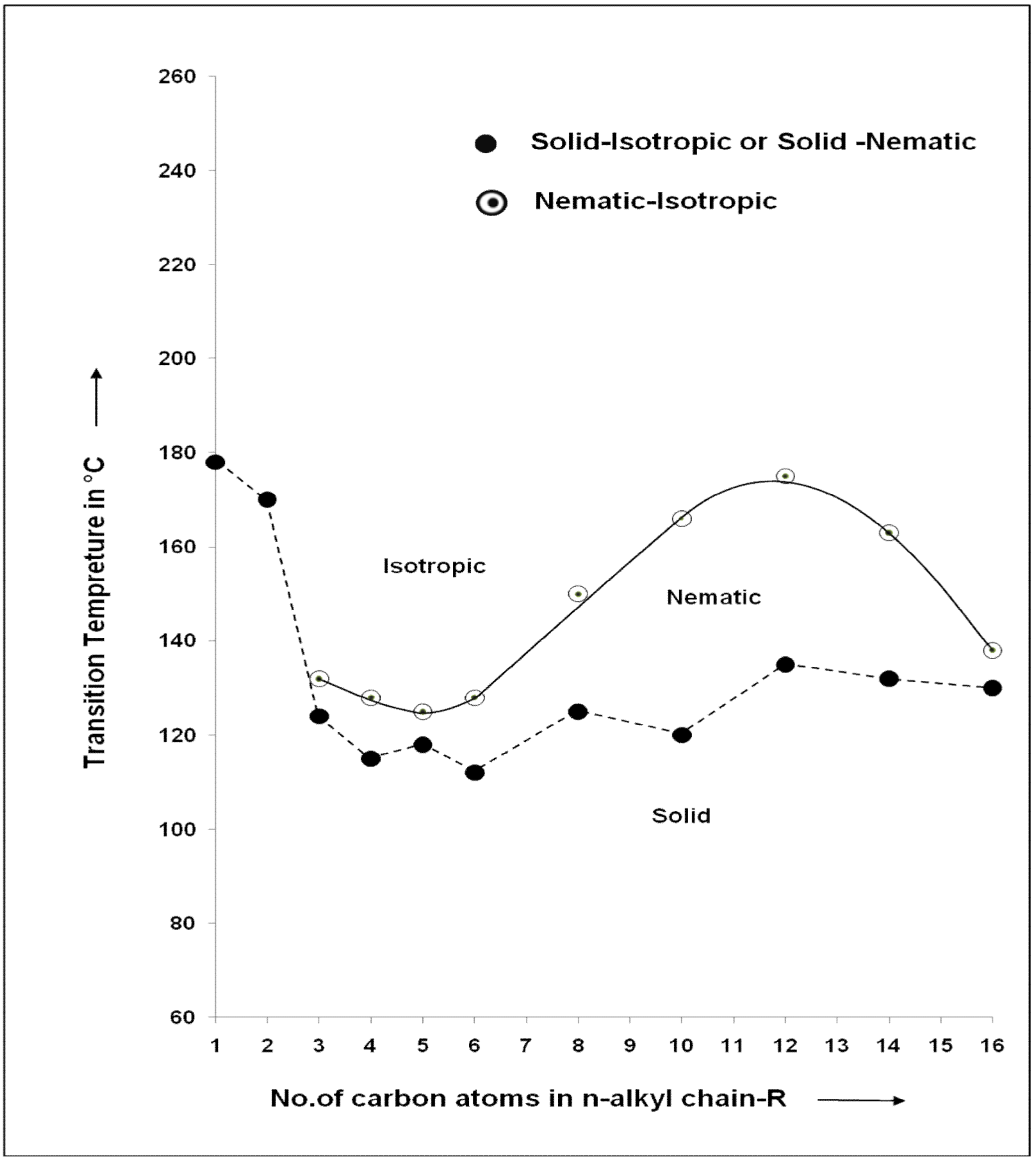
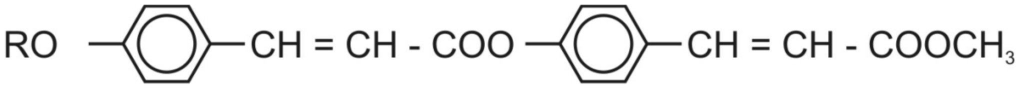


Fig- 14 , Homologous Series: Cis Methyl p- (p'- n-alkoxy cinnamoyloxy) cinnamate

Analytical data :



Cis Methyl–p-(p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

Table- 3 : Elemental Analysis:

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{20}H_{18}O_5$	71.10	5.33	71.18	5.38
2.	Ethyl	$C_{21}H_{20}O_5$	71.59	5.68	71.66	5.79
3.	Proxyl	$C_{22}H_{22}O_5$	72.13	6.01	72.25	6.09
4.	Butyl	$C_{23}H_{24}O_5$	72.63	6.32	72.67	6.25
5.	Pentyl	$C_{24}H_{26}O_5$	73.10	6.60	73.11	6.65
6.	Hexyl	$C_{25}H_{28}O_5$	73.53	6.86	73.45	6.98
7.	Octyl	$C_{27}H_{32}O_5$	74.31	7.34	74.38	7.67
8.	Decyl	$C_{29}H_{36}O_5$	75.00	7.76	75.21	7.86
9.	Dodecyl	$C_{31}H_{40}O_5$	75.61	8.13	75.50	8.35
10.	Tetradecyl	$C_{33}H_{44}O_5$	76.15	8.46	75.96	8.58
11.	Hexadecyl	$C_{35}H_{48}O_5$	76.64	8.76	76.75	8.68

NMR: in ppm

Propyl

1.84 → Confirms – CH_2-CH_2-CH_3

3.806 → Confirms – O-CH_3

4.00 → Confirms -O-CH2 of O-CH_2-CH_2-CH_3

4.44 & 4.02 → Confirms- CH=CH-

6.43 & 6.94, 6.97 & 7.20 →Confirms two p-sub. phenyl ring

7.23 & 7.55, 8.09 & 8.12 – →Confirms- two p-sub.phenyl ring

NMR confirms the structure.

Octyl

1.81 →Confirms -O-CH_2-CH_2-$(CH_2)_5$-CH_3

3.8 →Confirms- O-CH_3

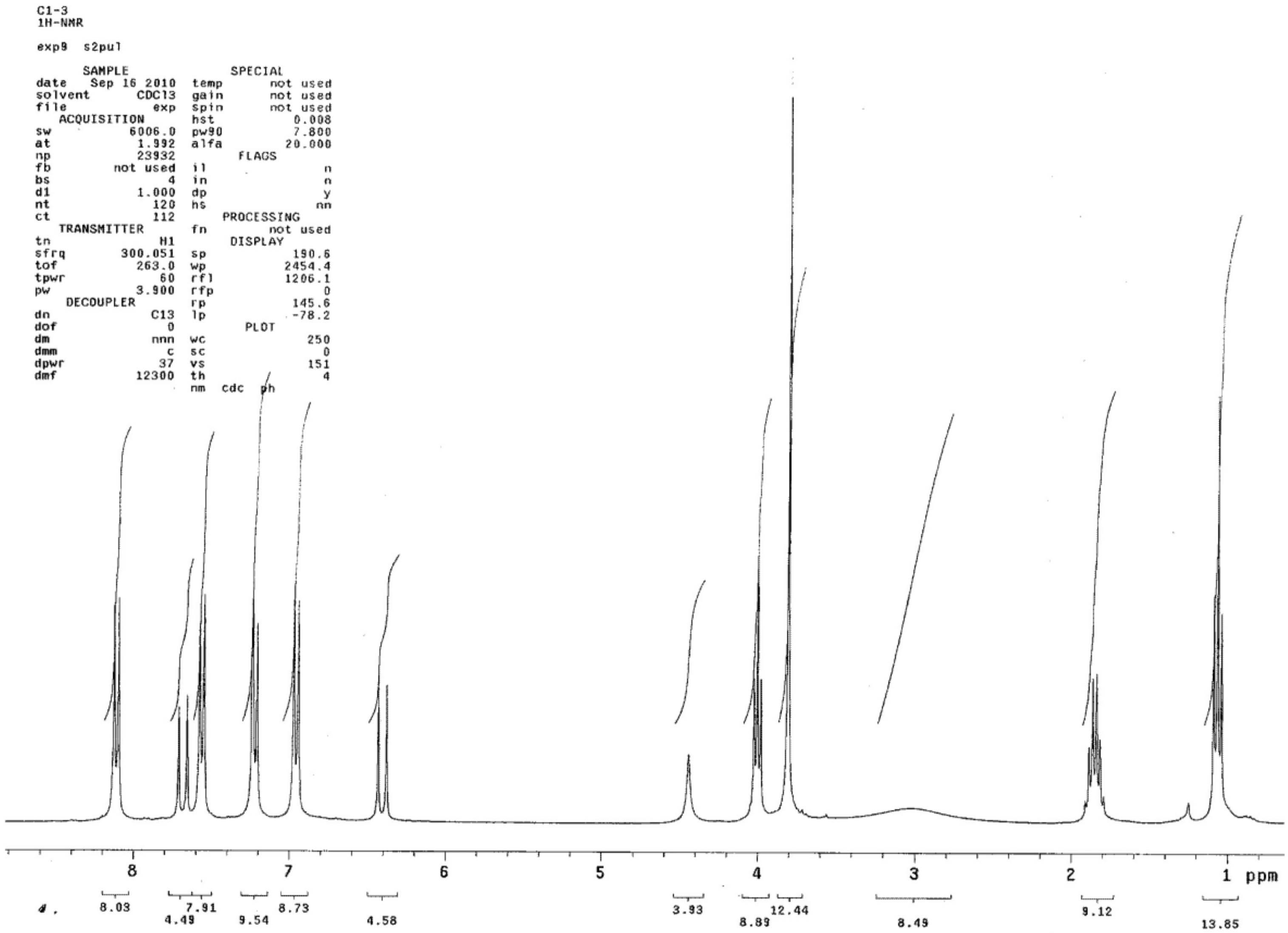
4.034 →Confirms- O-CH_2 of (O-CH_2-$(CH_2)_6$-CH_3)

4.41 →Confirms -CH=CH-

6.38 & 6.43, 7.23 & 7.24 →Confirms -two p-sub.phenyl ring

7.55 & 7.58, 8.09 & 8.12 →Confirms -two p-sub.phenyl ring

NMR confirms the structue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C1-3
1H-NMR

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file            exp  spin        not used
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at            1.992  alfa          20.000
np            23932          FLAGS
fb         not used  il                 n
bs                4  in                 n
d1            1.000  dp                 y
nt              120  hs                nn
ct              112        PROCESSING
   TRANSMITTER       fn          not used
tn               H1          DISPLAY
sfrq        300.051  sp             190.6
tof           263.0  wp            2454.4
tpwr             60  rfl           1206.1
pw            3.900  rfp                0
     DECOUPLER       rp             145.6
dn              C13  lp             -78.2
dof               0            PLOT
dm              nnn  wc               250
dmm               c  sc                 0
dpwr             37  vs               151
dmf           12300  th                 4
                     nm   cdc   ph
```

IR: in cm^{-1}

Pentyl

720.0 → Confirms Poly –CH_2 of pentyl

1050.0 →Confirms –CO- group of ester

820.0 →Confirms p-sub. Phenyl ring

1250. 0 →Confirms >C=O bend

698.2 →Confirms cis –CH=CH- group

1750.0 →Confirm of > C=O of ester

3000.0 →Confirms > C-H of aromatic

I R confirms the structure.

Tetradecyl

1050.0 →Confirms >C-O of estergroup

650.0 →Confirms cis –CH=CH- group

1250.0 →Confirms >C=O of ester group

840.0 →Confirms p-sub. Phenyl ring

750.0 →Confirms poly –CH2- of tetradecyl

1750.0 →Confirms > C=O of ester group

1250 →Confirms > C=O of ester group

3000.0 →Confirms =C-H of aromatic group

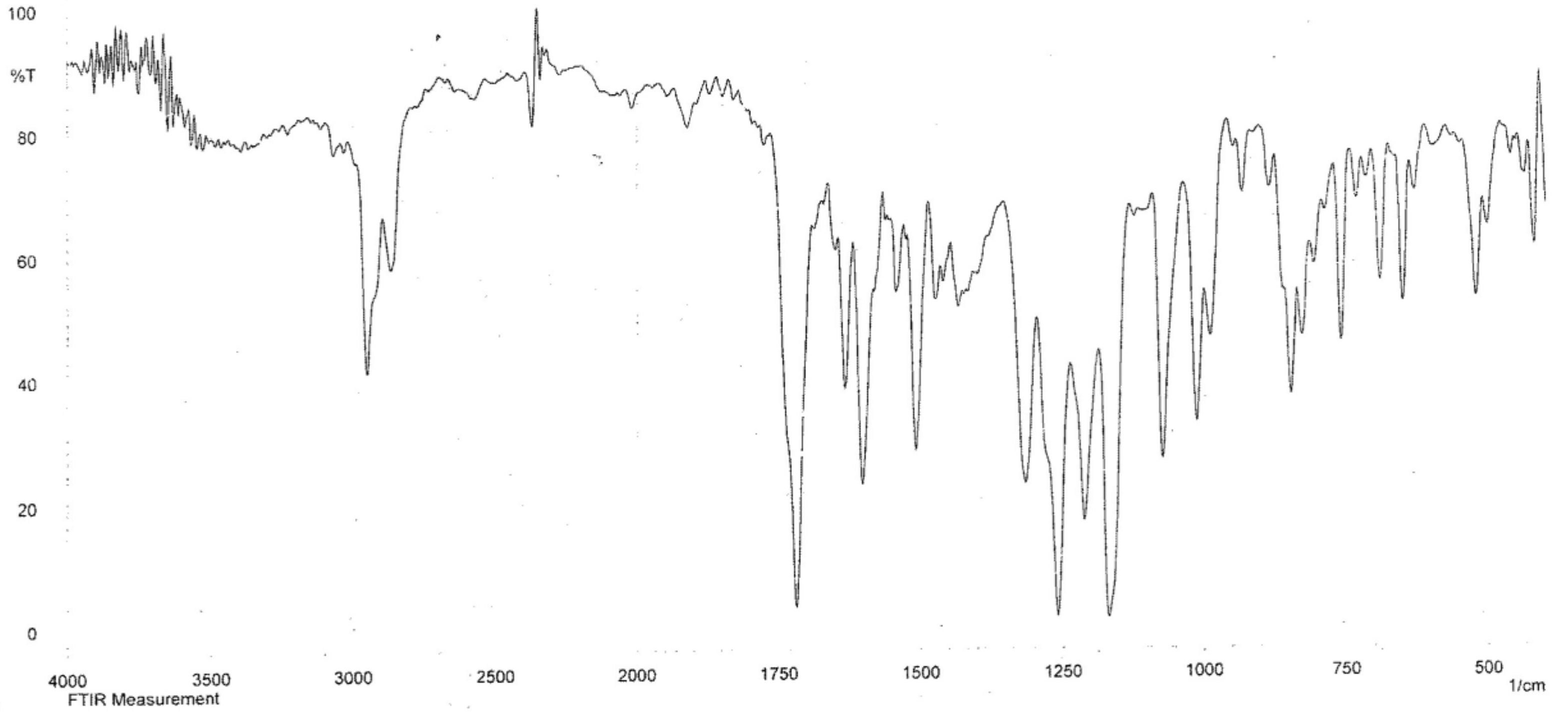
I R confirms the structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

SAMPLE NAME : C-1 , 15

DATE : 01/09/2010



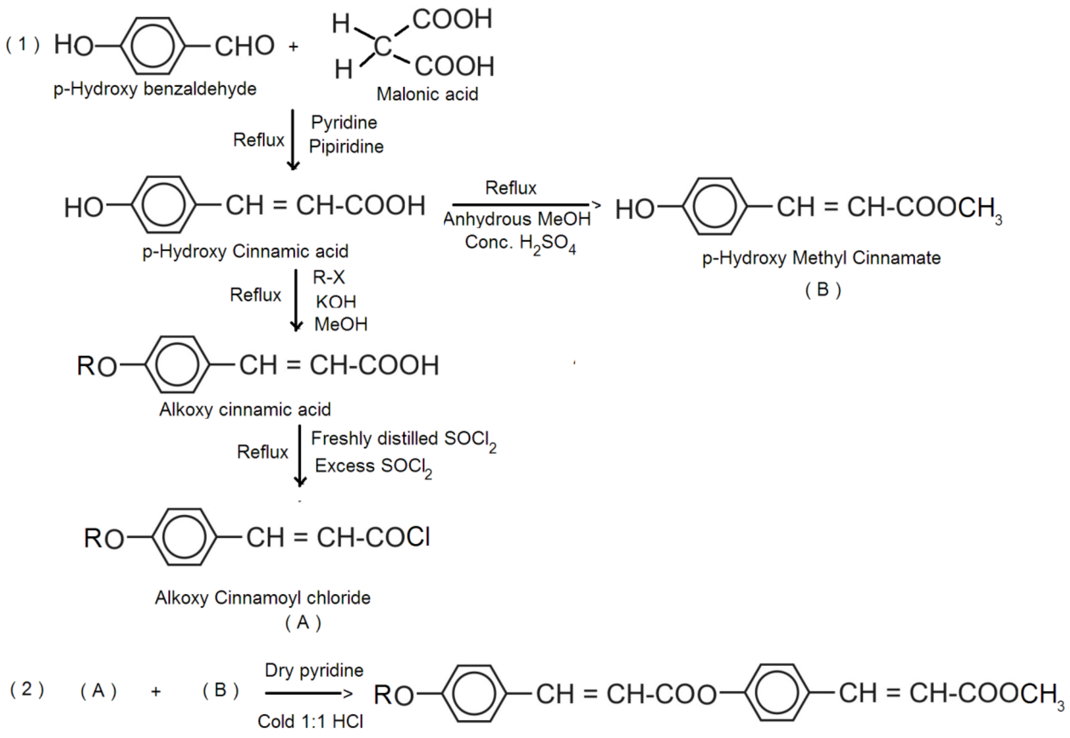
NO OF SCANS-16

RESOLUTION-4

ANALYST : J.R.

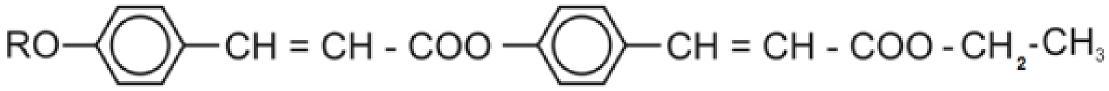
VAIBHAV ANALYTICAL SERVICES

Scheme of Synthesis:



Where R= $C_n H_{2n+1}$, n= 1 to 8, 10, 12, 14 and 16

Synthetic rout to series -1



Cis Ethyl-p-[p$^{/}$-n-alkoxy cinnamoyloxy] cinnamates**.**

Table-4: Transition temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	202.0
2	Ethyl	-	-	195.0
3	Propyl	-	-	164.0
4	Butyl	-	-	154.0
5	Pentyl	-	-	156.0
6	Hexyl	-	149.0	159.0
7	Heptyl	-	135.0	152.0
8	Octyl	-	129.0	147.0
9	Decyl	-	127.0	139.0
10	Dodecyl	-	125.0	144.0
11	Tetradecyl	-	130.0	152.0
12	Hexadecyl	-	130.0	164.0

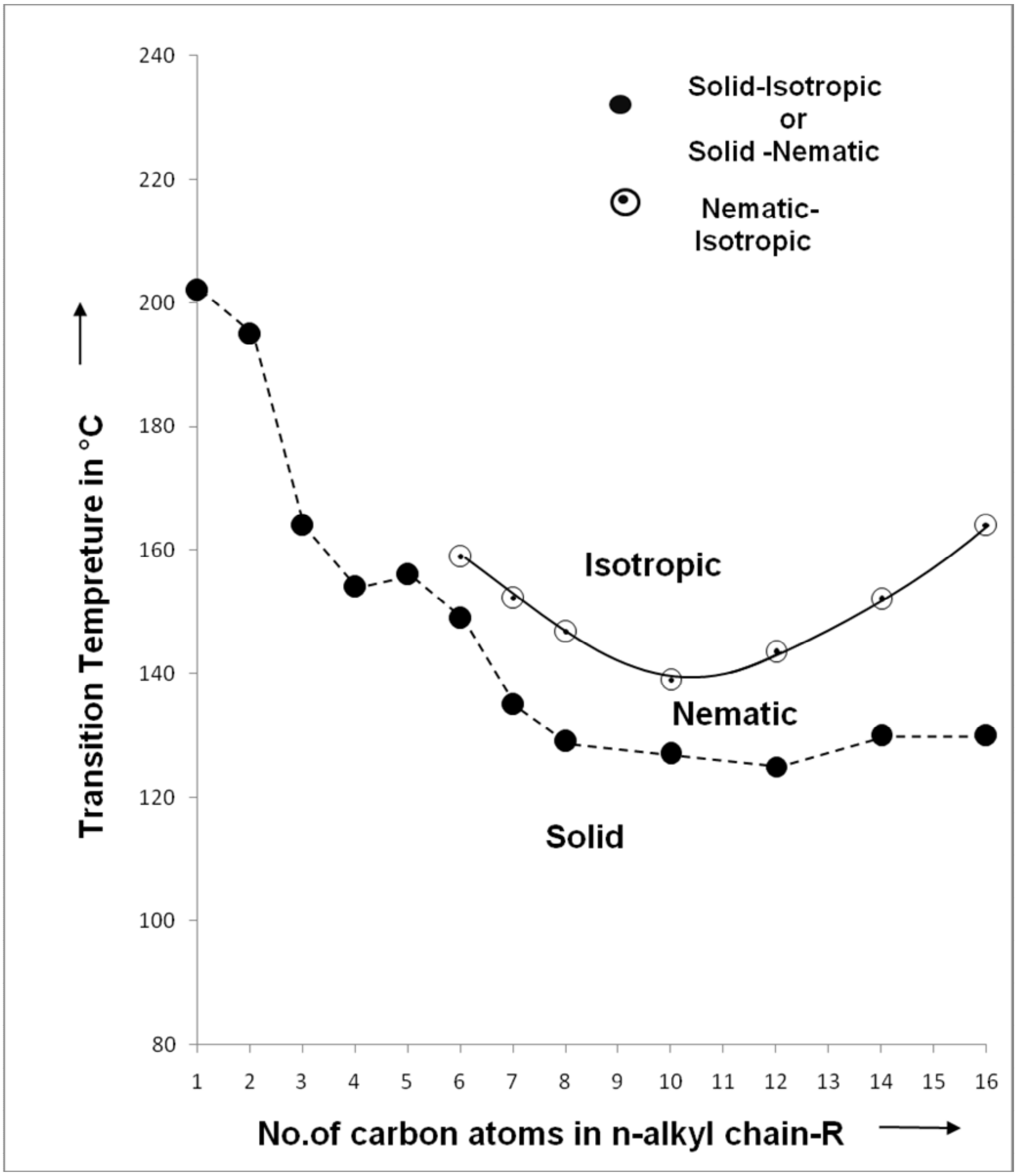
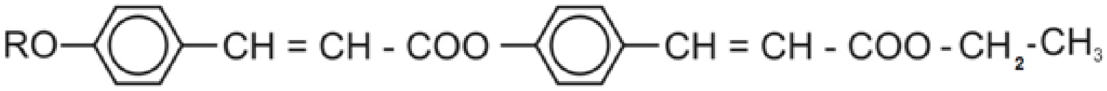


Figure-15 :Homologous series:Cis Ethyl- p-[-p$^{/}$-n-alkoxy cinnamoyloxy] cinnamates.

Analytical data :



Cis Ethyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

Table- 5: Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{21}H_{20}O_5$	71.59	5.68	71.49	5.58
2.	Ethyl	$C_{22}H_{22}O_5$	72.13	6.01	72.13	6.01
3.	Proxyl	$C_{23}H_{24}O_5$	72.63	6.32	72.53	6.22
4.	Butyl	$C_{24}H_{26}O_5$	73.1	6.60	73.1	6.60
5.	Pentyl	$C_{25}H_{28}O_5$	73.53	6.86	73.43	6.76
6.	Hexyl	$C_{26}H_{30}O_5$	73.93	7.11	74.03	7.11
7.	Heptyl	$C_{27}H_{32}O_5$	74.31	7.34	74.21	7.24
8.	Octyl	$C_{28}H_{34}O_5$	74.67	7.56	74.67	7.56
9.	Decyl	$C_{30}H_{38}O_5$	75.31	7.95	75.21	7.85
10.	Dodecyl	$C_{32}H_{42}O_5$	75.99	8.30	75.99	8.30
11.	Tetradecyl	$C_{34}H_{46}O_5$	76.40	8.61	76.41	8.51
12.	Hexadecyl	$C_{36}H_{50}O_5$	76.87	8.90	76.67	9.0

NMR: in ppm :

Hexyl

0.840 → Confirms $-CH_3$

2.490 → Confirms- $O-CH_2$ 4.20 – $O-CH_2$ of $-COOC_2H_5$

3.98→ Confirms $-O-CH_2$ of $-C_6H_{13}$

4.4 and 4.0 → Confirms – CH=CH-

6.80, 6.83, 7.74 and 7.78→ Confirms two p-sub.phenyl ring

7.24and 8.02 → Confirms two p-sub.phenyl ring

NMR confirms the structure.

Hexadecyl

0.88 → Confirms $-CH_3$

1.55 → Confirms $-CH_2$

2.40-→ Confirms $-OCH_2-CH_2-$

4.00→ Confirms- $O-CH_2$ of$-COOC_2H_5$

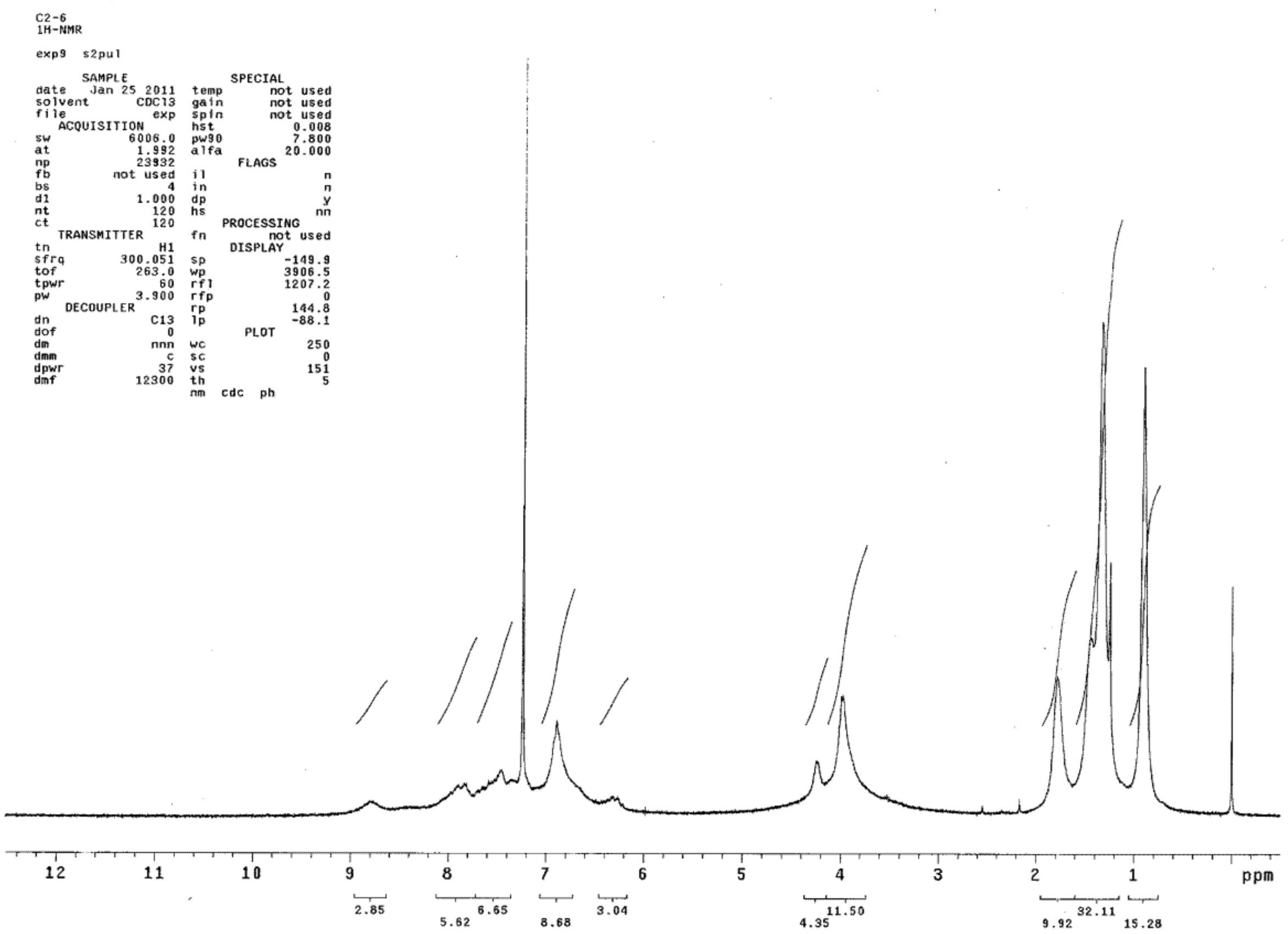
3.31→ Confirms $-O-CH_2$ of $C_{16}H_{33}$

4.48→ Confirms – CH=CH-

6.896 and 6.925, → Confirms two p-sub.phenyl ring

8.039 and 8.011, → Confirms two p-sub.phenyl ring

NMR confirms the structure.



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C2-6
1H-NMR

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at            1.992  alfa          20.000
np            23932          FLAGS
fb         not used  il                 n
bs                4  in                 n
d1            1.000  dp                 y
nt              120  hs                nn
ct              120       PROCESSING
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tof           263.0  wp            3906.5
tpwr             60  rfl           1207.2
pw            3.900  rfp                0
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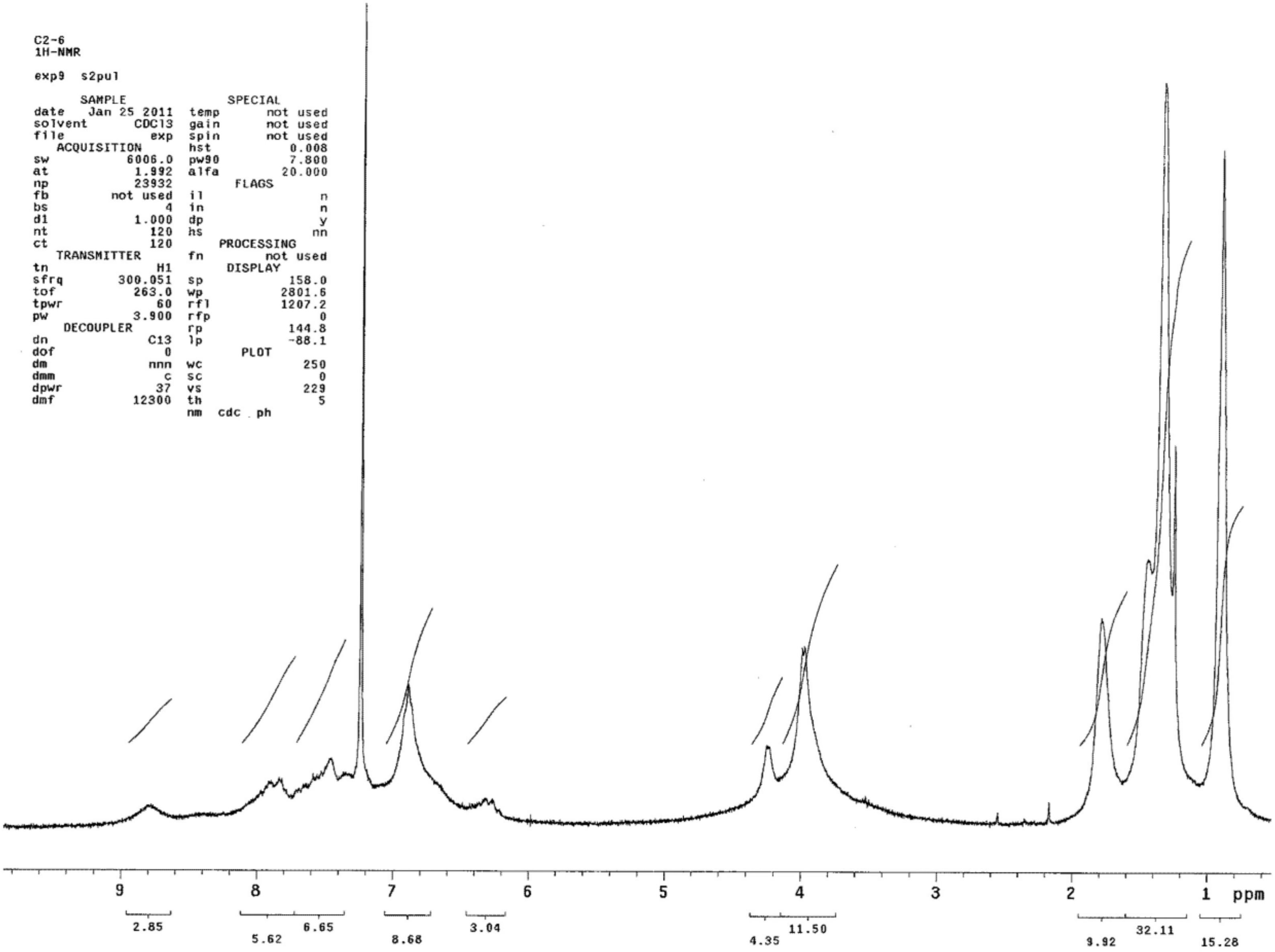

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C2-6
1H-NMR

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at           1.992  alfa        20.000
np           23932          FLAGS
fb        not used  il               n
bs               4  in               n
d1           1.000  dp               y
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ct             120        PROCESSING
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pw           3.900  rfp              0
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dn             C13  lp           -88.1
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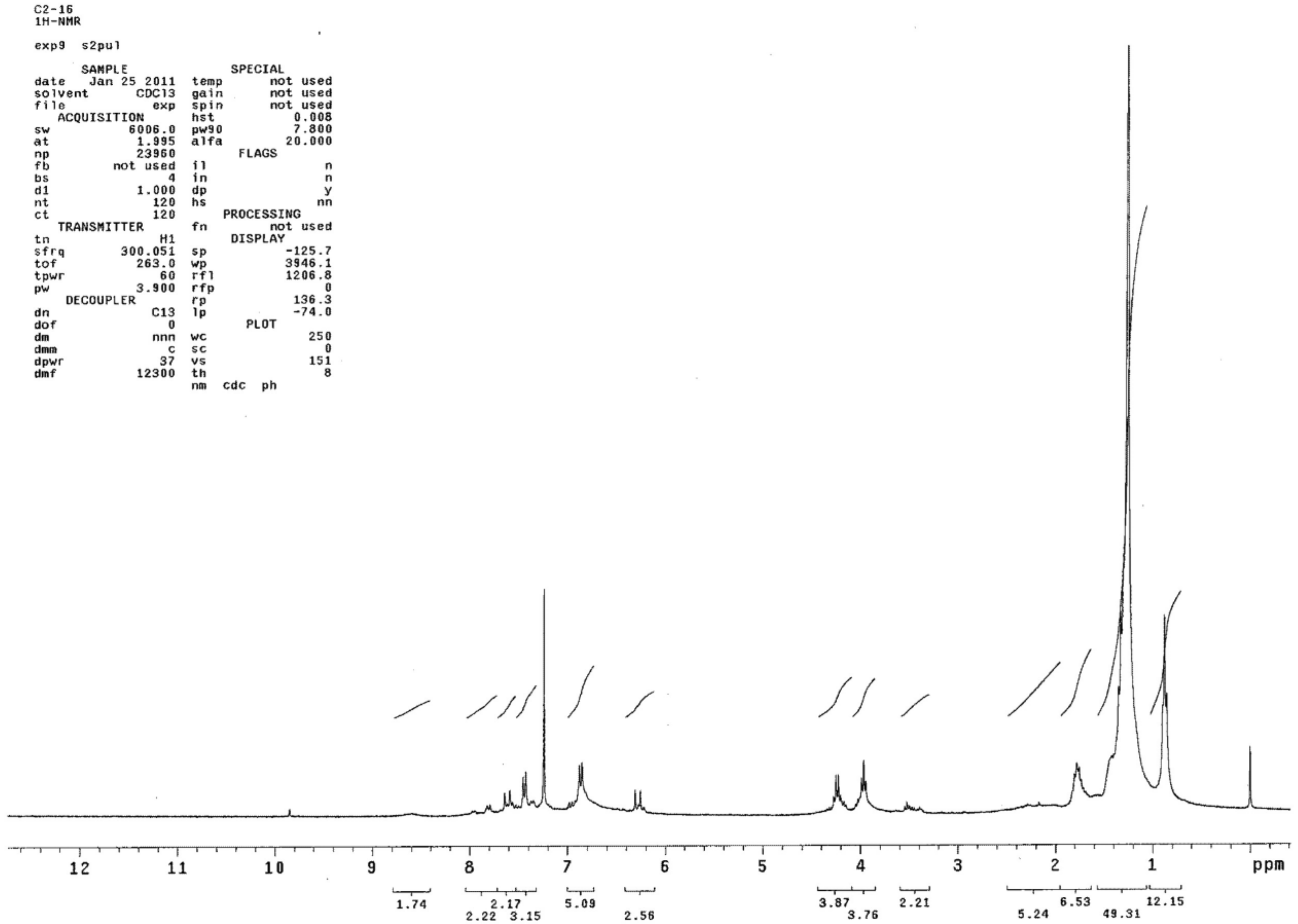

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1H-NMR

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np           23960         FLAGS
fb        not used  il                n
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d1           1.000  dp                y
nt             120  hs               nn
ct             120       PROCESSING
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pw           3.900  rfp               0
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                    nm   cdc   ph
```
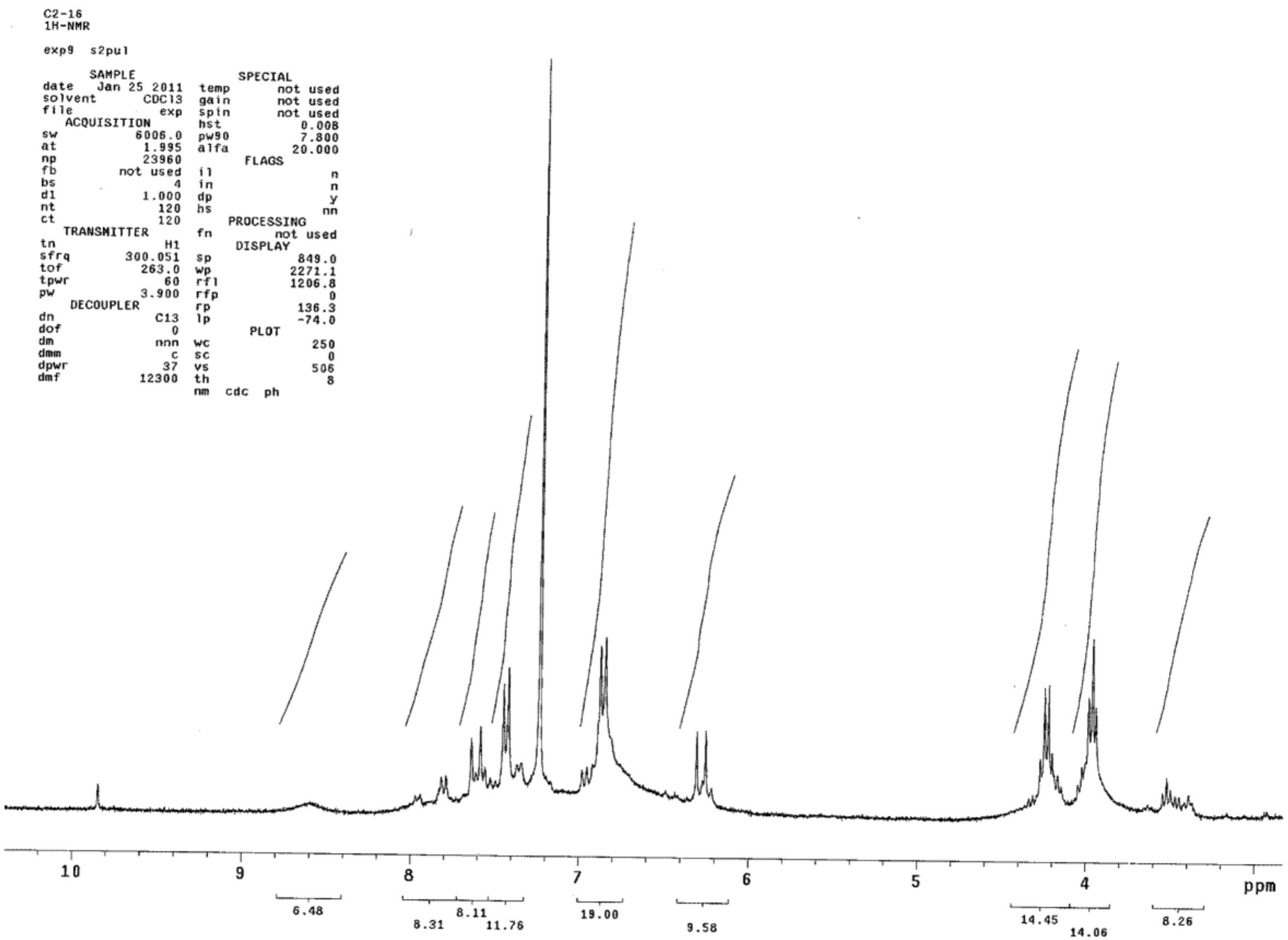



```
C2-16
1H-NMR

exp9  s2pul

      SAMPLE                 SPECIAL
date    Jan 25 2011  temp       not used
solvent       CDC13  gain       not used
file            exp  spin       not used
    ACQUISITION      hst           0.008
sw           6006.0  pw90          7.800
at            1.995  alfa         20.000
np            23960          FLAGS
fb         not used  il                n
bs                4  in                n
d1            1.000  dp                y
nt              120  hs               nn
ct              120       PROCESSING
   TRANSMITTER       fn         not used
tn               H1         DISPLAY
sfrq        300.051  sp            849.0
tof           263.0  wp           2271.1
tpwr             60  rfl          1206.8
pw            3.900  rfp               0
    DECOUPLER        rp            136.3
dn              C13  lp            -74.0
dof               0           PLOT
dm              nnn  wc              250
dmm               c  sc                0
dpwr             37  vs              506
dmf           12300  th                8
                     nm   cdc   ph
```

IR in cm^{-1}

Tetradecyl

2850.0→ Confirms alkyl group

1040, 1160, & 1720→ Confirms –COO- group

660 →Confirms cis –CH=CH- group

840→ Confirms p-sub. phenyl ring

2960 →Confirms aromatic ring

750 →Confirms polymethylene of $C_{14}H_{29}$

IR confirms above structure

Butyl

2850.0 →Confirms alkyl group

1040,1160, & 1700 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

840→ Confirms p-sub. phenyl ring

2960 →Confirms aromatic ring

750 →Confirms polymethylene of C_4H_9

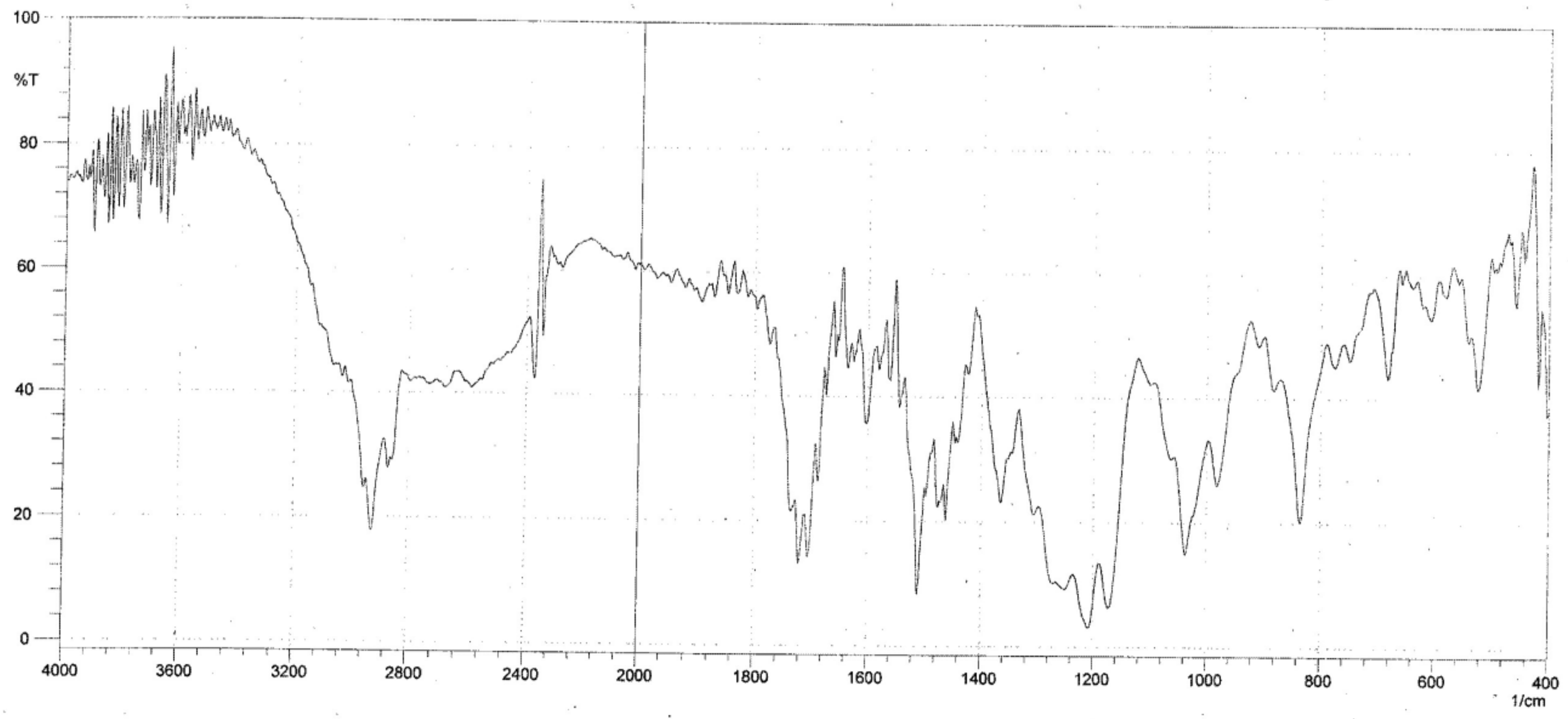
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

SAMPLE NAME : C2- 4

DATE : 10/01/2011



No. of Scans; 16

ANALYST : K.J.

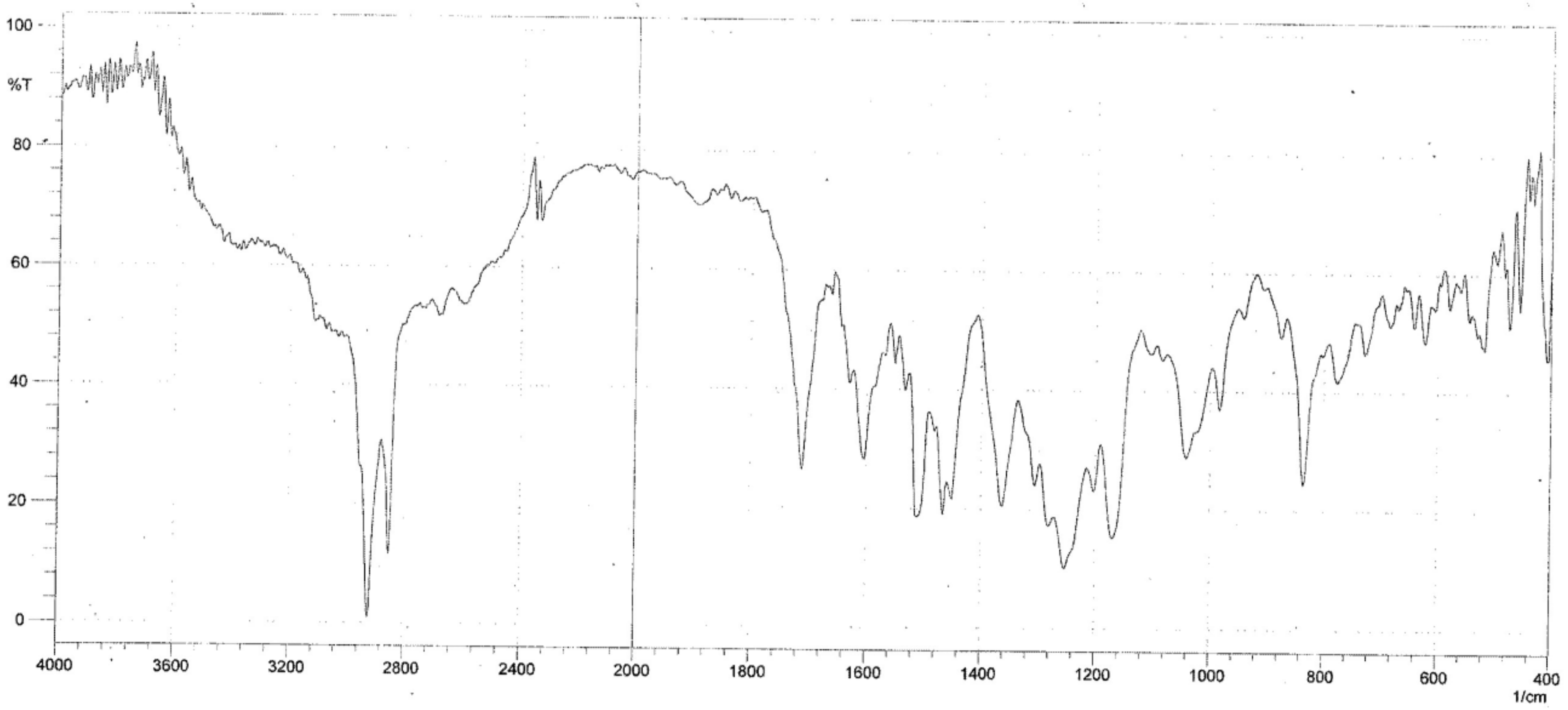
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

SAMPLE NAME : C2- 14

DATE : 10/01/2011

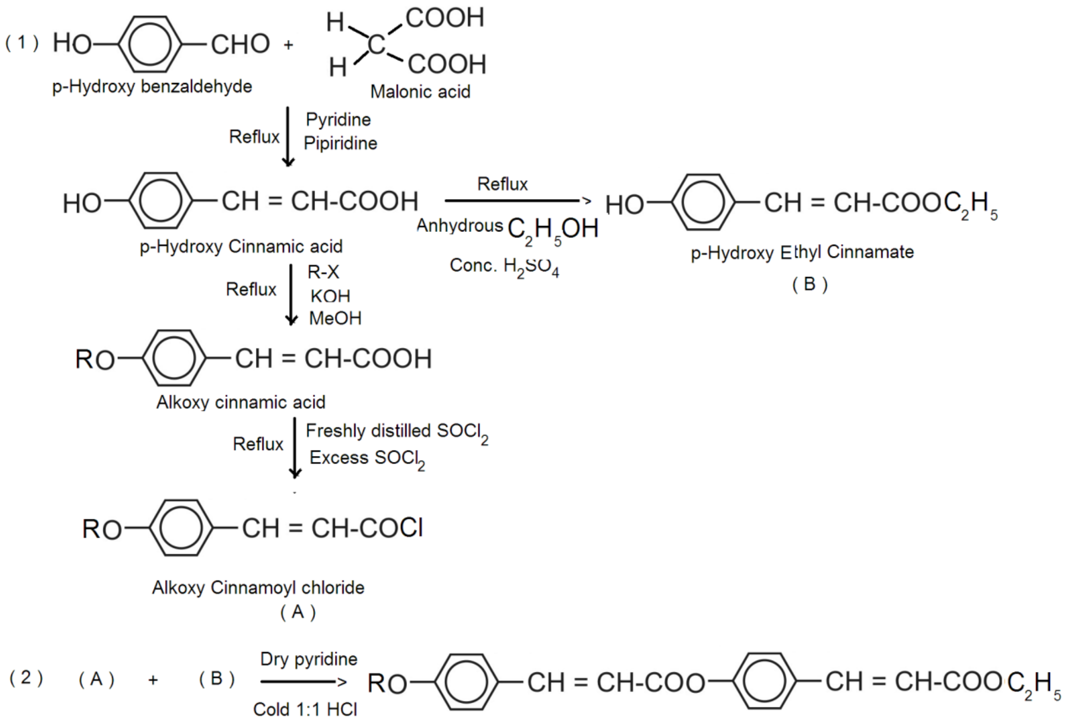


No. of Scans; 16

ANALYST : K.J.

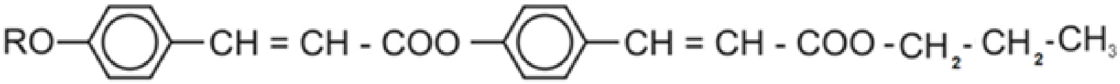
Resolution; 4

Scheme of Synthesis:



Where R= $C_n H_{2n+1}$, n= 1 to 8, 10, 12, 14 and 16

Synthetic rout to series -2



Cis n-propyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

Table-6: Transition temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	202.0
2	Ethyl	-	-	195.0
3	Propyl	-	-	164.0
4	Butyl	-	-	154.0
5	Pentyl	-	-	156.0
6	Hexyl	-	149.0	159.0
7	Heptyl	-	135.0	152.0
8	Octyl	-	129.0	147.0
9	Decyl	-	127.0	139.0
10	Dodecyl	-	125.0	144.0
11	Tetradecyl	-	130.0	152.0
12	Hexadecyl	-	130.0	164.0

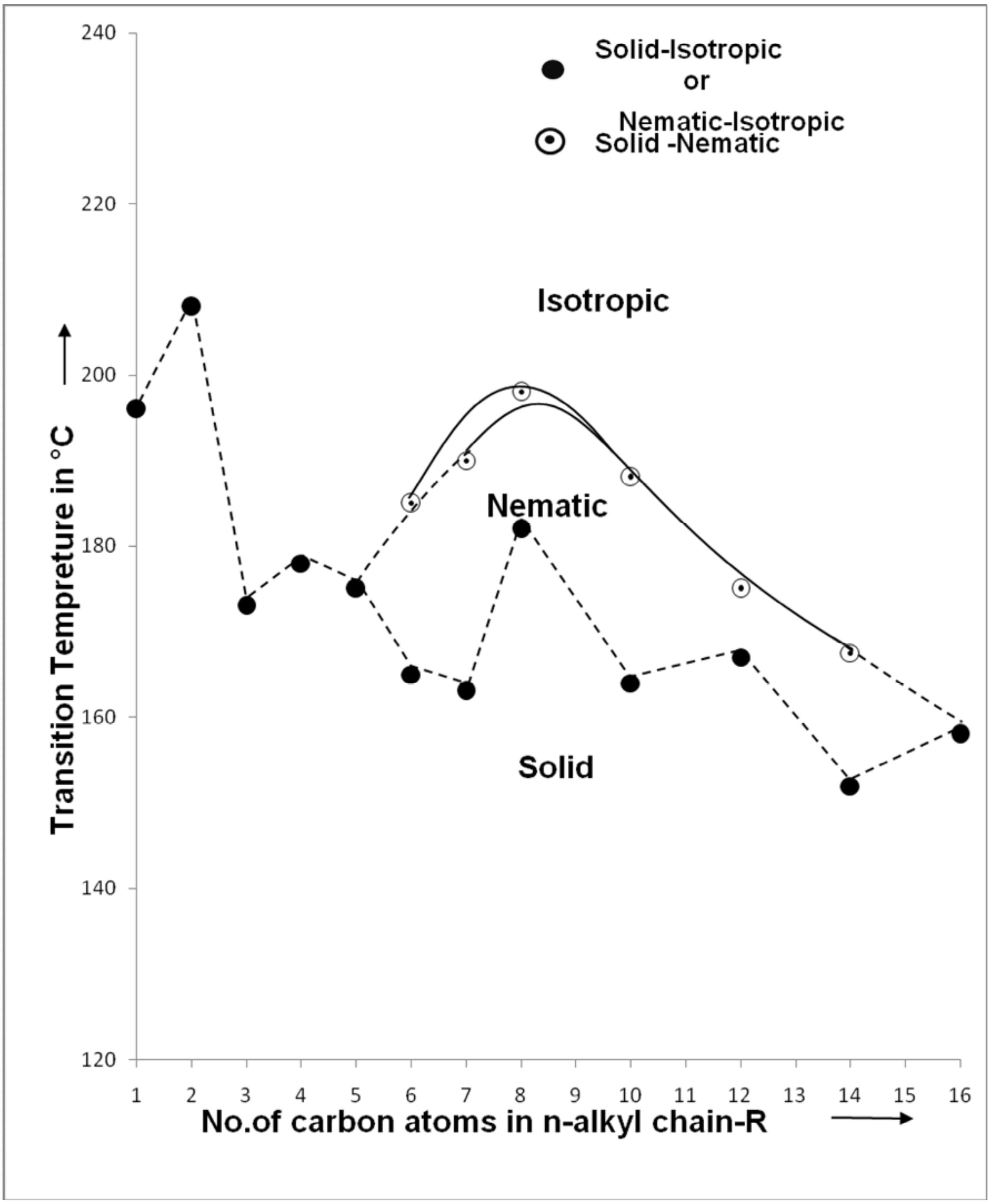
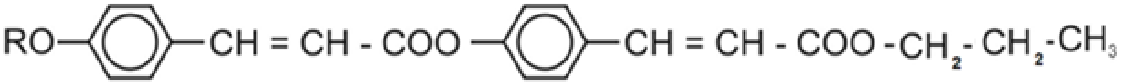


Figure-16 , Series: Cis n-propyl-p-[p′-n- alkoxy Cinnamoyloxy] Cinnamates



Cis n-propyl –p-(p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

Table-7 : Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{22}H_{22}O_5$	72.13	6.01	72.18	6.00
2.	Ethyl	$C_{23}H_{24}O_5$	73.02	6.35	73.16	6.36
3.	Proxyl	$C_{24}H_{26}O_5$	73.85	6.67	73.84	6.66
4.	Butyl	$C_{25}H_{28}O_5$	74.63	6.97	74.67	6.96
5.	Pentyl	$C_{26}H_{30}O_5$	75.16	7.25	75.12	7.24
6.	Hexyl	$C_{27}H_{32}O_5$	76.06	7.51	76.12	7.58
7.	Heptyl	$C_{28}H_{34}O_5$	76.71	7.76	76.76	7.78
8.	Octyl	$C_{29}H_{36}O_5$	77.33	8.00	77.38	7.96
9.	Decyl	$C_{31}H_{40}O_5$	78.48	8.44	78.52	8.46
10.	Dodecyl	$C_{33}H_{44}O_5$	79.52	8.84	79.50	8.84
11.	Tetradecyl	$C_{35}H_{48}O_5$	80.46	9.20	80.46	9.18
12.	Hexadecyl	$C_{37}H_{52}O_5$	81.32	9.52	81.32	9.58

NMR: in ppm :

Hexyl

0.840 → Confirms – CH_3

2.490 → Confirms – $O\text{-}CH_2$

4.20 → Confirms – $O\text{-}CH_2$ of $–COOC_3H_7$

3.98→ Confirms $-O\text{-}CH_2$ of $–C_6H_{13}$

4.4 and 4.0 → Confirms – CH=CH-

6.80, 6.83, 7.74 and 7.78 → Confirms two p-sub.phenyl ring

7.24and 8.02 → Confirms two p-sub.phenyl ring

NMR confirms the structure.

Hexadecyl

0.88 → Confirms $-CH_3$

1.55 → $-CH_2$

2.40 → Confirms $-OCH_2\text{-}CH_2\text{-}$

4.00 → Confirms – $O\text{-}CH_2$ of$–COOC_3H_7$

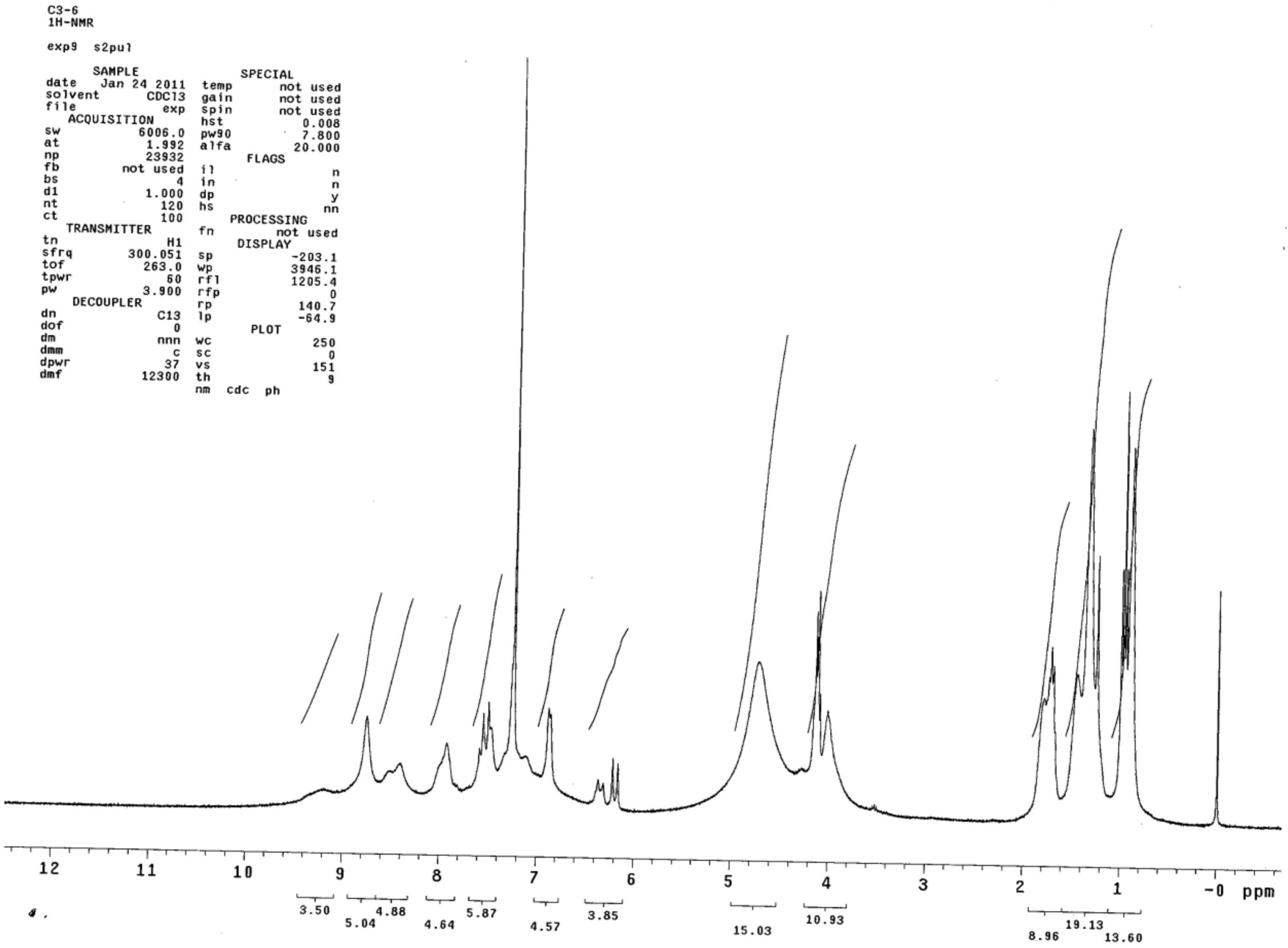
3.31 → Confirms $-O\text{-}CH_2$ of $C_{16}H_{33}$

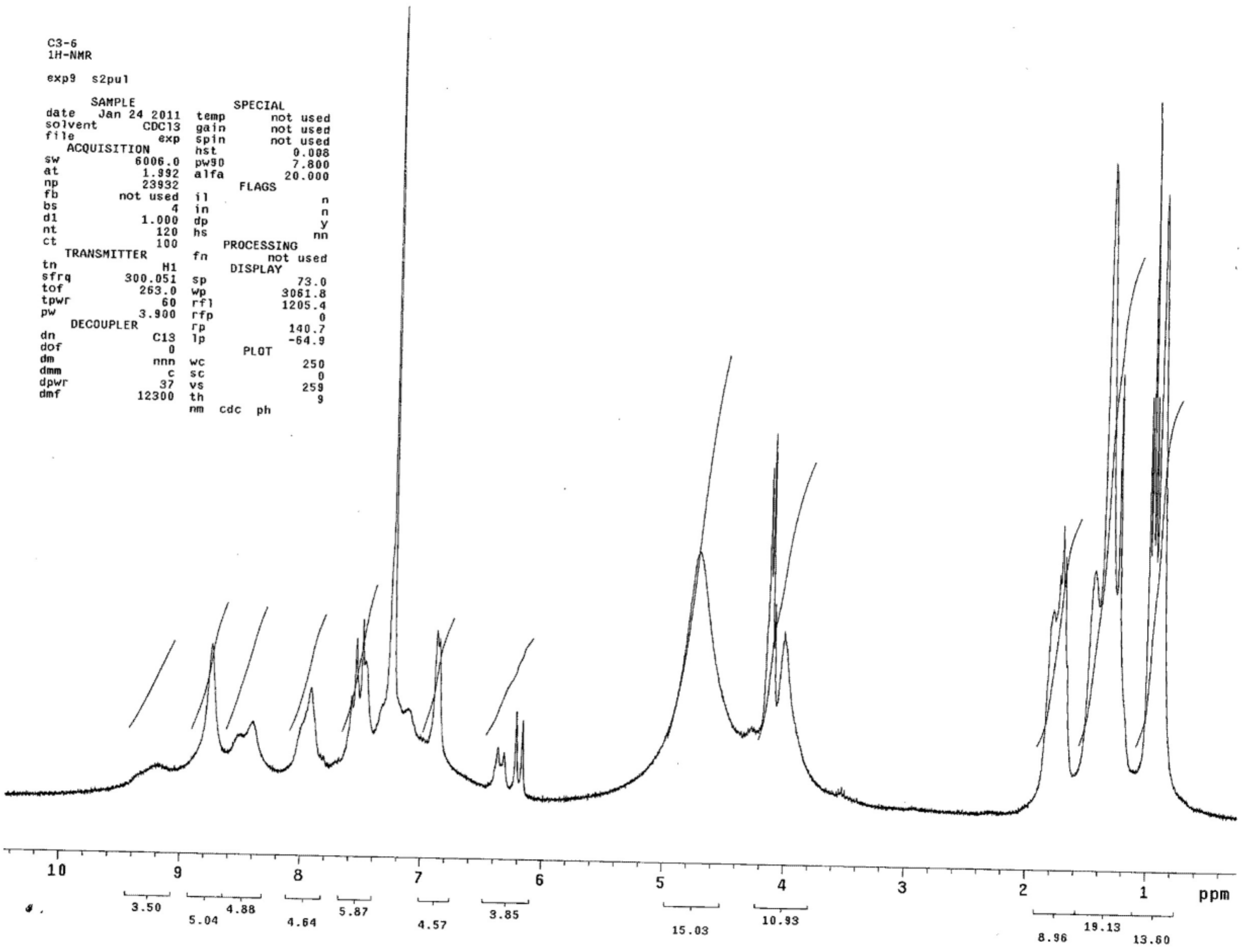
4.48 → Confirms – CH=CH-

6.896 and 6.925, → Confirms two p-sub.phenyl ring

8.039 and 8.011, → Confirms two p-sub.phenyl ring

NMR confirms the structure.





```
C3-6
1H-NMR

exp9  s2pul

      SAMPLE                  SPECIAL
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solvent      CDCl3  gain        not used
file           exp  spin        not used
   ACQUISITION      hst            0.008
sw          6006.0  pw90           7.800
at           1.992  alfa          20.000
np           23932          FLAGS
fb        not used  il                 n
bs               4  in                 n
d1           1.000  dp                 y
nt             120  hs                nn
ct             100        PROCESSING
  TRANSMITTER       fn          not used
tn              H1         DISPLAY
sfrq       300.051  sp              73.0
tof          263.0  wp            3061.8
tpwr            60  rfl           1205.4
pw           3.900  rfp                0
   DECOUPLER        rp             140.7
dn             C13  lp             -64.9
dof              0          PLOT
dm             nnn  wc               250
dmm              c  sc                 0
dpwr            37  vs               259
dmf          12300  th                 9
                    nm  cdc  ph
```
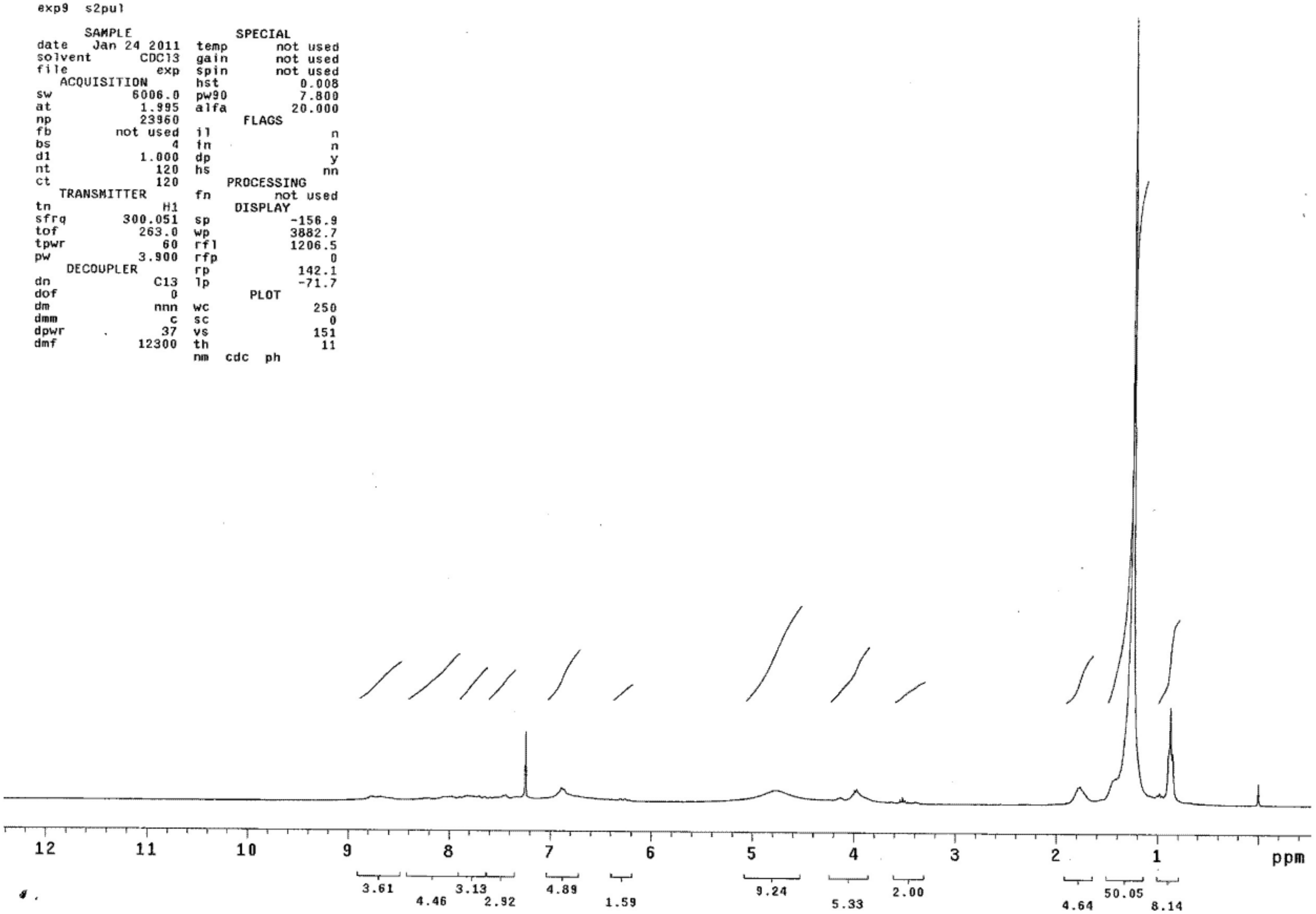
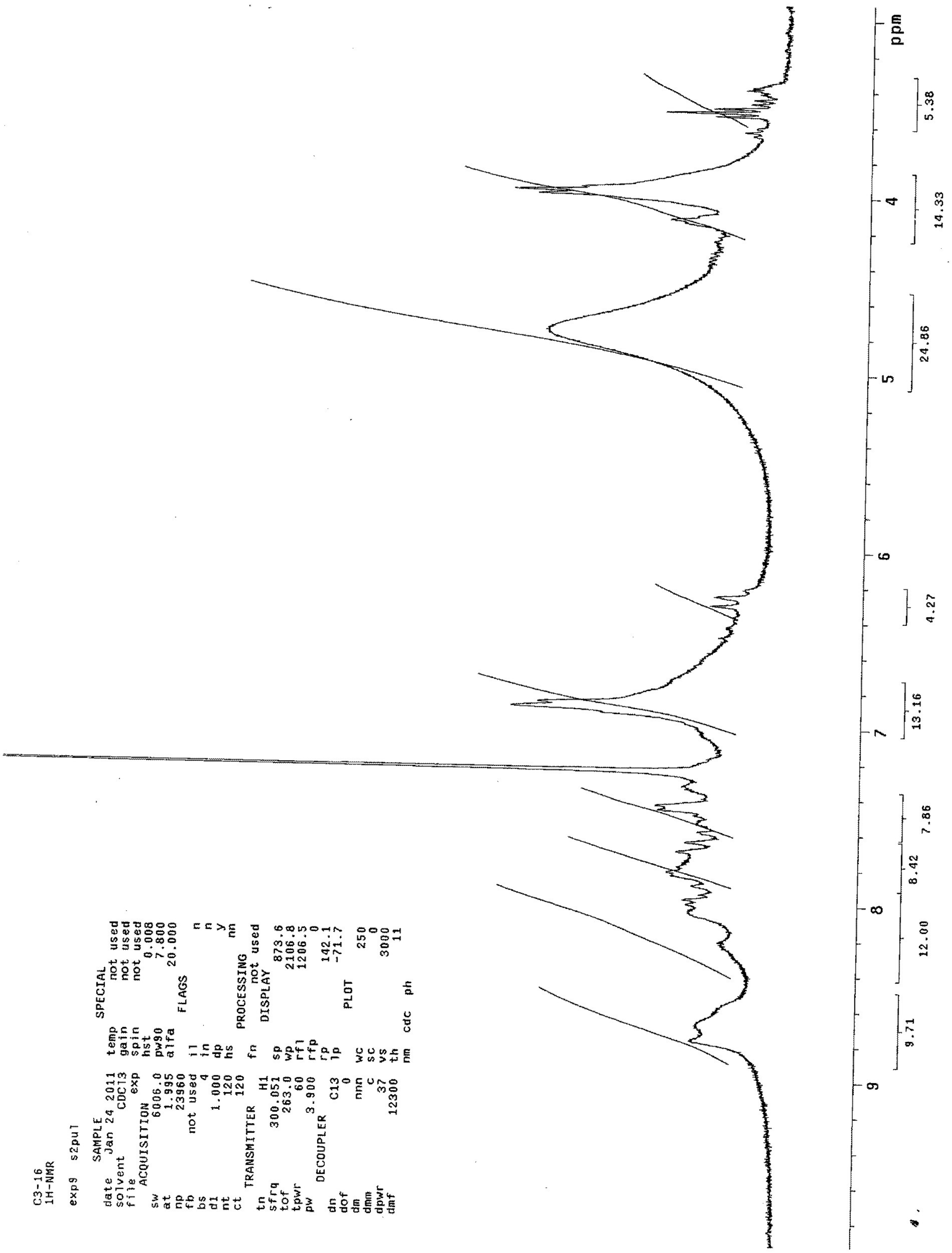
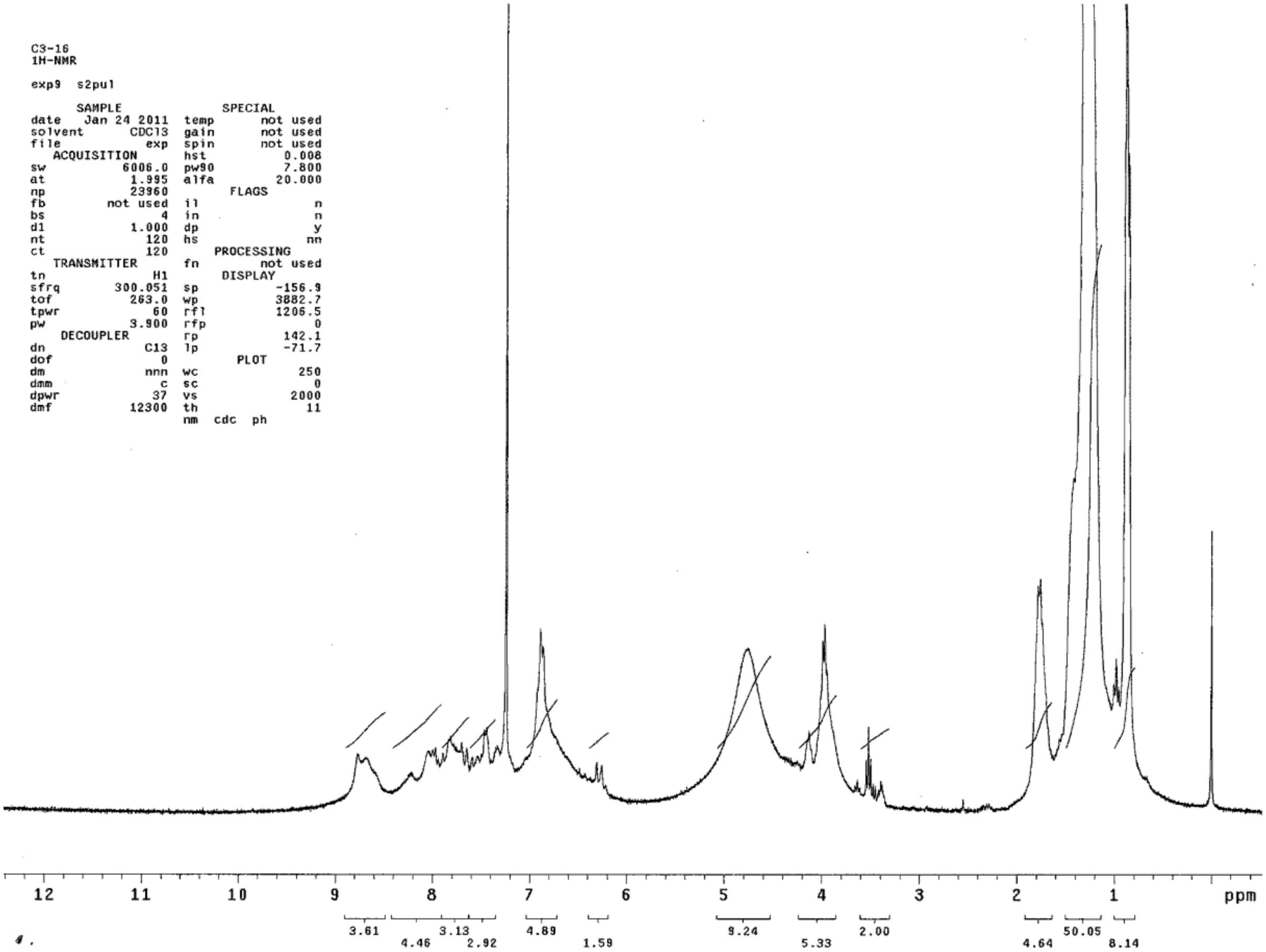

```
C3-16
1H-NMR

exp9  s2pul

      SAMPLE                 SPECIAL
date    Jan 24 2011  temp       not used
solvent       CDCl3  gain       not used
file            exp  spin       not used
    ACQUISITION      hst           0.008
sw           6006.0  pw90          7.800
at            1.995  alfa         20.000
np            23960          FLAGS
fb         not used  il                n
bs                4  in                n
d1            1.000  dp                y
nt              120  hs               nn
ct              120        PROCESSING
    TRANSMITTER      fn         not used
tn               H1          DISPLAY
sfrq        300.051  sp           -156.9
tof           263.0  wp           3882.7
tpwr             60  rfl          1206.5
pw            3.900  rfp               0
     DECOUPLER       rp            142.1
dn              C13  lp            -71.7
dof               0           PLOT
dm              nnn  wc              250
dmm               c  sc                0
dpwr             37  vs              151
dmf           12300  th               11
                     nm  cdc  ph
```




C3-16
1H-NMR
exp9 s2pul
SAMPLE
date Jan 24 2011
solvent CDCl3
file exp
ACQUISITION
sw 6006.0
at 1.995
np 23960
fb not used
bs 4
d1 1.000
nt 120
ct 120
TRANSMITTER
tn H1
sfrq 300.051
tof 263.0
tpwr 60
pw 3.900
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 37
dmf 12300
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 7.800
alfa 20.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 873.6
wp 2106.8
rfl 1206.5
rfp 0
rp 142.1
lp -71.7
PLOT
wc 250
sc 0
vs 3000
th 11
nm cdc ph
9
8
7
6
5
4
ppm
9.71
12.00
8.42
7.86
13.16
4.27
24.86
14.33
5.38



```
C3-16
1H-NMR

exp9  s2pul

     SAMPLE               SPECIAL
date   Jan 24 2011  temp      not used
solvent      CDCl3  gain      not used
file           exp  spin      not used
   ACQUISITION      hst          0.008
sw          6006.0  pw90         7.800
at           1.995  alfa        20.000
np           23960         FLAGS
fb        not used  il               n
bs               4  in               n
d1           1.000  dp               y
nt             120  hs              nn
ct             120       PROCESSING
   TRANSMITTER      fn        not used
tn              H1        DISPLAY
sfrq       300.051  sp          -156.9
tof          263.0  wp          3882.7
tpwr            60  rfl         1206.5
pw           3.900  rfp              0
   DECOUPLER        rp           142.1
dn             C13  lp           -71.7
dof              0          PLOT
dm             nnn  wc             250
dmm              c  sc               0
dpwr            37  vs            2000
dmf          12300  th              11
                    nm  cdc  ph
```

IR in cm^{-1}

Tetradecyl

2900.0→ Confirms alkyl group

1080, 1260, & 1700 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

860 →Confirms p-sub. phenyl ring

3000→ Confirms aromatic ring

750 →Confirms polymethylene of $C_{14}H_{29}$

IR confirms above structure

Butyl

2850.0 →Confirms alkyl group

1050,1150, & 1710 →Confirms –COO- group

660→ Confirms cis –CH=CH- group

850 →Confirms p-sub. phenyl ring

2900 →Confirms aromatic ring

750 →Confirms polymethylene of C_4H_9

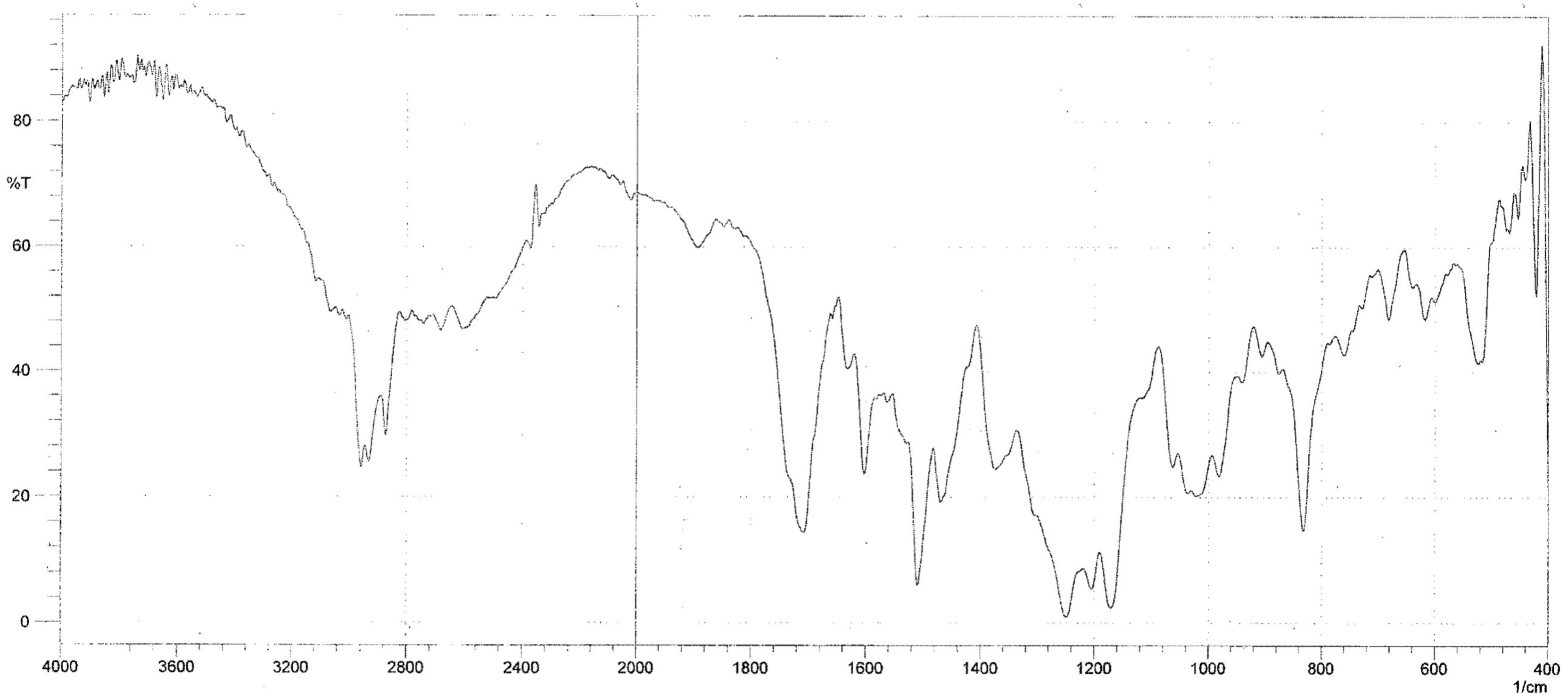
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 10/01/2011

SAMPLE NAME : C3-4



No. of Scans; 16

ANALYST : K.J.

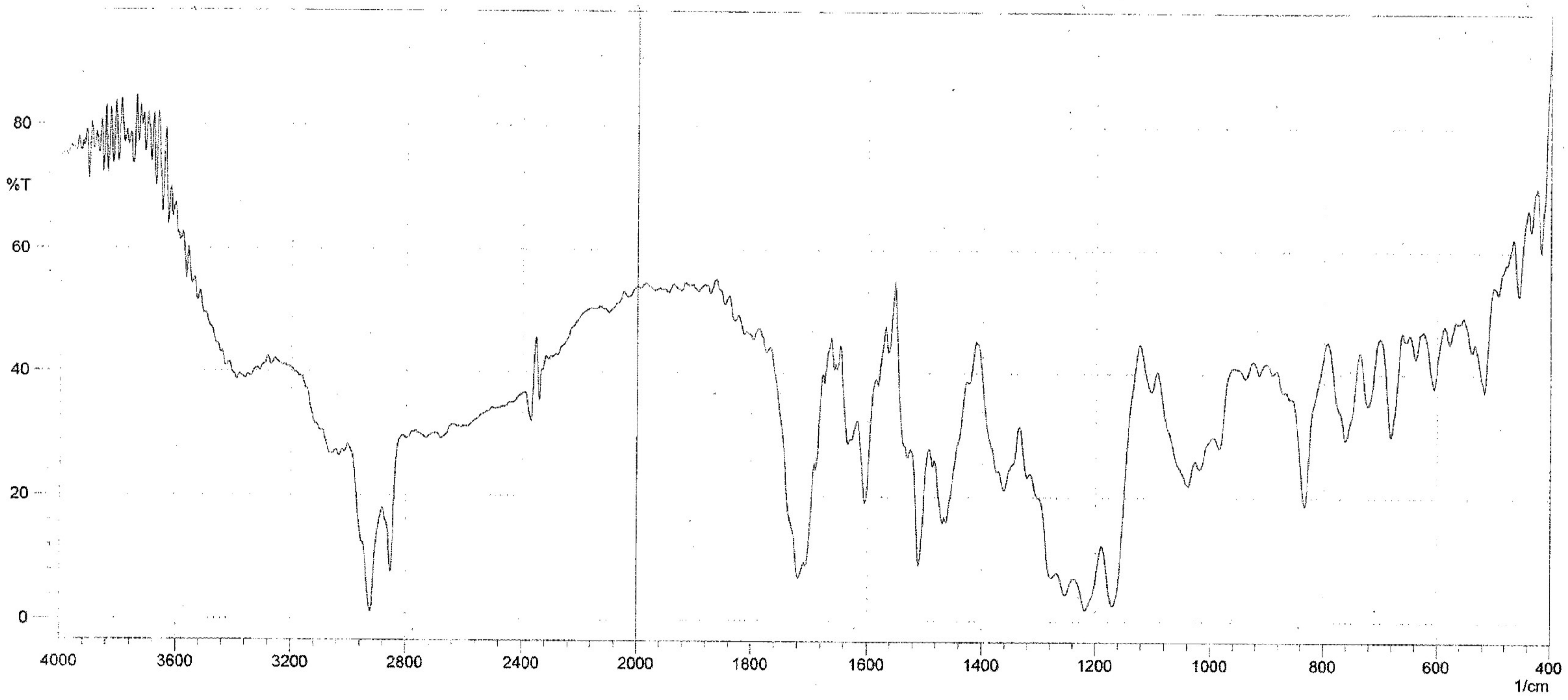
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

SAMPLE NAME : C3-14

DATE : 10/01/2011

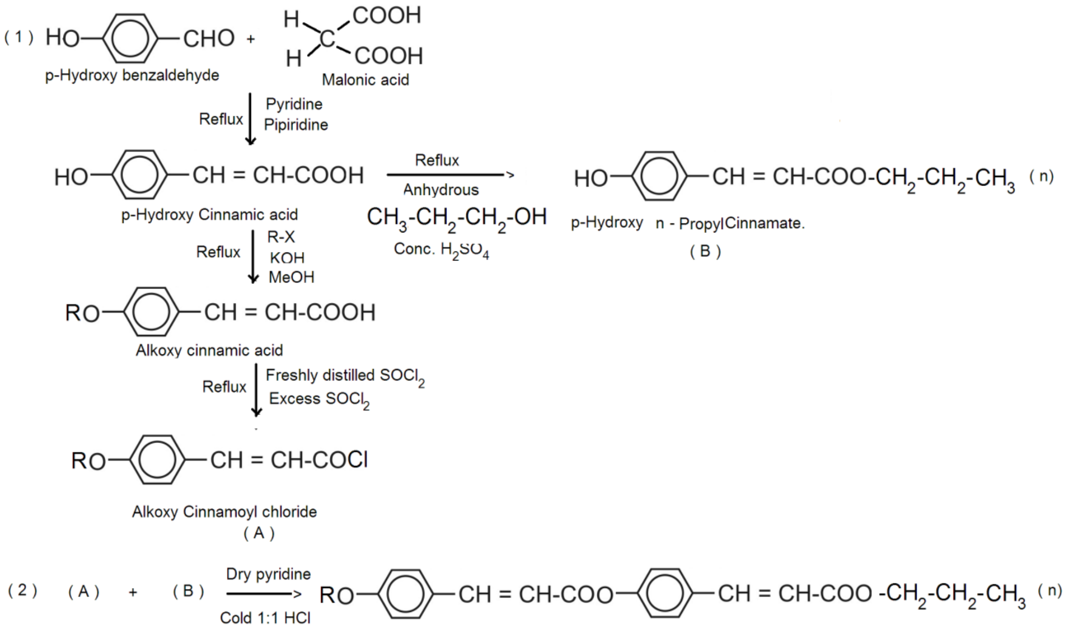


No. of Scans; 16

Resolution; 4

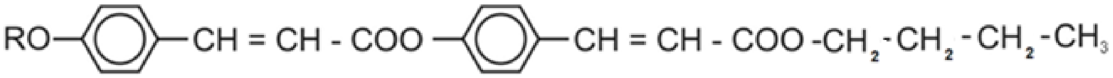
ANALYST : K.J.

Scheme of Synthesis:



Where R= $C_n H_{2n+1}$, n= 1 to 8, 10, 12, 14 and 16

Synthetic rout to series -3



Cis n-Butyl-p-(p/-n-alkoxycinnamoyloxy) cinnamates

Table- 8 : Transition temperatures in ^{0}C

Sr. No.	n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	200.0
2	Ethyl	-	-	215.0
3	Propyl	-	-	219.0
4	Butyl	-	-	180.0
5	Pentyl	-	-	142.0
6	Hexyl	-	130.0	142.0
7	Octyl	-	122.0	160.0
8	Decyl	-	140.0	189.0
9	Dodecyl	-	135.0	222.0
10	Tetradecyl	-	160.0	236.0
11	Hexadecyl	-	152.0	220.0

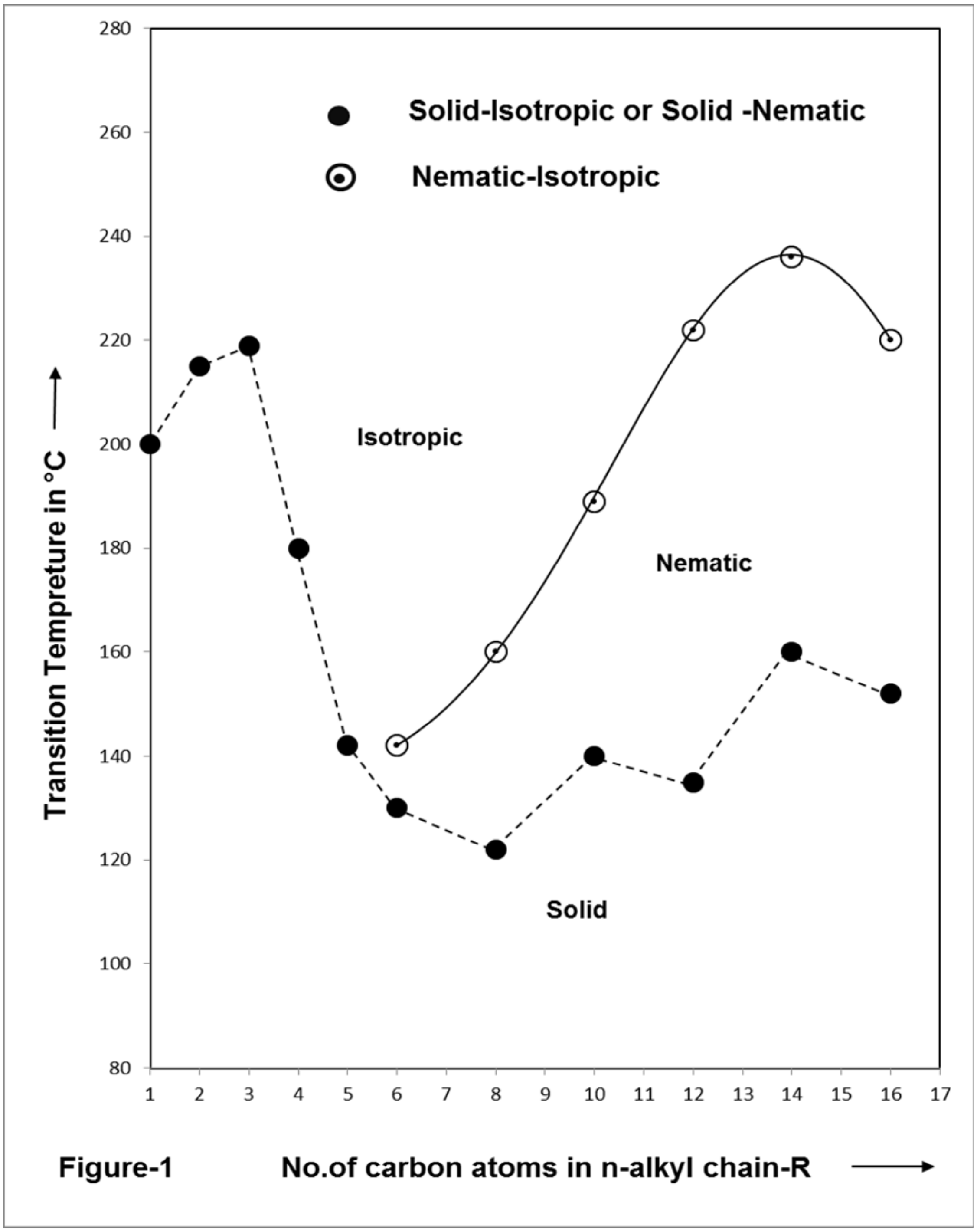
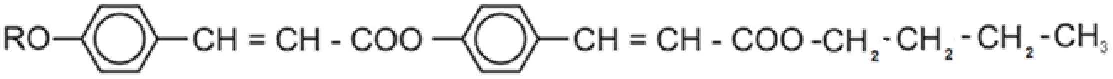


Figure- 17 **:** Cis n-Butyl-p-(p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

Analytical data:



Cis n-Butyl-p-(p/-n-alkoxy cinnamoyloxy) cinnamates

Table- 9 ; Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1	Methyl	$C_{23}H_{24}O_5$	72.63	6.32	72.94	6.8
2	Ethyl	$C_{24}H_{26}O_5$	73.1	6.6	73.58	7.14
3	Proxyl	$C_{25}H_{28}O_5$	73.53	6.86	73.72	7.38
4	Butyl	$C_{26}H_{30}O_5$	73.93	7.11	74.18	7.6
5	Pentyl	$C_{27}H_{32}O_5$	74.31	7.34	74.51	7.71
6	Hexyl	$C_{28}H_{34}O_5$	74.67	7.56	74.74	7.93
7	Octyl	$C_{30}H_{38}O_5$	75.31	7.95	75.54	8.64
8	Decyl	$C_{32}H_{42}O_5$	75.89	8.3	76.22	8.75
9	Dodecyl	$C_{34}H_{46}O_5$	76.4	8.61	76.39	8.96
10	Tetradecyl	$C_{36}H_{50}O_5$	76.87	8.9	76.9	9.38
11	Hexadecyl	$C_{38}H_{54}O_5$	77.29	9.42	77.12	9.42

NMR: in ppm :

Hexyl

1.25 →Confirms -CH_3

3.98 →Confirms- O-CH_2

4.01 →Confirms- O-CH2 of –$COOC_4H_9$

3.29 →Confirms -O-CH2 of C_6H_{13}

4.44 and 4.02 →Confirms – CH=CH-

6.89, 6.92, 8.00 and 8.03 →Confirms two p-sub.phenyl ring

7.24and 8.02 →Confirms two p-sub.phenyl ring

NMR confirms the structure.

Tetradecyl

0.83 →Confirms -CH_3

1.21 →Confirms -CH_2

2.49 →Confirms -OCH_2-CH_2-

3.5 →Confirms- O-CH_2 of–$COOC_4H_9$

3.31 →Confirms -O-CH2 of $C_{14}H_{29}$

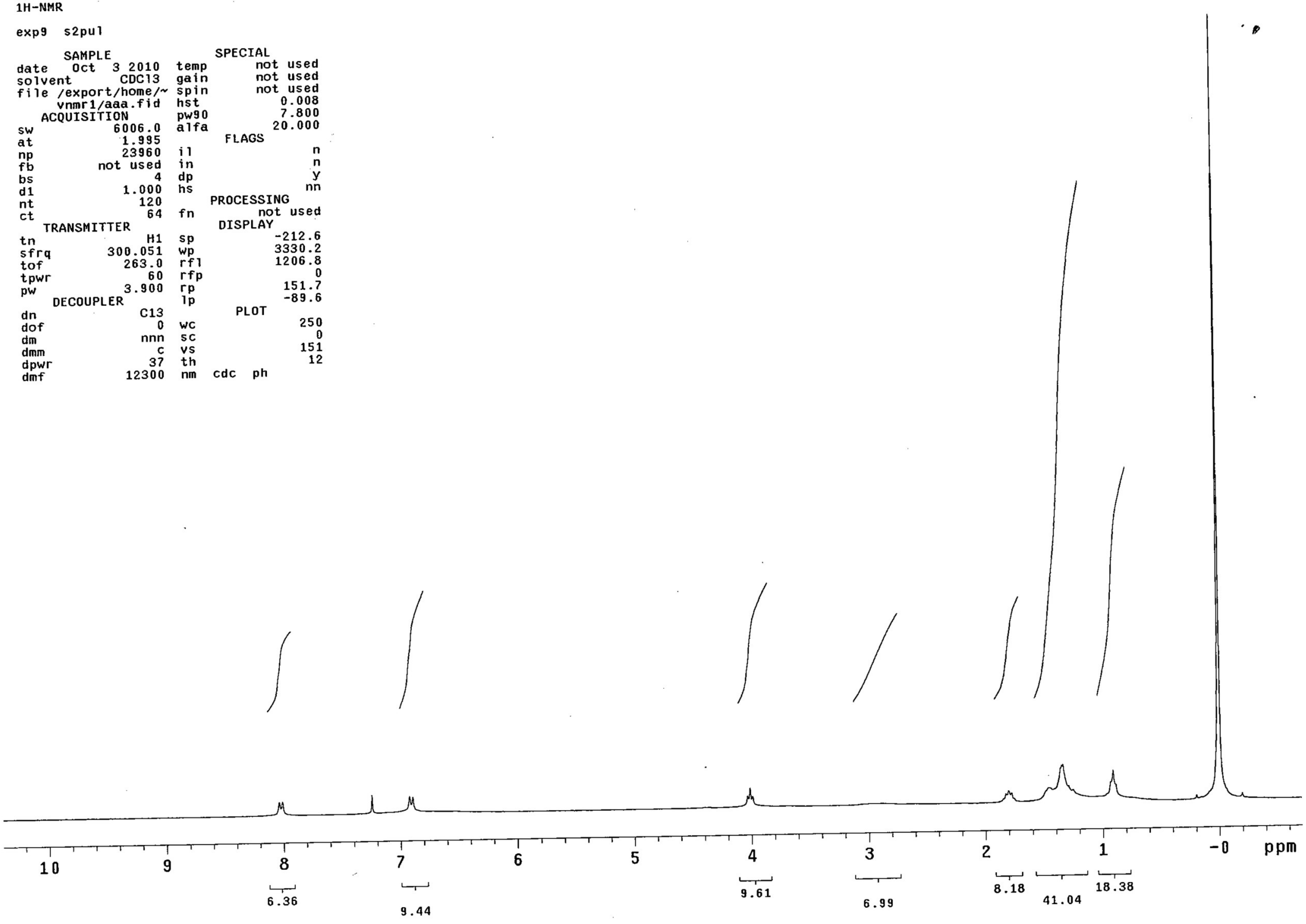
4.41 →Confirms- CH=CH-

6.80 and 6.83, →Confirms two p-sub.phenyl ring

7.75 and 7.78, →Confirms two p-sub.phenyl ring

NMR confirms the structure.

```
Cn-4-6
1H-NMR

exp9  s2pul

      SAMPLE             SPECIAL
date   Oct  3 2010  temp      not used
solvent      CDCl3  gain      not used
file /export/home/~ spin      not used
     vnmr1/aaa.fid  hst          0.008
   ACQUISITION      pw90         7.800
sw          6006.0  alfa        20.000
at           1.995         FLAGS
np           23960  il               n
fb        not used  in               n
bs               4  dp               y
d1           1.000  hs              nn
nt             120      PROCESSING
ct              64  fn        not used
    TRANSMITTER          DISPLAY
tn              H1  sp          -212.6
sfrq       300.051  wp          3330.2
tof          263.0  rfl         1206.8
tpwr            60  rfp              0
pw           3.900  rp           151.7
     DECOUPLER      lp           -89.6
dn             C13           PLOT
dof              0  wc             250
dm             nnn  sc               0
dmm              c  vs             151
dpwr            37  th              12
dmf          12300  nm  cdc  ph
```



IR in cm^{-1}

Octyl

2850.0 →Confirms alkyl group

1150,1270, & 1725 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

830 →Confirms p-sub. phenyl ring

3000 →Confirms aromatic ring

740 →Confirms polymethylene of C_8H_{17}

IR confirms above structure

Hexadecyl

2900.0 →Confirms alkyl group

1150, 1260, & 1710 →Confirms –COO- group

666 →Confirms cis –CH=CH- group

840 →Confirms p-sub. phenyl ring

2950 →Confirms aromatic ring

740 →Confirms polymethylene of $C_{16}H_{33}$

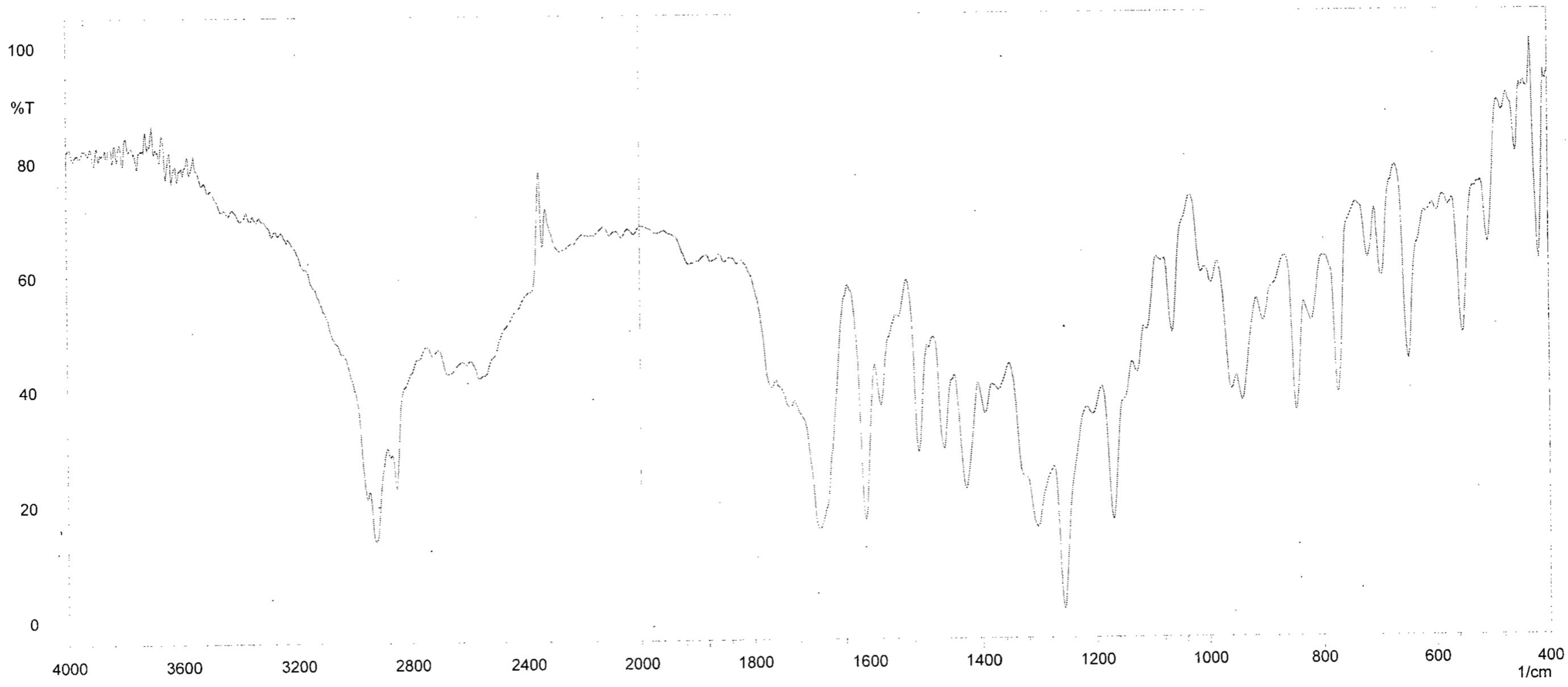
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

SAMPLE NAME : N.4. 8

DATE : 05/10/2010

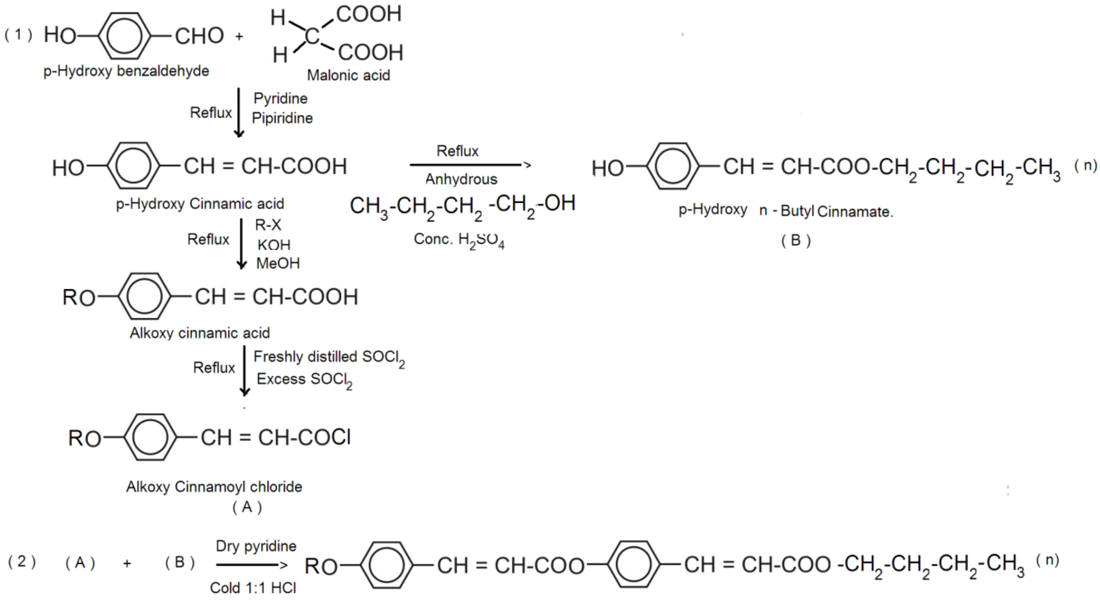


ANALYST :H.P.

No. of Scans; 16

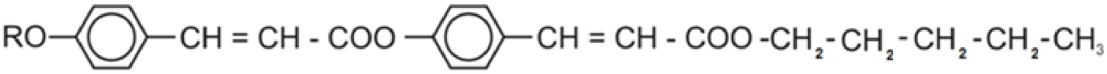
Resolution; 4

Scheme of synthesis:



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

Synthetic rout to series -4



Cis n-Pentyl-p-[p/-n-alkoxy cinnamoyloxy] cinnamates**.**

Table- 10 : Transition temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	174.0
2	Ethyl	-	-	170.0
3	Propyl	-	-	178.0
4	Butyl	-	-	168.0
5	Pentyl	-	135.0	156.0
6	Hexyl	124.0	133.0	150.0
7	Heptyl	119.0	139.0	164.0
8	Octyl	114.0	135.0	166.0
9	Decyl	110.0	135.0	163.0
10	Dodecyl	125.0	147.0	176.0
11	Tetradecyl	-	153.0	180.0
12	Hexadecyl	-	177.0	200.0

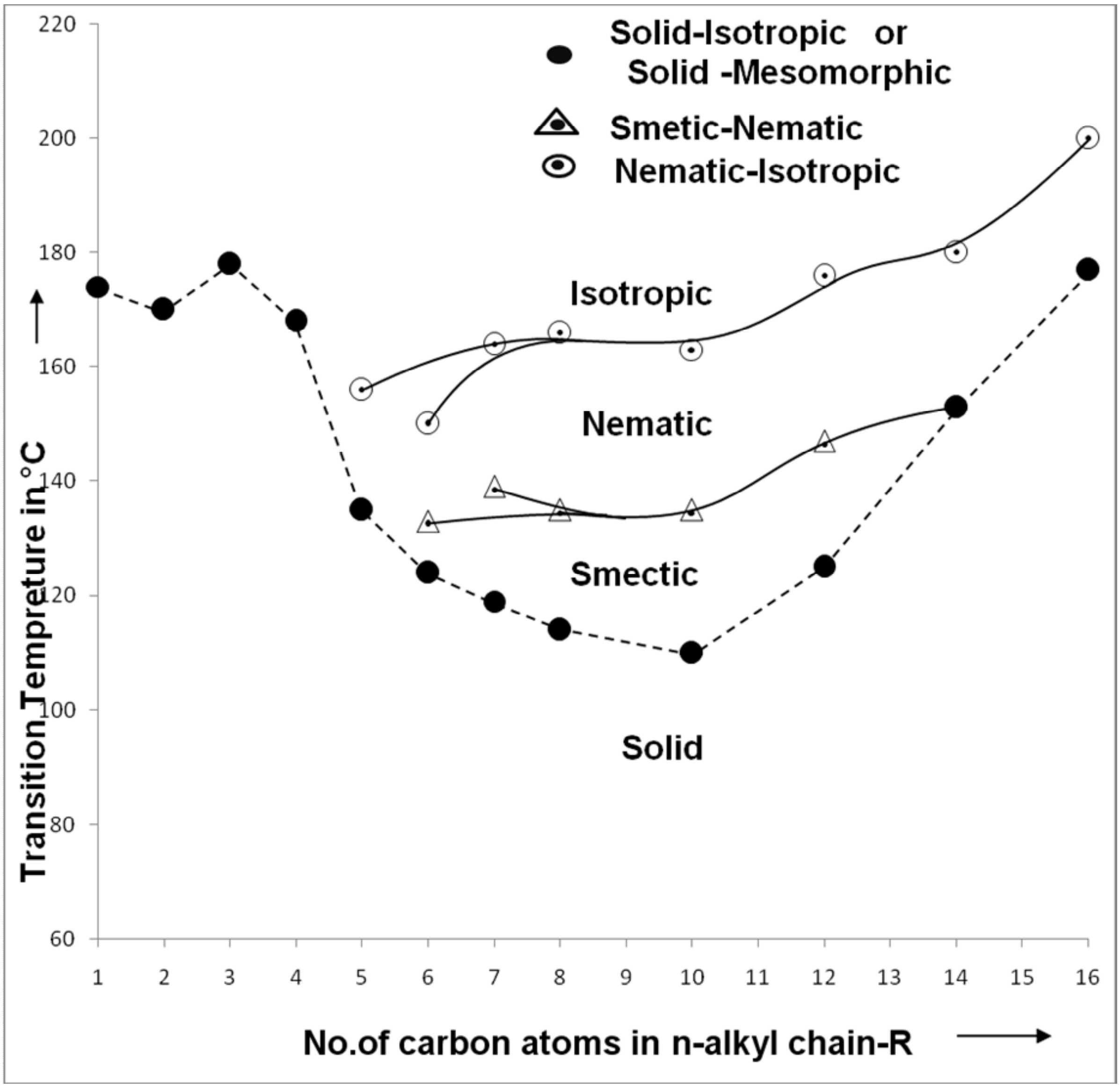
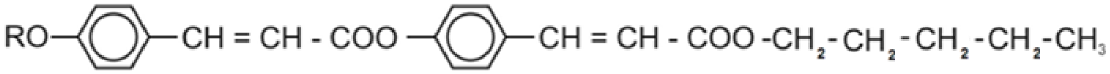


Figure – 18 : Cis n-Pentyl-p-[-p/-n-alkoxy cinnamoyloxy] cinnamates.

Analytical data :



Cis n-Pentyl –p-(p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

Table-21 : Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{24}H_{26}O_5$	73.10	6.60	73.18	6.60
2.	Ethyl	$C_{25}H_{28}O_5$	73.53	6.86	73.56	6.86
3.	Proxyl	$C_{26}H_{30}O_5$	73.93	7.11	73.84	7.12
4.	Butyl	$C_{27}H_{32}O_5$	74.31	7.34	74.36	7.36
5.	Pentyl	$C_{28}H_{34}O_5$	74.67	7.56	74.60	7.56
6.	Hexyl	$C_{29}H_{36}O_5$	75.00	7.76	75.12	7.78
7.	Heptyl	$C_{30}H_{38}O_5$	73.77	7.79	73.67	7.84
8.	Octyl	$C_{31}H_{40}O_5$	75.61	8.13	75.38	8.06
9.	Decyl	$C_{33}H_{44}O_5$	76.15	8.46	76.15	8.46
10.	Dodecyl	$C_{35}H_{48}O_5$	76.64	8.76	76.50	8.76
11.	Tetradecyl	$C_{37}H_{52}O_5$	77.08	9.03	77.06	9.08
12.	Hexadecyl	$C_{39}H_{56}O_5$	77.48	9.27	77.32	9.28

NMR: in ppm :

Hexyl

0.83 →Confirms -CH_3

2.49 →Confirms -O-CH_2

4.01 →Confirms O-CH2 of –$COOC_5H_{11}$

3.3 →Confirms O-CH2 of C_6H_{13}

4.44 and 4.02 →Confirms -CH=CH-

6.89, 6.83, 7.75 and 7.78 → Confirms two p-sub.phenyl ring

7.24and 8.02 →Confirms two p-sub.phenyl ring

NMR confirms the structure.

Tetradecyl

0.876 →Confirms -CH_3

1.25 →Confirms -$CH_{2\,-}$

2.49 →Confirms -OCH_2-CH_2-

4.00 →Confirms O-CH_2 of–$COOC_5H_{11}$

3.31 →Confirms O-CH2 of $C_{14}H_{29}$

4.48 →Confirms CH=CH-

6.896 and 6.925, →Confirms two p-sub.phenyl ring

8.039 and 8.011, → Confirms two p-sub.phenyl ring

NMR confirms the structure.

```
Cn-4-6
1H-NMR

exp9  s2pul

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date   Oct  3 2010  temp        not used
solvent       CDCl3  gain        not used
file /export/home/~ spin        not used
    vnmr1/aaa.fid   hst            0.008
   ACQUISITION      pw90           7.800
sw           6006.0 alfa          20.000
at            1.995          FLAGS
np            23960 il                 n
fb         not used in                 n
bs                4 dp                 y
d1            1.000 hs                nn
nt              120        PROCESSING
ct               64 fn          not used
   TRANSMITTER              DISPLAY
tn               H1 sp            -212.6
sfrq        300.051 wp            3330.2
tof           263.0 rfl           1206.8
tpwr             60 rfp                0
pw            3.900 rp             151.7
    DECOUPLER       lp             -89.6
dn              C13            PLOT
dof               0 wc               250
dm              nnn sc                 0
dmm               c vs               151
dpwr             37 th                12
dmf           12300 nm   cdc  ph
```
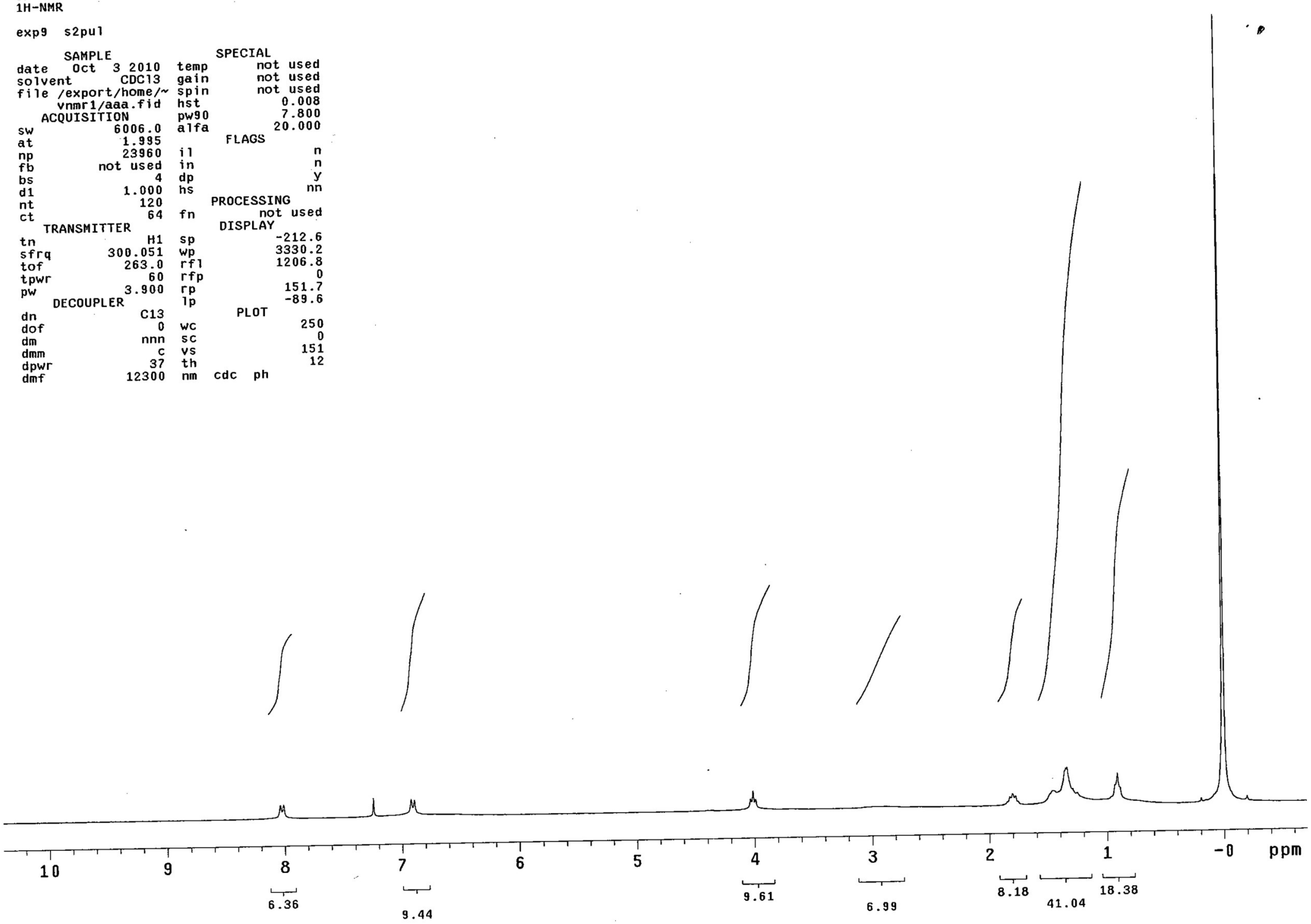



IR in cm^{-1}

Octyl

2900.0 →Confirms alkyl group

1050,1150, & 1710 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

850 →Confirms p-sub. phenyl ring

2900 →Confirms aromatic ring

750 →Confirms polymethylene of C_8H_{17}

IR confirms above structure

Hexadecyl

2850.0 →Confirms alkyl group

1080, 1150, & 1700 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

860 →Confirms p-sub. phenyl ring

3000 →Confirms aromatic ring

750 →Confirms polymethylene of $C_{16}H_{33}$

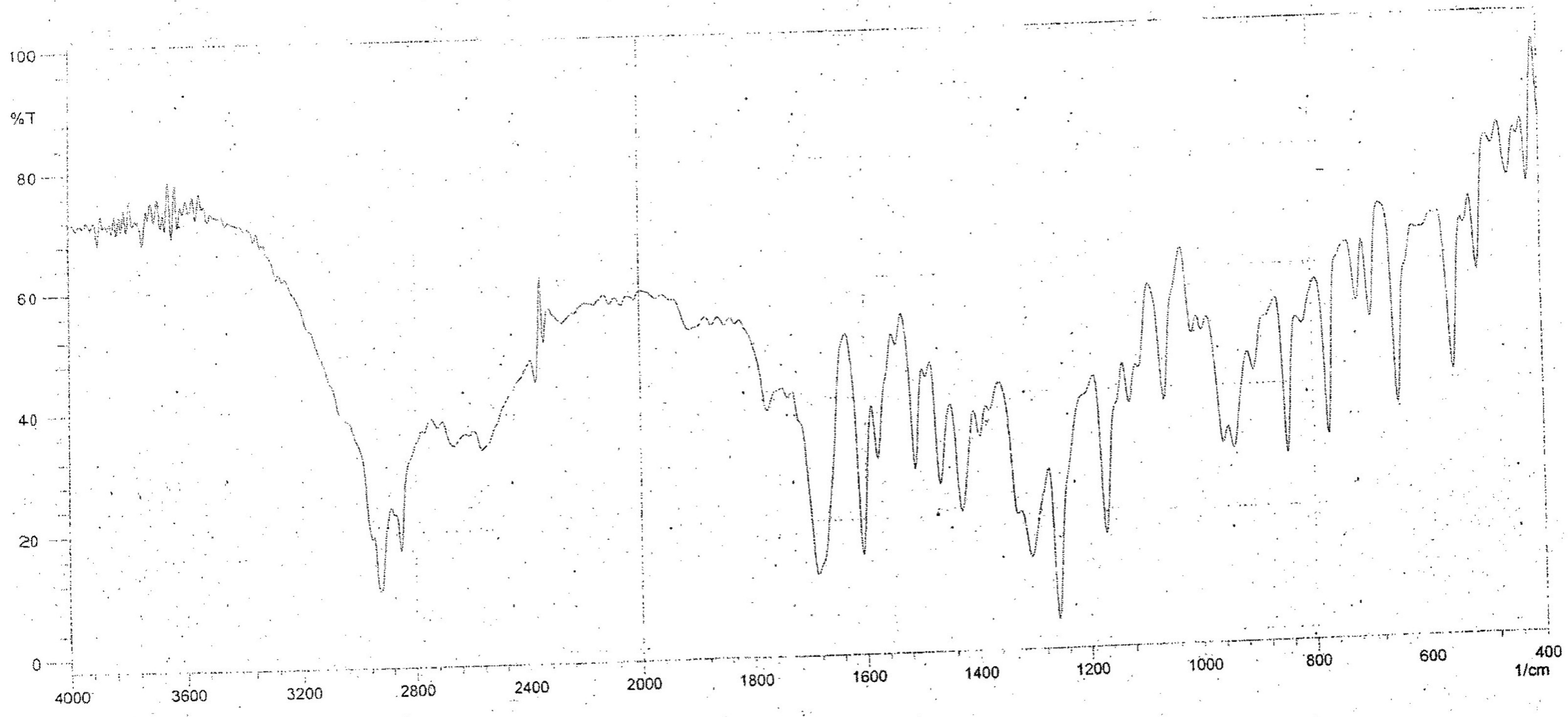
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 05/10/2010

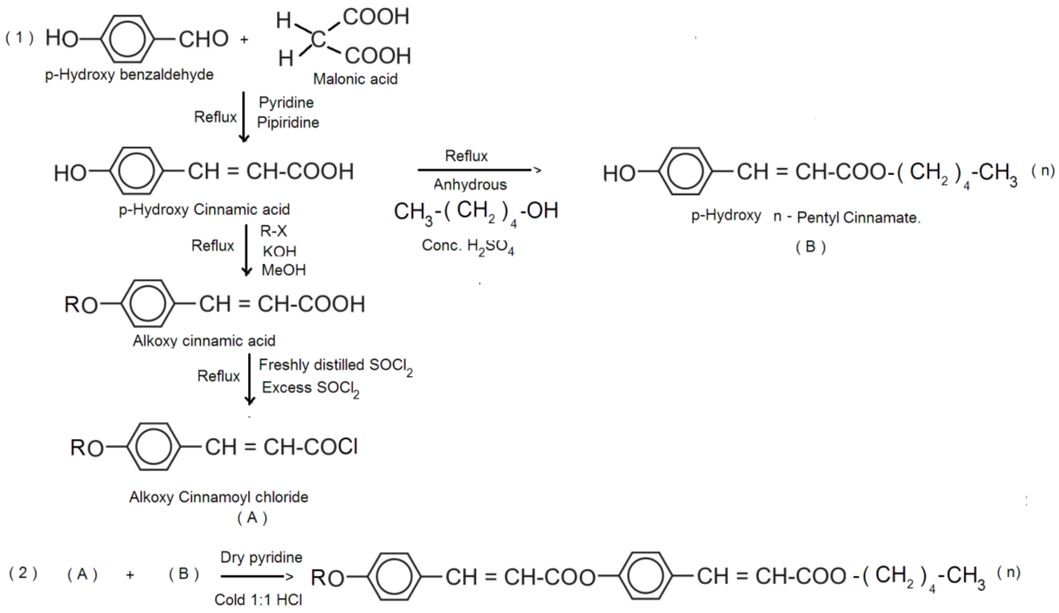
SAMPLE NAME : C.5.8



ANALYST :H.P.

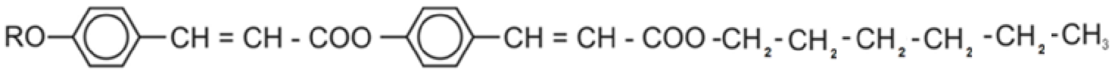
lo . of Scans; 16

Scheme of Synthesis:



Where R= $C_n H_{2n+1}$, n= 1 to 8, 10, 12, 14 and 16

Synthetic rout to series -5



Cis n-Hexyl-p-[p$^/$-n-alkoxy cinnamoyloxy] cinnamates**.**

Table- 12 : Transition Temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	192.0
2	Ethyl	-	-	186.0
3	Propyl	-	160.0	170.0
4	Butyl	-	167.0	187.0
5	Pentyl	-	170.0	192.0
6	Hexyl	-	178.0	206.0
7	Heptyl	171.0	195.0	213.0
8	Octyl	168.0	198.0	219.0
9	Decyl	172.0	190.0	208.0
10	Dodecyl	145.0	179.0	196.0
11	Tetradecyl	110.0	136.0	170.0
12	Hexadecyl	-	136.0	148.0

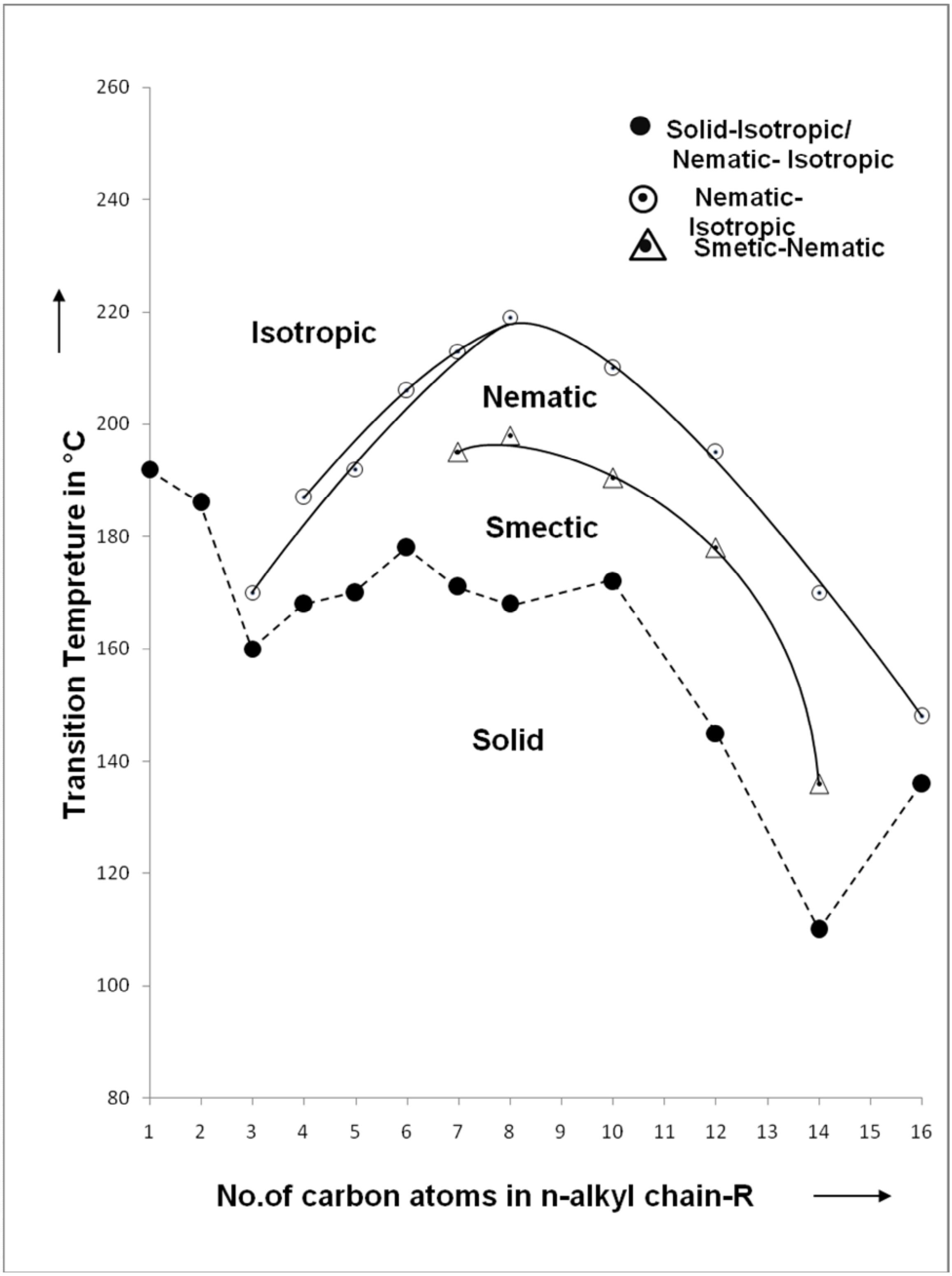
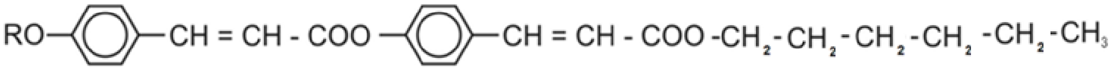


Figure-19:Homologous Series: Cis n-Hexyl-p-[p/-n-alkoxy cinnamoyloxy] cinnamates.

Analytical data :



Cis n-Hexyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

Table- 13 : Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{25}H_{28}O_5$	73.53	6.86	73.31	6.86
2.	Ethyl	$C_{26}H_{30}O_5$	73.93	7.11	73.63	7.11
3.	Proxyl	$C_{27}H_{32}O_5$	74.31	7.34	74,11	7.15
4.	Butyl	$C_{28}H_{34}O_5$	74.57	7.56	74.57	7.56
5.	Pentyl	$C_{29}H_{36}O_5$	75.00	7.76	75.13	7.36
6.	Hexyl	$C_{30}H_{38}O_5$	75.31	7.95	75.31	7.95
7.	Heptyl	$C_{31}H_{40}O_5$	75.61	8.13	75.56	8.13
8.	Octyl	$C_{32}H_{42}O_5$	75.89	8.30	76.11	8.56
9.	Decyl	$C_{34}H_{46}O_5$	76.40	8.61	76.13	8.61
10.	Dodecyl	$C_{36}H_{50}O_5$	76.87	8.90	76.87	8.89
11.	Tetradecyl	$C_{38}H_{54}O_5$	77.29	9.15	77.29	9.15
12.	Hexadecyl	$C_{40}H_{58}O_5$	77.67	9.39	77.67	9.19

NMR: in ppm :

Octyl

0.840 →Confirms -CH_3

2.490 →Confirms- O-CH_2

4.20 →Confirms- O-CH_2 of –$COOC_6H_{13}$

3.98 →Confirms -O-CH_2 of –C_8H_{17}

4.4 and 4.0 →Confirms – CH=CH-

6.80, 6.83, 7.74 and 7.78 →Confirms two p-sub.phenyl ring

7.24and 8.02 →Confirms two p-sub.phenyl ring

NMR confirms the structure.

Dodecyl

0.88 →Confirms -CH_3

1.55 →Confirms -CH_2

2.40 →Confirms -OCH_2-CH_2-

4.00 →Confirms- O-CH_2 of–$COOC_6H_{13}$

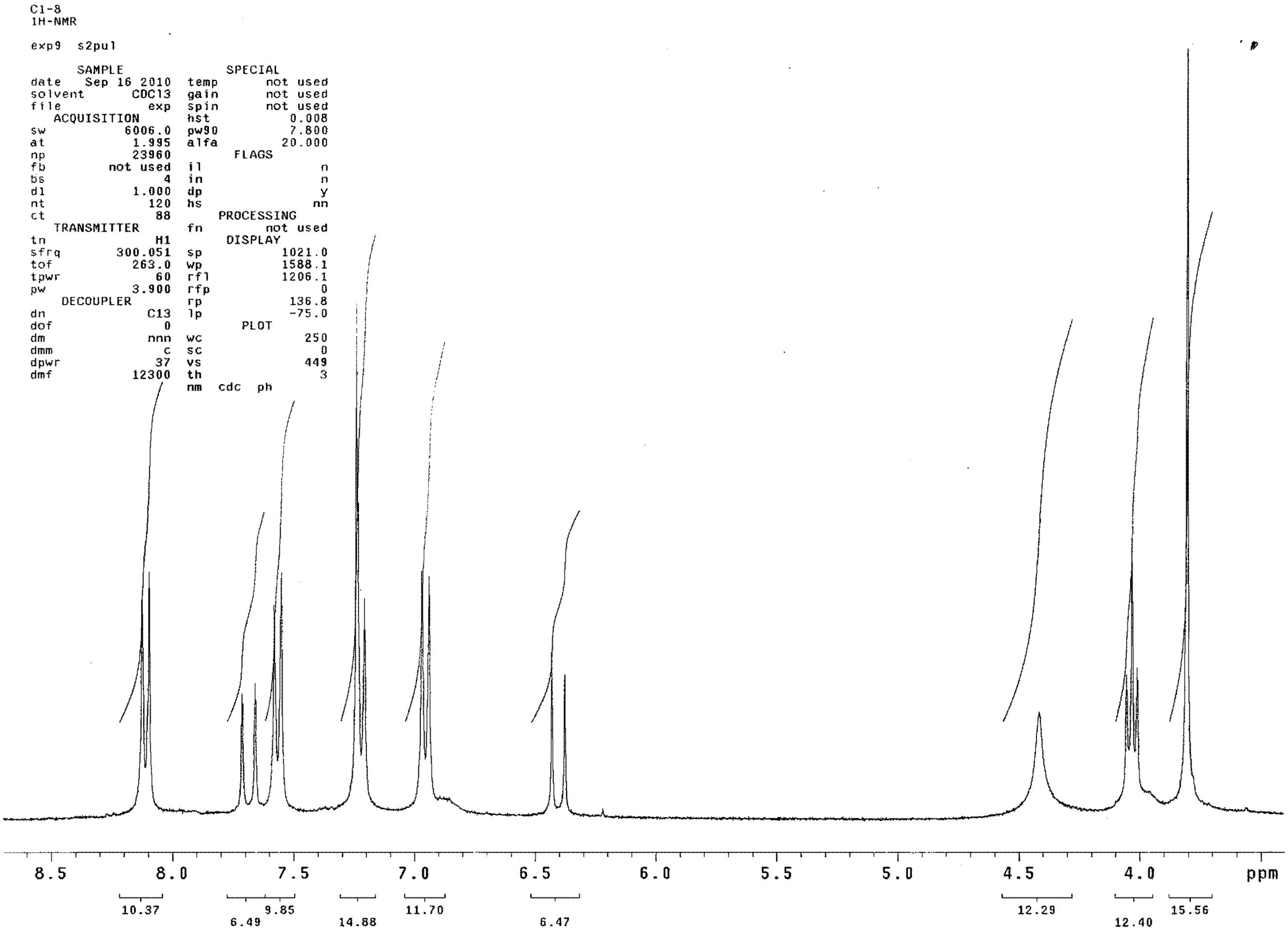
3.31 →Confirms -O-CH_2 of $C_{12}H_{25}$

4.48 →Confirms- CH=CH-

6.896 and 6.925, →Confirms two p-sub.phenyl ring

8.039 and 8.011, →Confirms two p-sub.phenyl ring

NMR confirms the structure.



C1-8
1H-NMR

```
exp9  s2pul

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solvent      CDCl3   gain        not used
file           exp   spin        not used
   ACQUISITION       hst            0.008
sw          6006.0   pw90           7.800
at           1.995   alfa          20.000
np           23960           FLAGS
fb        not used   il                 n
bs               4   in                 n
d1           1.000   dp                 y
nt             120   hs                nn
ct              88         PROCESSING
   TRANSMITTER       fn          not used
tn              H1            DISPLAY
sfrq       300.051   sp            1021.0
tof          263.0   wp            1588.1
tpwr            60   rfl           1206.1
pw           3.900   rfp                0
    DECOUPLER        rp             136.8
dn             C13   lp             -75.0
dof              0            PLOT
dm             nnn   wc               250
dmm              c   sc                 0
dpwr            37   vs               449
dmf          12300   th                 3
                     nm  cdc  ph
```

IR in cm^{-1}

Hexyl

2850.0 →Confirms alkyl group

1050,1150, & 1710 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

850 →Confirms p-sub. phenyl ring

2900→ Confirms aromatic ring

750 →Confirms polymethylene of C_6H_{13}

IR confirms above structure

Tetradecyl

2900.0 →Confirms alkyl group

1080, 1260, & 1700 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

860 →Confirms p-sub. phenyl ring

3000 →Confirms aromatic ring

750 →Confirms polymethylene of $C_{14}H_{29}$

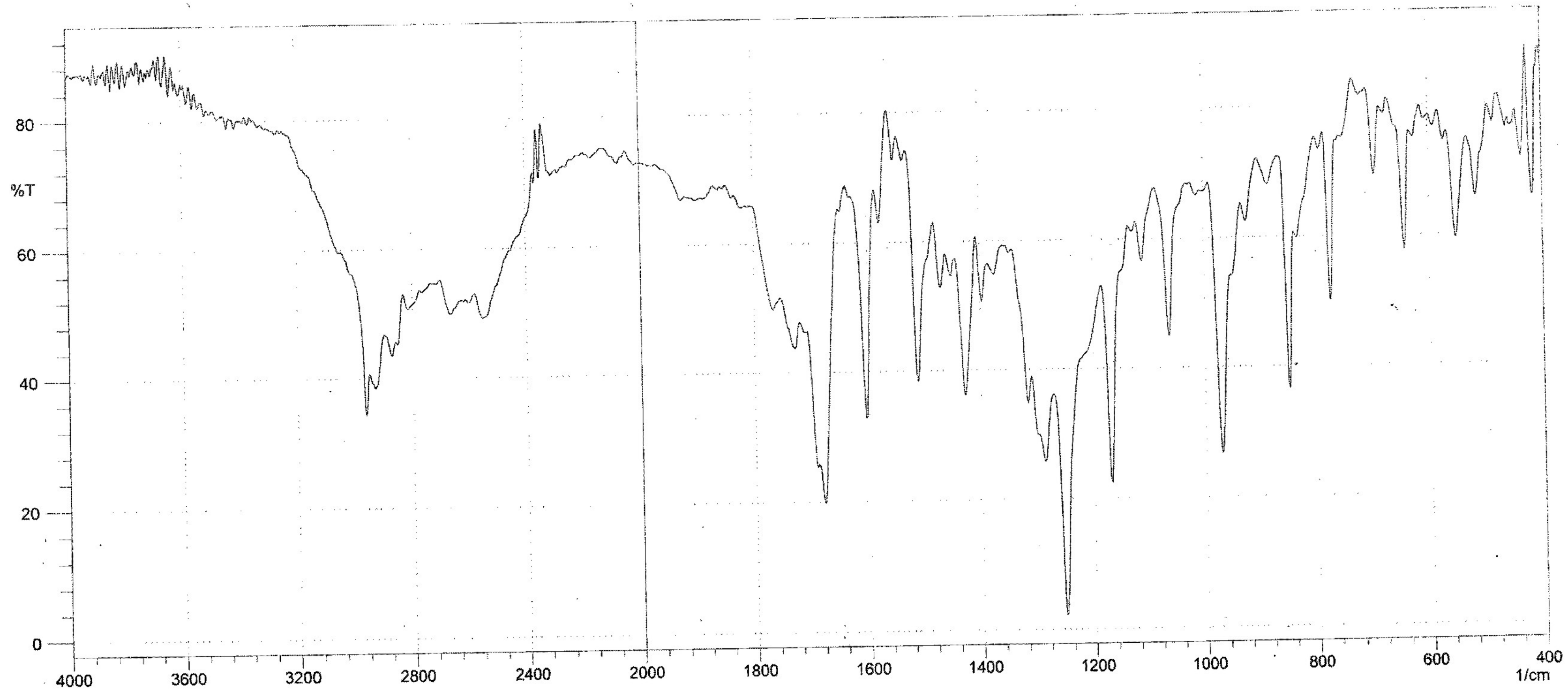
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 04/01/2011

SAMPLE NAME : C 6 - 3

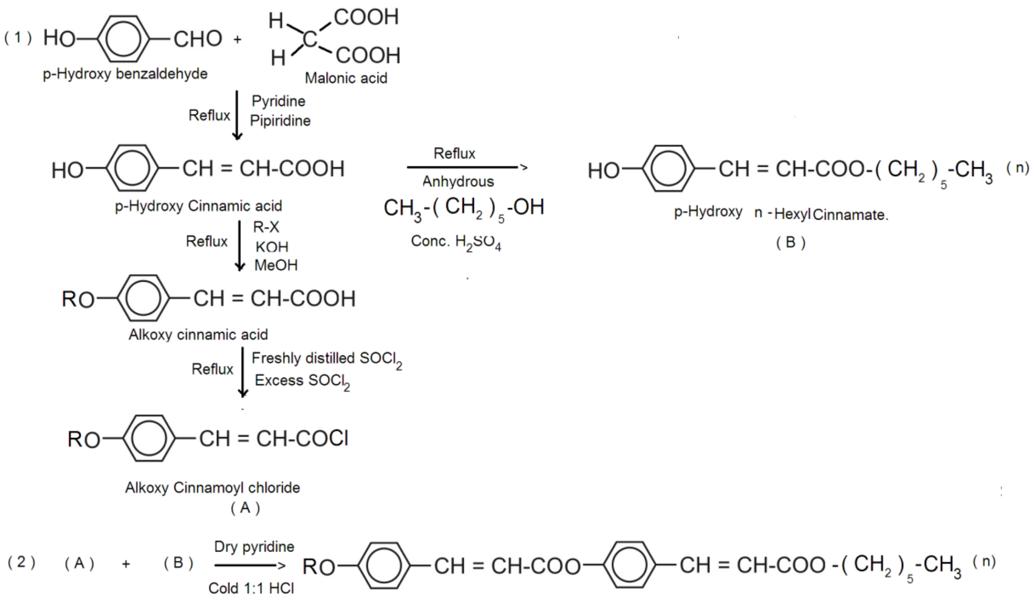


ANALYST : K.J.

No. of Scans; 16

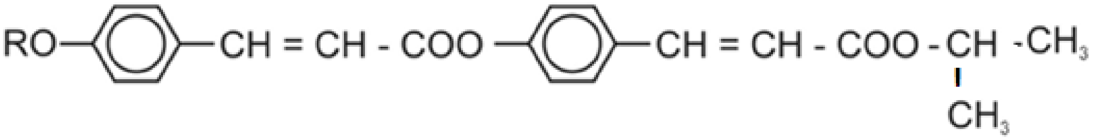
Resolution; 4

Scheme of Synthesis:



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

Synthetic rout to series -6



Cis Isopropyl-p-[p/-n-alkoxy cinnamoyloxy] cinnamates.

Table- 14 : Transition temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	208.0
2	Ethyl	-	-	216.0
3	Propyl	-	-	220.0
4	Butyl	-	-	200.0
5	Pentyl	-	140.0	184.0
6	Hexyl	-	140.0	244.0
7	Heptyl	-	131.0	207.0
8	Octyl	-	130.0	242.0
9	Decyl	-	130.0	220.0
10	Dodecyl	-	138.0	190.0
11	Tetradecyl	-	130.0	170.0
12	Hexadecyl	-	132.0	152.0

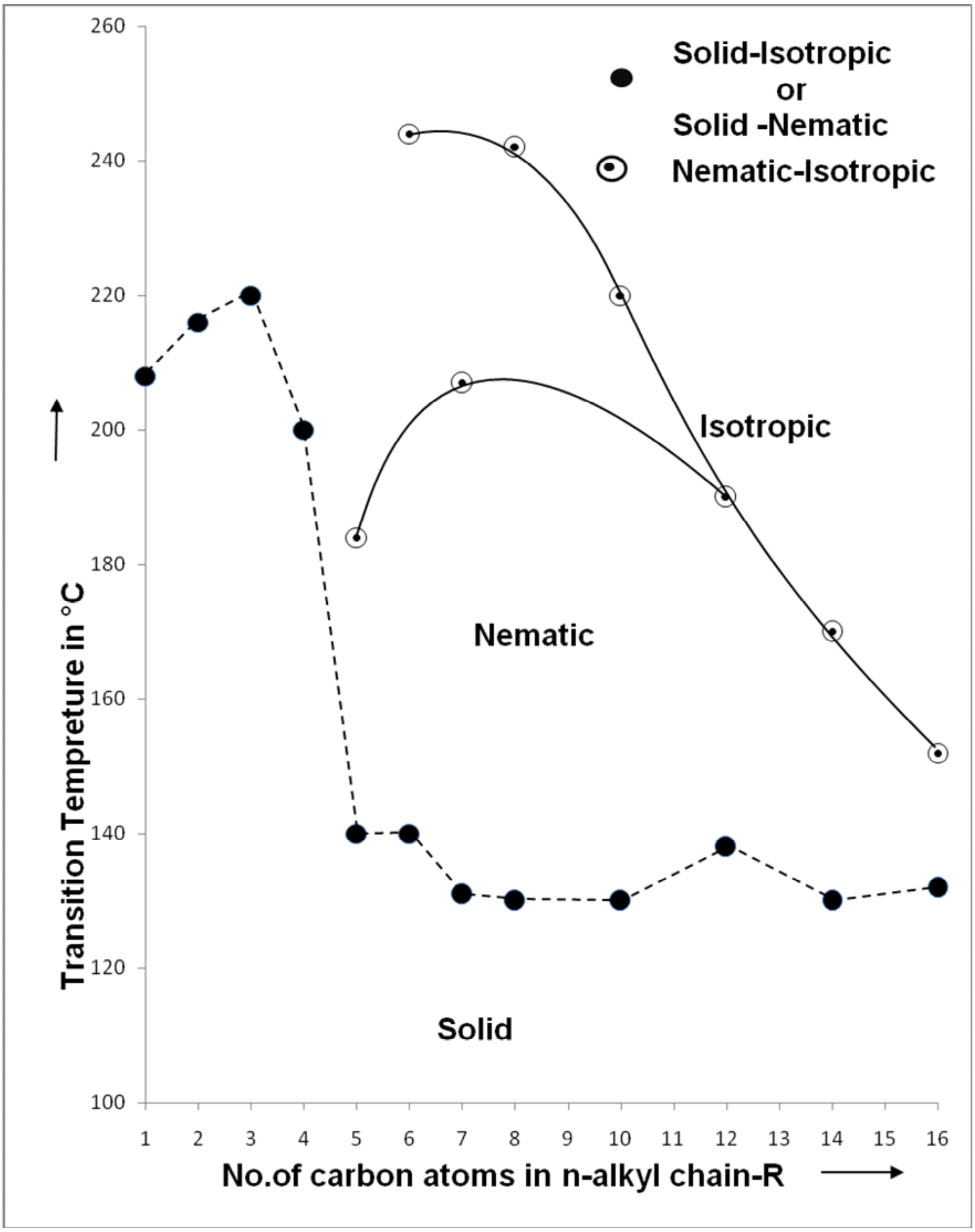
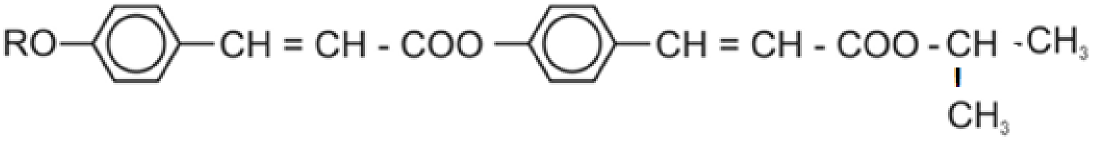


Figure- 20 : Cis Isopropyl-p-[p/-n-alkoxy cinnamoyloxy] cinnamates.

Analytical data :



Cis Isopropyl –p-(p$^/$-n-alkoxy cinnamoyloxy) cinnamates.

Table- 15 : Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{22}H_{22}O_5$	72.13	6.01	72.18	6.00
2.	Ethyl	$C_{23}H_{24}O_5$	73.02	6.35	73.16	6.36
3.	Proxyl	$C_{24}H_{26}O_5$	73.85	6.67	73.84	6.66
4.	Butyl	$C_{25}H_{28}O_5$	74.63	6.97	74.67	6.96
5.	Pentyl	$C_{26}H_{30}O_5$	75.16	7.25	75.12	7.24
6.	Hexyl	$C_{27}H_{32}O_5$	76.06	7.51	76.12	7.58
7.	Heptyl	$C_{28}H_{34}O_5$	76.71	7.76	76.76	7.78
8.	Octyl	$C_{29}H_{36}O_5$	77.33	8.00	77.38	7.96
9.	Decyl	$C_{31}H_{40}O_5$	78.48	8.44	78.52	8.46
10.	Dodecyl	$C_{33}H_{44}O_5$	79.52	8.84	79.50	8.84
11.	Tetradecyl	$C_{35}H_{48}O_5$	80.46	9.20	80.46	9.18
12.	Hexadecyl	$C_{37}H_{52}O_5$	81.32	9.52	81.32	9.58

NMR: in ppm :

Hexyl

0.84 →Confirms -CH_3

2.38 →Confirms -O-CH_2

3.98 →Confirms- O-CH2 of O-CH_2-CH_2-CH_3

3.32 →Confirms -O-CH2 of C_6H_{13}

4.34 and 4.26 →Confirms – CH=CH-

6.64, 6.83, 7.75 and 7.88 →Confirms - two p-sub.phenyl ring

7.22and 8.02 →Confirms two p-sub.phenyl ring

NMR confirms the structure.

Hexadecyl

1.16 → Confirms -CH_3

1.20 →Confirms -CH_2

2.38 →Confirms -OCH_2-CH_2-

4.00 → Confirms- O-CH_2 of–$COOC_3H_7$

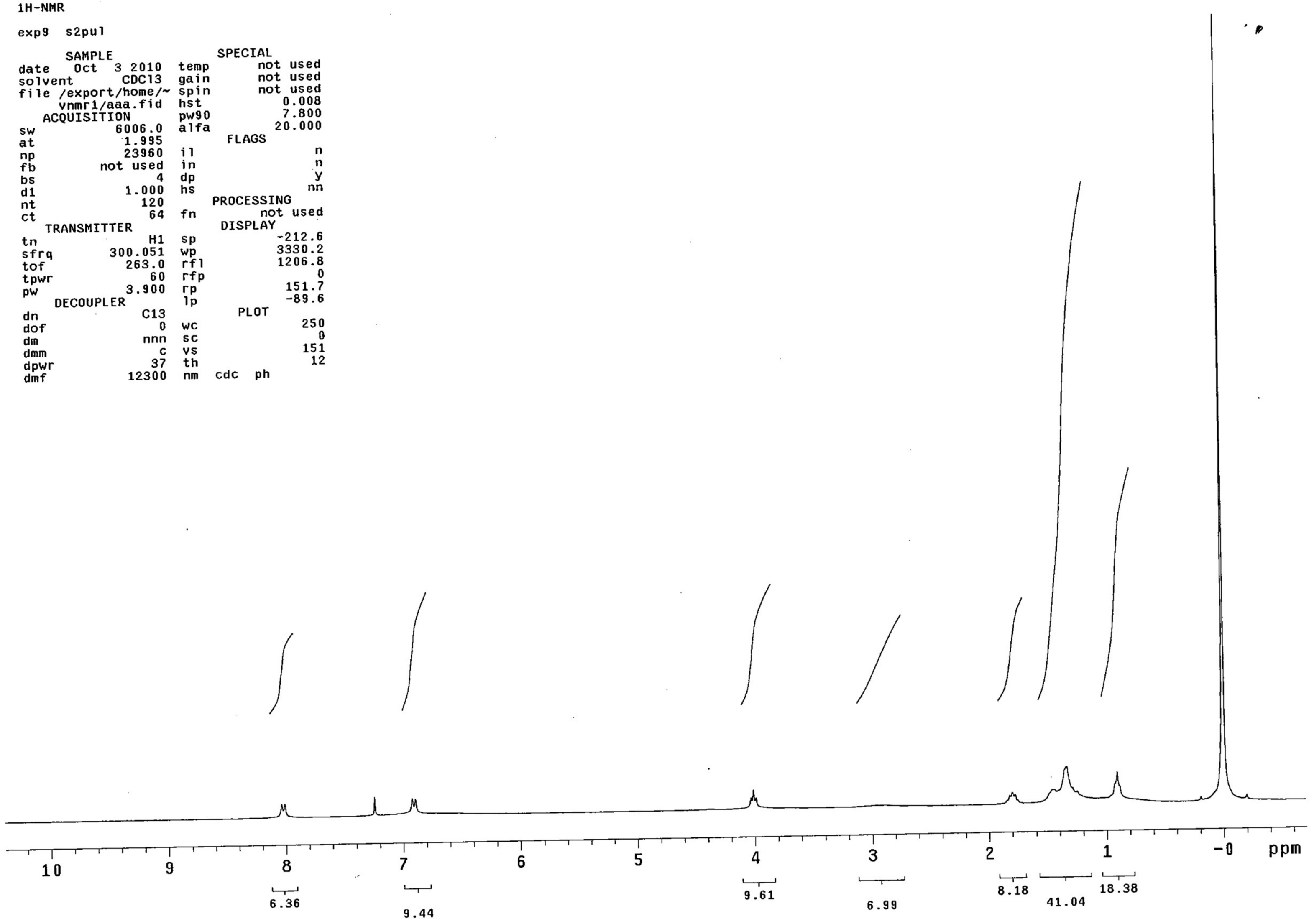
3.32 →Confirms -O-CH2 of $C_{16}H_{33}$

4.40 →Confirms- CH=CH-

6.88 and 6.90, →Confirms -two p-sub.phenyl ring

8.03 and 8.01, →Confirms -two p-sub.phenyl ring

NMR confirms the structure.



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Cn-4-6
1H-NMR

exp9  s2pul

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solvent       CDCl3  gain        not used
file /export/home/~ spin        not used
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   ACQUISITION      pw90           7.800
sw            6006.0 alfa          20.000
at             1.995           FLAGS
np             23960 il                 n
fb          not used in                 n
bs                 4 dp                 y
d1             1.000 hs                nn
nt               120        PROCESSING
ct                64 fn          not used
   TRANSMITTER                DISPLAY
tn                H1 sp            -212.6
sfrq         300.051 wp            3330.2
tof            263.0 rfl           1206.8
tpwr              60 rfp                0
pw             3.900 rp             151.7
    DECOUPLER        lp             -89.6
dn               C13           PLOT
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dmm                c vs               151
dpwr              37 th                12
dmf            12300 nm  cdc  ph
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C2-16
1H-NMR

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np           23960         FLAGS
fb        not used  il                n
bs               4  in                n
d1           1.000  dp                y
nt             120  hs               nn
ct             120      PROCESSING
    TRANSMITTER     fn         not used
tn              H1         DISPLAY
sfrq       300.051  sp           -125.7
tof          263.0  wp           3946.1
tpwr            60  rfl          1206.8
pw           3.900  rfp               0
     DECOUPLER      rp            136.3
dn             C13  lp            -74.0
dof              0          PLOT
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dmm              c  sc                0
dpwr            37  vs              151
dmf          12300  th                8
                    nm  cdc  ph
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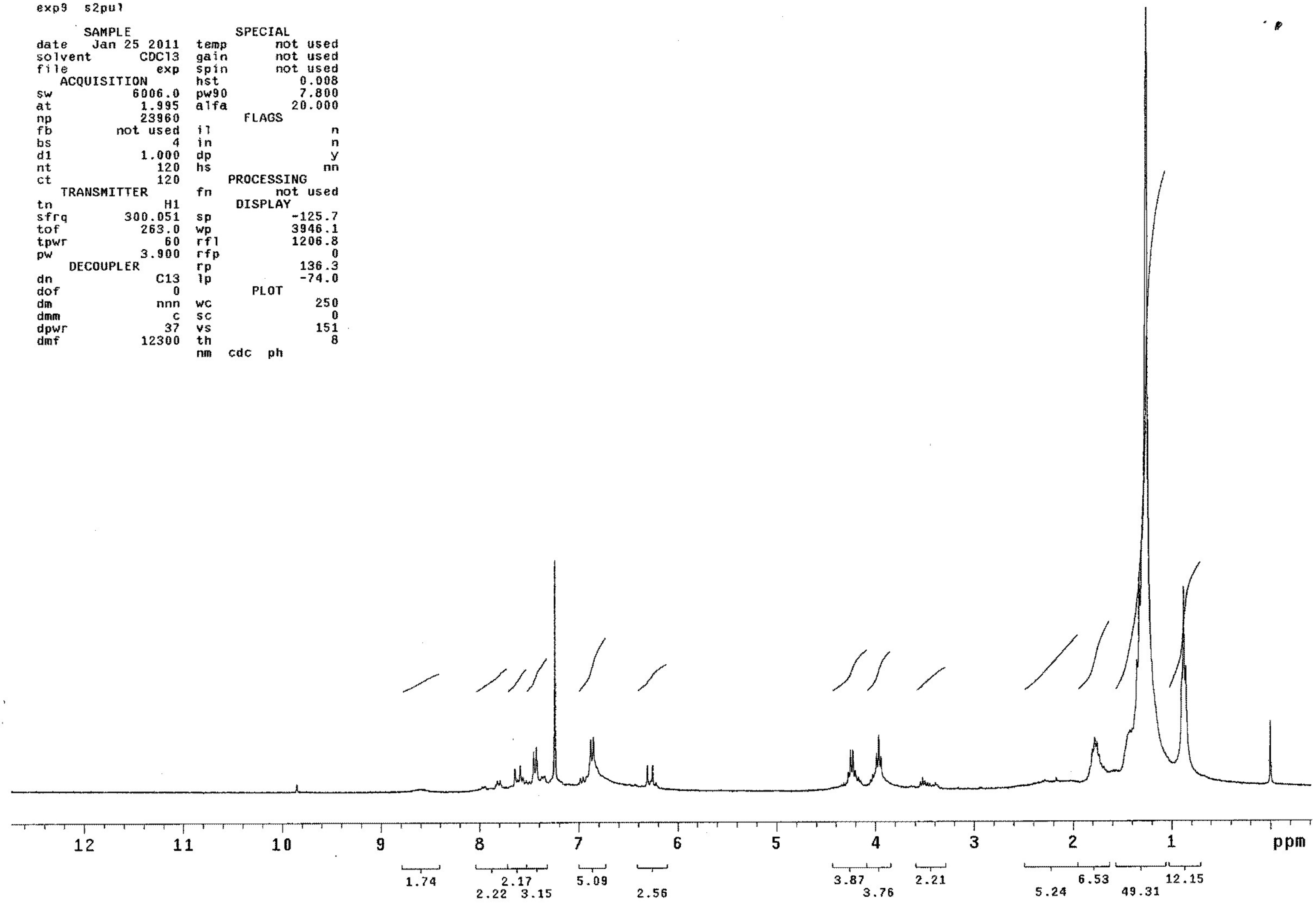


IR in cm^{-1}

Octyl

2800.0 →Confirms alkyl group

1100, & 1750→Confirms –COO- group

660 →Confirms cis –CH=CH- group

830 →Confirms p-sub. phenyl ring

3000 →Confirms aromatic ring

740 →Confirms polymethylene of C_8H_{17}

IR confirms above structure

Tetradecyl

2800.0 →Confirms alkyl group

1050, 1150, & 1700→Confirms –COO- group

725 →Confirms cis –CH=CH- group

820 →Confirms p-sub. phenyl ring

3100 →Confirms aromatic ring

1300 ,1350 Confirms polymethylene of $C_{14}H_{29}$

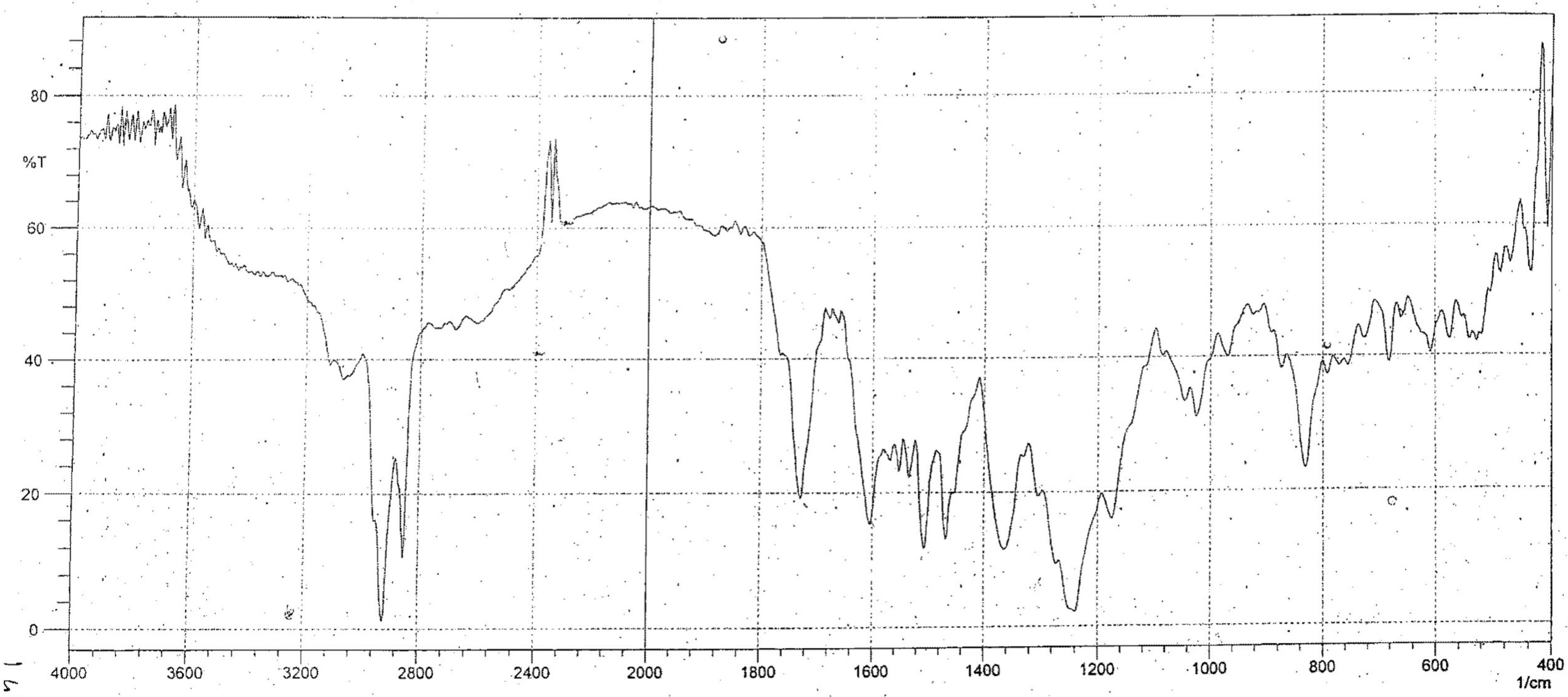
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

SAMPLE NAME: Ci $_{3,8}$

DATE : 04/01/2011

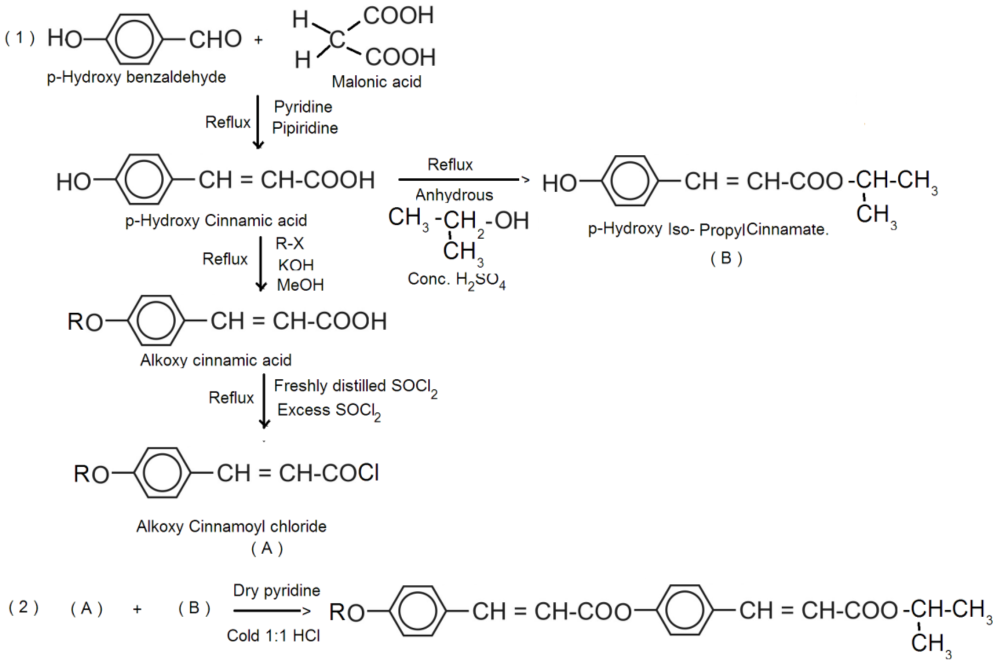


142

No. of Scans; 16

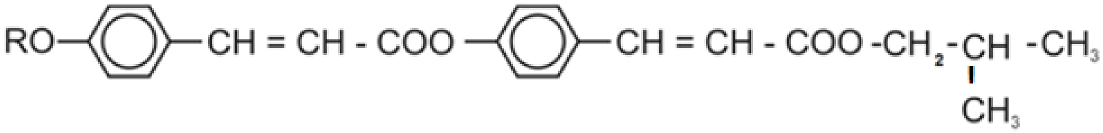
ANALYST : K.J.

Scheme of Synthesis:



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

Synthetic rout to series -7



Cis Isobutyl-p-(p/-n-alkoxycinnamoyloxy) cinnamates.

Table- 16 : Transition temperatures in ^{0}C

Sr. No.	R=n-alkyl chain C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	200.0
2	Ethyl	-	-	210.0
3	Propyl	-	-	144.0
4	Butyl	-	-	125.0
5	Pentyl	-	132.0	165.0
6	Hexyl	-	97.0	136.0
7	Octyl	-	110.0	125.0
8	Decyl	-	105.0	130.0
9	Dodecyl	-	115.0	142.0
10	Tetradecyl	-	110.0	143.0
11	Hexadecyl	-	105.0	129.0

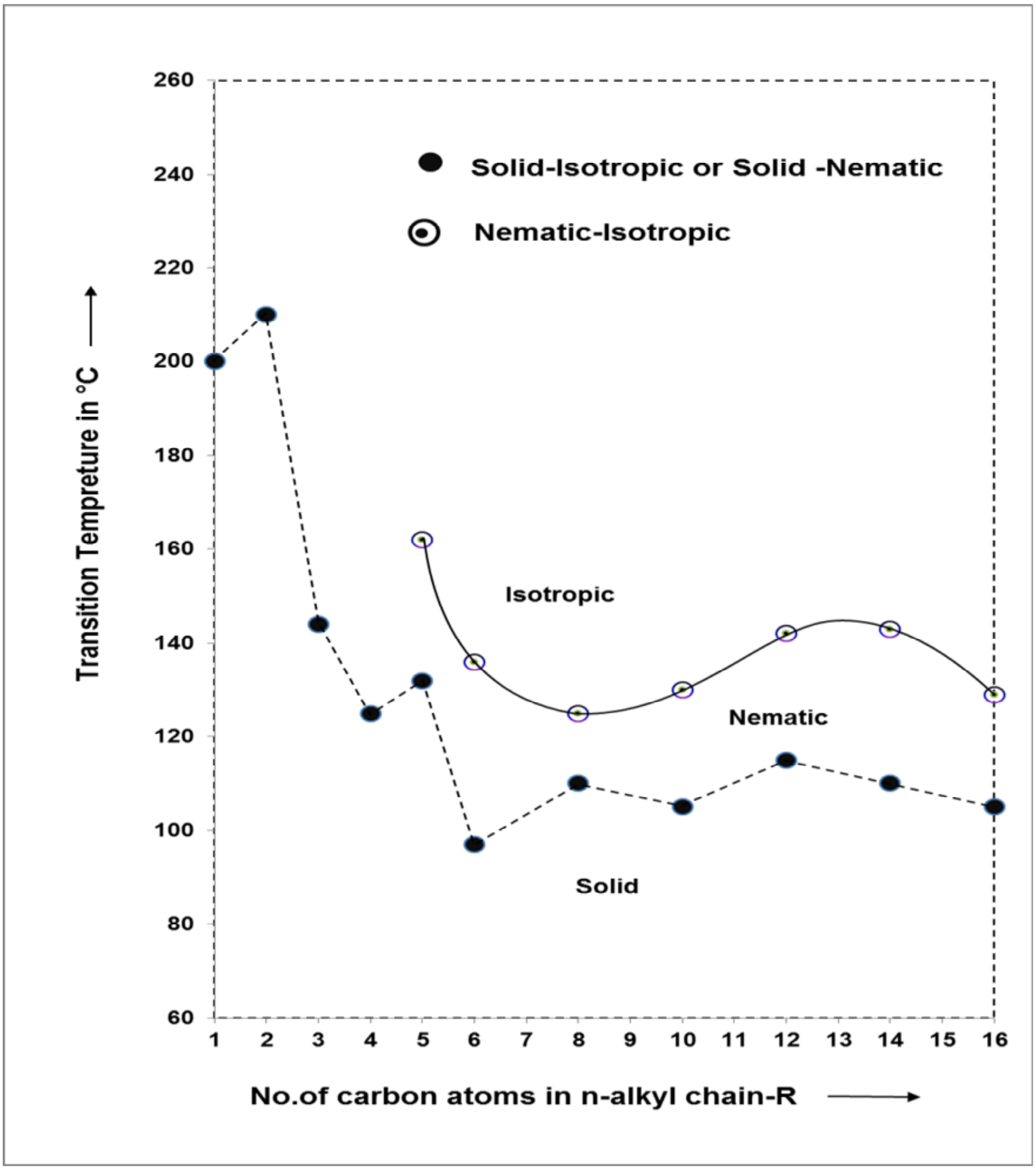
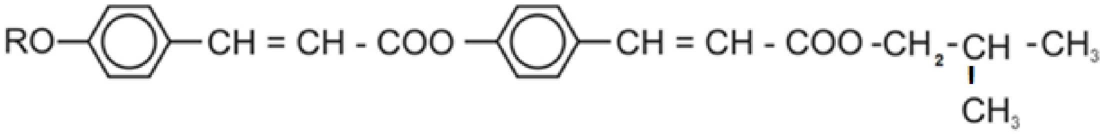


Figure-16 : Homologous Series: Cis Isobutyl-p- [p′- n-alkoxy cinnamoyloxy] cinnamates

Analytical data:



Cis Isobutyl-p-(p/-n-alkoxy cinnamoyloxy) cinnamates

Table- 17 ; Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{23}H_{24}O_5$	72.63	6.32	72.96	6.89
2.	Ethyl	$C_{24}H_{26}O_5$	73.10	6.60	73.61	7.14
3.	Proxyl	$C_{25}H_{28}O_5$	73.53	6.86	73.74	7.38
4.	Butyl	$C_{26}H_{30}O_5$	73.93	7.11	74.18	7.62
5.	Pentyl	$C_{27}H_{32}O_5$	74.31	7.34	74.51	7.71
6.	Hexyl	$C_{28}H_{34}O_5$	74.67	7.56	74.76	7.93
7.	Octyl	$C_{30}H_{38}O_5$	75.31	7.95	75.53	8.65
8.	Decyl	$C_{32}H_{42}O_5$	75.89	8.30	76.22	8.75
9.	Dodecyl	$C_{34}H_{46}O_5$	76.40	8.61	76.39	8.97
10.	Tetradecyl	$C_{36}H_{50}O_5$	76.87	8.90	76.90	9.38
11.	Hexadecyl	$C_{38}H_{54}O_5$	77.29	9.42	77.15	9.48

NMR: in ppm :

Octyl

0.83 →Confirms -CH_3

1.21 →Confirms -CH_2

2.49 →Confirms -OCH_2-CH_2-

3.5 →Confirms- O-CH_2 of–$COOC_4H_9$

3.31 →Confirms -O-CH2 of C_8H_{17}

4.41 →Confirms -CH=CH-

6.80 and 6.83, →Confirms -two p-sub.phenyl ring

7.75 and 7.78, →Confirms -two p-sub.phenyl ring

NMR confirms the structure.

Hexadecyl

1.25 →Confirms -CH_3

3.98 →Confirms- O-CH_2

4.01 →Confirms -O-CH2 of $COOC_4H_9$

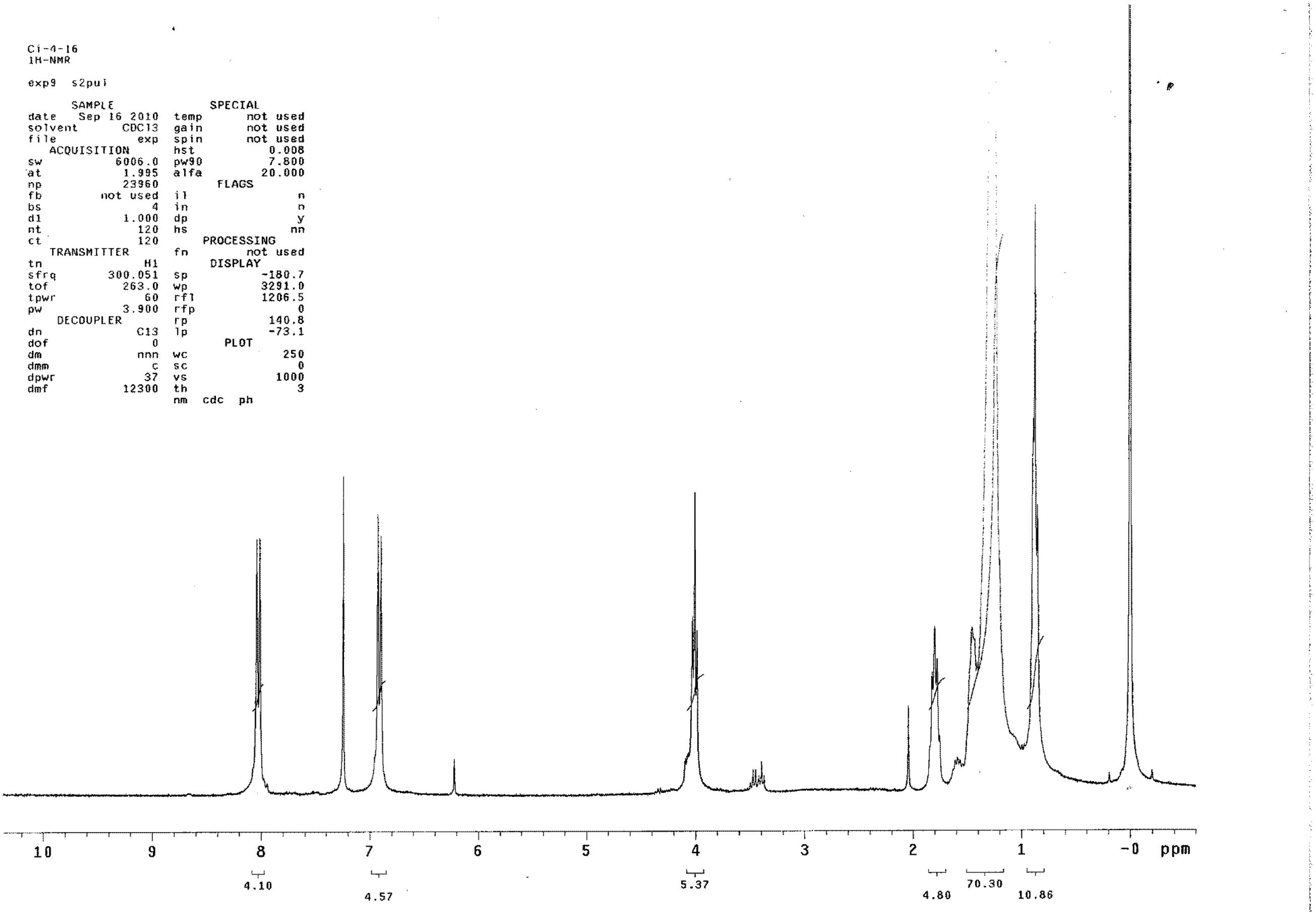
3.3 →Confirms -O-CH2 of $C_{16}H_{33}$

4.44 and 4.02 →Confirms – CH=CH-

6.89, 6.92, 8.00 and 8.03 →Confirms- two p-sub. .phenyl ring

7.24and 8.02 →Confirms- two p-sub. .phenyl ring

NMR confirms the structure.



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Ci-4-16
1H-NMR

exp9  s2pul

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solvent      CDCl3  gain        not used
file           exp  spin        not used
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sw          6006.0  pw90           7.800
at           1.995  alfa          20.000
np           23960        FLAGS
fb        not used  il                 n
bs               4  in                 n
d1           1.000  dp                 y
nt             120  hs                nn
ct             120       PROCESSING
   TRANSMITTER      fn          not used
tn              H1        DISPLAY
sfrq       300.051  sp            -180.7
tof          263.0  wp            3291.0
tpwr            60  rfl           1206.5
pw           3.900  rfp                0
    DECOUPLER       rp             140.8
dn             C13  lp             -73.1
dof              0          PLOT
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dmm              c  sc                 0
dpwr            37  vs              1000
dmf          12300  th                 3
                    nm  cdc  ph
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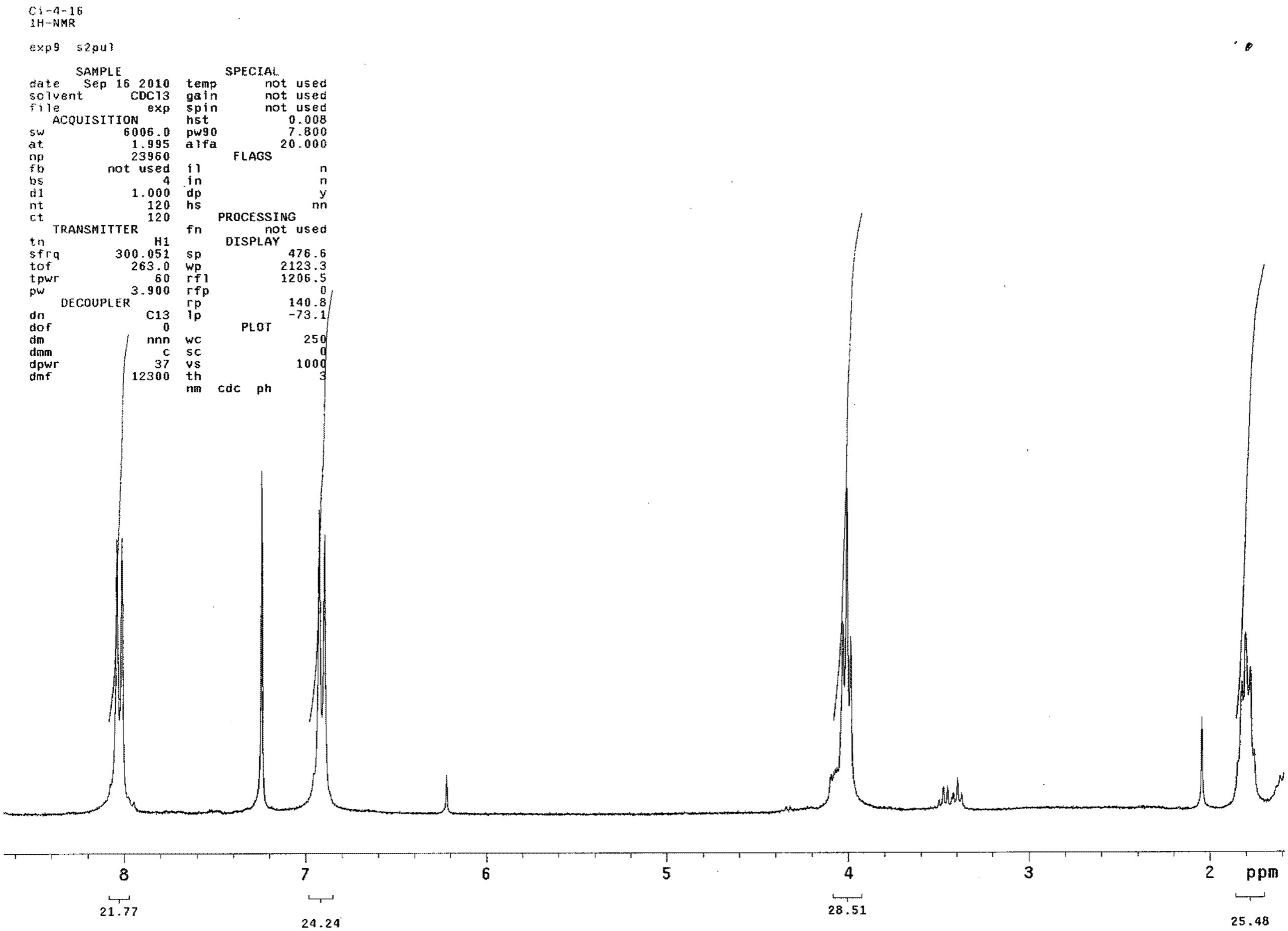

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Ci-4-16
1H-NMR

exp9  s2pul

      SAMPLE                 SPECIAL
date   Sep 16 2010  temp       not used
solvent      CDCl3  gain       not used
file           exp  spin       not used
   ACQUISITION      hst           0.008
sw          6006.0  pw90          7.800
at           1.995  alfa         20.000
np           23960         FLAGS
fb        not used  il                n
bs               4  in                n
d1           1.000  dp                y
nt             120  hs               nn
ct             120       PROCESSING
   TRANSMITTER      fn         not used
tn              H1         DISPLAY
sfrq       300.051  sp            476.6
tof          263.0  wp           2123.3
tpwr            60  rfl          1206.5
pw           3.900  rfp               0
    DECOUPLER       rp            140.8
dn             C13  lp            -73.1
dof              0            PLOT
dm             nnn  wc              250
dmm              c  sc                0
dpwr            37  vs             1000
dmf          12300  th                3
                    nm  cdc  ph
```

IR in cm^{-1}

Tetradecyl

2850 →Confirms alkyl group

1080,1150, & 1700 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

860 →Confirms p-sub. phenyl ring

3000 →Confirms aromatic ring

750→Confirms polymethylene of $C_{14}H_{29}$

IR confirms above structure

Hexyl

2850.0 →Confirms alkyl group

1050,1150, and 1710 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

850 →Confirms p-sub. phenyl ring

3000 →Confirms aromatic ring

750 →Confirms polymethylene of C_6H_{13}

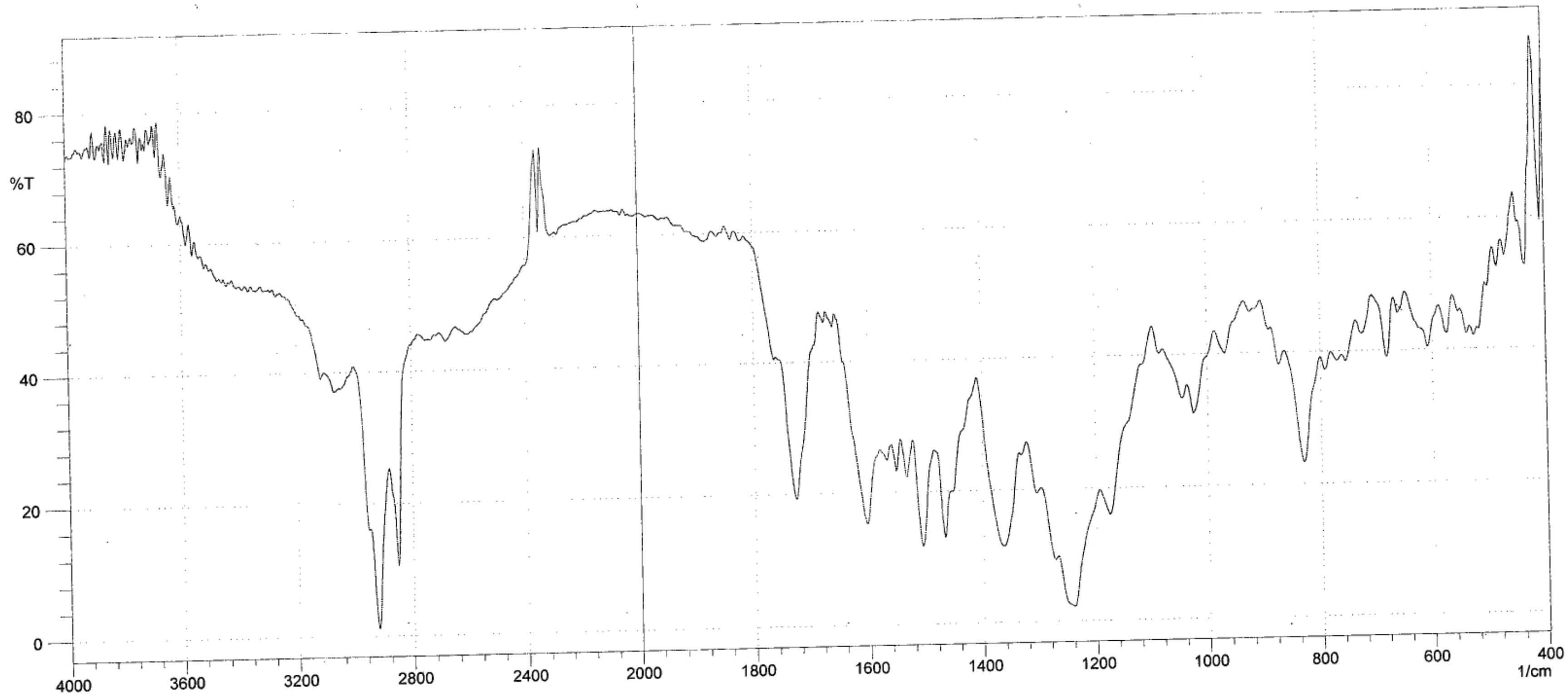
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 04/01/2011

SAMPLE NAME : C 4112

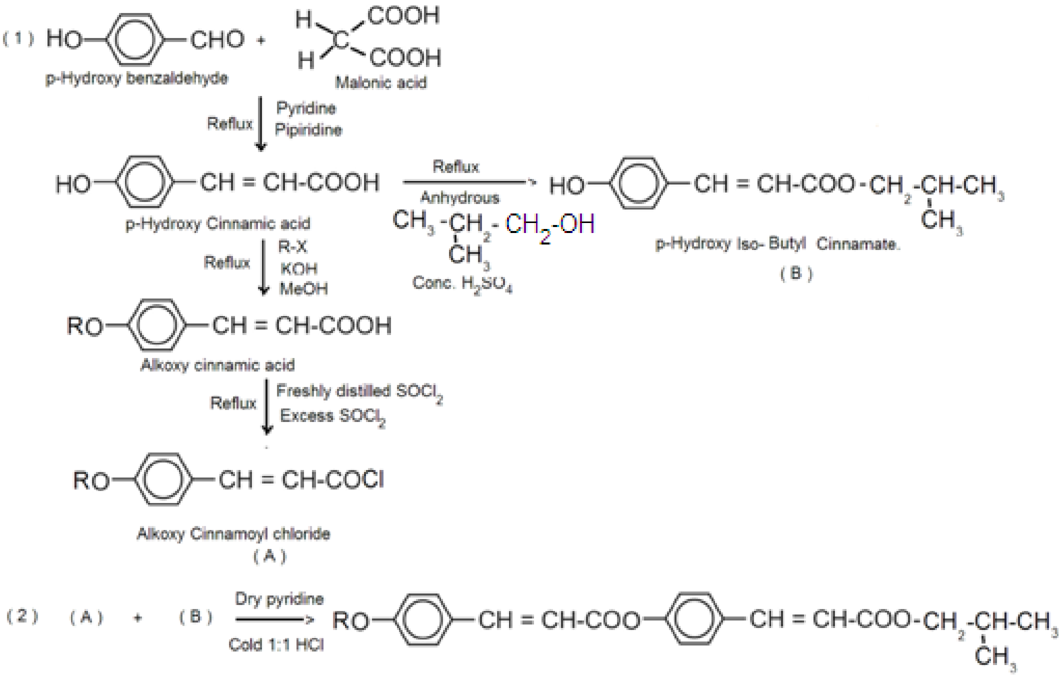


ANALYST : K.J.

No. of Scans; 16

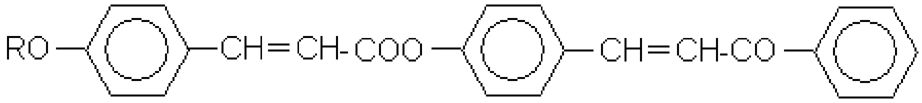
Resolution; 4

Scheme of Synthesis:



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

Synthetic rout to series -8



Cis p-(p'-n-alkoxy cinnamoyloxy) β-benzoyl styrenes.

Table- 18 : Transition Temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	162.0
2	Ethyl	-	-	172.0
3	Propyl	-	-	133.0
4	Butyl	-	-	135.0
5	Pentyl	-	-	172.0
6	Hexyl	-	164.0	179.0
7	Heptyl	-	170.0	178.0
8	Octyl	-	168.0	174.0
9	Decyl	-	115.0	145.0
10	Dodecyl		75.0	122.0
11	Tetradecyl	-	78.0	109.0
12	Hexadecyl	-	80.0	104.0

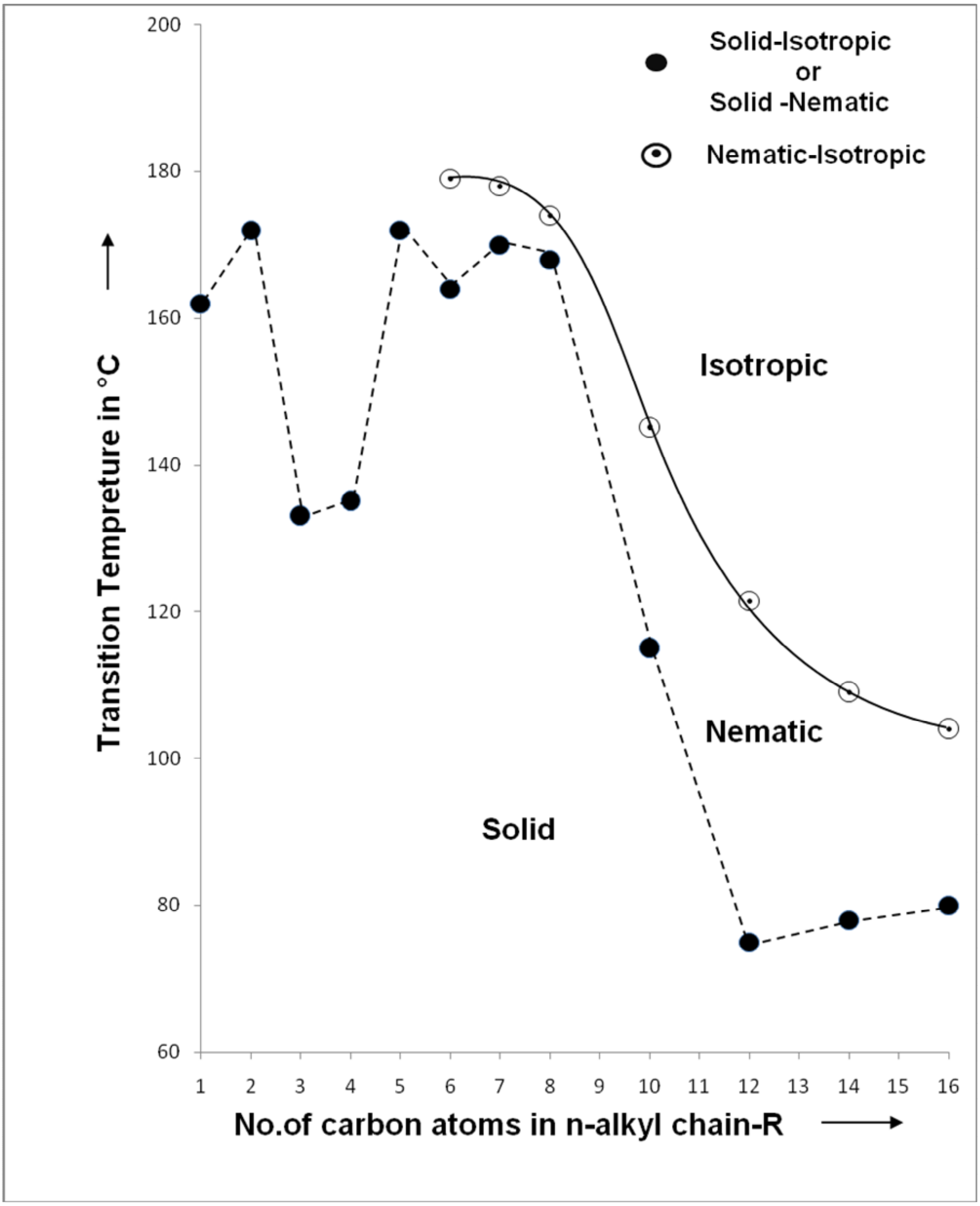
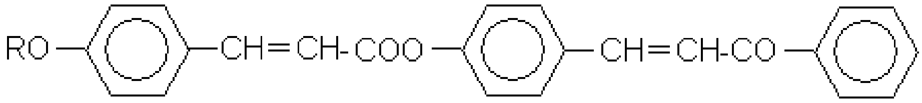


Figure – 22 :Series: p-[p′-n- Alkoxy Cinnamoyloxy] β-benzoyl styrenes

Analytical data:



Cisp-(p'-n-alkoxy cinnamoyloxy) β-benzoyl styrenes.

Table- 19 : Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{25}H_{20}O_4$	78.13	5.21	78.13	5.21
2.	Ethyl	$C_{26}H_{22}O_4$	78.39	5.53	78.33	5.56
3.	Proxyl	$C_{27}H_{24}O_4$	78.64	5.83	78.64	5.87
4.	Butyl	$C_{28}H_{26}O_4$	78.87	6.10	78.77	6.16
5.	Pentyl	$C_{29}H_{28}O_4$	79.09	6.36	79.09	6.39
6.	Hexyl	$C_{30}H_{30}O_4$	79.30	6.61	79.33	6.61
7.	Heptyl	$C_{31}H_{32}O_4$	79.49	6.84	79.59	6.82
8.	Octyl	$C_{32}H_{34}O_4$	79.67	7.05	79.67	7.05
9.	Decyl	$C_{34}H_{38}O_4$	80.00	7.45	80.03	7.46
10.	Dodecyl	$C_{36}H_{42}O_4$	80.30	7.81	80.33	7.81
11.	Tetradecyl	$C_{38}H_{46}O_4$	80.57	8.13	80.57	8.14
12.	Hexadecyl	$C_{40}H_{50}O_4$	80.81	8.42	80.81	8.42

NMR: in ppm :

Octyl

0.840 →Confirms -CH_3

2.490 →Confirms- O-CH_2

3.98 →Confirms -O-CH_2 of –C_8H_{17}

4.4 and 4.0 →Confirms – CH=CH-

6.80, 6.83, 7.74 and 7.78 →Confirms two p-sub. phenyl ring

7.24and 8.02 →Confirms two p-sub. phenyl ring

NMR confirms the structure.

Dodecyl

0.88 →Confirms -CH_3

1.55 →Confirms -CH_2

2.40 →Confirms -OCH_2-CH_2-

3.31 →Confirms -O-CH_2 of $C_{12}H_{25}$

4.48 →Confirms- CH=CH-

6.896 and 6.925, →Confirms Two p-sub.phenyl ring

8.039 and 8.011, →Confirms Two p-sub.phenyl ring

NMR confirms the structure.

```
CA-16
1H-NMR

exp9  s2pul

      SAMPLE              SPECIAL
date   Jan 25 2011   temp       not used
solvent      CDCl3   gain       not used
file           exp   spin       not used
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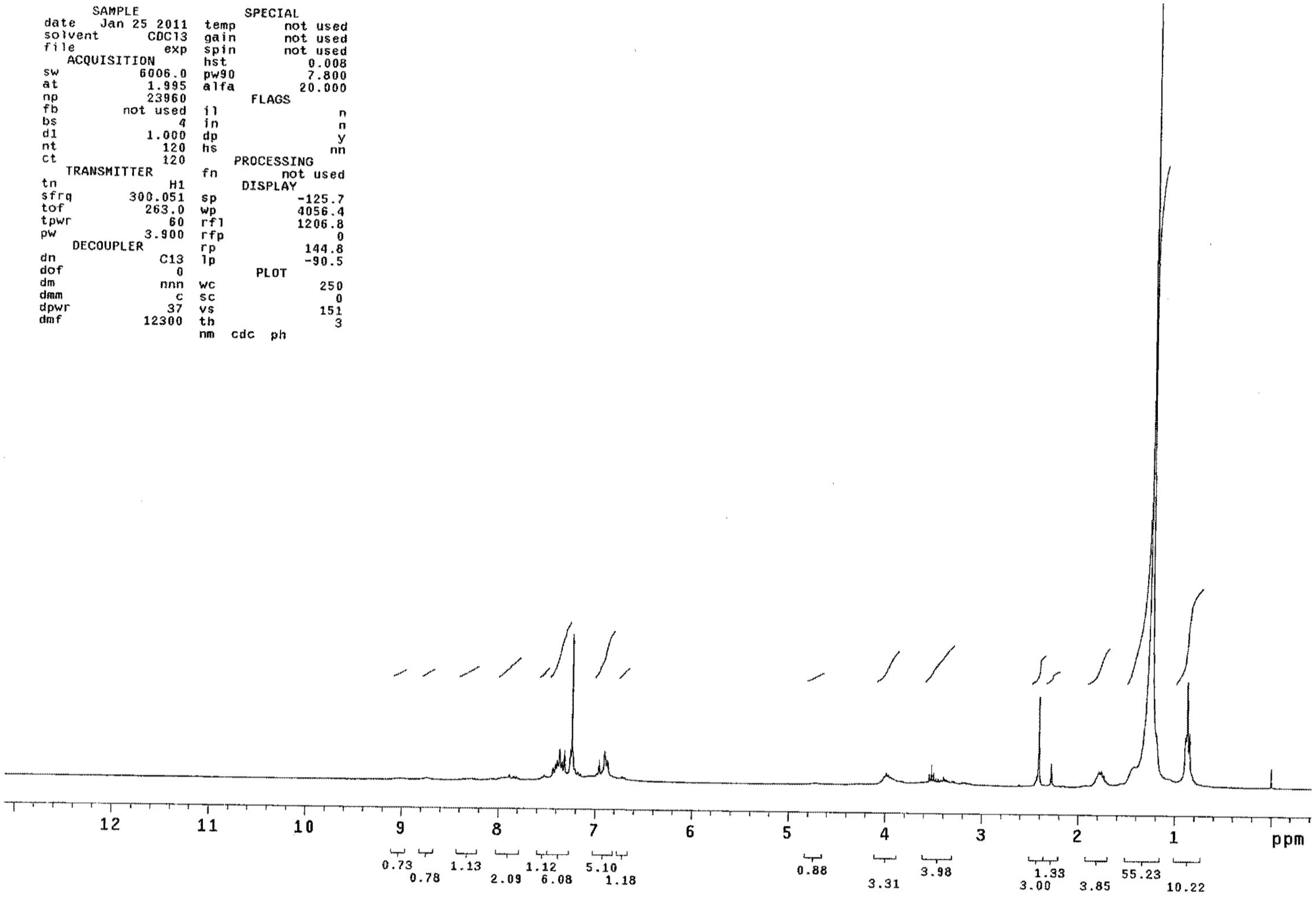
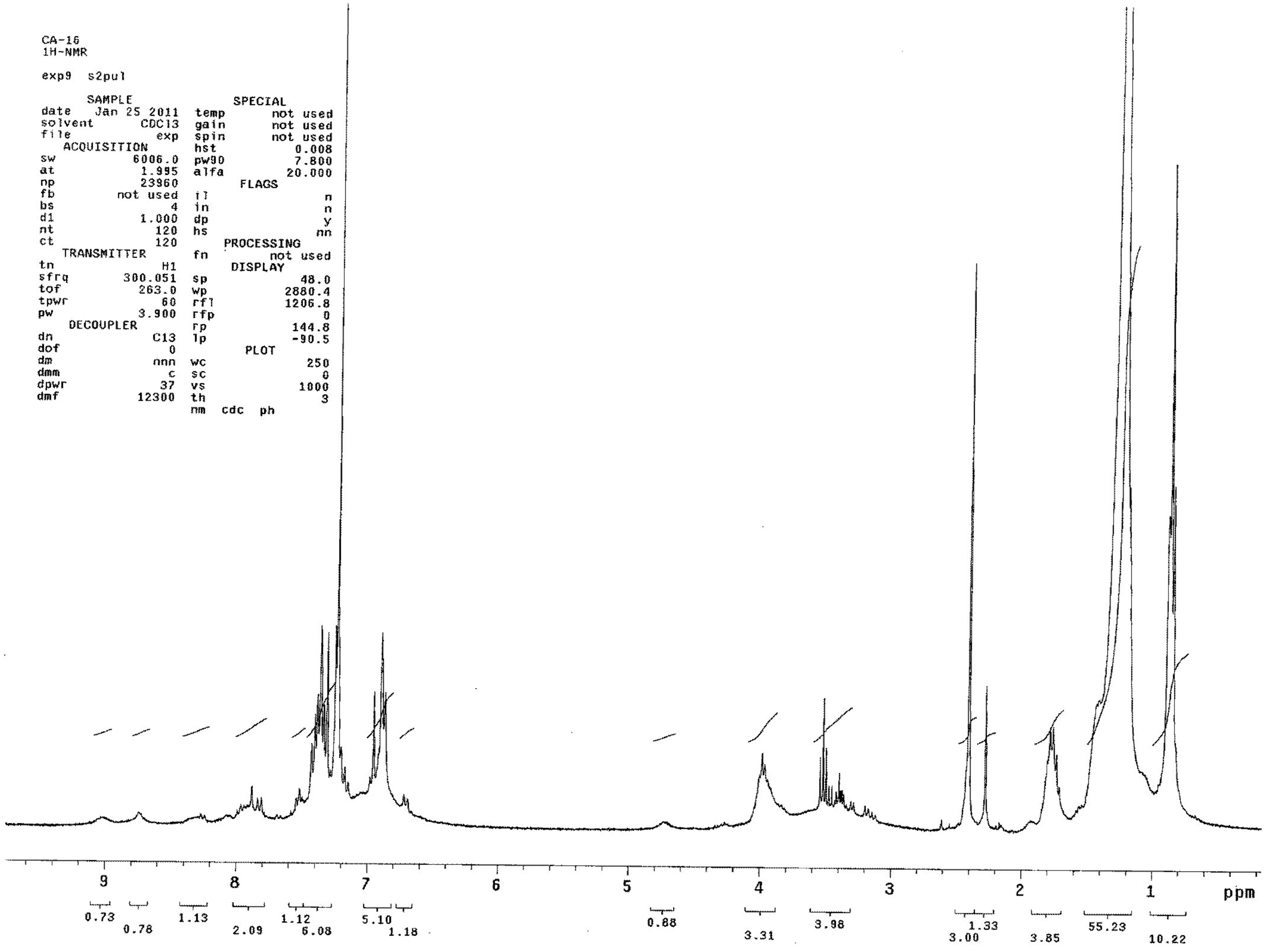
sw          6006.0   pw90          7.800
at           1.995   alfa         20.000
np           23960          FLAGS
fb        not used   il                n
bs               4   in                n
d1           1.000   dp                y
nt             120   hs               nn
ct             120       PROCESSING
   TRANSMITTER       fn         not used
tn              H1          DISPLAY
sfrq       300.051   sp           -125.7
tof          263.0   wp           4056.4
tpwr            60   rfl          1206.8
pw           3.900   rfp               0
    DECOUPLER        rp            144.8
dn             C13   lp            -90.5
dof              0          PLOT
dm             nnn   wc              250
dmm              c   sc                0
dpwr            37   vs              151
dmf          12300   th                3
                     nm   cdc  ph
```




CA-16
1H-NMR
exp9 s2pul
SAMPLE
date Jan 25 2011
solvent CDCl3
file exp
ACQUISITION
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at 1.995
np 23960
fb not used
bs 4
d1 1.000
nt 120
ct 120
TRANSMITTER
tn H1
sfrq 300.051
tof 263.0
tpwr 60
pw 3.900
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 37
dmf 12300
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 7.800
alfa 20.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
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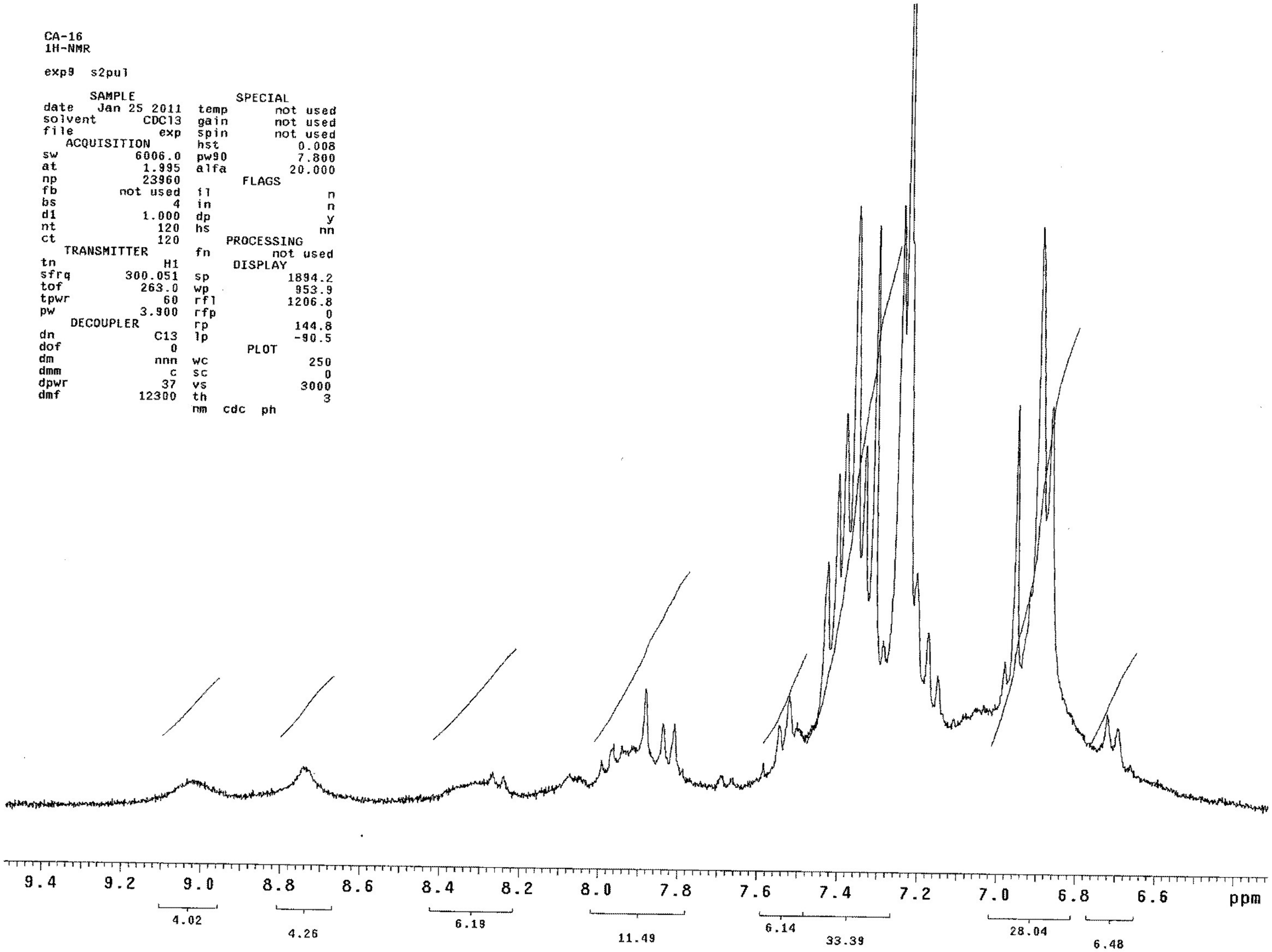
wp 2880.4
rfl 1206.8
rfp 0
rp 144.8
lp -90.5
PLOT
wc 250
sc 0
vs 1000
th 3
nm cdc ph
9
8
7
6
5
4
3
2
1
ppm
0.73
0.78
1.13
2.09
1.12
6.08
5.10
1.18
0.88
3.31
3.98
1.33
3.00
3.85
55.23
10.22



```
CA-16
1H-NMR

exp9  s2pul

       SAMPLE                 SPECIAL
date    Jan 25 2011   temp        not used
solvent       CDCl3   gain        not used
file            exp   spin        not used
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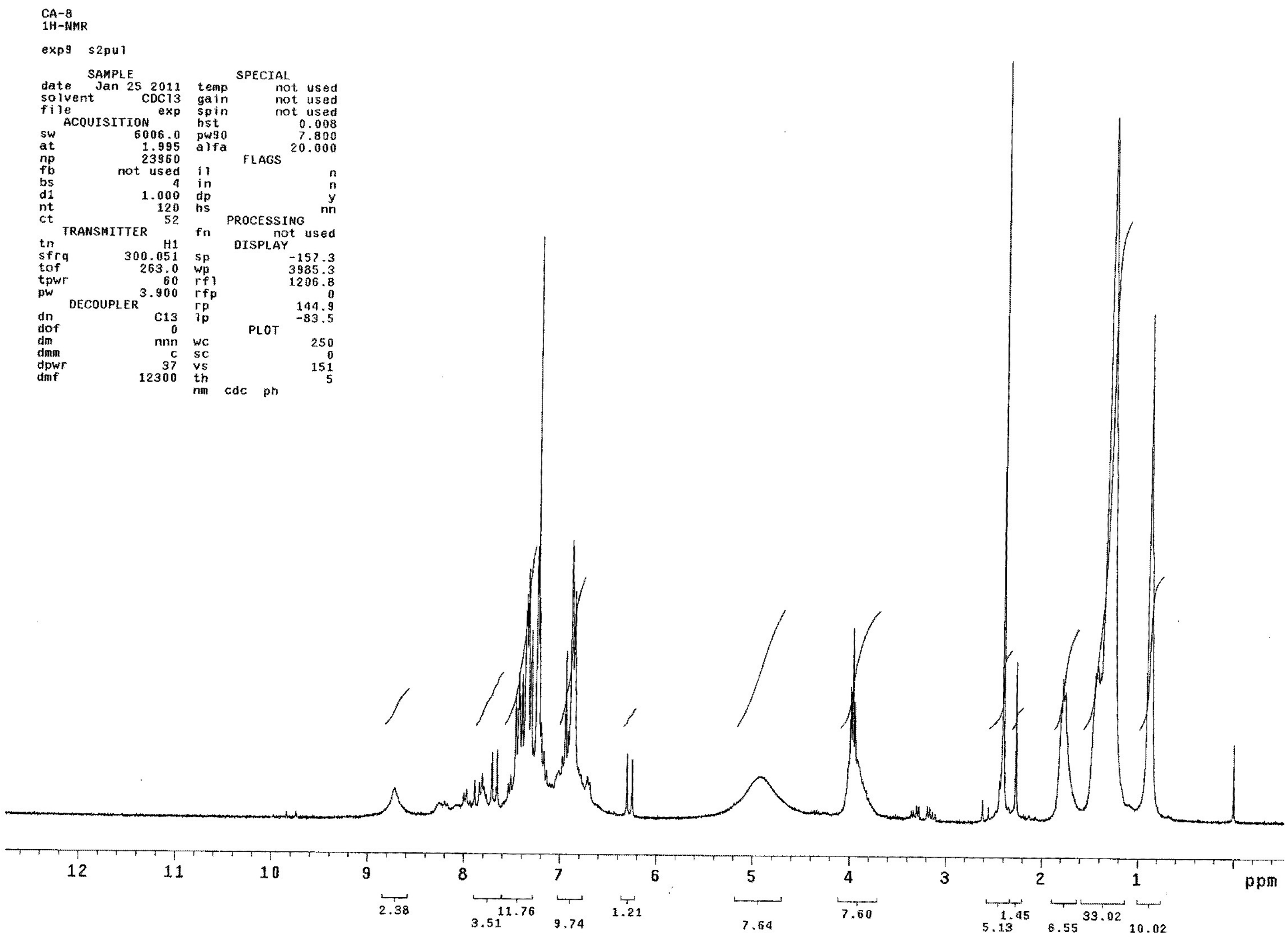
sw           6006.0   pw90           7.800
at            1.995   alfa          20.000
np            23960          FLAGS
fb         not used   il                 n
bs                4   in                 n
d1            1.000   dp                 y
nt              120   hs                nn
ct              120        PROCESSING
    TRANSMITTER       fn          not used
tn               H1          DISPLAY
sfrq        300.051   sp            1894.2
tof           263.0   wp             953.9
tpwr             60   rfl           1206.8
pw            3.900   rfp                0
     DECOUPLER        rp             144.8
dn              C13   lp             -90.5
dof               0           PLOT
dm              nnn   wc               250
dmm               c   sc                 0
dpwr             37   vs              3000
dmf           12300   th                 3
                      nm   cdc   ph
```



```
CA-8
1H-NMR

exp9  s2pul

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solvent       CDCl3   gain        not used
file            exp   spin        not used
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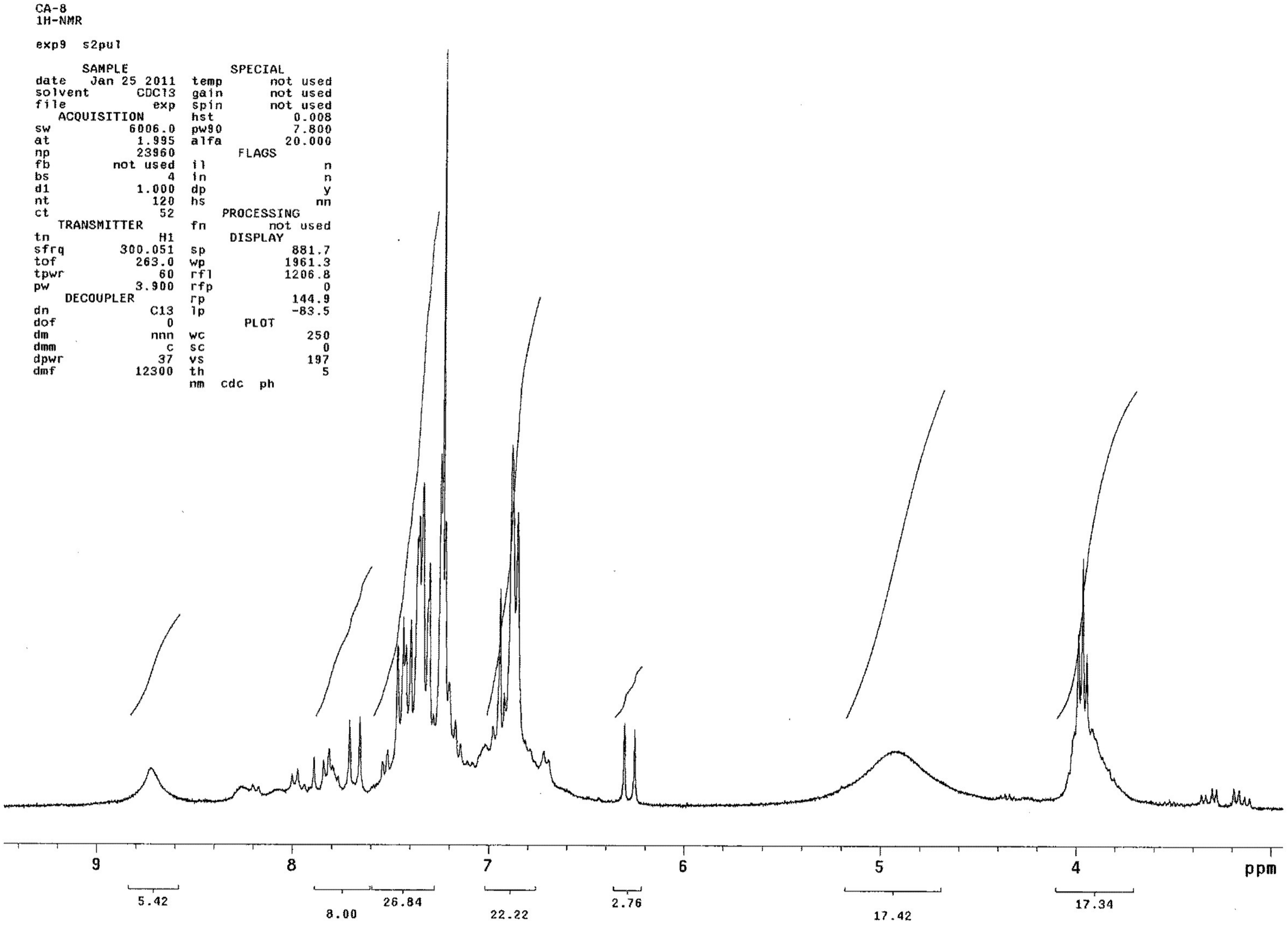
sw           6006.0   pw90           7.800
at            1.995   alfa          20.000
np            23960          FLAGS
fb         not used   il                 n
bs                4   in                 n
d1            1.000   dp                 y
nt              120   hs                nn
ct               52        PROCESSING
   TRANSMITTER        fn          not used
tn               H1          DISPLAY
sfrq        300.051   sp            -157.3
tof           263.0   wp            3985.3
tpwr             60   rfl           1206.8
pw            3.900   rfp                0
    DECOUPLER         rp             144.9
dn              C13   lp             -83.5
dof               0            PLOT
dm              nnn   wc               250
dmm               c   sc                 0
dpwr             37   vs               151
dmf           12300   th                 5
                      nm   cdc   ph
```



```
CA-8
1H-NMR

exp9  s2pul

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solvent       CDCl3  gain       not used
file            exp  spin       not used
   ACQUISITION       hst           0.008
sw           6006.0  pw90          7.800
at            1.995  alfa         20.000
np            23960           FLAGS
fb         not used  il               n
bs                4  in               n
d1            1.000  dp               y
nt              120  hs              nn
ct               52        PROCESSING
   TRANSMITTER       fn         not used
tn               H1          DISPLAY
sfrq        300.051  sp            881.7
tof           263.0  wp           1961.3
tpwr             60  rfl          1206.8
pw            3.900  rfp               0
    DECOUPLER        rp            144.9
dn              C13  lp            -83.5
dof               0           PLOT
dm              nnn  wc              250
dmm               c  sc                0
dpwr             37  vs              197
dmf           12300  th                5
                     nm  cdc  ph
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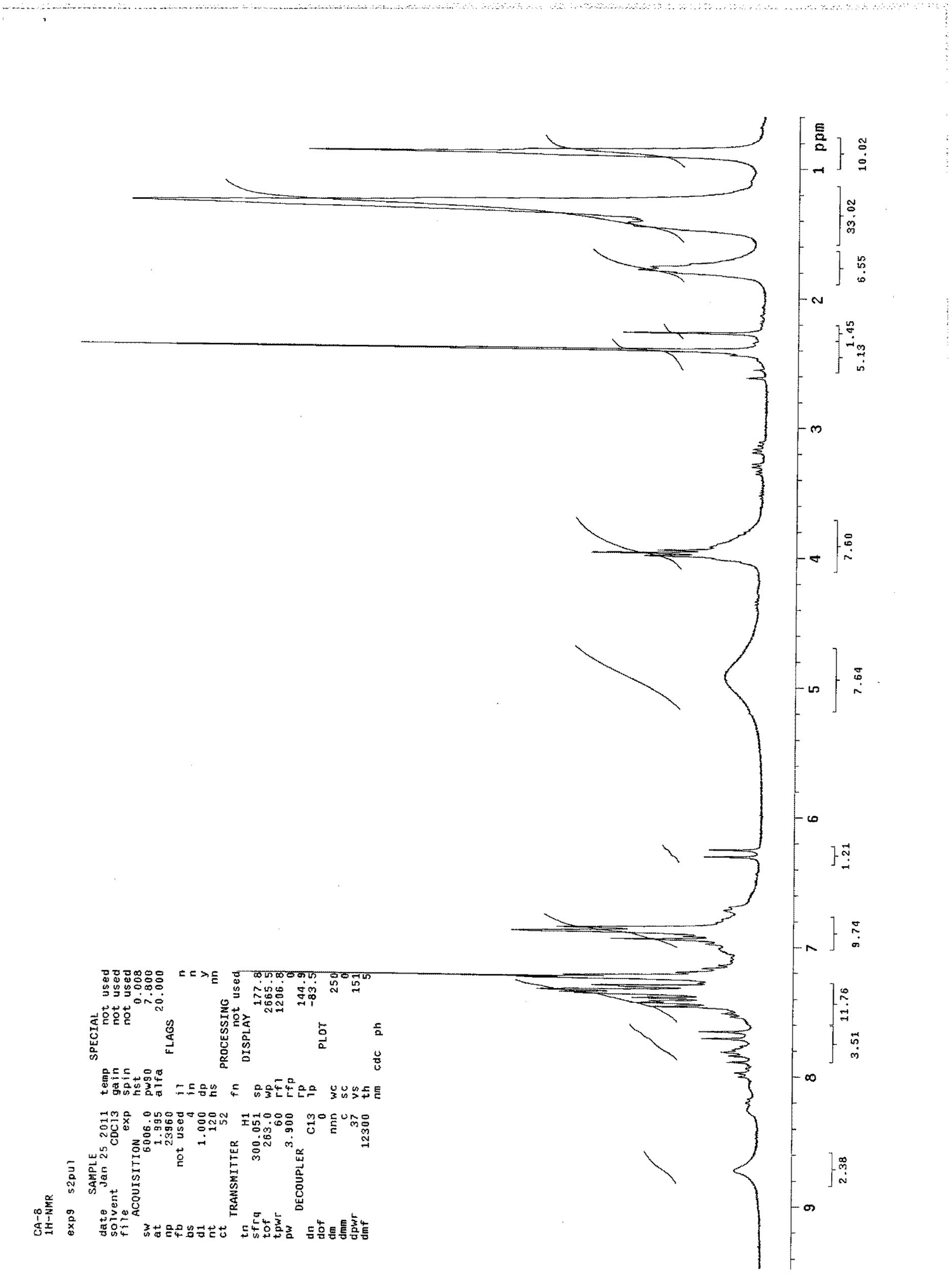
CA-8
1H-NMR
exp9 s2pul
SAMPLE
date Jan 25 2011
solvent CDCl3
file exp
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sw 6006.0
at 1.995
np 23960
fb not used
bs 4
d1 1.000
nt 120
ct 52
TRANSMITTER
tn H1
sfrq 300.051
tof 263.0
tpwr 60
pw 3.900
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 37
dmf 12300
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pw90 7.800
alfa 20.000
FLAGS
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in n
dp y
hs nn
PROCESSING
fn not used
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wp 2665.5
rfl 1206.8
rfp 0
rp 144.9
lp -83.5
PLOT
wc 250
sc 0
vs 151
th 5
nm cdc ph
9
8
7
6
5
4
3
2
1 ppm
2.38
3.51
11.76
9.74
1.21
7.64
7.60
5.13
1.45
6.55
33.02
10.02

IR in cm^{-1}

Hexyl

2900.0 →Confirms alkyl group

1040,1220, & 1690 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

830 →Confirms p-sub. phenyl ring

3000→ Confirms aromatic ring,=CH-

1170→ Confirms ether linkage –O-

740 →Confirms polymethylene of C_6H_{13}

IR confirms above structure

Tetradecyl

2830.0 →Confirms alkyl group

1030, 1200, & 1680 →Confirms –COO- group

660 →Confirms cis –CH=CH- group

840 →Confirms p-sub. phenyl ring

2950 →Confirms aromatic ring=CH-

1160→ Confirms ether linkage –O-

750 →Confirms polymethylene of $C_{14}H_{29}$

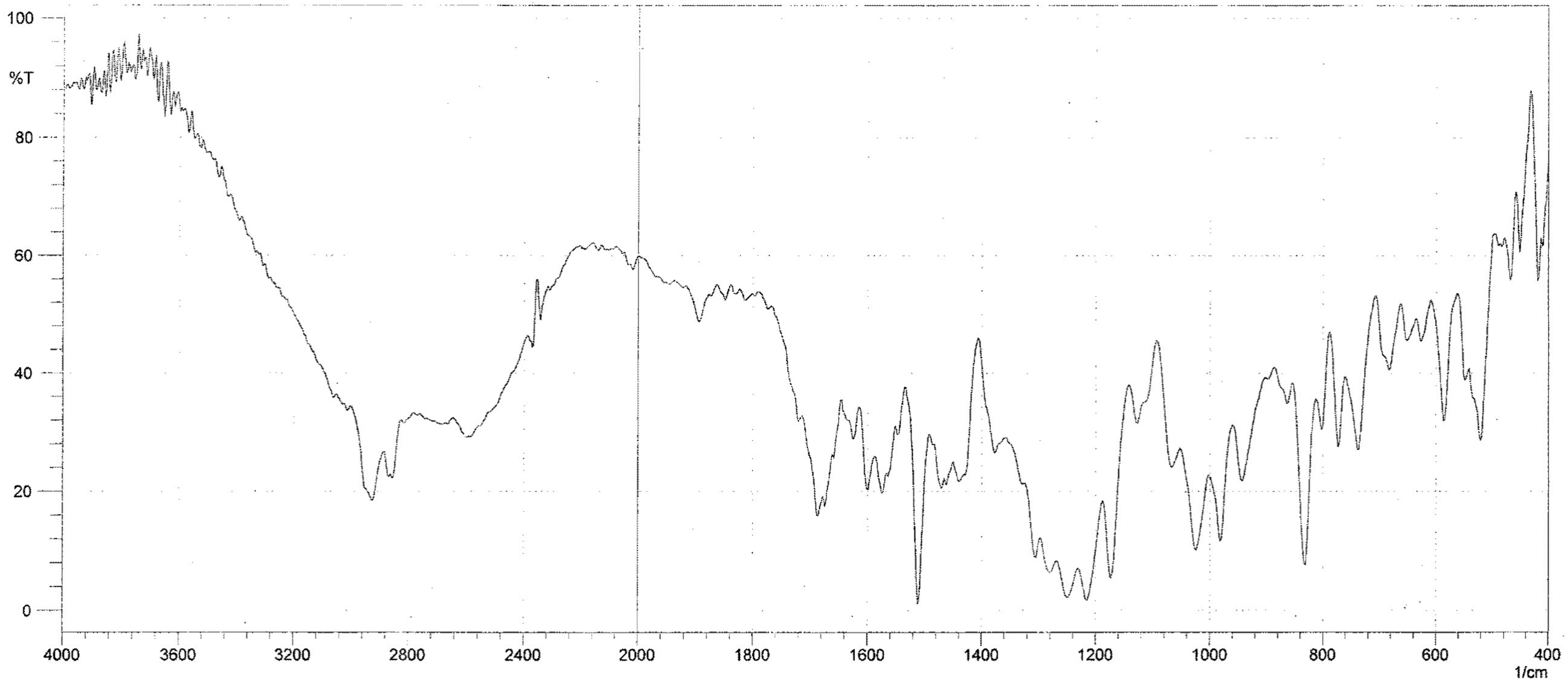
IR confirms above structure

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 10/01/2011

SAMPLE NAME : CA-6



No. of Scans; 16

ANALYST : K.J.

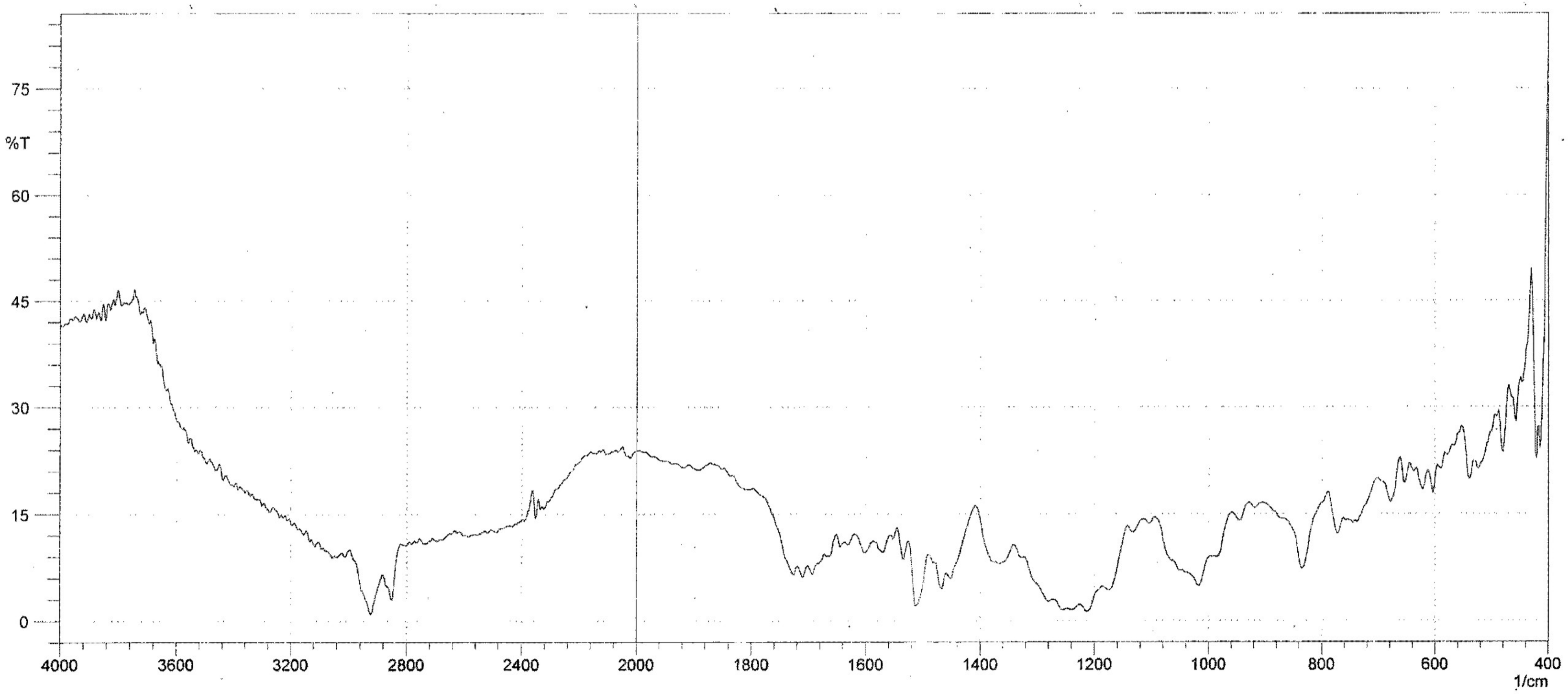
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 10/01/2011

SAMPLE NAME : CA-10

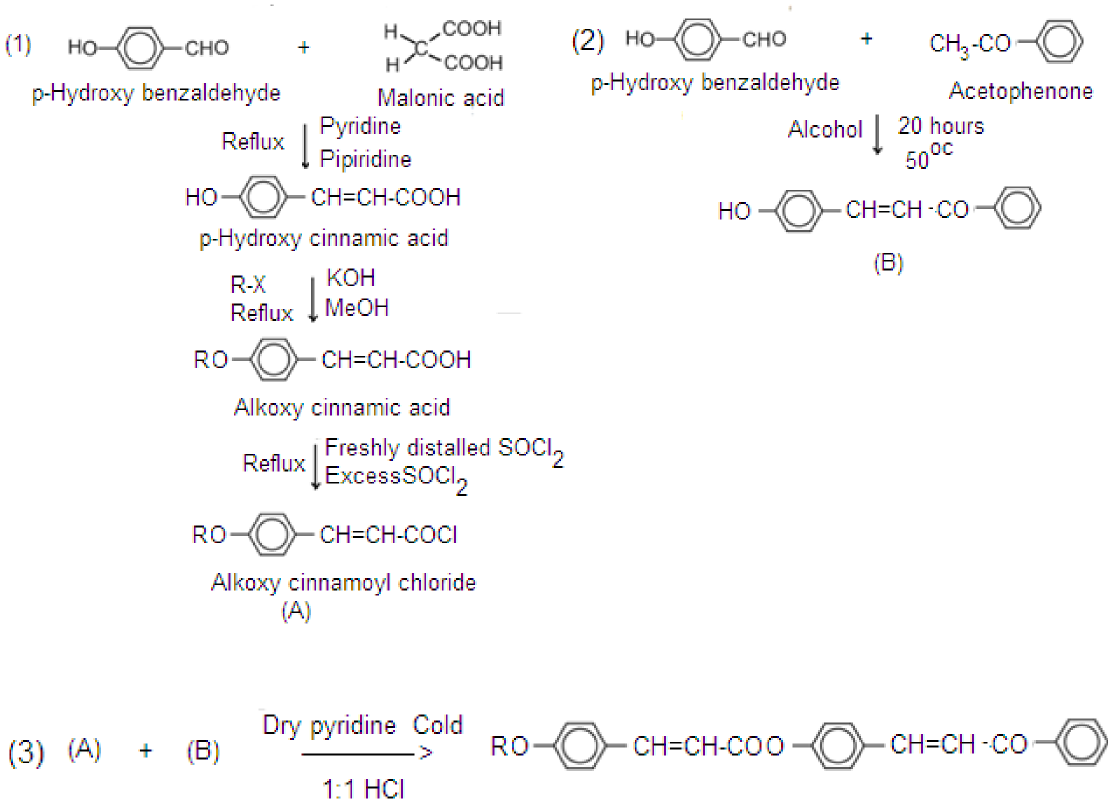


ANALYST : K.J.

No. of Scans; 16

Resolution; 4

Scheme of Synthesis:



Where R= C_nH_{2n+1}, n=1,2,3,4,5,6,8,10,12,14 and16.

Synthetic rout to series -9

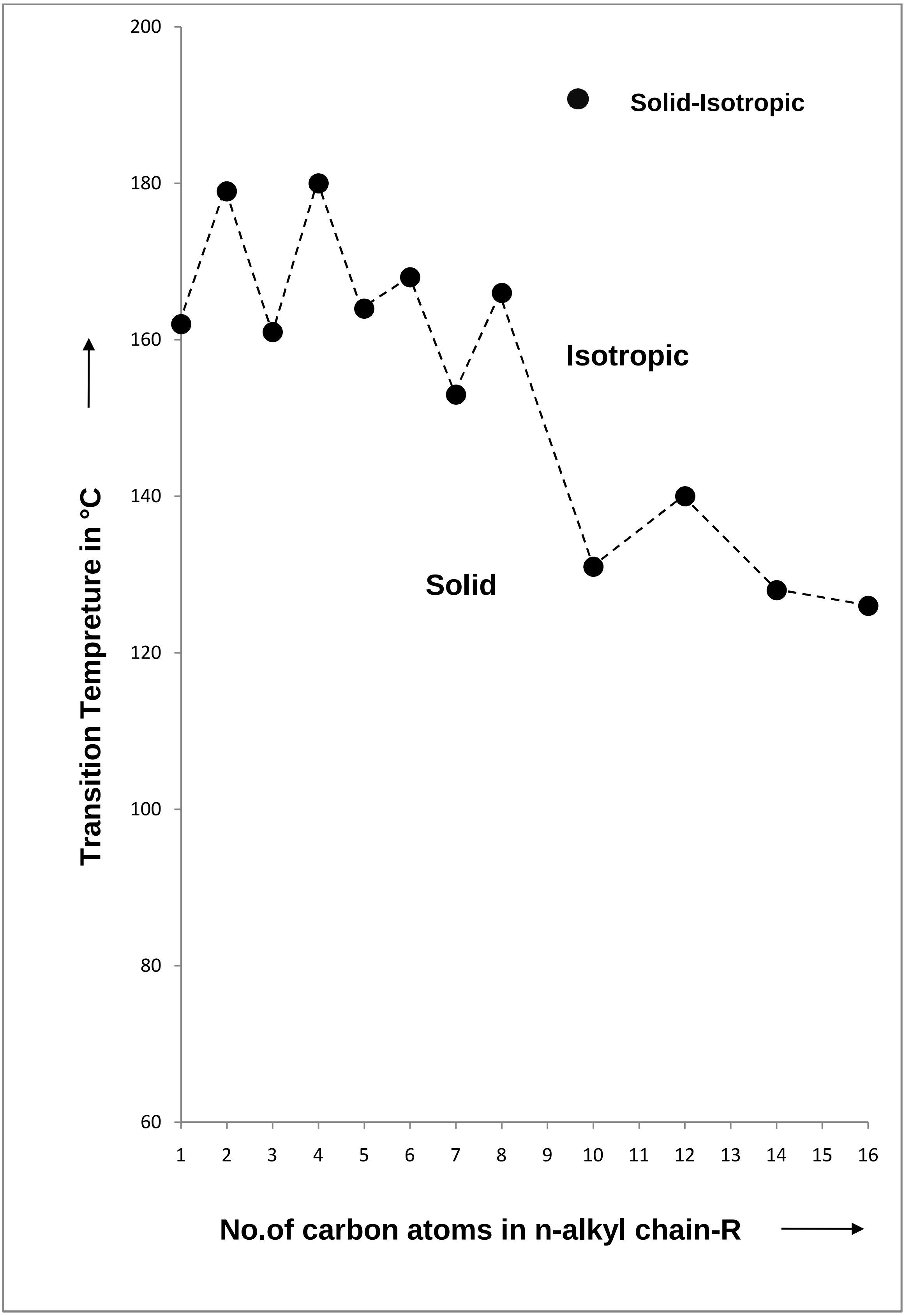


Figure- 22 (a) **: Cis n-Alkoxy Cinnamic acids**

IR: in cm^{-1}

Pentyl

720.0 → Confirms Poly –CH_2 of C_5H_{11}

1050, 1150, 1650 →Confirms –CO- group of ester

850.0 →Confirms p-sub. Phenyl ring

2500 to 2750 (broad peak) →Confirms (COOH) group

650 →Confirms cis –CH=CH- group

I R confirms the structure.

M.P. →164.0^{0C}

Hexyl

750.0 → Confirms Poly –CH_2 of C_6H_{13}

1240, 1700 →Confirms –CO- group of ester

830.0 →Confirms p-sub. Phenyl ring

2500 to 2900 (broad peak) →Confirms (COOH) group

670 →Confirms cis –CH=CH- group

I R confirms the structure

M.P. →168.0^{0C}

Octyl

110.0 → Confirms Poly –CH_2 of C_5H_{11}

1050, 1250, 1700 →Confirms –CO- group of ester

840.0 →Confirms p-sub. Phenyl ring

2800 to 3000 (broad peak) →Confirms (COOH) group

700 →Confirms cis –CH=CH- group

I R confirms the structure.

M.P. →166.0^{0C}

Decyl

735.0 → Confirms Poly –CH_2 of $C_{10}H_{21}$

1050, 1230, 1750 →Confirms –CO- group of ester

830.0 →Confirms p-sub. Phenyl ring

2500 to 2700 (broad peak) →Confirms (COOH) group

640 →Confirms cis –CH=CH- group

I R confirms the structure

M.P. →131.0^{0C}

Dodecy

740.0 → Confirms Poly –CH_2 of $C_{12}H_{25}$

1050, 1200, 1700 →Confirms –CO- group of ester

840.0 →Confirms p-sub. Phenyl ring

2800 to 2900 (broad peak) →Confirms (COOH) group

650 →Confirms cis –CH=CH- group

I R confirms the structure.

M.P. →140.0^{0C}

Tetradecyl

740.0 → Confirms Poly –CH_2 of $C_{14}H_{29}$

1150, 1250, 1700 →Confirms –CO- group of ester

840.0 →Confirms p-sub. Phenyl ring

2800 to 2900 (broad peak) →Confirms (COOH) group

670 →Confirms cis –CH=CH- group

I R confirms the structure

M.P. →128.0^{0C}

Hexadecyl

720.0 → Confirms Poly –CH_2 of $C_{16}H_{33}$

1150, 1250, 1700 →Confirms –CO- group of ester

850.0 →Confirms p-sub. Phenyl ring

2800 to 2900 (broad peak) →Confirms (COOH) group

670 →Confirms cis –CH=CH- group

I R confirms the structure

M.P. →126.0^{0C}

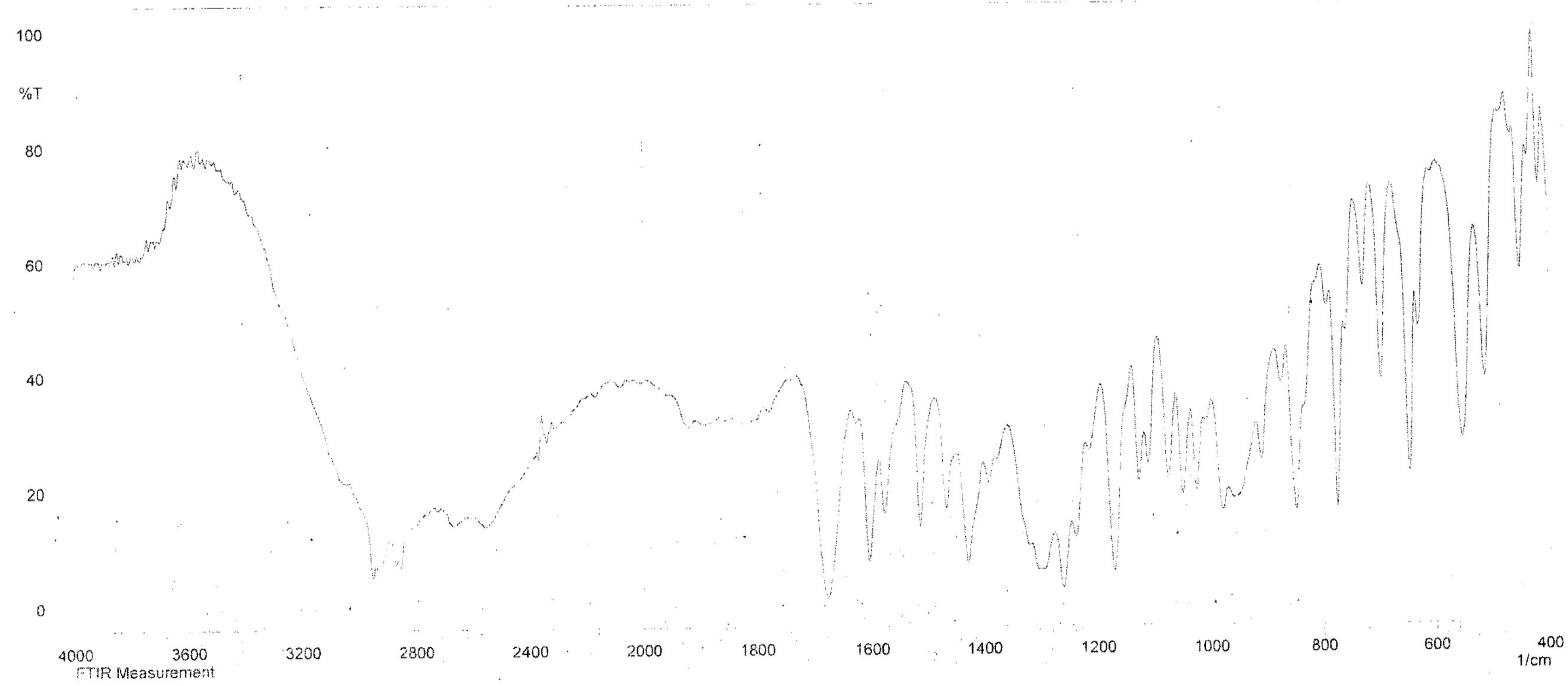
Note :- Methoxy derivatives was prepared by reaction of p-hydroxy cinnamic acid and dimethyl sulphate. Rest of the homologues alkylated by corresponding alklyhalide.

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 26/11/2010

SAMPLE NAME : 5



ANALYST : H.P.

No. of Scans; 16

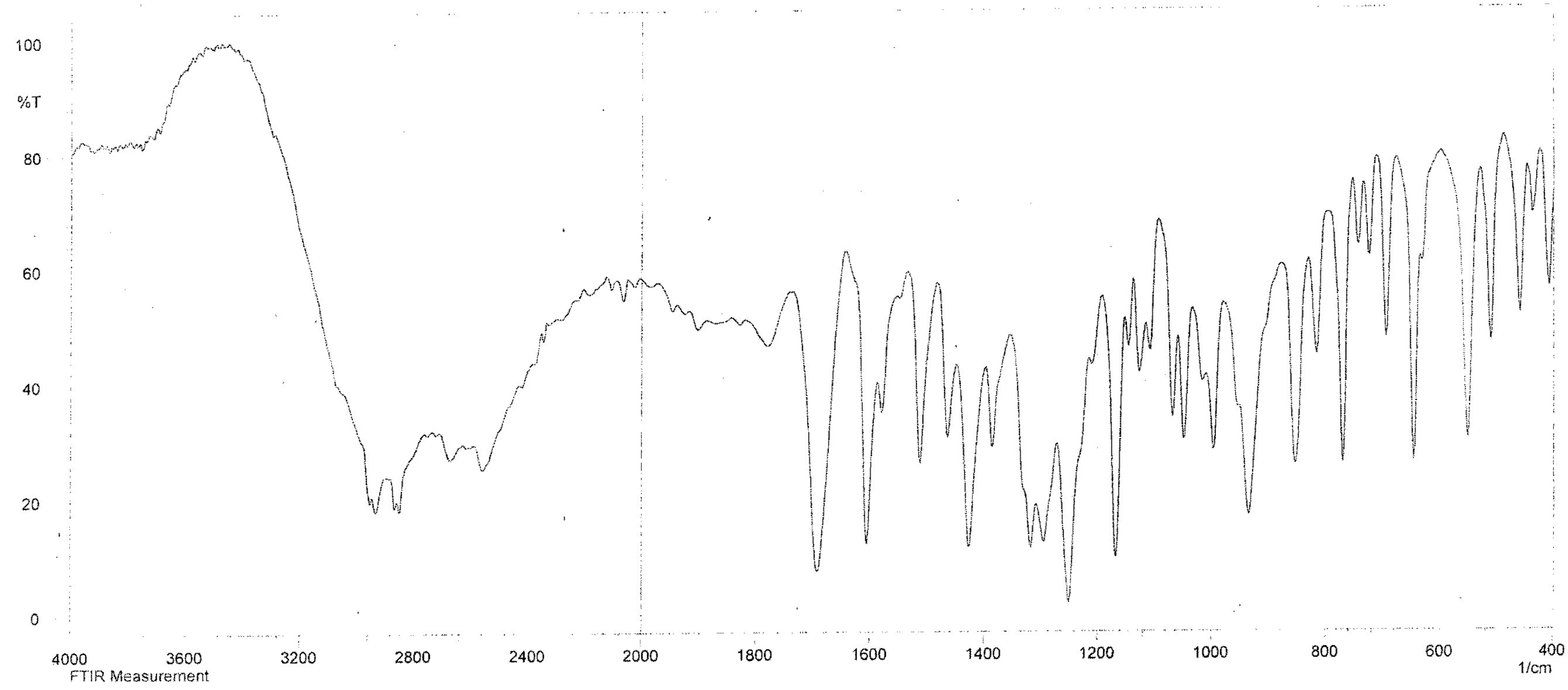
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 25/02/2011

SAMPLE NAME : C6



ANALYST : K.J.

No. of Scans; 16

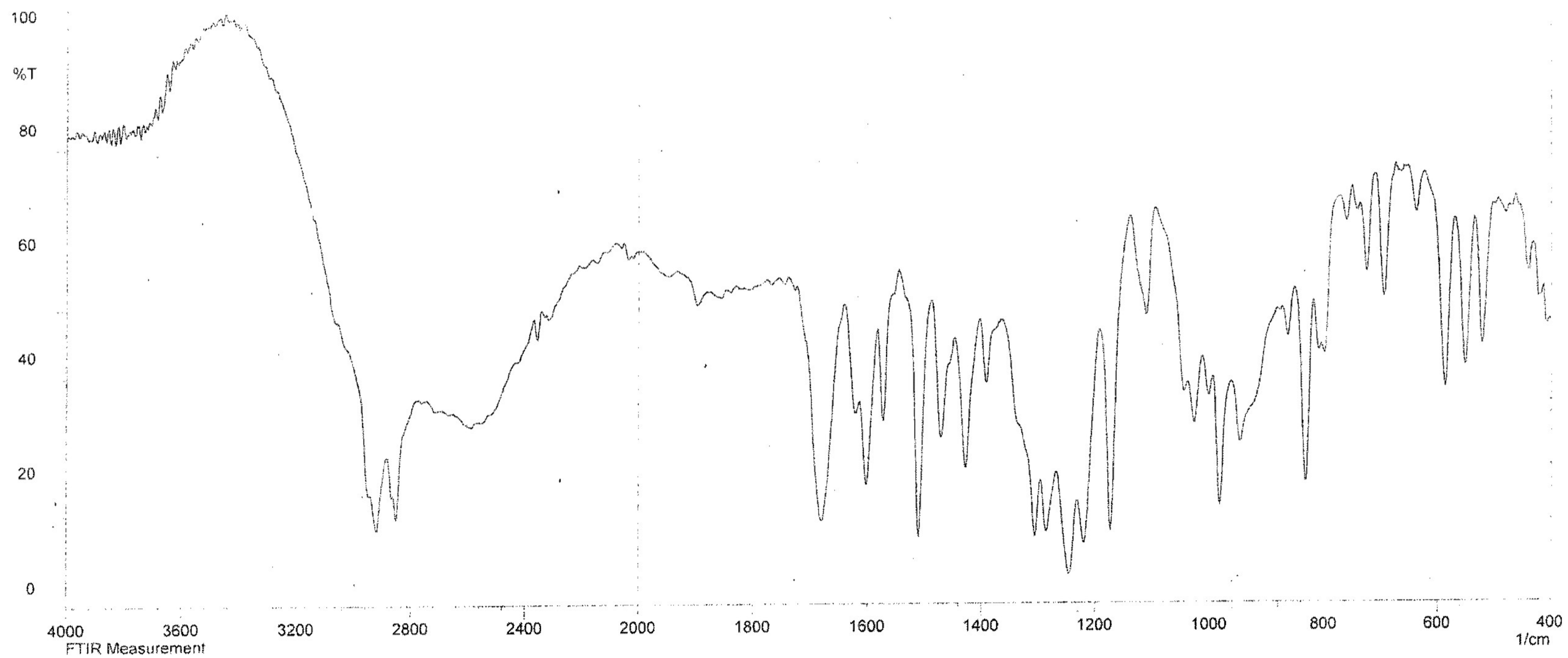
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 25/02/2011

SAMPLE NAME : P - OCTOXY CINNAMIC ACID ,B#C8



ANALYST : K.J.

No. of Scans; 16

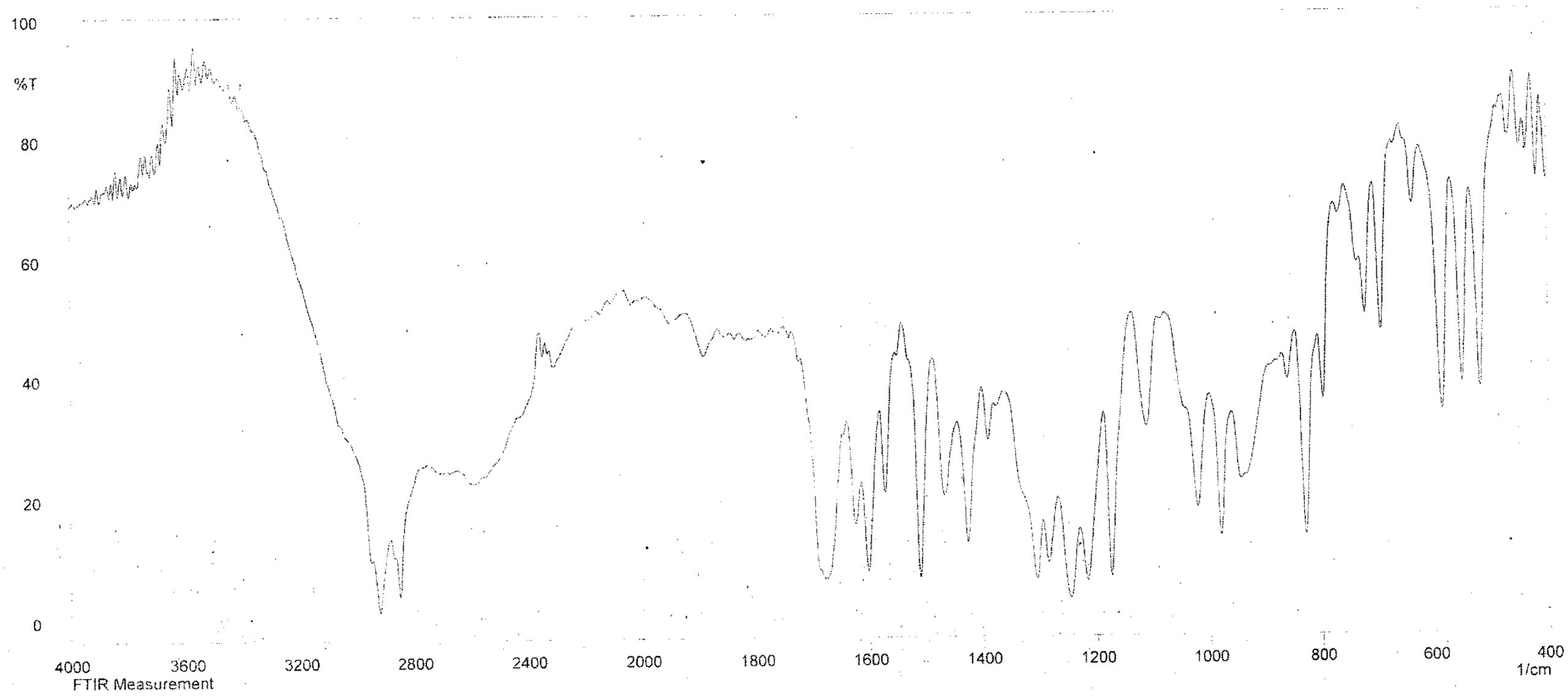
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 26/11/2010

SAMPLE NAME : 10



ANALYST : H.P.

No. of Scans; 16

Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 25/02/2011

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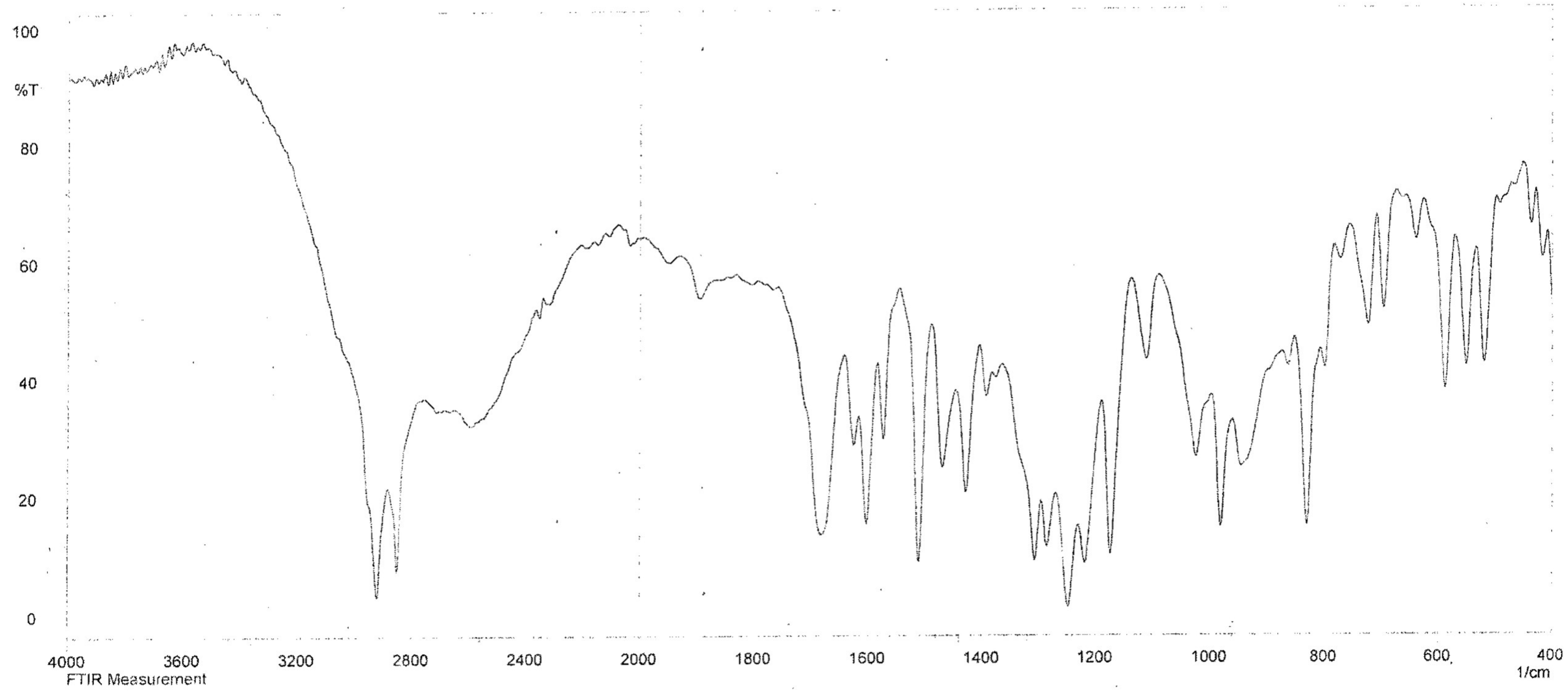

ANALYST : K.J.

No. of Scans; 16

Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 25/02/2011

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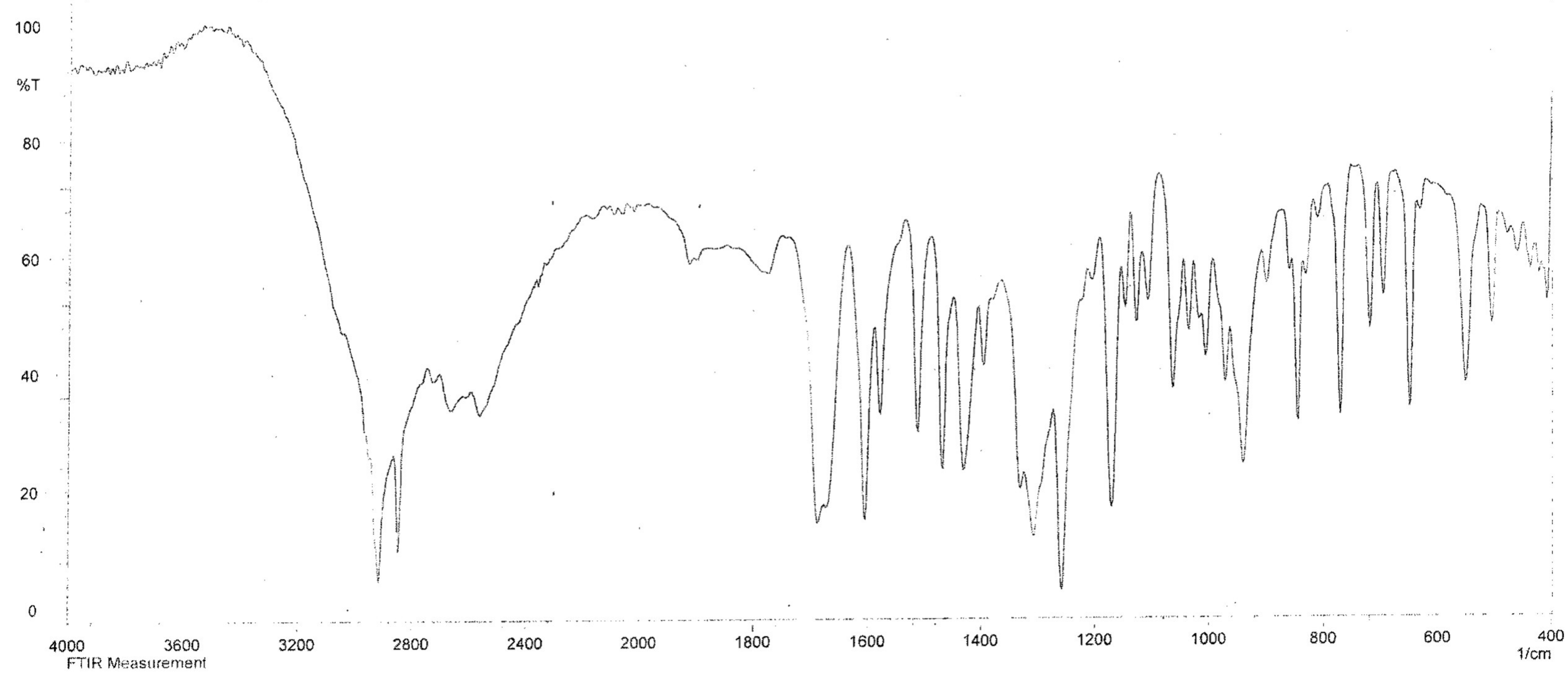


ANALYST : K.J.

No. of Scans; 16

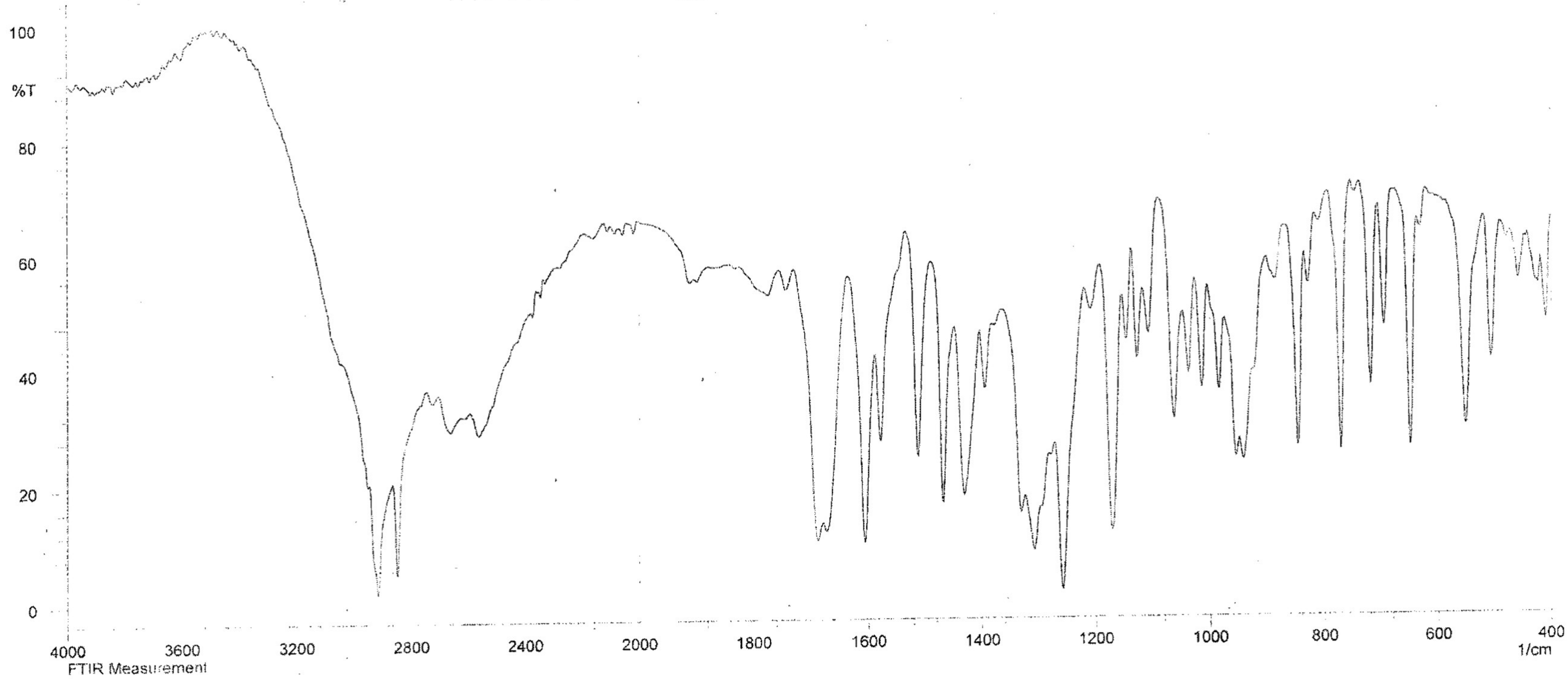
Resolution; 4

SHIMADZU

VAIBHAV ANALYTICAL SERVICES

DATE : 25/02/2011

SAMPLE NAME : C 16



ANALYST : K.J.

No. of Scans; 16

Resolution; 4

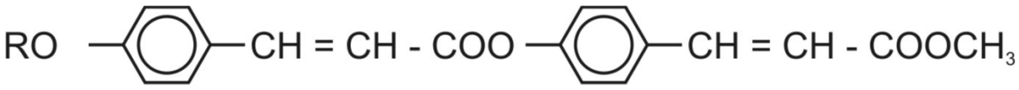
Chapter-4

RESULTS AND DISCUSSION:

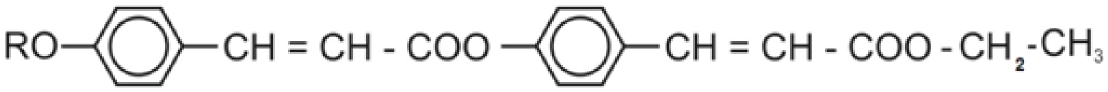
Homologus series:

The present investigation has been inspired with the desire to search for new liquid crystals or nonamphiphiles which may be endowed with specific characteristics. The synthesis had been undertaken after giving due consideration to the moleculer geomentry enhancing the potential probability of the new compounds to exhibit mesomorphism preferably in the lower range of temperature. The generalization concerning mesophases get strengthened from the present investigation, as the results obtained supports the generally accepted criteria and some new trends of transition curves and characteristics. The following homologous series have been synthesized and their characteristics have been determined.

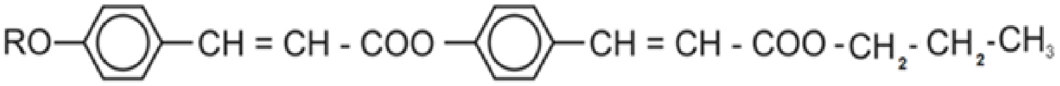
1.Methyl p-(-p'-n-alkoxy cinnamoyloxy) cinnamates.



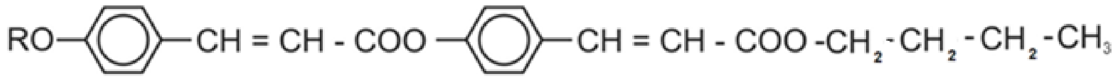
2.Ethyl p-(-p'-n-alkoxy cinnamoyloxy) cinnamates



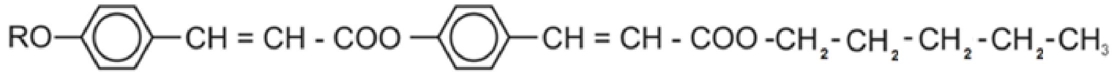
3.n-Propyl p-(-p'-n-alkoxy cinnamoyloxy) cinnamates



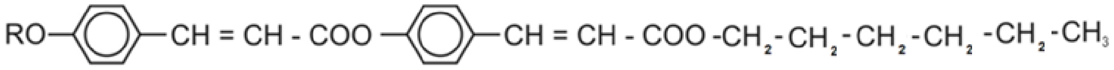
4.n-Butyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates



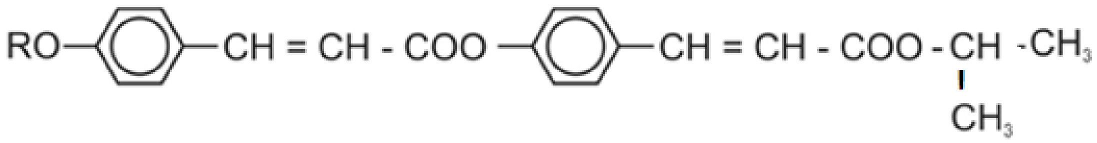
5.n-Pentyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates



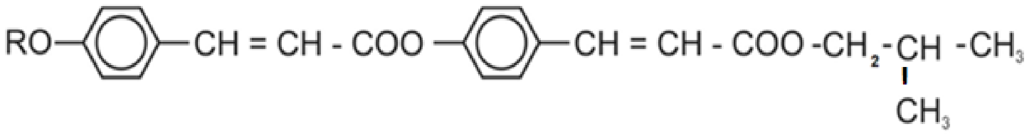
6.n-Hexyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates



7.Isopropyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates



8. Isobutyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates



Where R stands for n- alkyl chain in alkoxy group from C_1 to C_8, C_{10}, C_{12}, C_{14}, C_{16}..

9. p-(p’-n-alkoxy cinnamoyloxy) β-benzoyl styrene.

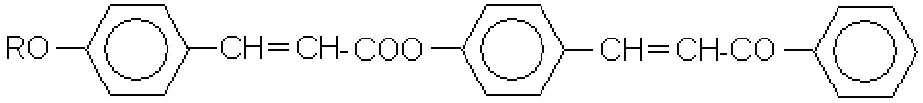


Figure-23

The synthesis involved four or five steps through known routes as discussed in experimental part of this thesis. Care was taken for obtaining the homologue substances in pure form. The elemental analysis conformed with the calculated one and structure of some homologues were confirmed by IR and ^{1}HNMR spectra. Enthalpy (ΔH) and entropy (ΔS) concept discussed qualitatively without peak value temperature from D.S.C. scan. Textures of homologues confirmed by miscibility method.

The 105 new compounds have been synthesized in this investigation, and 69 of them are found liquid crystals in nature. The molecular geometry as designed for the left hand and right hand alkyl chain is that of normal / iso linking with vinyl carboxy central bridge, in case of homologous series (1) to (8) and in case of homologous series (9) right handed terminal end group and central bridge varied as –H and –CH=CH-CO- respectively.

It can be seen that the molecules of all these homologous series from (1) to (6) possess.

(1). Two phenyl rings.

(2). Central bridge –CH=CH-COO- the stereochemistry of the unit does

however preserve the non-linearity of the molecule

(3). Terminal groups of varying polarity (-CH=CH-COOR’)

Where R’ = C_nH_{2n+1} where n = 1 to 6

(4). An overall length to breadth ratio besides linearity. 4- homologous series (7),(8)

and (9) differ in respect of terminal group viz; iso linkage C_3H_7 and C_4H_9 with –CH=CH-COO- (series-7 and -8) and –CH=CH-CO-C_6H_5 in series (9).

Above factors favour the exhibition of mesomorphic property in the homologues of the above mentioned cis configurated homologous series. However, some of the homologues [homologues] display nonmesomorphic behavior due to their high crystalising tendency, which arises due to the absence of anisotropic intermolecular forces of unsuitable magnitude as a consequence of molecular rigidity and flexibility.

Mesomorphic Characteristics of the Individual series:

1.Homologous series Methyl-p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

Methyl and ethyl derivatives of titled homologous series are nonmesomorphic, while propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives are enantiotropic nematic. None of the homologues is smectogenic even in the monotropic condition. Number of carbon atoms in the n-alkyl chain of left n-alkoxy end group are plotted versus the transition temperatures of homologues from **table-2**. Smooth curves are drawn through the like points and phase diagram **(figure-14)** is obtained. Careful observation of a phase diagram **(Figure-14)** shows that, solid-isotropic or solid-nematic transition curve directly falls from first to the fourth and than follows zigzag path of rising and falling upto fourteenth homologue and than, instead of subsequent rising, it falls to the hexadecyl derivative and behaves in a normal manner. Nematic-isotropic transition curve falls by five degree centigrade and then rises and again falls smoothly as series is ascended with normal behavior. Odd-even effect is not observed in nematic-isotropic transition curve. Transition temperatures and melting temperatures are relatively high as compared to other homologous series with -COO- central bridge. Nematogenic mesophase range varies from 7.0ºC to 46.0ºC. Thus Nematogenic phase length is minimum of 7.0ºC at the pentyl derivative and maximum of 46.0ºC at the decyl derivative. Nematic-isotropic temperatures are minimum 125.0ºC at the fifth homologue and maximum 175.0^{0}C at the twelfth homologue. Thus homologous series is of higher middle ordered melting type with absence of smectogenic character. The texture of nematic mesophase is of threaded type as judged directly by observing , the field of view of polarizing microscope and confirmed by miscibility method. Analytical data conforms the structure of molecules. The mesomorphic behavior of titled homologous series is compared with structurally identical homologous series.

First and second homologues of the homologous series, Methyl-p-(p^{l}-n-alkoxy cinnamoyloxy) cinnamate are nonmesomorphic and directly and smoothly passes into isotropic liquid from crystalline solid state without passing through an intermediate state of existence, called liquid crystalline state or mesomorphic state or mesogenic state or nonamphiphilic state. This type of nomesomorphic behavior is attributed to the high crystallizing tendency of molecules arising out of strong intermolecular forces of attractions due to the presence of shorter methyl and ethyl groups linked through $-\underset{\cdot\cdot}{\ddot{O}}-$ with left phenyl ring and -CH=CH-COOCH$_3$ right terminal end group. Stronger intermolecular forces of attractions abruptly breaks the crystal structure on heating. The adhering forces of attractions are unable to maintain two dimentional array of molecules in floating condition. Thus first and second members of the series smoothly pass into isotropic liquid or molecules are randomly oriented without display of any kind of mesophase.

Nematogenic mesophase commences from third member of series enantiotropically and it continue upto sixteenth homologue without exhibition of any smectic character even in the monotropic condition. On heating the samples of homologues from and beyond propyl derivative of the series. Average themal stability for nematic mesophase is 145.88 in absence of smectic mesophase.

2. Homologous series Ethyl-p-(-p'-n-alkoxy cinnamoyloxy) cinnamates.

p-Hydroxy ethyl cinnamate is nonmesomorphic substance but on linking it with nonmesomorphic cis p-n-alkoxy cinnamic acids through p-n-alkoxy acid chlorides give rise to corresponding Ethyl–p-($p^{/}$-n-alkoxy cinnamoyloxy) cinnamate esters with cis spatial configuration. Seven, out of twelve homologues are mesomorphic and remaining five viz; methyl to n-pentyl homologues are nonmesomorphic. i.e. n-heptyl, n-octyl, n-decyl, n-dodecyl n-tetradecyl and n-hexadecyl homologues are not smectogenic even in the monotropic condition. All the seven mesomorphic homologues are only and entirely nematogenic in enantiotropic manner. Transion temperatures are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group. Like points are joined to obtain solid-isotropic or solid-nematogenic transition curve and nematic-isotropic transition curve. The resulted phase diagram obtained is shown in the **figure-15** from **table-4.** Solid -nematic/isotropic transition curve falls from methyl to n-butyl homologue and than rises to n- pentyl by two degree and again falls upto decyl homologue. Finally it rises by five degrees to hexadecyl homologue through tetradecyl homologue. Thus, it follows zigzag path of rising and falling as series is ascended in normal manner. Nematic-isotropic transition curve follows descending tendency from n-hexyl to n- decyl homologue in normal manner, then it passes through minima (264- 270) at decyl homologue and rises abnormally from decyl to hexadecyl homologue as series is ascended. Odd-even effect is not observed for nematic-isotropic transition curve. Mesomorphic properties like average thermal stability, commencement of mesophase, mesophase length, degree of mesomorphism etc. are compared with structurally similar homologous series.Mesomorphic range varies minimum of 12^{0C} at the decyl homologue to maximum 34^{0C} at the hexadecyl homologue of series under discussion. Thus, titled homologous series is entirely nematogenic with short range of liquid crystallinity. Mesomorphic properties of titled homologous series is compared with structurally similar homologous series. Average themal stability for nematic mesophase is 138.1 in absence of smectic mesophase. Average themal stability for nematic mesophase is 151.0 in absence of smectic mesophase.

3. Homologous series n-Propyl-p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

Cis n-alkoxy cinnamic acids and p-hydroxy n-propyl cinnamic ester are nonmesomorphic in nature. However, on linking chemically both of them, they combine and gives rise to liquidcrystal property from n-hexyl derivative of the homologous series:n-propyl-p-[p’-n-alkoxy cinnamoyloxy] cinnamates. First five and sixteenth homologues i.e. methyl to n-pentyl and hexadecyl derivatives of the series are nonmesomorphic in character. Transition temperatures of the homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end groups from **table-6**. Like points are linked and a phase diagram is obtained, which is shown in **figure –16**. Nematic-isotropic transition temperature curve for n-hexadecyl and n-pentyl derivatives are extrapolated from n-tetradecyl and n-heptyl homologues respectively to predict hypothetical nematic-isotropic (or vice versa) transition temperatures for pentyl and hexadecyl derivatives of the series. The extrapolated curve for pentyl and hexadecyl derivatives merge into the isotropic temperatures of both nonmesomorphic homologues at 175.0^{0C} and 158.0^{0C} respectively. This observation indicate, that nematogenic mesophase start to commence from hexyl derivative and ends to tetra decyl derivative i.e. intermolecular anisotropic force of suitable magnitude are occurred from hexyl to tetradecyl derivatives of the series to cause properly required type of molecular alignment to keep and maintain statically parallel orientations of molecules as a consequence of molecular rigidity and flexibility in floating condition. Careful examination of a phase diagram (figure-2) reveals that, solid-isotropic or solid-mesomorphic transition curve follows zigzag path of rising and falling as series is ascended in usual manner. Nematic-isotropic transition curve initially rises and then adopt descending tendency as series is ascended with overall descending manner following expected trend of behavior. Mesomorphic range varies between 8.0^{0C} at the dodecyl homologue to 27.0^{0C} at the heptyl homologue with 183.8^{0C} nematogenic thermal stability. Thus, mesomorphic range is short and series is of middle ordered melting type without exhibition of any smectic character, even in the monotropic condition. Odd-even effect is observed for nematic-isotropic transition curve. Transition curves for odd and even homologues merge into each other between nonyl and decyl homologues.

Intermolecular force of attractions due to molecular rigidity and flexibility are not anisotropic and of suitable magnitude of n-propyl-p-hydroxy cinnamate and cis p-n-alkoxy cinnamic acid but, on linking them through cis n-alkoxy cinnamoyl chloride, the enantiotropic nematogenic messophase is induced for hexyl homologue to tetradecyl homologue with absence of smectogenic character. The titled homologous series induce thermotropic mesomorphism i.e. mesophase appears by application of thermal energy from surrounding [Rest of the universe other than system] to system [crystalline homologue under study]. When a crystalline unlayered homologue undergo formation and reaches to crystalline solid state, it releases energy (ΔH) and tend to move towards a state of higher entropy (ΔS) to as far as lower entropy to acquire the most, thermodynamically stable state of existence. Now, heat (ΔH) is supplied to a thermodynamically stable system (homologue) from surrounding to a system, a system under investigation tend to absorb heat energy which acts against the intermolecular end to end and lateral attractive forces, fighting against binding forces of solid homologue. Thus, loosely bonded molecules undergo translational motion to vibrational motion through rotational motion. As a result of this, molecules of a system tend to acquire interstate transition of thermodynamically more stable state to less stable state of high entropy or randomness. As temperature exposed upon system rises, the vibrating molecular system may or may not resist thermal vibrations imposed upon them. The molecular system which resist thermal vibrations resisting disalignment of molecules at an angle less than 90^0, are able to maintain statically parallel orientational order of molecules in floating condition causing formaton of nematic mesophase at temperature t_1 at constant pressure as observed for n-hexyl homologue to n-tetradecyl homologue. Thus, nematic mesophase commence to appear from temperature t_1 and continue till the higher temperature t_2 for enantiotropic nematic mesophase corresponding to randomness or entropy, $\Delta S= \Delta H/ T$ where $T= t+273$, Absolute temperature in ^{0}K. and t= temperature of transition in ^{0}C. The range of liquid crystallinity of a homologue or a substace $t_R = t_2- t_1 = T_2-T_1$. If a molecular system is unable to resist the thermal vibrations exposed upon it, $t_2- t_1 = 0$ or $t_2 = t_1 = t$. Thus,molecular system under examination undergo disalignment of molecules in floating condition without formation of mesomorphic state and passes directly into isotropic liquid state from unlayered crystalline solid state. i.e.a solid crystalline material directly melts at temperature t^{0C} without passing through an intermediate state of existence, called liquid crystal state or mesomorphic state or nonamphiphilic state as observed for the, methyl to pentyl and n-hexadecyl homologues of titled homologous series. The appearance of zigzag path of solid-isotropic or mesomorphic curve and alternation of transition temperatures for odd and even homologues are attributed to the sequentially and progressively added methylene unit to the left n-alkyl chain of n-alkoxy terminal end group. Exhibition of odd-even effect by nematic-isotropic transition curve is also due to the sequentially added methylene unit at the n-alkyl chain of left n-alkoxy terminal end groups. Nematic-isotropic transition curves for odd and even homologues merges into each other between nonyl and decyl homologue. The odd-even effect for higher homologues from and beyond decyl homologue diminishes because longer left n-alkyl chain of left n-alkoxy group may coil or bend or couple to lie in the line with major axis of core. Thus, end to end contacts would then ultimately be the same for odd and even homologue. Average themal stability for nematic mesophase is 183.8 in absence of smectic mesophase.

4. Homologous series n-Butyl-p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

On synthesis of titled homologous series, resulted eleven homologues.Microscopic examination of the homologues resulted, methyl, ethyl, n-propyl, n-buty, and n-pentyl derivatives as nonmesogenic homelogues and hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives as mesogenic homologues. p-Hydroxy n-butyl cinnamate is nonmesogenic, but on linking it with nonmesomorphic p-n-alkoxy cinnamic acid with cis confugration through esterification gave mesogenic homologues from hexyl to hexadecyl derivatives. A phase diagram **(Figure-17)** is obtained by plotting a graph for number of carbon atoms present in n-alkyl chain of left n-alkoxy end group versus the transition temperatures of the homologues **(Table-8)** .Transition temperatures of homologues are determined by polarizing microscope with heating stage, as recorded in table-. Analytical data support the structures of molecules. Texture of the nematic mesophase is of threaded type as judged directly from microscopic field of view. A nematogenic type of mesophase is exhibited by the members of the series showing mesogenic character. Smetic type of mesophase is not exhibited by any of the homologues. Careful observation of a phase diagram **(Figure-17)** obtained, indicate that, solid-isotropic or solid-nematic transition curve shows falling tendency as series is ascended up to octyl derivative of the series without following zigzag path of rising and falling. However from and beyond octyl derivative it follows zigzag path of rising and falling tendency upto hexadecyl derivative of series. Nematic –

isotropic transition curve inially rises and than falls in a normal manner. Odd even effect is not observed for nematic-isotropic transition curve, because nematogenic character is exhibited by only even numbered homologues viz. hexyl, octyl, decyl, dodacyl, tetradecyl and hexadecyl derivatives. None of the odd numbered member of the series exhibit nematogenic character. Nematogenic mesophase length ranges from 12^0c to 87^0c in hexyl homologue and dodecyl homologue respectively. Transition and melting temperatures are relatively high. Thus, series is of high melting type with long range of nematogenic character and without exhibition of smectogenic character.

Inability for exhibition of mesogenic character by methyl,ethyl, propyl,bultyl and pentyl derivatives of titled homologous series is attributed to their high crystalisation tendency ,arising from irregular heat absorption and abrupt breaking of crystal lattices, which leads to the smooth passing of solid substance directly in to isotropic liquid without exhibition of an intermediate state of existence between solid and liquid, called liquid crystal state or mesomorphic state or mesogenic state or nonamphiphilic state at definite temperature and constant pressure. Absence of dimerisation in cis configurated p-n-alkoxy cinnamic acids causes disappearance of mesophase automatically which on linking with non mesomorph p-hydroxy n-butyl cinnamate, bridged through –CH=CH-COO- increases length of a molecule by phenyl ring and its para substituted n-butyl group induces mesomorphism. Thus, extended molecular length,introduces mesogenic character from hexyl to hexadecyl derivatives of the series.

Homologues of titled homologous series from hexyl to hexadecyl derivatives are of enantiotropic nematogenic in character. Extent of nematogenic phase length (87.0^0C) occurred at the cost of eliminated smectic mesophase. Methylene unit is progressively added in n-alkyl chain of left n-alkoxy terminal end group keeping remaining part of a homologue molecule intact. This causes variation in homologue to homologue molecular length of same series. Hence, length to breadth ratio gradually varies from homologue to homologue. Mesogenic properties are compared with structurally similar homologous series. Average themal stability for nematic mesophase is 194.8 in absence of smectic mesophase.

5. Homologous series n-Pentyl-p-(-p'-n-alkoxy cinnamoyloxy) cinnamates.

The final products i.e. ester homologues of the series are cis isomers as determined from IR spectra. Cis para n-alkoxy cinnamic acids are not being dimeric, their absence of dimerization results into occurrence of linking them with nonmesomorph p-hydroxy n-pentyl cinnamate being nonmesomorphic in characteristics which on esterification, results into esters formed, are mesomorphic in nature except methyl to butyl homologues. Methyl to butyl homologues are unable to resist thermal vibrations and melts sharply at their melting point from crystalline solid state to isotropic liquid state without passing through mesogenic state. Transition temperatures are determined by hot stage polarizing microscope as recorded in **table–10** Pentyl, tetradecyl and hexadecyl derivatives of homologues are only nematogenic, while, hexyl, octyl, decyl and dodecyl derivatives are polymesomorphic i.e. smectic and nematic mesophases are exhibited by these homologues of the series. Texture of smectogenic homologues are of the type smectic -A, as determined by miscibility method and also judged directly from field of view of microscope. Texture of nematic mesophase is of the threaded type. None of the mesomorphic homologues show monotropic mesophase exhibition. Transition temperatures **(table-10)** are plotted versus the number of carbon atoms in n-alkyl chain of left n- alkoxy terminal end group.Like points are linked and a phase diagram obtained is shown in the figure.

A careful examination of a phase diagram **(figure-18)** indicate that, solid-isotropic or solid-mesophase transition curve follow a zigzag path of rising and falling from methyl to butyl homologue. Then it steeply falls to decyl homologue at the minima and again steeply rises to hexadecyl homologue making its overall rounded shape. The smectic-nematic transition curve rises to decyl homologue and then its extrapolated extension merges to tetradecyl derivative, at solid-nematic point of solid mesomorphic curve. Thus, theoretically a smectic mesophase should disappear in tetradecyl derivative and really disappeares practically also for tetradecyl homologue. Thus, smectic-nematic transition curve behaves in normal manner showing minima instead of maxima. Nematic-isotropic transition curve rises from pentyl to hexadecyl derivative of homologues in serpentile shape and behaves in normal manner without showing descending tendency as series is ascended and with alternation of transition temperatures. Odd-even effect is observed in solid-smectic transition curve and nematic-isotropic transition curve. Transition curves for odd and even homologues merges into decyl and octyl homologues for smectic-nematic and nematic-isotropic transition curve respectively. Mesogenic range which ranges minimum of 21.0^{0C} at the pentyl homologue to maximum of 53.0^{0C} at the decyl homologue. Thus, mesomorphic range is enough and series is of middle ordered melting type. Textures of the homologues are determined by miscibility method. nematogenic mesophase is of treaded type and that of smectic mesophase is of focal conic fan shaped with smectic A or C variety. Analytical data matches with the structures of molecules.

The nonmesogenic behavior of methyl to butyl derivative of the homologues is attributed to their high crystallizing tendency which arises from stronger intermolecular forces of attractions, which are not anisotropic and of the suitable magnitude, of which correspond to amount of energy (ΔH) released from system (Formation of homologue) to surrounding (Rest of the univers other than system). According to third law of thermodynamics, the entropy (ΔS) (i.e. randomness or disorder) of perfectly crystalline substance is zero at absolute zero degree Kelvin (-273^{0C}).Therefore as heat energy (ΔH) is supplied to a sample substance from external source [i.e. from surrounding to system], the applied heat energy tend to break crystal structure and sample substance acquire disruption to move towards higher or less stable state of existence. n-Alkyl chains of left n-alkoxy terminals from methyl to n-butyl caused, stronger intermolecular forces of attractions which required relatively higher amount of energy to undergo interstate transformation. But molecules are disaligned under cohesive forces which are not anisotropic from ordered arrangement, preventing parallel orientations or sliding layered arrangement of molecules in floating condition. Thus, molecules of substance from methyl to butyl homologues at required high temperature are unable to resist thermal vibrations in bearable regular manner to have in controlled motion and sharply passes into isotropic liquid state from crystalline solid state without passing through an intermediate state of existence called mesogenic state. The uncontrolled motion or Brownian motion of molecules at their melting point causes high order of molecular disorder; i.e. the entropy change (∆S) causes to occure high level of randomness or disorder amongst the randomly oriented disaligned molecules of a sample homologue, as transformed directly into isotropic liquid. Thus, high order of disorder or randomness or entropy (∆S) resulted from the combine effects of molecular rigidity, flexibility and bending of molecule which disturbed alignments of molecules causing generation of intermolecular cohesion which is not anisotropic and of suitable magnitude which restricts mesophase formation.

As n-alkyl chain of left n-alkoxy terminal increase their length by sequentlial addition of methylene unit, crystallinity of a sample homologues gradually diminishes and amorphous character rises, introducing mesogenic character favourbly. The amount of energy released (∆H) during their formation of stable solid crystal structure, which on heating tend to destabilize require heat energy which correspond to such a magnitude of randomness or entropy change (∆S) that, molecules of pentyl to hexadecyl derivatives of the series are able to resist thermal vibrations imposed upon them,due to generation of anisotropic intermolecular forces of adhesion by suitable combination of effects caused by molecular rigidity, by flexibility and molecular bending. As a result of this, two dimensional array of molecules is maintained in floating condition. i.e. Lamellar molecular packing and hence the sliding layered arrangement of molecules in floating condition of hexyl,heptyl, octyl, decyl and dodecyl homologues give rise to smectic-A mesophase formation, while, pentyl, tetradecyl, hexadecyl, hexyl, heptyl, octyl, and decyl derivatives of homologues acquiring balanced anisotropic intermolecular cohesive forces of suitable magnitude emerging from molecular rigidity, molecular bending or flexibility without restricting statistically parallel orientational order of properly aligned molecules in floating condition which gives rise to the formation of nematogenic mesophase. Thus, hexyl, heptyl, octyl, decyl and dodecyl homologues show smectic and nematic mesophases one after another enantiotropically while, pentyl, tetradecyl and hexadecyl derivatives show only enantiotropic nematic mesophase formation. The mesogenic properties of titled homologous series are compared with structurally similar homologous series. Average themal stability for nematic mesophase is 169.3 in presence of smectic mesophase is118.6 respectively.

6. Homologous series n-Hexyl-p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

Homologues of the homologous series entitled n-hexyl-p-[p/-n-alkoxy Cinnamoyloxy] Cinnamates are geometrically cis isomers as determined from spectroscopic data. Methoxy and ethoxy homologues are nonmesogenic while, propyloxy to octyloxy, decyloxy,dodecyloxy, tetradecyloxy and hexadecyloxy derivatives are enantiotropically nematogenic. Heptyloxy, octyloxy, decyloxy, dodecyloxy and tetradecyloxy homologues exhibits enantiotropically smectogenic mesophase in addition to nematogenic mesophase. Smectogenic character is missing in hexadecyloxy homologue. Transition and melting temperatures are carefully observed through hot stage polarizing microscope and recorded in **table-12** Transition temperatures of homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n- alkoxy termally situated end group. Like points are linked and a phase diagram is obtained as shown in **figure-19.**

Carful examinations of a phase diagram **(Figure-19)** reveals that, solid-isotropic / mesomorphic transition curve adopt a descending tendency as series is ascended following a zigzag path of overall rising and falling tendency. It falls from methoxy to propyloxy homologue and rises to hexyloxy homologue, then it falls to tetradecyloxy homologue with intermitant rise of only four degree centigrad at decyloxy homologue and considerable rise at hexadecyloxy homologue take place without disturbing overall falling tendency. Thus, solid-isotropic / mesomorphic transition curve behaves in normal manner.

Smectic-nematic transition curve slightly rises from heptyloxy to octyloxy homologue and then it falls to the tetradecyloxy homologue in usual manner without exhibition of odd-even effect. Texture of nematic and smectic mesophases determined by miscibility method. Smectic-A type of mesophase is exhibited by heptyloxy, octyloxy, decyloxy and dodecyloxy derivatives. Tetradecyloxy derivative shows smectic-C texture as judged directly from fields of view of microscope. Texture of nematic mesophase is of threaded type.

Nematic- isotropic transition curve initially rises, passes through maxima at the octyloxy derivative and than it smoothly falls to the hexadecyloxy derivative in normal manner. Odd-even effect is observed for nematic-isotropic transition curve. Thus, nematic isotropic transition curve fits two curves which rises to late maxima at the octyloxy homologue and merge into each other at the maxima (15 to 20) before smooth falling to hexadecyloxy homologue.(14).

Methoxy and ethoxy derivatives of titled homologous series are nonmesogenic, though the geometrical shape of molecules is long linear lath like or rod like with sufficient rigidity and flexibility. However, because of their shorter left n-alkoxy terminals viz. Methoxy and ethoxy causes strong intermolecular forces of attractions amongst the molecule inducing high crystalising tendency. High crystalising tendency gives rise to formation of thermodynamically more stable system of crystal lattices by releasing energy (ΔH) from system to surroundings. Conversely on heating the thermodynamically stable system, it destabilizes by absorbing heat energy (ΔH) from surrounding to system which correspond to magnitude of intermolecular adhesion forces. Thus, intermolecular end to end and lateral attractive forces being too strong, the thermal vibrations exposed upon the molecules having highly polarizable methoxy and ethoxy left terminal end groups become unable to resist such high energetic thermal vibrations. So that, thermodynamically stable system (crystals) tend to destabilize to a state of higher entropy or randomness at particular temperature t_1^{0C} and continue for higher temperature t_2^{0C} where ($t_2 - t_1$) = range of temperature and entropy, $\Delta S = \Delta H / T$ and $T = t^{0C} + 273$. Where T = absolute temperature in degree Kelvin and t = transition temperature in degree centigrade. For, nonmesomorphic homologues like methyl and ethyl derivatives of series ($t_2 - t_1$) = 0 i.e. $t_2 = t_1 = t$ but for enantiotropic transition $t_2 > t_1$ and for monotropic $t_2 < t_1$. Thus, sample molecules of methyl and ethyl homologues under examination are unable to maintain adequate ordered arrangement of molecules in floating condition because, inter molecular forces are neither anisotropic nor of suitable magnitude as a consequence of molecular bending, molecular rigidity and flexibility. Hence, molecules of methyl and ethyl homologues having individually lath like shape disalign on the plane of surface and molecules are randomly oriented without any ordered arrangement in floating condition corresponding to inadequate magnitude of entropy. Under this situation, disaligned molecules restricts the formation of statistically parallel orientational order of molecules as intermolecular cohesion forces are neither anisotropic, nor of suitable magnitude, which inhibits the formation of nematogenic mesophase. Thus, high order of disorder exists amongst the molecules under very low intermolecular mutual adhesion forces resulting into direct normal melting (8) of solid crystals into isotropic liquid without passing through an anisotropic liquid state called liquid crystal state or mesogenic state. Hence, molecular arrangement on thermal disturbance causes molecules to move out of alignment adopting Brownian movement. Thus, entropy (ΔS) or randomness or disorderness cause thermodynamically stable system to destabilize, preventing exhibition of mesogenic state of existence. Mesomorphic range varies minimum from 10.0^{0C} at the propyloxy homologue to maximum 60.0^{0C} at the tetradecyloxy homologue. Nematic-isotropic transition temperature varies between 148.0^{0C} at hexadecyl homologue and 219.0^{0C} at the octyloxy homologue. Thus, series is of low mesomorphic length and middle ordered melting type.

Mesomorphic properties like thermal stability, range of liquid crystallinity, odd-even effect, commencement of smectic and nematic mesophase, extent of noncoplanarity causing early or late commencement of smectic mesophase etc. are compared with structurally similar homologous series. Average themal stability for nematic mesophase is 190.9 in presence of smectic mesophase is 179.6 respectively.

7. Homologous series Iso-propyl-p-(-p’-n-alkoxy cinnamoyloxy) cinnamates

Titled homologous series,Isopropyl–p-[p/-n-alkoxy cinnamoyloxy] cinnamates consist of twelve homologues of cis configuration as determined from spectral data. Methyl to butyl homologues are nonliquid crystals while , rest of the homologues are liquid crystals. Liquid crystal homologues exhibit enantiotropic nematogenic type of mesophase only. Smectic mesophase exhibition is totally absent, even in the monotropic condition. Transition temperatures and melting temperatures are determined by polarizing microscope with heating stage. Transition temperatures of homologues **(table-14)** are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end groups. A phase diagram is obtain by linking like or related points. **(figure-20)** Careful examination of a phase diagram **(figure-20)** indicate that, solid-isotropic or solid-nematic transition curve rises from methyl to propyl and than steeply falls to pentyl through butyl derivative of series. Then it follows zigzag path, as series is ascended. Thus, it behaves in normal manner. Nematic-isotropic transition curve shows descending tendency as series is ascended, in normal manner. Odd-even effect is observed for nematic-isotropic transition curve with alternation of transition temperatures. Mesophase length varies from 20.0^{0C} at hexadecyl homologue to 112.0^{0C} at the octyl homologue. Thus mesomorphic range is wide, and series is of higher middle ordered melting type. Liquid crystal properties of titled homologous series are compared with structurally similar homologous series.

Cis n-Alkoxy cinnamic acids are not dimeric molecules, and are nonmesomorphic. p-Hydroxy isopropyl cinnamate molecule is also nonmesomorphic which on esterification yields eight homologues as liquid crystals, out of twelve homologues. Methyl to butyl homologues are missing liquid crystal properties because shorter n-alkyl chain causes stronger intermolecular end to end forces of attractions which leads to high crystallizing tendency. The high crystallizing tendency arising from the amount of heat energy released thermodynamically (ΔH) from system to surrounding when crystal formation take place. The equivalent amount of heat energy required (ΔH) to supply from surrounding (part of universe other than system) to system (homologue) to break the crystal structure and transform it to isotropic liquid, relatively at high temperature causing disalignment of molecules which restricts statically, parallel orientational order of molecules or/and lamellar packing and sliding layered arrangement of molecules in floating condition. Thus, molecules of methyl to butyl homologues have to resist relatively high energetic unbearable thermal vibrations, which forces molecular species to face self uncontrolled random orientational motion to move in all possible directions with high magnitude of disorder. Thus, entropy (ΔS) of system rises to such an extent that, crystalline solid homologues sharply pass directly into isotropic liquid without passing through an intermediate state of existence, called liquid crystals. Thus, end to end inter molecular forces of attractions related to enthalpy (ΔH) change and hence responsible for high level entropy (ΔS) change or highly disordered random motion of the specy. Average themal stability for nematic mesophase is 201.11 in absence of smectic mesophase is compared with structurally similar other series.

8. Homologous series Iso-butyl-p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

All the members of the homologous series are geometrically cis isomeric structure. The possible isomer being two. viz. cis and trans, but spectroscopic data confirms only cis isomer, the only cis isomer of a molecule containing isobutyl terminal group will occure. Thus, cis isomer of isobutyl group being a single substance, all the homologues are a single substance and not a racemic mixture.

p-Hydroxy isobutyl cinnamate is nonliquid crystalline, while on linking it with p-n-alkoxy cinnamoyl chloride by way of esterification resulting, ester homologues with liquid crystalline character from pentyl to hexadecyl homologues and are nonliquid crystalline from methyl to butyl homolgues.

Homologues of the titled homologous series are enantiotropically nematogenic from pentyl to hexadecyl derivatives without exhibition of any smectic character even in the monotropic condition. Phase transition temperatures **(Table-16)** are plotted against the number of carbon atoms present in n-alkyl chain of left n-alkoxy end group. A phase diagram **(figure-21)** is obtained by joining like and related points. Careful observations of a phase diagram **(figure-21)** indicate that, solid-isotropic or solid-nematic transition curve follows zigzag path of rising and falling as series is ascended with occurrence of drastic fall from second to third member and with a negligible fall from twelfth to sixteenth member of the series. Hence solid-Isotropic or solid-nematic transition curve behaves in normal manner. Nematic-isotropic transition curve also behaves in normal manner, with negligible abnormality at dodecyl and tetradecyl homologue, which may be due to “iso” linking at the terminal end group. Odd-even effect is not observed in nematic-isotropic transition curve because nematic character is exhibited by all even numbered homologues except odd numbered, fifth member of the series. Methyl to butyl derivatives are being nonliquid crystalline, which eliminates the possibility of odd-even effect.

The lowering or highering of phase transition temperatures of titled homologous series by esterification of corresponding p-n-alkoxy cinnamic acids is not due to breaking of hydrogen bonding of dimerised p-n-alkoxy cinnamic acids, homologoues are cis isomer of p-n-alkoxy cinnamic acids. The nonliquid crystalline behavior of methyl, ethyl, propyl and butyl homologues is, due to the high crystallizing tendancy of molecules; arising out of imbalanced intermolecular forces of attractions which are not anisotropic and of suitable maguitude. n- Alkyl chains of left n-alkoxy terminal of methyl to butyl homologues are relatively short. Therefore intermoleculare forces of lateral and end to end attractions are relatively stronger. i.e. these four homologues are thermodynamically more stable by releasing more energy from system (formation of homologue) to surrounding (part of universe other than a system). Thus, heat of formation (ΔH) being higher, the crystal lattices are strongly bonded with each other by low magnitude of randomness or entropy (ΔS). Now on heating the crystalline homologue the amount of heat enegy (ΔH) supplied from surrounding to system, the intermolecular forces of attractions are weakened and entropy (ΔS) increases. Thus, on increasing the temperature, molecules of any homologue tend to destabilizes from stabilized state of existence acquiring molecular motion in sequence from translational motion to rotational motion and from rotational motion to vibrational motion, increasing value of molecular randomness or disorder or entropy. Hence, higher value of enthalpy change (ΔH) require high amount of heat energy or higher temperature to break or to rupture the crystal structure. Under this condition the molecules of methyl to butyl homologues of titled homologous series move out of alignment and / or molecule may bend and flex causing inability to resist thermal vibrations, causing disalignment of molecules. Thus, disaligned molecules are individually lath like linear, are randomly orientated in floating condition without two dimensional array. Therefore intermolecular cohesive forces are being not anisotropic and of suitable magnitude due to combined effect of molecular rigidity in combination with molecular flexibility or molecular bending are unable to resist thermal vibrations which restricts the possibility of occurring statistically parallel orientational order of molecules to maintain ordered molecular arrangement in floating condition. Thus, uncontrolled motion of randomly orienting molecules with high order of disorder directly passes into isotropic liquid without passing through intermediate state of existence, called liquid crystal state or mesogenic state. Pentyl to hexadecyl homologues are liquidcrystalline of the type with enantiotropic nematogenic mesophase without exhibition of any smectic type of mesophase. Homologous series, Isobutyl-p-(p’-n-alkoxy cinnamoyloxy) cinnamates is entirely nematogenic with relatively shorter nematogenic mesophase length between 15.0ºC to 39.0ºC. Average thermal stability and other mesomorphic behavior of titled homologous series is compared with structurally similar homologous series. Average themal stability for nematic mesophase is 138.1 in absence of smectic mesophase.

9. Homologous series p-(p$^{/}$-n-alkoxy Cinnamoyloxy) β-benzoyl Styrenes.

Cis p-n-alkoxy cinnamic acids and p-hydroxy – benzoyl styrene are originally nonliquid crystal in nature, however on combining them together under favourable and suitable condition, results into the new products which are homologues of this titled series, the liquidcrystal property is induced from and beyond hexyl homologue. Methyl to pentyl homologues are nonliquidcrystal in character. All the liquidcrystal homologues i.e. hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives of the titled homologous series are enantiotropic nematogenic in character without exhibition of any smectic character even in the monotropic condition. Transition temperatures **(table-18)** of the homologues are plotted versus the number of carbon atoms presents in n- alkyl chain of left n-alkoxy group. Like points are linked and a phase diagram obtained is represented as **figure-22**. Careful examination of a phase diagram reveals that, the solid-isotropic or solid-nematic transition curve follows a zigzag path of rising and falling throughout the series with one or two exceptions, otherwise curve shows overall decending tendency as series is ascended and behaves in usual expected manner. Nematic-isotropic transition curve exhibits descending tendency as series is ascended and curve behaves in normal manner without showing up of odd-even effect, because, transition temperatures do not alternate in regular manner as well as nematogenic mesomorphism commences late, i.e.from and beyond sixth homologue. The mesomorphic properties of a homologous series are compared with structurally similar homologous series (A) and (B) as shown in **figure-30**.

The nonmesomorphic behavior of methyl to pentyl homologues observed is due to the high crystallizing tendency of the molecules which arises due to the intermolecular forces occurred between the molecules are not anisotropic and of suitable magnitude to keep molecules in proper alignment under the influence of heat from surrounding to system. Thermodynamically stable state achived by all the homologue substance (system) by exchanging energy (ΔH) from surrounding (Rest of universe other than a system) to system or vice versa. Now a thermodynamically stable unlayered substance is supplied heat i.e. heat is supplied from surrounding to system, the molecules of a homologue substance under the influence of heat start to pass from transitional motion to vibrational motion through rotational motion. Thus, vibrating molecules may or may not resist the thermal vibrations exposed upon them. If the victim vibrating molecules are unable to resist applied thermal vibrations, such molecules exhibit disaligned position on the plane of the surface with high entropy ($\Delta S=\Delta H/T$) or randomness or high order of disorder at higher temperature. Under this situation molecules of a sample homologue under examination are restricted to maintain statistically parallel orientations of molecules in floating condition due to insufficient intermolecular forces of end to end and lateral attractions occurred as a consequence of molecular rigidity and flexibility. Thus, molecules of methyl to pentyl homologues are directly converted from solid to isotropic state without passing through an intermediate state of existence, called liquid crystal state or mesomorphic state or nonamphiphilic state or mesogenic state. Thus, interstate transition of first five homologues takes place in titled homologous series, without formation of either nematogenic or smectogenic mesophase.

However the vibrating molecules resist the thermal vibrations exposed upon them from the heat supplied from surroundings, the molecules of the molecular system under examination has intermolecular lateral and end to end attractions are stronger enough to withstand the effect of exposed heat. Therefore molecules of a homologue are not disaligned i.e. molecules of a homologue make an angle less than 90^0 with the plane of the surface. Such molecular system which maintains net intermolecular anisotropic forces of attractions of suitable magnitude caused by the favourable molecular rigidity and flexibility. Thus, in such case, the statistically parallel orientations of molecules are not restricted to form nematic mesophase in floating condition in absence of sliding layered arrangement of molecules under identical condition. Hence under such situation, hexyl to hexadecyl homologues exhibit only nematic mesophase without exhibition of smectic mesophase in case of homologous series under discussion. Absence of odd-even effect in nematic-isotropic transition curve is attributed to the late commencement of mesophase i.e. mesophase appears from and beyond sixth homologue and it is a known fact that, n-alkyl chain of left n-alkoxy terminal of higher homologues may be coupled or coiled to lie on the line with major axis of the core. Thus, effect due to odd and even homologues diminishes i.e. end to end contact would then ultimately be the same for odd and even homologues.

The variation in mesomorphic properties from series to series for same homologue keeping molecular part unchanged except right terminal end group. The variation of right terminal end groups of series (1), (A) and (B) causes difference in mesomorphic properties due to diffence in molecular length, polarity of right terminal end group, molecular polarizability, rigidity, flexibility etc. The variation in mesomorphic properties among the molecules of homologues in the same series occurs due to sequencially and progressively added methylene unit at the left n-alkoxy terminal keeping right terminal intact viz; phenyl ring. Thus, varying part of the molecules causes variation in mesomorphic properties. The nematic-isotropic transition temperature maximum is 179.0^{0C} at the hexyl homologue and minimum is 104.0^{0C} at the hexadecyl homologue, varying mesomorphic range minimum of 6.0^{0C} at the octyl derivative of the series to maximum 47.0^{0C} at the dodecyl homologue. Thus, series (1) under discussion is entirely nematogenic with middle ordered melting type and of short rang liquid crystallinity. . Average themal stability for nematic mesophase is 144.5 in absence of smectic mesophase.

Evaluation of the homologous series:

Attempt has been made to evaluate mesomorphic characteristics in comperitive manner for the homologous series under discussion. Molecular geometry and the forces arising there from would be the important factors in the process of evaluating mesomorphism and degree of mesomorphism. The core geometry of the new ester series may be represented as under.

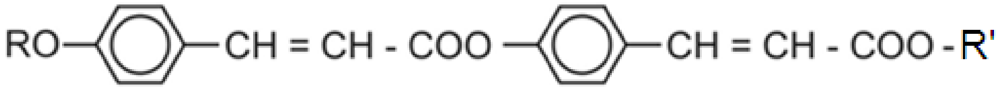


Figure-24

Where R= $-CH_3$ to $–C_7H_{15}$, $-C_8H_{17}$, $-C_{1O}H_{21}$, $-C_{12}H_{25}$, $-C_{14}H_{28}$, $-C_{16}H_{33}$.

R’= $-CH_3$, $-C_2H_5$, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13},iso-C_3H_7, iso-C_4H_9

Several homologous series with this core structure except right terminal end group are known to exhibit mesomorphism. The varied display of molecular forces which in their peculiar combination affect the mesomorphic property has been significantly used for proper understanding and evaluation of the phenomenon. Polarity, polarizability, length to breadth ratio, rigidity and linearity of molecule, steric hinderance caused by certain groups attached to the molecule, planner nature, π-electron density [35] etc. have been considered to be sufficiently important, besides several other untraced factors in desiding mesomorphic characteristics of the molecules. With above core structure, excluding the terminal groups, the basic length due to two phenyl rings and central linking unit, aromaticity of the molecule etc. are the constant unchanging feature and the display of molecular forces on account of these will remain the same for series 1, 2, 3, 4, 5, 6, 7, 8.

The homologous series have their changing parts at both terminals, but in a sequential manner. In the first place, the n-alkyl (R) chain of the alkoxy group at the left terminal progressively increases as the number of carbon atoms increases in the case of the various homologues of the same series, keeping the right terminal group R’ constant. At the second stage, along with the progressive increase in the sequentially added the number of carbon atoms of the n-alkyl chain at the left terminal, the right terminal R’ iso(series-7 and 8) and n-alkyl (series-1 to 6) chain changes from series 1 to 8 in a stepwise manner.

Thus, two phenyl rings, central bridge, and varying n-alkoxy left terminal end group are the common identical parts of the homologous series 1, 2, 3, 4, 5, 6, 7 and 8. The only thing that differs from series to series is the terminal substituents at the right end. The terminal substituents at right terminal increases the length or breadth of the substituent with the introduction of a methylene unit –CH_2- gradually from series to series [1 to6 and 7, 8]. The increase in the length of the n-alkyl chain in the right end terminal substituent,

(a).Will enhance the length to breadth ratio and the overall polarizability of the molecules.

(b).The longer molecules will be more difficult to disalign.

(c).The frequency with which readily polarizable parts e.g.core parts of the molecules lie side by side will decrease.

(d). The terminal separation of readily polarizable parts e,g. core parts of the molecules will increase.

It should thus be possible to assign the variations in the degree of mesomorphism and its characteristics to the changing right end terminal substituents. For series (7) and (8) which has ‘iso’ propyl and isobutyl linkage at the right terminal, which causes two opposing effects, operating at a time due to broadening of a molecule.

(1).’iso’linking reduces length of molecules and increases intermolecular distance due to widening of molecules. Decrease in molecular lenth will reduce lenth to breadh ratio and increase in intermolecular distance will diminish intermolecular attractions. However, at the same time,

(2). The broadening of a molecule results into increase of molecular polarizability, which increases intermolecular attractions.

Thus, when two opposing effects, operating at a time, the resultant effect concerning intermolecular forces of attractions will depend upon predominating effect, out of two opposing effects.

(i). Intermolecular hydrogen bonding and mesomorphism:

Cis p-n-alkoxy cinnamic acids are nonmesomorphic with relatively high transitions. Their nonmesomorphic characteristics are due to the cis configuration of the acid molecules. Esterification of cis n-alkoxy cinnamic acids yields mesomorphs with lower transitions,by linking with non mesomorph or iso or n-alkyl p-hydroxy cinnamate ester.

(ii) Mutual comparison of series 1, 2, 3, 4, 5 and 6.

Sequentially and progressively a methylene unit at the terminally situated end group to the R’ terminal group, the mesomorphic-isotropic transitions for the corresponding homologues are lowered with corresponding variations in the polarity of the end groups, polarizability also enhanced in case of ‘iso’ linked alkyl and n-alkyl group and yet the inductive effect due to the added methylene unit does not seem to be operative effectively. It is possible that with addition of a methylene unit, the increased chain length of the terminal group will have a bearing on the overall polarity across the molecule. Hence the ratio of polarity to polarizability is decreased as methyl is substituted by ethyl, n-propyl, n-butyl, n-pentyl and n-hexyl as well as isopropyl and isobutyl groups in the alkyl chain at the other end. This would explain the lowering (or highring) of transitions of the homologues of the homologous series (1) to (6) and (7) to (8) in sequential manner.

The upper transitions of the homologues displaying mesomorphism are recorded in Table- as under.

Table-20:

No.of carbon atoms in alkyl chain	Upper transition temperatures in 0C					
	Series-1	Series-2	Series-3	Series-4	Series-5	Series-6
C_1		-	-	-	-	-
C_2	-	-	-	-	-	-
C_3	140.0	-	-	-	-	170.0
C_4	128.0	-	-	-	-	187.0
C_5	125.0	-	-	-	156.0	192.0
C_6	128.0	159.0	185.0	142.0	150.0	206.0
C_7	-	152.0	190.0	-	164.0	213.0
C_8	150.0	147.0	198.0	160.0	166.0	219.0
C_{10}	166.0	139.0	188.0	189.0	163.0	208.0
C_{12}	175.0	144.0	175.0	222.0	176.0	196.0
C_{14}	163.0	152.0	167.5	236.0	180.0	170.0
C_{16}	138.0	164.0	-	220.0	200.0	148.0

From **Table-20** it is seen that, the upper transitions of the corresponding homologues are gradually not decreasing as methylene group is added at the right terminal R' from series to series but adopt irregular trend of increasing or decreasing. The variation of the smectic and / or nematic phase length from homologue to homologue in same series and series to series are recorded in **Table-21.**

Table-21: Mesophase length

No.of carbon atoms in alkyl chain	Mesophase length in 0C					
	Series Sm+Nm=	Series-2 Sm+Nm=	Series-3 Sm+Nm=	Series-4 Sm+Nm=	Series-5 Sm+Nm=	Series-6 Sm+Nm=
C_3	0+16=16	-	-	-	-	0+10=10
C_4	0+13=13	-	-	-	-	0+20=20
C_5	0+07=07	-	-	-	0+21=21	0+22=22
C_6	0+16=16	0+10=10	0+20=20	0+12=12	9+17=26	0+28=28
C_7	-	0+17=17	0+27=27	-	20+25=45	24+18=42
C_8	0+25=25	0+18=18	0+16=16	0+38=38	21+31=52	30+21=51
C_{10}	0+48=48	0+12=12	0+24=24	0+49=49	25+28=53	18+18=36
C_{12}	0+40=40	0+19=19	0+08=08	0+87=87	22+39=51	34+17=51
C_{14}	0+21=21	0+22=22	0+15.5=15.5	0+76=76	0+27=27	26+34=60
C_{16}	0+08=08	0+34=34	-	0+68=68	0+23=23	0+12=12

A glance at figure- and brings out another interesting variation. In all the homologous series under discussion, the initial five [four in series-5 and three in series-1 and 6] homologues are nonmesomorphic. Nonmesomorphic behavior is due to their high crystalising tendency which arises due to disalignment of molecules and disturbed sliding layered arrangement of molecules in floating condition as a concequence of molecular rigidity and flexibility or molecular bending which restricts statistically parallel oriantational order of molecules in floating condition. Commencement of mesomorphism takes place from third fifth or sixth member of series in enantiotropic manner.

The common features as observed in series 1, 2, 3, 4, 5 and 6 are

(i)Absence of smectic property from series 1 to 4 and

(ii)Exhibition of the only nematic property by series 1, 2, 3, 4 and smectic property in addition to nematic property by series 5 and 6. and (iii)Alteration of transition temperature effect in nematic-isotropic transition curve is observed in n-propyl, n-pentyl and n-hexyl series while, methyl, ethyl and n-butyl series do not display alternation of transition temperatures i.e. odd-even effect is observed in nematic-isotropic transition curve for series 3, 5, 6 and not observed for the series 1, 2 and 4.

The absence of smectic property is attributed to the rigidity displayed bycentral group which does link the phenyl rings through at least one multiple bond. The stereochemistry of the unit, however does not preserve the linearity of the molecule due to cis configuration but usually result in unusual thermally stable mesophase and unexpected thermal behavior. The first five (or two and four in case of series-5) homologues of series under discussion melt directly in to isotropic liquid on heating at comparatively higher temperatures. From this comparison, it can be said that, due to increased length at right terminal with 'normal' linking of the alkyl chain, these homologues resist the forces of thermal break down well enough to yield isotropic liquid at quite a later stage, until the alkyl chain at the left terminal also has increased in case of series 2, 3, 4, 5 but a little bit earlier in case of series -1 and 6 i.e. from third member of the series. For, these higher homologues do get broken down into isotropic liquid relatively at high or low temperature in irregular manner. On cooling, the first five (four in series-5 and two in series 1 and 6) homologues exhibit high crystallizing tendency precluding any showing up of smectic or nematic property even in monotropic conditions. It also appears that, the terminal attractions are not sufficiently strong enough to induce nematic or smectic property even when supercooling has been possible from the last nonmesomorph homolologue, obviously, because, the overall polarizability of the molecules is insufficient in series 1, 2, 3, 4 and sufficient in series 5 and 6 to cause a sliding layered molecular order to show up, and hence these homologues of the present series 1,2,3and 4 do not exhibit monotropic or enantiotropic smectic property, while series 5 and 6 exhibit enantiotropic smectic property. Exhibition of nematogenic mesophase property by all the homologous series 1, 2, 3, 4, 5 and 6 is due to the arisen of the intermolecular anisotropic attractive forces of suitable magnitude to cause molecular alignment at an angle less than 90^{0C} to the plane of a surface, so that, statically parallel orientational order of molecules is maintained in floating condition.Thus, mesophase formation occure for the series under discussion.

Thus, display of only nematic property in absence of smectic property in series 1,2,3,4 and display of smectic property in addition to nematic property in series 5 and 6 indicate that, the forces holding the planes of the layers together in the rigid crystal are weaken relatively to the attractions between the molecules within a given layer at solid-mesomorphic transition temperature and the layers may become free to slide (and rotate) over one another giving smectic phase in case of series 5 and 6 and on heating the smectic to a higher temperature the, molecular forces between the sides of the molecules weakens to such an extent that, resultant intermolecular force do permit molecules to slide out of the layer and statistically parallel orientations are maintained in addition to sliding layers for the homologous series 5 and 6 while, only parallel orientations are maintained in series 1, 2, 3, 4, through out the series. Hence, abcence of smectic property and exhibition of only nematic property in series 1, 2, 3, and 4 occurred and both mesophases viz;smectic and nematic mesophases occurred one after another in case of series 5 and 6.

Alternation effect is not generally observed in smectic-isotropic transition curve because mesomorphism commences in each series quite later and from and beyond sixth homologue and onwards enatiotropically which are of even numbered. With higher homologues, the longer chain may be constrained to lie in the line with the major axis of the core due to bending or flexing, the end to end contact would then ultimately be the same for odd and even homologues and the alternation diminishes with increasing tendency of the alkyl chain.

The thermal stabilities when compared offer, interesting information leading to molecular characteristics. Since the homologous series 1, 2, 3, 4, 5 and 6 have all other characteristics the same except the vinyl carboxylate terminal group R’ which varies from methyl to n-hexyl. Thus, the variations in the thermal stabilities of the homologous series under comparison can be directly linked with the chain length.

Smectic-isotropic or smectic-nematic and nematic-isotropic thermal stabilities are recorded in **Table-22**

Table-22: Relative thermal stabilities.

	Average thermal stabilities in ^{o}C					
Series. ⟶	1	2	3	4	5	6
Smectic-isotropic or smectic-nematic	- -	- -	- -	- -	118.5 (C_6-C_{12})	179.6 (C_7-C_{14})
Commencement of smectic phase	-	-	-	-	C_6	C_7
Nematic isotropic or smectic nematic	145.88 (C_3-C_{16})	151.0 (C_6-C_{16})	183.8 (C_6-C_{14})	194.8 (C_6-C_{16})	169.3 (C_5-C_{16})	190.3 (C_3-C_{16})
Commencement of nematic phase	C_3	C_6	C_6	C_6	C_5	C_3

It can be seen from the **table-22** that the, smectic-isotropic thermal stabilities [zero for series 1 to 4] for the homologous series 1, 2, 3, 4, 5 and 6 are in the increasing order as the number of methylene group increases in the vinyl carboxylate terminal in the right hand side. Smectic-isotropic thermal stabilities for the homologous series 1, 2, 3, 4, 5 and 6 also do not alternate with a decreasing ratio of the difference. The inductive effect due to addition of methylene –CH_2- unit at left terminal is rather less effective through –O- linking; while increase in polarizability of the molecules there by providing grounds for enhancing thermal stabilities, yet due to inductive effect as mentioned above, the terminal attractions are strengthened of these ester series resulting into increase in thermal stabilities as progressively methylene units are added.

The commencement of mesophase [for nematic series 1 to 6 and smectic phase for series 5,6] from fifth or sixth member in all the six [1 to 6] homologous series except in first and sixth series where commencement of the mesophase takes place from third homologue. Dave and Kurian [271] relates extent of non-coplanarity with early or late commencement of smectic phase. According to them, early commencement of the smectic phase is related with less non-coplanarity of the molecules. Molecules of series 1, 2, 3, 4, 5 and 6 are almost equally non-coplaner mutually. The extent of non-coplanarity and lateral attractions due to the central bridge being almost the same for the molecules of all the six series under comparison, the added polarizability due to increased chain length at the vinyl carboxylate end seems almost equally effective for series 1, 2, 3, 4, but it is more effective to reduce the non-coplanarity for series 5 and 6 because the smectic phase appears in case of series 5 and 6 from sixth and seventh member of the series respectively, while, it does not appear till the last homologue in case of series 1, 2, 3, 4. In methyl homologous series i.e. series 1,the right terminal methyl has to have straight linking, the overall display of mesomorphism is richer than that shown by the very next homologus series 2 and 3 in sequence but less richer than the present homologous series 4,.5,and 6.

Therefore, taking into consideration, the above discussion for series 1, 2, 3.4.5 and 6 the smectic and nemetic group efficiency order derived in terms of the terminal substituent from table is as under.

Group efficiency order for nematic:-

$-CH=CH-COOC_4H_9(n) > -CH=CH-COOC_6H_{13}(n) > -CH=CH-COOC_3H_7(n) > -CH=CH-COOC_5H_{11}(n) > -CH=CH-COOC_2H_5 > -CH=CH-COOCH_3$

Group efficiency order for smectic :-

$-CH=CH-COOC_6H_{13}(n) > -CH=CH-COOC_5H_{11}(n) > -CH=CH-COOR'$

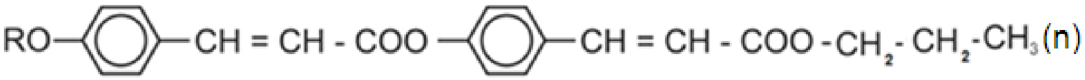
Where $R' = -CH_3, -C_2H_5, -C_3H_7(n), -C_4H_9(n)$

Comparison of series 3,4 with series 7,8 with reference to series 1 and 2:

From **fig.–23** the molecules with above core structure excluding the right terminal group, the basic length due to two phenyl rings, the central bridge –CH=CH-COO- left n-alkoxy terminal linking groups, aromaticity of the molecules are the constant unchangimg features and the display of molecular forces on account of these factors will remain constant. All these homologous series represented in figure- have their changing part at right linking are n-alkyl and iso-alkyl branched carbon chain in carboxylate terminal groups. Therefore, change in mesomorphic characteristics have direct relation with the difference in the stereoisomerism of the right terminals.

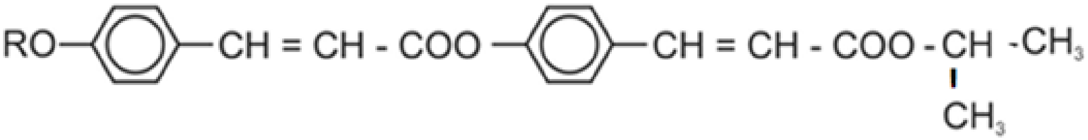
In the methyl and ethyl homologous series **(figure-23),**

(3)



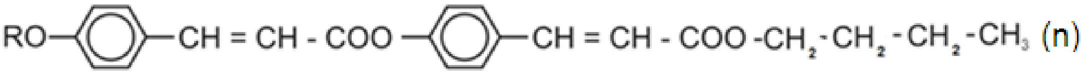
Cis n-propyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

(7)

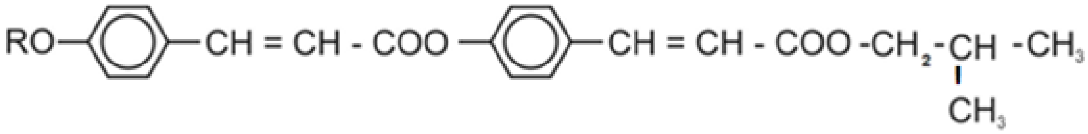


Cis Isopropyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

(4)



Cis n-butyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

(8) 

Cis Isobutyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

Figure-25

Where the right terminal methyl or ethyl or in general alkyl chain have though straight linking **(figure-25),** the overall display of mesomorphism is poorer than that shown by the very next series in the sequence i.e. homologous series -7.

Table-23 .

No. of carbon atoms in left alkylchain	Upper transition in ^{0}C			Difference in the transition temperatures ^{0}C	
	Series-1	Series-2	Series-7	(7-1)	(7-2)
3	140.0	*	*	-	-
4	128.0	*	*	-	-
5	125,0	*	184.0	59.0	-
6	128.0	159.0	241.0	116.0	85.0
7	-	152.0	207.0	-	55.0
8	150.0	147.0	242.0	92.0	95.0
10	166.0	139.0	220.0	54.0	81.0
12	175.0	144.0	190.0	15.0	46.0
14	163.0	152.0	170.0	07.0	18.0
16	138.0	164.0	152.0	14.0	12.0

*indicate nonmesomorphic.

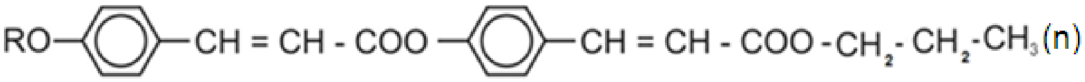
Observations recorded in **table-23** clearly convey that, while both ‘methyl’ and ethyl groups at the right terminal of the homologous series under comparison are shorter than the corresponding ‘propyl’ group of the homologous series-7, the upper transitions of the series-7, due to ‘iso’ disposition of the right terminal propyl chain should be lower than the series 1 and 2. But are actually higher than the series 1 and 2 (except C_{16} homologue of series-2). This unexpected experimental observation suggests that, ‘iso’ terminal linking should reduce the intermolecular attractions due to widening of molecules on one hand, but on the other hand, widening of molecules increases molecular polarizability and consequently increases intermolecular attractions. Thus, two opposingeffects are operating at the same time. Therefore resultant net effect depends upon the effect which predominates out of these two opposing effects. In case of present comparison of methyl and ethyl homologous series with ‘iso’ linked propyl homologous series-7, the predominating factor is, increased molecular polarizability due to widening of isopropyl homologous series-7 as compared to molecular polarizability caused by methyl and ethyl homologous series which do not surpass the magnitude of intermolecular attractions caused by isopropyl series (7). Hence, greater the magnitude of intermolecular attraction, more heat energy or rather high temperature will be required to occure mesophase or to disrupt the molecular structure. Therefore upper transitions of ‘iso’ linked propyl series are higher than corresponding methyl and ethyl homologous series 1 and 2. This is indeed a very striking effect to emerge from the comparative study.

Further, the homologous series 1 and 2 (figure-) display mesomorphism from their third and sixth homologue while, mesomorphism is displayed from fifth, homologue of homologous series-7. Only nematic property is exhibited by two series i.e. series -1 and -2 and by series-7. However, smectic property is not displayed by any of the series 1, 2 and 7 under comparison.

It seem that, the isopropyl chain being longer than methyl or ethyl group, its isodisposition is accilarating factor which raises the mesomorphic characteristics to a more or less extent as if the ‘iso’ linked propyl group is longer than the either otherwise smaller group. Nevertheless, all the series considered so far under comparative evaluation of the mesomorphic characteristics, predominantly and entirely nematogenic including series which is also entirely nematogenic without exhibition of smectic property. This would point out to say that ‘iso’ or ’normal’ linking is more conducive to the smectic property than nematic orientations in ester series involving –CH=CH-COO- central bridge or / and terminal end group.

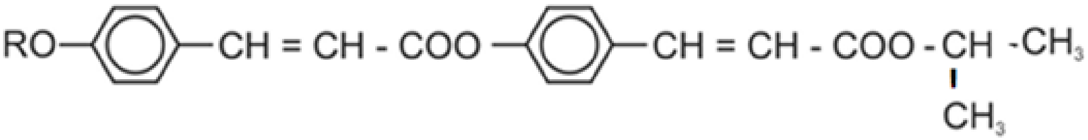
Taking now homologous series-3 and-7, which differ only in right terminal groups. In case of n-propyl –p-(p'-n- alkoxy cinnamoyloxy) cinnamates, the alkyl chain at the right terminal has a straight normal linking (series-3) while, that in the series 7, it has 'iso' disposition linking (figure).

(3)



Cis n-propyl –p-(p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

(7)



Cis Isopropyl –p-(p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates.

Figure-26

The net effect is seen in the total length of the two molecules in the face of the fact that, the core geometry of the moieties is the same. In the case of the homologous series-7, the length of the molecules is shortened by almost two carbon linking in space as compared to that of the molecules of series-3. At the same time, however, breadth of the molecules of series-7 is increased by one –CH_3 unit assuming iso-linking in space. This difference results into several alteration in the mesomorphic characteristics of the two homologous series under comparison.

Firstly, with the length shortened and breadth widened, the mesomorphic transitions are expected to scale down, in table- . Difference values of the transitions are given.

Table-24.

No. of carbon atoms in left alkylchain	Upper transition in ^{0}C		Difference in the transition temperatures ^{0}C
	Series-3 (Fig.)	Series-7 (Fig.)	(7-1)
5	*	184.0	Not deducible
6	157.0	274.0	85.0
7	153.0	207.0	55.0
8	147.0	242.o	95.0
10	139.0	220.0	81.0
12	144.0	190.0	46.0
14	152.0	170.0	18.0
16	164.0	152.0	12.0

*Indicate nonmesomorphic.

From **table-24**, it can be seen that, increase in the upper transitions is rising between 12^{0C} and 95^{0C} in case of the series-7 with the branched ‘iso’ linking of the right alkyl chain, the breadth has increased sufficiently to cause some what odd fitting of the molecules throwing or pusing apart the molecules, but increased polar molecular polarizability due to widening predominatly raises itermolecular attractions. Consequently, they need more thermal agitation to break down partially so as to give rise to a mesomorphic order of molecules in the fluid state; than that needed for the molecules of the series-3 **(figure-26)** where the right alkyl chain linking is just straight.

Secondly the absence of smectic property in series-7 is obviously understood because series-3 with ‘normal’ linking exhibit tatally nematogenic property, supporting the view that terminal ring –CH=CH-COO- group strongly favours nematic mesophase formation. In case of series n-propyl-p-(p’-n-alkoxy cinnamoyloxy)cinnamates,first five homologues are non-mesomorphic;

enantiotropic nematic property is exhibited from sixth homologues onwards without persistence of any monotropic smectic or nematic property. In contrast, the homologous series isopropyl-p-(p'-n-alkoxy cinnamoyloxy) cinnamates with just one terminal linkage being changed, the first four homologues are without cut in mesomorphism produces one more mesogenic homologue. From this comparison it can be said that higher homologues do get broken down into isotropic liquid relatively at higher temperature between 152.0^{0C} and 244.0^{0C}. On cooling, the first five homologues in series-3 **(figure-16)** exhibit high crystallizing tendency precluding any showing up of either nematic or smectic property even in the monotropic condition. Same is the case with the first four members of the series -7, where no monotropic mesophase has been detected on supercooling due to high crystalising tendency. It also appears that, the terminal attractions are insufficient which do not induce nematic or smectic property in the monotropic condition on supercooling in case of straight or branched alkyl chain at the right terminal vinyl carboxylate group.

Thirdly the display of mesomorphism from sixth homologue onwards in series -3 **(figure-16)** enantiotropically which indicate that the intermolecular packing in the right terminal resulting into the stable mesophase formation. But, if 'normal' linking is replaced by 'iso' linking in the right carboxylate terminal, the terminal attractions are simultaneously increased, into enhancement in the mesomorphic behaviour as observed in series-7, where early commencement of the mesophase persisted by one more mesogenic homologue.

Thus, the statement that, "broading of molecule reduce the thermal stability of the molecules" is not an universal truth but thermal stability due to iso linking at the end group may increase or decrease, depending upon predominancy of the two opposing effects operating at a time due to widening of molecules

Fourthly odd-even effect in the nematic transitions of both series under comparison (3 to 7) is observed even if mesophase commemces late, i.e. higher homologues preserves their molecular n-alkyl chain intact without bending or flexing in floating condition, upto decyl homologue.

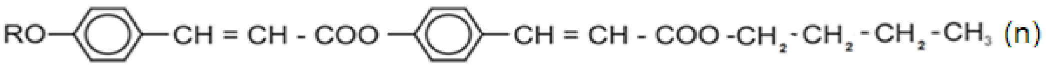
Table-25 depicts the difference value of the upper transitions for series 4 and 8.

Table-25:

No. of carbon atoms in left alkylchain	Upper transition in ^{0}C		Difference in the transition temperatures ^{0}C
	Series-4 (Fig.)	Series-8 (Fig.)	(4-8)
5	nonemeshomorphic	165.0	Not deducible
6	142.0	136.0	06.0
8	160.0	125.0	35.0
10	189.0	130.0	59.0
12	222.0	142.0	80.0
14	236.0	143.0	93.0
16	220.0	129.0	91.0

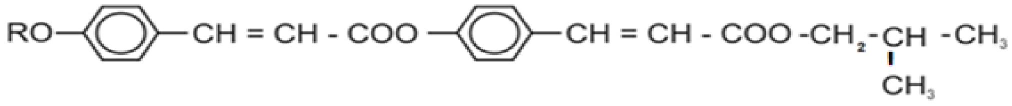
From **table-25**, it is seen that, the branching of the alkyl chain or keeping straight alkyl chain at the right carboxylate terminal causes difference in mesomorphic properties. The mesomorphism is reduced (series-4 and 8) by replacing straight n-alkyl chain to iso linked alkyl chain.

(4)



Cis n-butyl –p-(p$^/$-n-alkoxy cinnamoyloxy) cinnamates.

(8)



Cis isobutyl –p-(p$^/$-n-alkoxy cinnamoyloxy) cinnamates.

Figure-27

Compering the series 4 and 8, the first five members in series 4 **(figure-17)** are nonmesomorphic and melting relatively at high temperature. Remaining members are enantiotropic nematic. Similarly in series-8, the first four members are nonmesomorphic, and rest of the homologues are enantiotropic nematic. Thus, mesomorphism displayed by the series-4 is richer than series-8 which exhibits only nematic type of mesomorphism. This is quite an expected because genaraly branching of alkyl chain can cause mesomorphism with lower transitions in case of series-8. Thus, overall polarizability and polarity in combination with sreric effect and inductive effect results into the molecules of series-4 and 8 in such a way that net cohesive forces in series-4 due to end to end attraction in straight linking (n-Butyl) predominantly operates as compared to effect due to polarisability caused due to branching which becomes greater than series-8. Therefore, packing of the molecules in series-4 is stronger than the packing of molecules of series-8. Thus, series-4 displays mesomorphism to a greater extent than series-8. Hence, the extentof mesomorphism is less disturbed as number of carbon atoms in alkyl chain increases beyond four (i.e. butyl group) either in form of ‘iso’ linking or ‘normal’ linking at the right carboxylate terminal.

The relative nematic-isotropic thermal stabilities for homologous series-3 and 4 as well as 7 and 8 are calculated and recorded in **table-26** .

Table-26: . Relative thermal stabilities.

-	Average thermal stability in ^{0}C			
	Series-3	Series-4	Series-7	Series-8
Nematic isotropic	183.8 (C_6-C_{14})	194.8 (C_6-C_{16})	201.11 (C_5-C_{16})	138.1 (C_5-C_{16})
Commencement of smectic phase	C_6	C_6	C_5	C_5

From **table-26**, it can be seen that nematic isotropic thermal stabilities for the homologous series-3 and 4 **(figure-16,17)** are in the increasing order as one passess from series-3 to 4. It means that, thermal stabilities increases as the methylene unit is added causing increase in the alkyl chain length at the ester end. This variation in the thermal stabilities which is of increasing sequence as chain length is increased at the ester end is in good agreement with the generalization derived from previous wark. However, looking to the relative thermal stabilities of series -7 and 8 are in decreasing order. Moreover, thermal stability of series-3 **(figure-16)** is less than the thermal stability of series-7 **(figure-20)** which is not in agreement with the generalization made earlier i.e. instead of lowering of thermal stability it, increases in series-7 as compared to series-3. But however, the relative thermal stability of series-4 and 8 are fitting with the generalization as made earlier that irrespective of branching of molecule, thermal stability of series-8 is less than series-7 and 4 which is expected feature.

The molecules of the series-3 and 4 are identical with these series 7 and 8 in all respect except the type of linking in alkyl chain at the right carboxylate terminal; which is ‘iso’ instead of the ‘normal’ chain. With this change, while the polarizability of the molecules is affected, the breadth is indeed enhanced. The effect of these factors in case of series-3 and 7 operates in respect of consequence of polarizability. A termination in transition temperature is not expected in the ester series; of the alkyl chain at the right terminal of the series-7 and 8.

Thus, it can be concluded that nematic isotropic thermal stability though generally decreases from series to series in ester series, but however, it may or may not alternate from series to series irrespective of the type of linking in alkyl chain at the right vinyl carboxylate terminal group.

Thus, from above comparison discussed, the nematic group efficiency in terms of ‘normal’ and ‘iso’ stereoisomerism on the basis of thermal stability is as under:

–CH=CH-COO-C_3H_7(iso) > -CH=CH-COO-C_4H_9 (n) > -CH=CH-COO-C_3H_7(n) > -CH=CH-COO-C_4H_9(iso).

Comparison of series 1, 2, 3, 4, 6, 7, 8, 9 with A_1, A_2, A_3, A_5, A_8, A_4, A_6, A_9

From **figure-28**, the molecules with above core structure excluding the central bridge, the basic length due to two phenyl rings and the both terminal linking group, aromaticity of the molecule etc. are the constant unchanging feature and the display of molecular forces on account of these will remain the same. All these homologous series represented in **figure-28**, have their changing part at central linking are –CH=CH-COO- in series 1,2,3,4,6,7,8,9 while –COO-in series A_1, A_2, A_3, A_5, A_8, A_4, A_6, A_9 . This difference brings in with, other differences in the display of molecular forces. The overall length of the molecules of the series A_1, A_4, A_6, A_8, A_9 is decreased as compared to series 1 to 4 and 6 to 9. Normally the length to breadth ratio is affected, simultaneously with the π-electron density due to delocalized electrons on account of an added double bond would be absent in series A_1 to A_3 and A_4 and A_6 which would affect the overall polarizability of the molecules. In other words, it can be seen that the series symbolised by A with lesser polarizability and length, these two difference would cause the mesomorphic characteristics to udergo variations.

The new homologous series as investigated in present investigation are designated as 1, 2, 3, 4, 6, 7, 8, 9. These series compered with other homologous series viz; A_1, A_2, A_3, A_5, A_8, A_4, A_6, A_9 (62(b)) and (62(a)) for

(1)

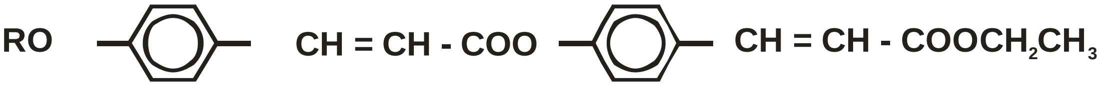
Cis Methyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(A_1)

[62 (b)]

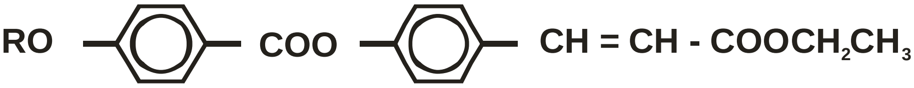
Methyl p-(-p’-n-alkoxy benzoyloxy) cinnamates.

(2)



Cis ethyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

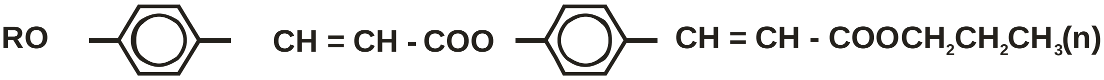
(A2)



[62 (b)]

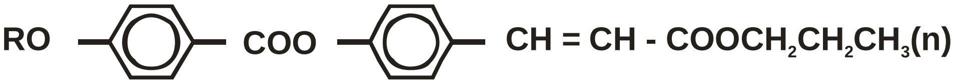
Ethyl p-(-p’-n-alkoxy benzoyloxy) cinnamates.

(3)



Cis n-propyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(A3)



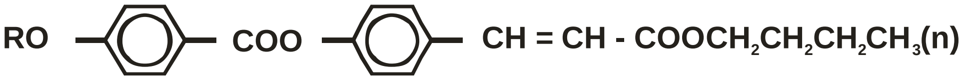
[62 (b)]

n-Propyl p-(-p’-n-alkoxy benzoyloxy) cinnamates.

(4)

Cis n-butyl –p-(p/-n-alkoxy cinnamoyloxy) cinnamates.

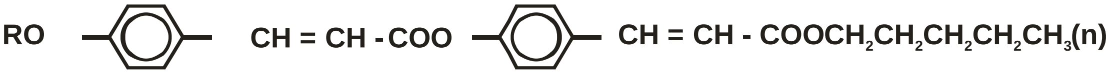
(A5)



[62 (b)]

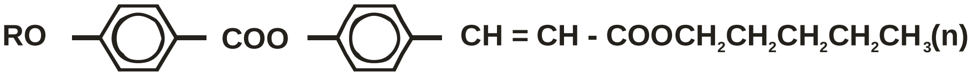
n-Butyl –p-(p/-n-alkoxy benzoyloxy) cinnamates.

(6)



Cis n-Hexyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

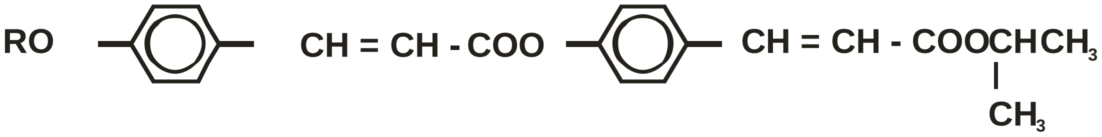
(A8)



[62 (b)]

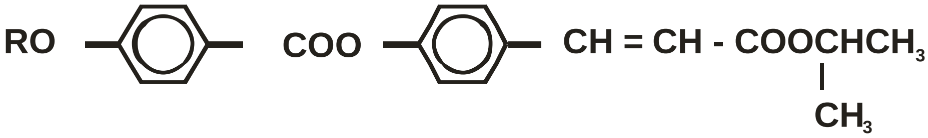
n-Hexyl p-(-p’-n-alkoxy benzoyloxy) cinnamates.

(7)



Cis Isopropyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

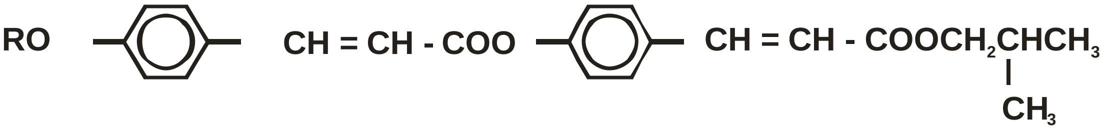
(A_4)



[62 (b)]

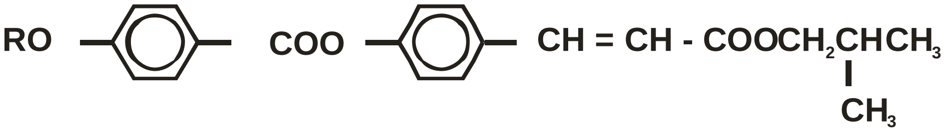
Isopropyl p-(-p’-n-alkoxy benzoyloxy) cinnamates.

(8)



Cis Isobutylyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

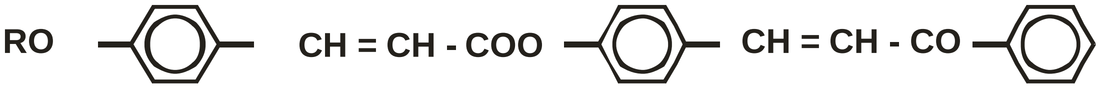
(A_6)



[62 (b)]

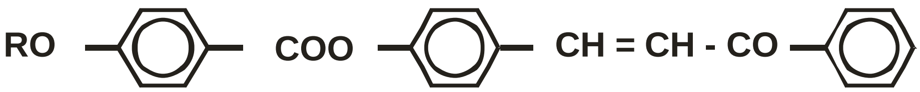
Isobutylyl p-(-p’-n-alkoxy benzoyloxy) cinnamates.

(9)



Cis p-(p’-n-alkoxy cinnamoyloxy) B-benzoyl styrene.

(A_9)



[62 (b)]

p-(p’-n-alkoxy benzoyloxy) B-benzoyl styrene.

Figure-28

evaluating their characteristics as associated with thermal stabilities. Both smectic-nematic or smectic-isotropic and nematic isotropic thermal stabilities are recorded in table- ; for all the above homologous series under comparison.

From **table-27,** it can be seen that occurrence of smectic mesophase being absent, smectic isotropic thermal stabilities for the homologous series 1, 2, 3 and 4 are considered as zero, the thermal stability for series-6 can be compared with series A_8, which is 179.6 and 93.2 respectively and therefore thermal stabilities for smectic is in the increasing order as one passess from series-1 to series-6. In other words, the smectic-isotropic thermal stability increases as the methylene unit is added causing increase in the alkyl chain length at the ester end.

This variation in the thermal stability which is of increasing sequence as chain length is increased at the ester end is not in agreement with the thermal stability characteristics of the homologous series A_1,A_2, A_3, A_5, A_6, A_8, (62 (b)) and A_9 (62 (a)) which differ in their molecular geomentry from the homologous series 1, 2, 3, 4, 6, 7, 8, 9 in the linking of the central bridge joining two phenyl rings and their difference of spatial configurated homologous series. The smectic isotropic thermal stability of homologous series 1, 2, 3, 4, 7, is in increasing order and in case of series 6 and 8 , it decreases as methylene unit is added to alkyl chain of right terminal, vinyl carboxylate. This observation clearly indicate that, cis configurated series 1 to 4 adversely behave than to behave in expected manner. This is because, nematic-isotropic transition temperatures rises as series is ascended for the series under investigation. This, suggests that, by changing the arrangement of atoms in space by varying molecular geomentry, the intermolecular attractions may get stringed by sequentially added methylene unit due to increased polarizability for the reason, replacing trans configurated molecule to cis configurated molecule. Thus, cis configurated isomers can also display mesomorphic behavior showing rise of transition temperature from homologue to homologue and after passing through maxima, transition temperatures may fall or may not fall down as series in ascended. [264].

Table No.27 : Relative thermal stability.

series	Average transition temperatures in^{0}C							
	1	2	3	4	6	7	8	9
Smectic-isotropic or smectic-Nematic	-	-	-	-	179.6 (C_7-C_{14})	-	-	-
Commencement of Smecticphase					C_7			
Nematic-isotropic	145.0 (C_3-C_{16})	151.0 (C_6-C_{16})	183.0 (C_6-C_{14})	194.8 (C_6-C_{12})	190.3 (C_3-C_{16})	201.1 (C_5-C_{16})	138.8 (C_5-C_{16})	144.5 (C_6-C_{16})
Commencement of Nematicphase	C_3	C_6	C_6	C_6	C_3	C_5	C_5	C_6

series	Average transition temperatures in^{0}C							
	A_1	A_2	A_3	A_5	A_8	A_4	A_6	A_9
Smectic-isotropic or smectic-Nematic	-	74.8 (C_6-C_{16})	107.5 (C_8-C_{10})	101.0 (C_{10}-C_{16})	93.2 (C_8-C_{14})	104.8 (C_5-C_{16})	-	106.6 (C_{10}-C_{16})
Commencement of Smecticphase	-	C_6	C_8	C_{10}	C_8	C_5	-	C_7
Nematic-isotropic	105.0 (C_2-C_{16})	98.6 (C_4-C_{16})	121.0 (C_6-C_{16})	140.0 (C_5-C_{16})	136.6 (C_8-C_{14})	133.3 (C_3-C_{16})	108.8 (C_6-C_{14})	119.8 (C_8-C_{16})
Commencement of Nematicphase	C_2	C_4	C_6	C_5	C_8	C_3	C_6	C_8

The above contention that the ester series give decreasing or increasing transitions as the chain length is increased or may be supported will depend upon arrangement of atoms in space i.e. either cis or trans configuration by the thermal stabilities of the homologous series under comparision. The homologous series designated A1, A2, A3, - - - (62 (a)) are alkyl-p-(p'-n-alkoxy benzoyloxy) cinnamates; of ester series have their thermal stabilities neither dcreasing nor increasing order but alternates [excluding exception] as a methylene unit –CH2- gets added. But, in case of the present homologous series, it generally increases. In all other respects except the central bridge which is –CH=CH- COO- in case of homologous series 1, 2, 3, 4, 6, 7, 8, 9, under study and carbboxy –COO- in case of series A_1, A_2, A_3, A_5, A_8, A_4, A_6 and A_9 under comparison are closely, similar to each other. Both these central bridges are comparable, though the vinyl carboxylatye –CH=CH-COO- has greater length and causes more noncoplanarity due to a twist obtained as the oxygen atoms of the vinyl carboxy group bump in to the nonbonded adjacent hydrogen atoms of the aromatic rings. On account of these differences the smectic -isotropic thermal stabilities are general way lower than the corresponding smectic themal stabilities of homologous serirs A_1, A_2, A_3, A_5, A_8, A_4, A_6 and $A_{9.}$ However, the characteristics neither of decreasing nor increasing but alternating order of the thermal stabilities on addition of the methylene unit, to the increasing order obtained in the present ester series of mesogens under study. Along with this desimilarity of the decreasing order of the smectic and nematic thermal stability, there is one more striking similarity and that is of the ratio of the difference in the values of the thermal stabilities i.e. 1-2 / 2-3=0.15 and A_1-A_2 /A_2-A_3=0.30 (2 x 0.15). This would strengthen the view that with addition of each methylene unit, the effect should be of equitable or multiple of equitable value is verywell supported by present investigation. Series 1, 2, 3, 4, 6, exhibit the nematic mesophases. Therefore, a comparison to this effect is discussed with reference to nematic property. Thus, the ratio of the difference in the consective series would have been in case of the homologous series 1, 2 and 3 is almost the same or in multiple of it as exhited by the homologous series A_1, A_2, and A_3.

The enhanced length of the vinyl carboxy –CH=CH-COO- central group, increased conjugation by –CH=CH- and length which increases the rigidity of the molecule and lateral attractions and hence intermolecular attractions increases; while in case of –COO- central bridge, the relative length is shorter and do not link the phenyl rings through atleast one multiple bond or a hydrogen bonded ring system. Consequently the stereochemistry of the molecule does however, preserve linearity of the molecule but results in less thermally stable mesophase. In case of series 1, 2, 3, 4. 6 the presence of cis configuration increase in the rigidity and polarizability of the molecules. Hence the molecules tend to pack efficiency and relatively higher thermal stability persisted for series under investigation as compared to series under comparision.

Thus, keeping both terminal same and varying central bridge, the variation in mesophase observed is given in **table-28**.

Table-28

series	Thermal stability (Nm)	series	Thermal stability (Nm)
1	145.88	A_1	105.0
2	151.10	A_2	98.6
3	183.8	A_3	121.0
4	194.8	A_5	140.0
6	190.3	A_8	136.6
7	201.1	A_4	139.3
8	138.8	A_6	108.8
9	144.5	A_9	109.8

It is observed that, as the central bridge becomes shorter by –CH=CH- unit length and lesser in an equivalent manner in π- electron density as is the case in series A_1, A_2, A_3, A_5, A_8, A_4, A_6 and A_9 the nematic-isotropic thermal stabilities are lowered considerably due to overall decrease length and polarizability of the molecules. The relative difference in the average thermal stabilities of the two sets of the series designated by A_1, A_2, A_3, A_5, A_8, A_4, A_6 and A_9 series 1, 2, 3, 4, 6, 7, 8, and 9can be obtained. The difference value in the thermal stability is due to the difference of the –CH=CH- unit in the respective homologue of the two sets of series. The difference value put good impact due to the shortening of the central bridge.

Exhibition of smectic characteristics in series involving viz; -COO- central bridge A_1, A_2, A_3, A_5, A_8, A_4, A_6 and A_9 differes from corresponding present homologous series 1, 2, 3, 4, 6, 7, 8, and 9with –CH=CH-COO- under investigation. This is due to the difference of conjugated part –CH=CH- causing difference in favorable length, breadth and hence the favourable polarizabilty and length to breadth ratio. Smectogenic character commence to appear late from homologous series-5 i.e. n-pentyl alkyl chain of terminal group.

Thus, the order of group efficiency order for smectic and nematic derived in terms of thermal stability, while both terminal substituents are same, can be given as under:

Smectic group efficiency order: -COO- > -CH=CH-COO-

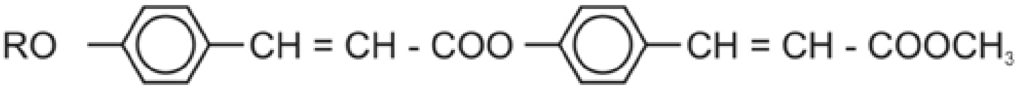
Nematic group efficiency order: -CH=CH-COO- > -COO-.

Comparison of the series 1, 2, 3, 4, 5, 6, 7, 8 and 9 :

From **figure –29** it is seen that the series 1, 2, 3, 4, 5, 6, 7, 8, 9, A_1, A_2 and A_3 which have the core geometry of their molecules, with two phenyl rings linked by the same central bridges and the same varying left terminal alkyl chains but differ in the right terminal groups. Therefore, the variation in mesomorphic characteristics and the extent of mesomorphism exhibited are related to the variation in the right terminal group. The smectic-isotropic and nematic-isotropic thermal stabilities are calculated and recorded in table-   .

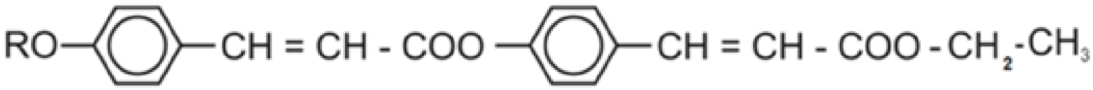
From table- it is seen that the smectic isotropic thermal stability of series-6 is maximum because the right terminal group –CH=CH-COO-C6H13(n) is having longest n-alkyl chain at right terminal end group amongst the series under comparison (Table-), involving vinyl carboxylate system.

(1)



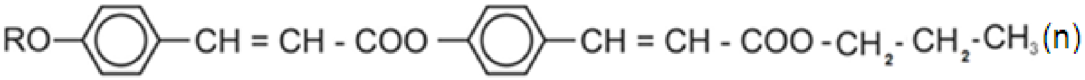
Cis Methyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(2)



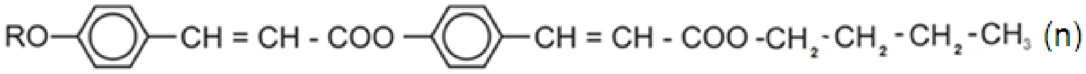
Cis Ethyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(3)



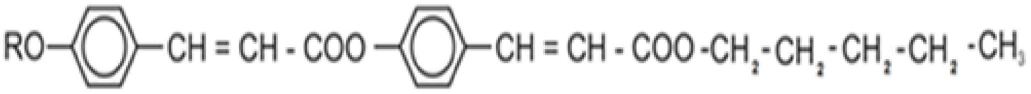
Cis n-Propyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(4)



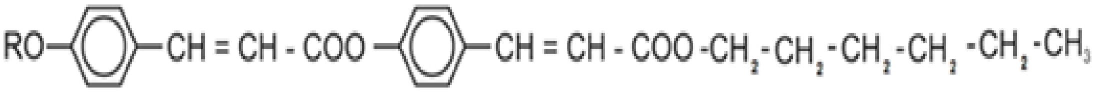
Cis n-Butyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(5)



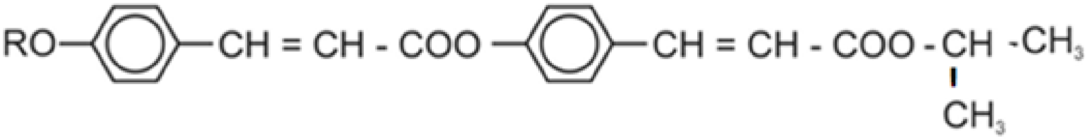
Cis n-Pentyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(6)



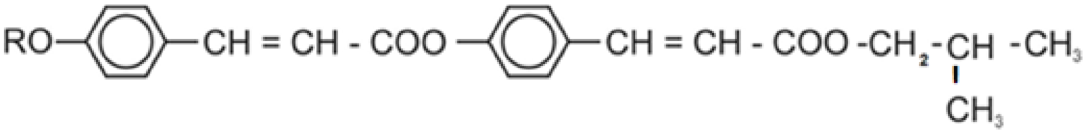
Cis n-Hexyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(7)



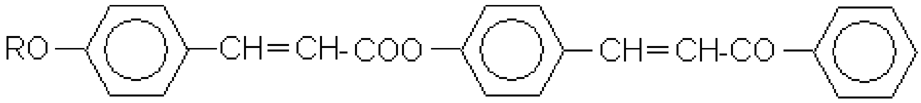
Cis iso propyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(8)



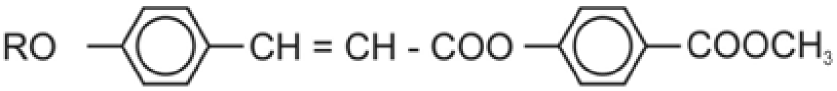
Cis isobutyl p-(-p’-n-alkoxy cinnamoyloxy) cinnamates.

(9)



Cis p-(p’-n-alkoxy cinnamoyloxy) B-benzoyl styrene.

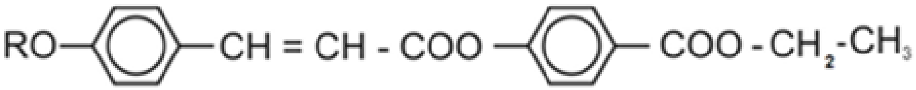
(A1)



[272]

Methyl p-(-p’-n-alkoxy cinnamoyloxy) benzoates.

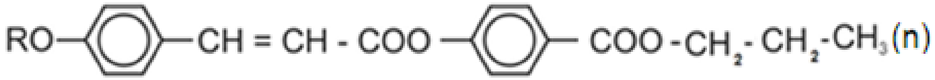
(A2)



[272]

Ethyl p-(-p’-n-alkoxy cinnamoyloxy) benzoates.

(A3)



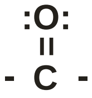
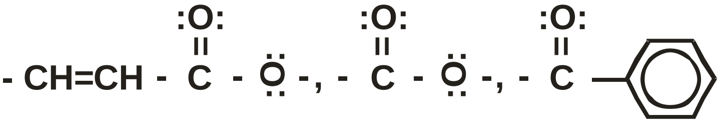
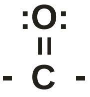
[272]

n- Propyl p-(-p’-n-alkoxy cinnamoyloxy) benzoates.

Figure-29

The terminal attractions due to overall polarizability of the molecule is so strong that the smectic-isotropic thermal stability increases to the highest extent amongst the series under comparison. The thermal stability of series A_1 is less than series 6 but greater than series A_2, A_3 and 5. The rest of the homologous series 1, 2, 3, 4 and 9 exhibit only nematic mesophase without exhibition of smectic property.

All homologous series undercomparison contain $-\overset{:O:}{\overset{\|}{C}}-$ part in the right terminal but difference in linking with $-\overset{:O:}{\overset{\|}{C}}-$ part differs i. e. in series-1 to 8; n-alkyl (methyl to n-hexyl) and (isopropyl and isobutyl) groups are linked through $-\ddot{\underset{\cdot\cdot}{O}}-$ part but, phenyl group is directly liked with $-\overset{:O:}{\overset{\|}{C}}-$ part in series-9. However, $-\overset{:O:}{\overset{\|}{C}}-$ group contained by series 1, 2, 3, 4, 5, 6, 7, 8 and 9differs from series A_1, A_2 and A_3 by –CH=CH-unit which is absent in series A_1, A_2 and $A_{3.}$

The normal or isolinked alkyl chain is linked with ketonic section through oxygen atom in series 1,2,3,4,5,6,7,8, A_1, A_2 and A_3 but in case of series-9, a phenyl ring is directly linked with ketonic section. The inductive effect and /or steric hinderance due to n- alkyl or iso alkyl group through oxygen linking rather than direct linking with  $-\overset{:O:}{\overset{\|}{C}}-$ is more effective in case of series-6 because of the difference in polarity of the bond  in case of series 1 to 8, series-A_1 to A_3 and series-9 respectively and related with the difference in electron negativity of sp^3 hybridised carbon atom linked through or not through oxygen atom and with or without –CH=CH- unit. Thus, the terminal attractions are strengthened in case of ester series with $-CH=CH-COO-C_6H_5$ resulting in to increase in thermal stability. However, smectic-isotropic thermal stability of series 1, 2, 3, 4, 7 ,8, and 9 are zero or less than the thermal stability of series 5, 6, A_1, A_2 and A_3 because the inductive effect due to addition of methylene $-CH_2$-unit is rather more effective through –O- linking than direct linking with sp^2 carbon atom, while increase in chain length may work towards increase in polarizability of the molecules thereby providing grounds for enhanceing smectic and nematic thermal stabilities. Yet due to inductive effect as mentioned above, the terminal attractions weakens in case of ester series with carboxylate end group resulting into decrease in nematic isotropic thermal stability of series A_1, A_2 and A_3 as progressively added methylene units; while, nematic-isotropic and smectic-isotropic thermal stability increases from series 1 to 8 (except-5) in case of vinyl carboxylate terminal end group as methylene unit is sequentially added. Obviously the inductive effect due to hydrogen atom is being zero while it is relatively positive in case of alkyl group. Moreover, sp^3 hybridised alkyl group being more than the steric effect caused by sp^2 carbon phenyl ring directly linked at  $-\overset{:O:}{\overset{\|}{C}}-$ part. These two factors in combination with other effects results in enhancement of the terminal attractions between the molecules of series-9 resulting into higher thermal stability (nematic-isotropic) than the molecules of series A_1, A_2 and A_3 but less than nematic isotropic thermal stability of series 1, 2, 3, 4, 5, 6, 7, and 8.

The commencement of the smectic mesophase in all the polymesomorphic series under comparison (Table-) takes place quite later from and beyond sixth homologue (except series-A_1) because the central group linking two phenyl rings in all these series under comparison is common i.e. –CH=CH-COO- producing almost equal non-coplanarity in the molecules. Morever, the series under comparison are either predominantly or partly smectogenic, supporting the view, that, ester series with –COO- carboxy central or / and end group are favourably and only or predominantaly smectogenic and partly nematogenic but, ester series with vinyl carboxy –CH=CH-COO- central and / or terminal end group are favourably and only nematogenic or predominantly nematogenic and partly smectogenic. Thus, group effeciency order derived for smectic and nematic in terms of terminal end group is as under.

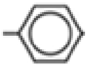
Table – 29 : Relative thermal stability

Series	Average transition temperatures in^{0}C								
	1	2	3	4	5	6	7	8	9
Smectic-isotropic or smectic-Nematic	-	-	-	-	118.5 (C_6-C_{12})	179.6 (C_7-C_{14})	-	-	-
Commencement of Smecticphase					C_6	C_7			
Nematic-isotropic	145.0 (C_3-C_{16})	151.0 (C_6-C_{16})	183.0 (C_6-C_{14})	194.8 (C_6-C_{12})	169.3 (C_5-C_{16})	190.3 (C_3-C_{16})	201.1 (C_5-C_{16})	138.8 (C_5-C_{16})	144.5 (C_6-C_{16})
Commencement of Nematicphase	C_3	C_6	C_6	C_6	C_5	C_3	C_5	C_5	C_6

Series	Average transition temperatures in^{0}C		
	A1	A2	A3
Smectic-isotropic or smectic-Nematic	138.25 (C_1-C_{14})	120.75 (C_7-C_{12})	123.5 (C_6-C_{12})
Commencement of Smecticphase	C_1	C_7	C_6
Nematic-isotropic	95.5 (C_8- C_{18})	135.9 (C_5- C_{16})	95.5 (C_3- C_{16})
Commencement of Nematicphase	C_8	C_5	C_3

Smectic group

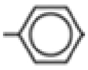
effeciency order : $-CH=CH-COO-C_6H_{13}$ (n) > $-COO-CH_3$ > $-COO-C_2H_5$ > $-CH=CH-COO-C_5H_{11}$(n)

> $-COO-C_3H_7$ (n) > -CH=CH- CO 

Nematic group

effeciency order : $-CH=CH-COO-C_3H_7$(iso) > $-CH=CH-COO-C_4H_9$(n) > $-CH=CH-COO-C_6H_{13}$ (n)

> $-CH=CH-COO-C_3H_7$ (n) > $-CH=CH-COO-C_5H_{11}$(n) > $-CH=CH-COOC_2H_5$ >

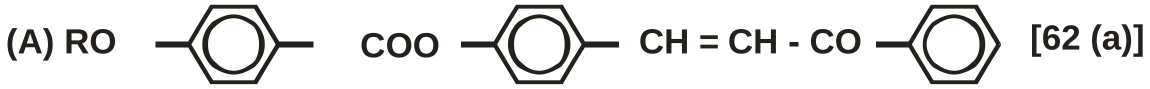
$-CH=CH-COO-CH_3$ > -CH=CH- CO  > $-COO-CH_3$ >

$-CH=CH-COO\ C_4H_9$ (iso) > $-COO-C_2H_5$ > $-COO-C_3H_7$(n)

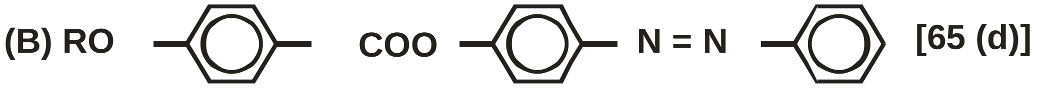
Comparison of the series 9 with series (A) and (B):

The average thermal stability and other liquid crystal properties of structurally similar homologous series (A) and (B) are compared with titled homologous series (1) as under in **table-30** from the **figure –30**.

p-(p’-n-alkoxy cinnamoyloxy) β-benzoyl styrenes



p-(p’-n-alkoxy benzoyloxy) β-benzoyl styrenes



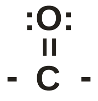
p-(p’-n-alkoxy benzoyloxy) phenyl azo benzenes

Figure- 30

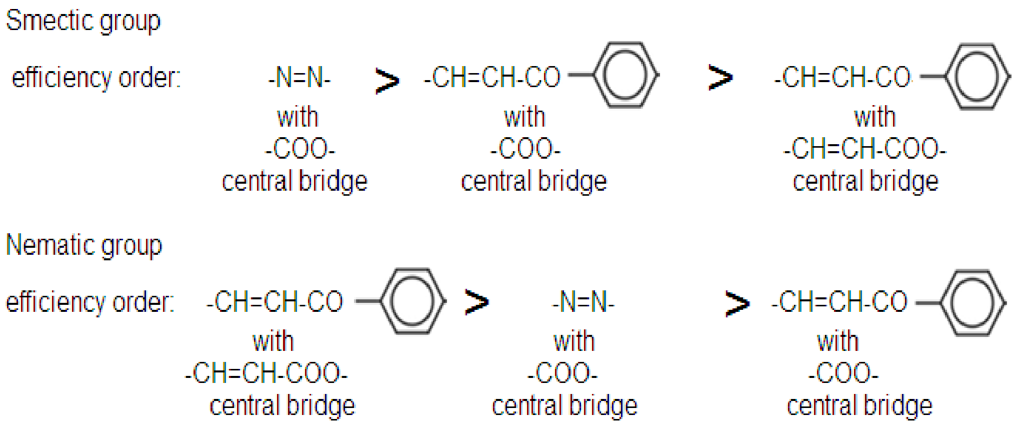
Table - 30 Average thermal stability:

Series	**(1)**	**(A)**	**(B)**
Smetic – isotropic or smectic-nematic	-	106.66 ($C_{10} – C_{14}$)	114.0 (C_{10}-C_{16})
Commencement of smetic phase	-	C_{10}	C_{10}
Nematic - Isotropic	144.5 (C_6-C_{16})	119.8 ($C_8 – C_{16}$)	138.54 (C_1-C_{16})
Commencement of nematic phase	C_6	C_8	C_1

The molecular geometry of the homologous series (1), (A) and (B) is common with respect to three phenyl rings, left n-alkoxy terminal and without right terminal (terminal-H) but, they differ in central bridges –COO-, -CH=CH-COO-, -N=N- and –CH=CH-CO-. Homologous series (1) and (A) under comparison resemble with eacher except a central bridge –CH=CH-COO- and –COO-, linking first and second phenyl rings while, series (B)differs from series (1) in respect of both central bridges. However series (A) and (B) differs from each other with respect to central bridge –N=N- linking second and third phenylrings. Thus, the aromaticity left n-alkoxy terminal and right –H terminal and only one or both central bridge or bridges differ. Therefore the variation in the mesomorphic properties and degree of mesomorphism depend upon the changing part of the molecules. Thus, intermolecular net isotropic or anisotropic forces of attractions vary according to resultant effect caused by overall aromaticity, polarity, polarizability, length to breadth ratio, molecular planarity, molecular rigidity and flexibility, conjugated double bond etc. The smectic-isotropic thermal stability of series (1) is zero or smectic mesophase is not exhibited by homologous series (1) or the lowest among the series under comparison, but, only nematic mesophase is exhibited by the series (1). Therefore nematic-isotropic thermal stability of series (1) is the highest among the series (1), (A) and (B). the presence of –CH=CH- unit at the both central bridges increases molecular rigiditry in addition to molecular length in case of series (1) as compared to series (A) and (B) (which contains only one double bond). This, suggests that intermolecular anisotropic forces of attraction due to end to end and lateral cohesion which are relatively higher for series (1) as compared to series (A) and (B). The electronagativity of nitrogen is more than the carbon but presence of only one double bond between two nitroges i.e. –N=N- while series (1) involve two –CH=CH- units in a molecules. Therefore molecular rigidity of series (1) due to two vinyl linkages surpasses the rigidity possessed by series (B) because of electronic interactions.

The early or late commencement of a smectic mesophase depend upon extent of noncoplanarity (271) caused by the molecule. Less extent of noncoplanarity causes early commencement of smectic mesophase. Vinyl carboxy central bridge is relatively longer than –COO–. Therefore ester groups –CH=CH–COO– causes more noncoplanarity than –CO– due to a twist obtained as the oxygen atoms of the vinyl carboxy or carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings causing considerable strain on the molecule. Therefore the twist around C-O bond forces the phenyl ring out of the plane relatively more incase of –CH=CH–COO– than –COO–. Thus, the noncoplanarity of the molecule is reduced to some extent in case of series (A) and (B) involving –COO– as central bridge and noncoplanarity extended by the molecules of series (1) which will be more than the series (A) and (B). Moreover SP^2 carbon of third phenyl ring is linked directly with  $-\overset{\overset{:O:}{\|}}{C}-$ part of the molecule in case of series (1) and (A) while SP^2 carbon of third phenyl ring in series(B) is linked with –N=N-, in which electronegativity of nitrogen is more than a carbon. On account of these differences, smectic mesophase commemces from decyl homologue of the series (A) and (B), but it does not commence to appear till the hexadecyl homologue of the series (1), as the molecules of a series (1) involve two –CH=CH- unit while only one –CH=CH- is contained by the molecules of the series (A) and (B) series involve –N=N- unit under comparison.

Thus, group efficiency order derived on the basis of thermal stability for smectic and nematic are as under.



Titled homologous series is entirely nematogenic without exhibition of any smectogenic property with middle ordered melting type with low mesomorphic range.

CHAPTER-5

SUMMARY

Salient features of the "Results and discussion" are presented as prominent gains of the present investigation under taken are mentioned below. The pointwise list of work done on new homologous series of liquid crystal and nonliquidcrystal materials are as under.

1. All the nine homologous series consisting of 105 new substances, sixty nine substances, are liquid crystals and exhibit mesogenic property over considerable mesomorphic range.
2. Homologous series (1 to 9) are ester homologous series with vinyl carboxy central bridge and –CH=CH-COOR series (1 to 6) as well as –CH=CH-COC_6H_5 (series 9) terminal group. Where R= C_nH2_{n+1} with iso and normal linking.
3. Molecules of all the homologous series (1 to 9) are having sufficient rigidity, and flexibility with usual polarity, breadth and polarizability to cause anisotropic intermolecular forces of attractions of suitable magnitude to from mesogenic mesophase.
4. All the homologous series (1), (2), (3), (4), (7),(8) and (9) are entirely nematogenic while, series (5) and (6) are predominantly nematogenic and partly smectogenic in character.
5. Absence of smectic property in homologous series(1), (2), (3), (4), (7),(8) and (9) with presence of two –CH=CH– units in the molecules support the view, that an ester homologous series with –CH=CH–COO– linkage favours more to occur nematogenic character as compared to an ester homologous series containing –COO– group.
6. Commencement of mesophase generally takes place from fifth sixth homologue of homologous series except first and sixth homologous series in which mesophase commences from third homologue.

7. None of the homologous series exhibit smectic or nematic mesophase in monotropic condition. i.e. All the 69 new mesogenic substances exhibit enantiotropic smectic or / and nematic liquid crystalals.
8. Polymesomorphism is exhibited by some members of series (5) and (6) enantiotropically proving a view that, as molecular length increases, the ratio of the length to breadth increases and intermolecular forces of attractions are strengthened to cause lamellar arrangement of molecules in crystal lattices resulting into sliding layered arrangement of molecules in floating condition.
9. Nematic-isotropic transition curve initially rises and then falls after passing through early maxima, or it rises and passes through late maxima or it falls initially and rises after passing through minima or it shows descending tendency without passing through early or late maxima or minima and behaves in normal manner as expected and observed in case of other homologous series. Thus, it can be concluded that nematic-isotropic transition curve may adopt any trend of transition temperatures as series is ascended with or without odd-even effect.
10. Generally nematic-isotropic thermal stability increases from series(1) to (6) except series (5) with normal strait alkyl end group while it decreases from series (7) to (8) with iso linking at terminal end group. A series with phenyl end group instead of alkyl linkage present in end group has nematic thermal stability more than series (8) and less than serie (7).
11. Transition temperatures of some homologues for smectic and / or nematic are predictable by extrapolating transition curves.
12. Presence of –CH=CH- part and long alkyl chain plays a specific role in nematic-isotropic transition and exhibition of liquid crystal property.
13. Study is useful for the devices to be operated thermotropically.

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Research papers

Publications:

(A). Research papers published:

(1). Synthesis and Study of New Homologous Series of Mesogens:
n- Butyl-p-(p/-n-alkoxy cinnamoyloxy) Cinnamates.

(B). Research paper accepted:

Following research papers have been accepted for publication in Vol. 3 of Derpharmachemica Journal U.K by 1st March 2011.

(1). Synthesis and Study of Mesogenic Material Through Homologous Series n-pentyl-p-(p/-n-alkoxy cinnamoyloxy) Cinnamates**.**

(2). Synthesis and Study of a New Homologous Series of Cis Cinnamate Esters of Mesogens: n-Hexyl-p-(p/-n-alkoxy cinnamoyloxy) Cinnamates.

(3). Synthesis and Study of a New Ester Homologous Series: Ethyl-p-(p/-n-alkoxy Cinnamoyloxy) Cinnamates**.**

(4). Synthesis and Study of a New Homologous Series of Cis n-Propyl-p-(p/-n-alkoxy Cinnamoyloxy) Cinnamates.

(5). Synthesis and Study of a New Mesomorphic Series: p-(p'-n-alkoxy Cinnamoyloxy) β-benzoyl Styrenes.

(C). **Research papers accepted for publication**, the copy of which note received ill the date which were likely to receive by February, 2011 from the publisher of the journal “Acta ciencia indica” Meerut.

(1). Study of Mesomorphism and its Relation to Molecular Structure with Special Reference to Central Bridges viz. -COO- and -CH=CH-COO- of the Homologous Series.

(2). Study of New Homologous Series of Liquid Crystals:Viz. Isopropyl-p-($p^{/}$-n-alkoxy cinnamoyloxy) Cinnamates.

(D). **Research paper under publication** from Journal of Indian Chemical society entitled:Study of new Mesogenic Homologous Series :Methyl -p-(p^{l}-n- alkoxy cinnamoyloxy) cinnamates.

(E). **Research paper presented** in poster session at the 17th national conference of liquid crystals held at, Department of chemistry, Vir Narmad South Gujarat university Surat (Gujarat) in September. 2010 and submitted for publication in the journal [MCLC] “Molecular Crystal Liquid Crystal” U.K. entitled: Synthesis and Study of new Liquid-Crystalline material through Homologous seris : Isobutyl-p(p’-n-alkoxy cinnamoyloxy) cinnamates.

A copy of each research paper with its status for publication is enclosed at the end of the present thesis after references section.