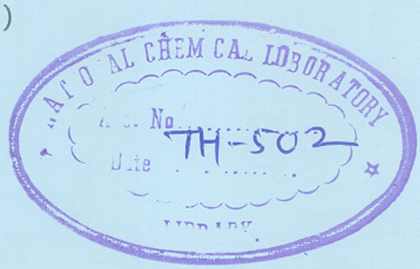
STUDIES IN LIQUID CRYSTALS AND THEIR APPLICATIONS IN GAS CHROMATOGRAPHY

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)



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SEPTEMBER 1986

DEDICATED TO MY PARENTS/IN-LAWS

A C K N O W L E D G E M E N T

It is a pleasure to express my profound sense of gratitude to Dr. B.B. Ghatge for his valuable guidance, constant encouragement and enthusiastic supervision throughout the course of my research.

I am indebted to Dr. D.G. Panse for the invaluable assistance, helpful discussions and suggestions. The assistance rendered by Dr.B.V. Bapat is recorded with high sense of appreciation. It will be out of place if I don't mention the immense help, timely advice and inspiration rendered by Mr. V.K. Bhalerao. I cannot omit thanking Miss A.L. Jadhav, Dr.(Miss) M.V. Natekar and Dr.(Miss) Z. Muljiani for their help and keen interest in this work.

I take the privilege of mentioning my obligation to my colleagues for their timely co-operation. Finally I am grateful to Dr. R.B. Mitra, Head, Organic Chemistry Division and Dr. L.K. Doraiswamy, Director, National Chemical Laboratory for the opportunity offered to me for submission of this research work in the form of a thesis.

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C E R T I F I C A T E

Certified that the work incorporated in the thesis "STUDIES IN LIQUID CRYSTALS AND THEIR APPLICATIONS IN GAS CHROMATOGRAPHY" submitted by Mrs. Nalini Vinayak Bhalerao was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. B.B. Ghatge)
Supervisor

GENERAL REMARKS

1. Melting points and transition point temperatures are uncorrected.
2. PMR spectra were recorded on Varian T-60 and FT-80-A-spectrometers using TMS as internal standard. The chemical shifts are given in δ values.
3. IR spectra were recorded on Perkin-Elmer infra-cord spectrophotomers, Models 137B and 599B.
4. DSC spectra were recorded on Perkin-Elmer DSC-2
5. Pet.ether used refers to the fraction boiling between 60-80°C.
6. C-N: Crystal to nematic transition point.
   N-I: Nematic to isotropic liquid transition point.
7. Microanalyses were carried out in the micro-analytical section of this laboratory.
8. The numbers assigned to the structures, figures and tables refer to that particular chapter only.

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CHAPTER III

Application of liquid crystalline substrates in Gas Chromatography for the study of reaction kinetics and identification of the products in Friedel-Crafts reaction

CHAPTER I A

Synthesis of laterally disubstituted and nitro-substituted liquid crystalline compounds

INTRODUCTION

The success of any organic chemist depends mostly on the selection of specific techniques and physical methods for the isolation, purification and identification of different compounds.

The determination of composition of complex mixtures, trace impurities that contaminate the main substance and physico-chemical characteristics of substances is the main problem in analytical chemistry.

Separation of intricate mixtures into pure components is possible by chromatographic methods where two mutually immiscible phases are brought into contact with each other wherein one is made to flow over a static stationary phase (solid support).

The sample is introduced into the above system which gets equilibrated or distributed between two phases and separates into pure components which are being eluted.

At present, gas chromatography is the most versatile and widespread method for the analysis of organic compounds because of

1. Rapidity of analyses
2. High efficiency
3. Use of microlitre quantity of sample.

In a single analysis it is possible to determine the qualitative and quantitative composition of a

complex mixture in concentration as low as p.p.m. and p.p.b. range by the use of high sensitivity detectors.

History of chromatography

Day[1] and Tswett[2] are credited for the discovery of chromatography in 1903-1906, although the word "Chromatography" was used since 1731. Tswett recognised that chromatographic process consists of sorption-desorption interactions from his experiments on separation of plant pigments which were separated as coloured bands on a calciumcarbonate column, thus named as chromatography.

In 1855[3] F.F. Runge, a German dye chemist, described a separation process known today as paper chromatography . Carotenoids and related pigments were separated by Palmer[4] in 1922 while Kuhn and Lederer[5] reported the separation of carotene and xanthophyll isomers by liquid solid chromatography proving it as an analytical tool.

Wilson[6] in 1940 was the first to describe the chromatographic method mathematically. Following the suggestion of Martin[7] and Synge who introduced the partition column chromatography in 1941, James and Martin[8] introduced gas liquid chromatography in 1952 for which they were awarded the Nobel Prize. There was a stepwise improvement in the sensitivity of detectors.

Techniques and apparatus for GLC

In the GLC method of analysis the sample is rapidly volatised in the injection part at a suitable temperature which is further carried by the carrier gas stream in a very thin, sharp and narrow zone at the inlet of the column. The carrier gas called the mobile phase flows through the column continuously and sample components get distributed between the two phases i.e. the stationary and the mobile phase. Finally the components emerging out of the column are detected and recorded. The time required for the elution of each component is called the retention time (t'R). It is the measure of the interaction of a component with the stationary phase. This is measured from the time of sample injection to the time at which peak height is maximum. The important part is a column which is along tube packed with an inert solid support, coated with the liquid stationary phase. The column is maintained at required constant temperature and a current of an inert gas passed through it.

Separation of complex mixtures of volatile substances with wide range in boiling points (-200° to 400°C) can be achieved in a very short time by GLC technique. Qualitative as well as quantitative

analysis of steroids[9], alkaloids[10], carbohydrates[11], lipids[12,13], carotinoids[14], amino acids[15], pesticides[16], drugs[17] and inorganic alloys[18] is possible by this technique.

Over 20,000 papers have been published wherein almost each and every aspect of the application of this technique to analytical problems has been dealt with. GLC thus forms a powerful analytical tool in the hands of chromatogaphers. (Analytical chemists all over).

Instrumentation

Block diagram of GLC apparatus is shown in Fig. I. The gas chromatographic unit consists basically of the following elements:

I Carrier gas assembly

II Sampling device

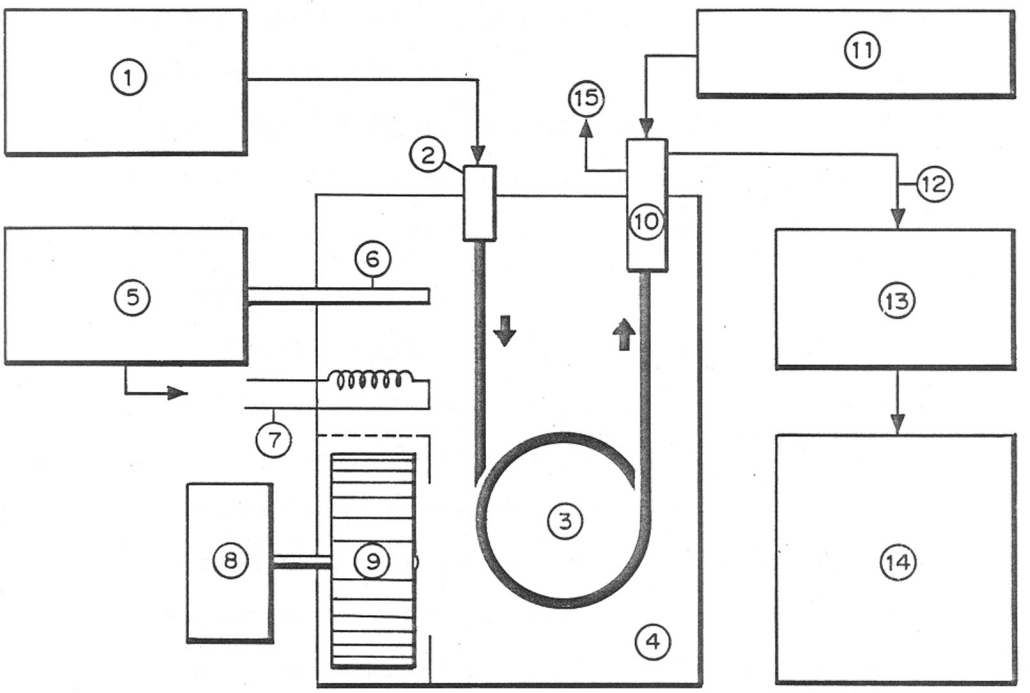
III Chromatographic column and oven

IV Detectors

V Recording and evaluating system

I) Carrier gas

The most commonly used carrier gases are the inert gases like Nitrogen, Hydrogen, Helium and Argon. The selection of carrier gas is done on the basis of its cost, availability and most important, the detector system employed.



1. CARRIER GAS CONTROL
2. INJECTOR
3. COLUMN
4. OVEN
5. TEMPERATURE CONTROLLER
6. RESISTANCE THERMOMETER
7. HEATER
8. MOTOR
9. FAN
10. DETECTOR
11. DETECTOR GASES
12. SIGNAL LEAD
13. DETECTOR AMPLIFIER AND SUPPLY
14. RECORDER
15. GAS OUTLET

FIG. I. CHROMATOGRAPHIC APPARATUS SHOWN SCHEMATICALLY

For accurate results the carrier gas is purified[19] by passing through simple molecular sieve and fine filter to remove the impurities like water, oxygen,oil, vapour etc. which can affect the liquid phase or the detector. At present highly purified Iolar gases are available which can be directly used.

II) Sampling devices

Liquid samples are injected on the column via injection port through a septum by a precision gas-tight, microlitre hypodermic syringe[20] while gas samples are introduced with by-pass gas pipettes or mercury burettes[21,22]. It is necessary to ensure that the temperature at the injection port is higher than the column oven temperature by 20° to 50°C to avoid slow vapourisation of the sample which will result in peak broadening. Number of injection methods are quoted in the Purnell's[23] book.

III) Chromatographic column

The columns used for this purpose are of various shapes viz. straight, coiled or U-shaped. The commonly used materials for these columns are glass, copper, aluminium and stainless steel[24].

Basically there are three types of columns used in GLC. These are packed, capillary and preparative columns. Packed columns used for routine analysis are

3 to 10 feet long or more with internal diameter of 2 to 4 mm. Capillary columns[25] are used for the separation of complex mixtures and may be 30(to 40(: meters long with internal diameter between 0.25 and 0.5 mm., whereas the internal diameter of preparative GLC columns is about 9 to 12 mm. The liquid stationary phase is coated on a porous solid support which is inert, thermally stable and has high crushing strength. The size of the particles used is60/80, 80/100, 100/120 mesh. Commonly used supports are celite, chromosorb, embacel and crushed fire brick. The porous supports are preferable over non-porous one[26]. The liquid phase is dissolved in a volatile solvent and is coated (as a slurry) over the solid support material. The solvent is removed from the slurry by agitating at low temperature (50° to 60°C). The solid support material thus impregnated with the liquid phase is evenly packed in the column by vibrating the column tubing to ensure uniform packing. The column needs a period of 20 hrs conditioning at 20°-30°C above its proposed operating temperature with a stream of carrier gas passing through it to remove the moisture, solvent or other volatile contaminants if any. This column is enclosed in an oven made of metal block. The temperature of which is controllable to ± 0.5°C.

IV) Detectors

The chromatographic detector is a device which indicates and measures the amount of separated component in the carrier gas.

There are two major types of detectors.

(A) Integrating detectors

(B) Differentiating detectors

(A) Integrating detectors give a response proportional to the total mass of the components in the eluted zone, e.g. titrating burette detector.

(B) Differentiating detector gives a response proportional to the concentration or mass flow rate of the eluted component e.g. Thermal conductivity detector,[27] flame ionization detector etc.[28]

Selectivity, sensitivity, good response, noise, minimum detectable quantity and linear range are the essential requirements to be considered for the usefulness of the detector. A simple, inexpensive, rugged detector which is insensitive to changes in flow rate is more advantagious.

V) Recording and evaluating system

The recorder does the main function of reproducing the output of the detectors graphically as accurately as possible to obtain a permanent record of the results in the form of chromatograms.

Electronic chart potentiometers are commonly used as recorders. They operate on the principle of balancing the input signal by a feed-back signal of the same intensity but of the opposite sign. Recently computers are being used to process GLC data.

Factors responsible for the separation

Several factors influence the separation on GLC columns. These factors are classified into two types. The first type covers column parameters like length, internal diameter, inlet and outlet pressure ratio, the nature of support material, particle size of support material, column temperature and flow rate of the carrier gas. Type two includes the most important factor, that is, nature of stationary phase.

Stationary Phase

The selection of a proper stationary phase to get good separation of the components of a mixture is always very critical. Principal factors in selecting appropriate liquid phases are summarized below.

The liquid phase should have low vapour pressure and low viscocity at operating temperature. Chemical stability, reasonable solubility in some common solvent and selectivity towards the components to be separated determine the utility of the liquid phase.

The selectivity of a given stationary phase is the ability of the stationary phase to separate a pair of solutes having very similar properties such as boiling points[29], molecular weights[30], number of carbon atoms in the molecule[31] or vapour pressures[32]. Littlewood[33] has suggested the following four groups of stationary phases.

I) Non-polar or paraffinic stationary phases

These include all alkanes and alkyl silicones. The hydrocarbons are much more soluble in these stationary phases than any polar solute with similar boiling point. These phases do not interact specifically with the solutes to be separated. They can be used in gas chromatography as reference stationary phases, e.g. Methyl silicones, squalane and Apiezon greases.

II) Dilute stationary phases

These phases can be used for polar as well as non-polar solutes, thus being of universal use.

III) Concentrated stationary phases

These stationary phases contain polar groups. Strongly electronegative atoms, F, O, N or electron attracting groups such as $-NO_2$, -CN and $-CF_3$ or electron repelling groups such as $-N(Me)_2$ $-C(Me)_3$ and -OMe constitute the polar part. Many stationary phases from this class interact with solutes

to be separated forming hydrogen bonds.

IV) Specific stationary phases

These stationary phases react specifically with a particular class of solutes.

The transition metal complexes form a group of specific stationary phases showing selectivity towards the separation of olefins[34], butenes[35] etc. Wasik and Tsang[36] used aqueous silver nitrate as the stationary phase.

Isomeric xylenes are separated selectively on Bentone-34[37].

In recent years liquid crystals have gained predominance in this class of specific stationary phases.

Liquid crystals as stationary phases

Discovered at the end of 19th century liquid crystals were merely scientific curiosity initially. But presently these compounds are found to possess a wide range of applications. In 1963 use of Liquid-crystalline compounds was made for the first time in GLC[38-40]. The interest in liquid crystals for chromatography is due to the possibility of using them as selective substrates for the separation of positional isomers, particularly p- and m- substituted benzenes, whose separation is difficult on the usual commercially available stationary phases. Reviews have been devoted

to the use of liquid crystals in Gas Liquid Chromatography[41-46]. These intriguing liquid-crystalline compounds gave inspiration to many researchers and recent literature shows the popularity of these compounds in use as stationary phases. K. Watabe and co-workers[47-49] have made a detailed study of the influence of an electrical field on the nematic phase. Dewar and Schroeder[40] and Cook and Spangelo[50] applied the anisotrotropic mesophase properties of these compounds for the use as column substrates and separated the xylene isomers. Janini et al. investigated the effect of solid support on liquid-crystalline phases[51]. An uptodate review on liquid crystal stationary phases for GLC has been written by Z. Witkiewicz[52].

Use of optically active liquid crystalline compounds has been made for the separation of d- and l-enantiomorphs[40,41,53,54]. Effect of lateral substitution on selectivity is studied[55,56]. Likewise the effect of solid surface on the properties of liquid-crystalline compounds (film) was studied and comparison of the properties of liquid crystal films on silica gel and on a graphite surface has been done[57]. The liquid-crystalline phases which are operated at high temperatures are prepared by Witkiewicz Z. et al.[58,59] having naphthalene fragment in their molecule. Synthesis of

new liquid crystalline Schiff's bases showing wide mesophase range for the analysis of higher polynuclear hydrocarbons has been carried out[60].

Disc like liquid-crystalline stationary phases are prepared and compared with the rod-like liquid-crystalline compounds[61]. Witkiewicz et al.[62] have synthesised liquid-crystalline phases possessing cyclohexyl moiety in the molecule with different terminal groups.

History

It is generally accepted that matter exists in three states: solid, liquid and gas. However, this is not quite correct in case of certain organic compounds. These compounds show a fourth state of matter, intermediate between a crystalline solid and isotropic liquid showing mechanical properties specific to liquids and anisotropic properties of a solid crystal and so have been called "Liquid Crystals". Earliest clear recognition of "Liquid Crystals" is usually attributed to Reinitzer[63] who in 1888 noted the colour phenomenon now known to be characteristic of many cholesteric mesophases, which arise when melts of cholesteryl acetate or benzoate are cooled. This colour phenomenon was observed earlier by others also but in addition to this effect he observed that it melts at 145.5°C to give a cloudy fluid which on further heating, suddenly clarified at 178.5°C. Reinitzer found that on slow cooling this mass showed colour effect for some time, then slowly the colour vanished and again the mass changed into turbid liquid. Subsequent cooling showed another colour effect and then the mass crystallized . These observations were confirmed by Lehmann[64] using polarizing microscope. He showed that the turbid liquid was birefringent and hence anisotropic

and therefore classified it as liquid crystalline. Friedel[65,66] proposed the name mesophases as they lie between the solid and liquid phases

"Liquid Crystals" the term used by Lehmann, although remains in the general use, was strongly opposed by Friedel. In his opinion liquid crystals were neither true liquids nor true crystals but represented two new states of matter intermediate between the solid crystal and the amorphous liquid. Their molecular structures are between periodic perfectly ordered structure which is that of a crystal type and the perfectly disordered structure of the amorphous type. Thus, for this situation the term"mesomorphic" would seem suitable.

Classification of Liquid Crystals

There are two major classes of these compounds (1) Thermotropic (2) Lyotropic.

Thermotropic Liquid Crystals: Liquid crystalline state is established after the solid is melted. The resulting liquid preserves or possesses in a certain temperature range, properties intermediate between those of the solid and the liquid. But upon further heating a transition takes place at a given temperature, called the clearing temperature, to form the isotropic liquid.

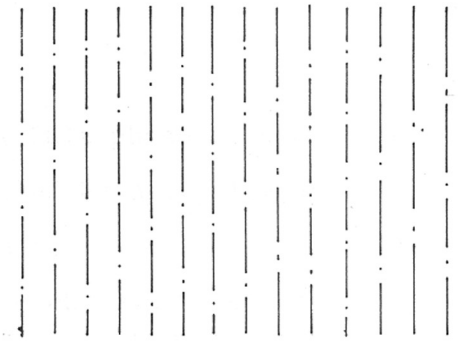
Lyotropic Liquid Crystals: This class of liquid crystalline compounds show Liquid-crystalline properties over a wide range of concentrations in a suitable solvent. They are obtained by mixing two or more components and are usually solutions of surface-active agents or polymers.

So far only thermotropic liquid crystals have been used in GLC as stationary phase but lyotropic liquid crystal could find some application in the form of mixed phases.

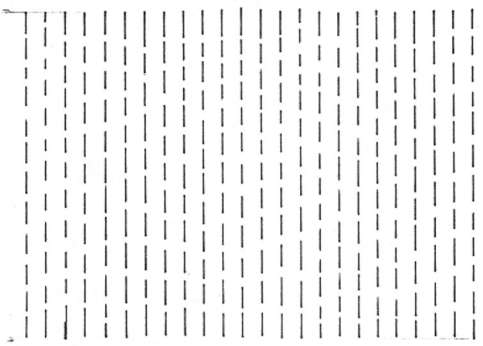
Thermotropic liquid crystals are further sub-divided depending on the mode of arrangement of molecules.

1. Nematic - The molecules are arranged approximately parallel along their long axes (Fig. 2(b) The molecules are not perfectly parallel owing to the thermal movement. The degree of ordering of the molecules is determined by the parameter "S", the value of which varies from zero for molecules arranged at random to unity for molecules ordered ideally. For nematics "S" assumes the value of 0.3 to 0.8. Nematic phase owes its name to its microscopic thread-like appearance[67]. At higher temperatures the nematics undergo a transition to an isotropic liquid phase (Fig. 2(d). The cholesteric phase is assumed to be a variety of the

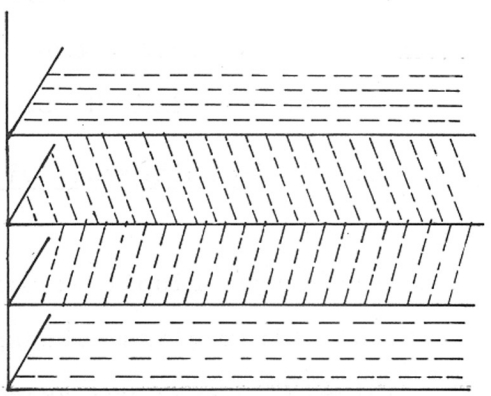
a) SMECTIC



b) NEMATIC



c) CHOLESTERIC



d) ISOTROPIC

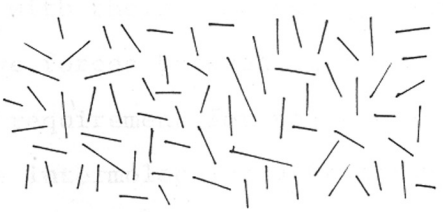


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FIG. 2.

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nematic phase. This phase is a chiral nematic phase as it is exhibited by optically active substances. In this structure, the molecules are arranged in layers. Within each layer the molecular arrangement resembles the nematic mesophase but the direction of the long axes of the molecules in each layer is systematically displaced with respect to the direction in adjacent layers, with the overall displacement tracing a helical path in the direction normal to the molecular planes (Fig. 2(c))

Smectic - In smectic structure the molecules are not only arranged parallel to one another but also are fixed in layers "S" attains the values greater than 0.8. Demus[68] and Halle[69] described the seven different smectic phases named A,B,C,D,E,F,G. Recently Eighth phase of smectic, H, has been identified[70].

Requirements for formation of thermotropic liquid crystals

Thermotropic liquid crystalline property is shown only by elongated, fairly rigid rodlike or lath-like molecules. X-ray spectroscopic evidence[71] indicates that rod-like molecules tend to pack in the solid crystal state with their long axes parallel. Anisotropy of the cohesive forces between elongated molecules is therefore the requirement for the formation of liquid crystals. The intermolecular attraction must not be

very strong which would effect into high melting points with loss of liquid crystalline property. Weak intermolecular cohesive forces may make the liquid crystal low melting but the order in the fluid state may be destroyed. Thus the cohesive forces operating between the elongated molecules must be anisotropic and of a suitable magnitude.

Properties of Liquid crystals significant for GLC

Most conventional (especially non-polar) stationary phases are unable to separate the isomeric mixtures because of their ability to separate the mixtures on the basis of boiling points. Such positional isomers differing in their molecular structure but having similar boiling points can be separated on liquid-crystalline phases which have an ordered structure in the smectic and nematic phase. The liquid crystalline compounds exhibit different solvent properties than conventional isotropic solvents. Thus it was expected that liquid crystals would be good stationary phases for separation of geometrical and optical isomers.

The first work by Kelker[38,39] and later by Dewar and Schroeder[40,72] was very promising and prompted studies on liquid crystalline phases. Literature gives the idea of application of liquid crystals in GLC through the surveys[41,43,45,46,73-83].

The liquid crystalline compounds used as stationary phases in GLC should have:

High thermal stability, low vapour pressure at operating temperature, good adhesion power towards the support and melting points higher than 50°C.

In GLC with temperature programming liquid crystals with wide mesophase range are used[84-86].

The use of mixed liquid crystal stationary phases increases the range of their applicability as stationary phases. These mixed liquid-crystalline stationary phases show a prominent tendency to become supercooled i.e. they can be used even below their nematic transitions.

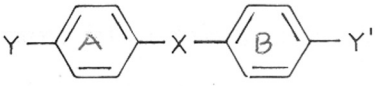
Compounds forming thermotropic liquid crystals

Mesomorphism is found in aromatic, aliphatic, multi-ring and polymeric compounds. Aromatic compounds form the largest group of known compounds exhibiting mesomorphism. Bernal and Crowfoot[87] proposed that an aromatic molecule to show mesomorphism must possess the following characteristics:

1) The molecule must be geometrically anisotropic and either rod shaped, flat or lath shaped.
2) There must not be more than one group in the molecule with a high dipole and

3) The molecules should contain moderately active groups such as -C-O-C-, -CH=CH-, and -C-O-, N=N towards the extremiteis of the molecule.

The basic structure of aromatic type compounds can be represented by the general formula:



where,  and  are aromatic systems with one or more aromatic rings, X is a central group capable of electronic conjugation with the aromatic systems and y and y' are para-terminal substituents.

Liquid crystals are rarely formed by aliphatic compounds due to relative flexibility of the long chains. Liquid crystal compounds with a nematic mesophase have been most thoroughly investigated and it has generally been well established that this nematic phase is superior to smectic and cholesteric phases for GLC separations of positional isomers[44,88]. But cholestric phases show higher selectivity towards cis and trans-isomer of n-alkenes than nematic, smectic and also non-liquid-crystalline stationary phases[89].

Separation mechanism on liquid crystal stationary phases

The interaction forces liberated in the sorbate-liquid crystal melt system, due to the ordered arrangement of molecules in the temperature range of mesophase are responsible for the separation of aromatic meta- and para-isomers with similar boiling points. Long and planar molecules fit better in the ordered structure of the liquid crystal and therefore non-linear and non-planar molecules (which do not permeate so easily between the liquid crystal molecules) are eluted easily from the column. This is confirmed experimentally[90-92]. Liquid crystal phases have been proved much superior to especially Bentone-34 which is best phase in conventional columns. Separation mechanism on nematic and cholesteric stationary phases is obtained from investigations carried out using an electric field applied perpendicular to the walls of capillary columns[93-101].

The properties of separated components to be observed in case of conventional columns are:
(1) Boiling points (2) Size (3) Polarity (4) Polarizability (5) Elasticity of the molecules.

While in case of liquid crystal column only two factors play important role: (1) Chemical structure
(2) Related polarity

Liquid crystals are reasonably good solvents as the solution in a mesophase requires more energy than solution in the isotropic liquid of the same compound because the energy required to overcome the steric restraints on entrance of solute molecules into ordered "lattice".

In GLC going from the disordered vapour state (similar for both isomers) to the ordered liquid state, the para substituted molecule sacrifies more translational and rotational freedom but, in return, its favourable geometry promotes stronger interaction with mesophase. Nematics are highly effective orderly matrics because of which separation of isomeric mixture is possible. Optimum selectivity of a nematic is obtained at the lowest possible operating temperature[38,40,102].

Several reports on the separation of alkyl naphthalenes[103] polycyclic aromatic hydrocarbons and their derivatives[104-107] disubstituted benzenes[108-110] phenol ethers[111] high boiling hydrocarbons[112], poly-chlorinated biphenyl[113], methyl esters of methoxy benzanthrazene and benoxaprofen[114] have appeared in the literature. M.S. Vigdergauz et al. have reviewed the analytical and physico-chemical aspects of GLC using liquid crystal sorbents upto-date[115].

Experimental considerations

Deposition of liquid-crystalline compound on a solid support is done from solution in a volatile solvent (dichloromethane, chloroform etc.) if suitable solvent cannot be found, dry blending of the solid stationary phase and support gives satisfactory results[41]. Columns used for conventional stationary phases with respect to both column material as well as dimensions are used for liquid-crystalline phases. Recently, capillary columns[116-133,47,48,89] and micropacked columns[134-137] with liquid-crystalline phases have been increasingly used. The liquid-crystalline phase in capillary columns is coated on the walls of capillaries. A method has also been applied in which liquid crystal phase is directly obtained in the capillary column[129].

Uniform column temperature is important. Zones of uncoated solid support at the ends of the column have been recommended as "temperature buffers"[41].

Study of stationary phases in this laboratory

A systematic study of stationary phases and their properties with respect to the separation of a wide variety of components is being carried out by Ghatge et al., the organic synthesis group, in this laboratory since long back. Systematic studies were earlier carried out for the development of polyesters and their proper evaluation[138-143].

There are a number of projects undertaken in this laboratory which necessitate the separation of different positional isomers by routine GLC analysis. The need of a specific stationary phase to solve the difficult problem of isomeric separations has always been felt. Realizing the potential of liquid crystals as selective stationary phases, recently our group has synthesised[144-146] several new unsubstituted and laterally substituted liquid crystalline stationary phases and has studied the applications[147-149] of these phases for the separations of various positional isomers.

Introduction to present work undertaken

Enantiotropic nematic azobenzenes with two benzene rings have been reported by Pohl and Steinstrasser[150]. After that Schubert et al.[151] have synthesised liquid crystalline azo benzenes with three benzene rings.

The comparison of these two types of compounds exhibit that there is tremendous increase in nematic temperature range with the addition of one more benzene ring.

Schroeder[88] in his review, noted that nematic range, rigidity and minimum usable temperature are the important factors for selectivity of liquid crystalline phases. He also pointed out that relative retention values are more for stationary phases of liquid crystalline compounds having longer nematic range as compared to stationary phases of short ranged liquid crystalline compounds. Also long terminal alkyl chain liquid crystals enhance the anisotropy and polarizability and raise the nematic range provided they increase the molecular length to-breadth ratio.

Thus realising the importance of liquid crystalline stationary phases in the solution of problem of separating different positional isomers recently our group has synthesised several new laterally substituted liquid crystalline stationary phases[144-146] and has studied the applications[147-149] of these phases for the separations of various positional isomers. As the laterally mono-substituted phases showed selectivity over unsubstituted and disubstituted (on the same side)

it was felt necessary to see the effect of disubstitution on opposite sides of the longer axis of the molecule.

Also the effect of an electron withdrawing $-NO_2-$ group when it is substituted in the middle ring was felt interesting to investigate.

A new series of liquid-crystalline compounds was synthesised keeping in mind the above mentioned facts and was investigated for its utility as stationary phases in GLC.

General method of synthesis

p-Substituted aniline was diazotised and subsequent phenyl diazonium chloride was coupled with 3,5-, 2,5-, 2,6-dimethyl or dichloro phenol and 2-nitro-phenol by following the method of Bolotin et al.[152] Purity of these compounds was checked by TLC, IR and elemental analysis.

p-Alkoxy benzoic acids and their acid chlorides were synthesised by known methods[153,154]. Azo compounds were then condensed with distilled acid chlorides to get final liquid crystalline compounds. Final compounds were crystallized with different solvents or solvent mixtures depending upon their solubilities.

Transition temperatures

Transition temperatures of liquid crystalline compounds can be observed using "Heating stage polarizing microscope", differential thermal analysis method, differential scanning ~~colourometry~~ calorimetry method and capillary melting point method. Crystal to nematic transition can be observed using gas chromatography[155]. In the present work capillary melting point method is employed. and the results are confirmed by DSC method.

EXPERIMENTAL

Synthesis of laterally disubstituted and nitro substituted new liquid crystals[155]

Total synthesis of laterally mono and disubstituted liquid crystalline compounds consists of two steps:

Step I: Synthesis of

(1) 4'-substituted-4-hydroxy-3-substituted azobenzene and (2) 4'-substituted-4-hydroxy-3,5-, 3,6- and 2,6-substituted azobenzenes.

Step II: Condensation of substituted azobenzenes with p-alkoxy benzoyl chloride.

Starting materials such as p-substituted aniline, 3,5-, 2,5-, 2,6-dimethyl and dichloro phenols and p-hydroxy benzoic acid were commercial products and were used after checking their purity.

Reaction Scheme

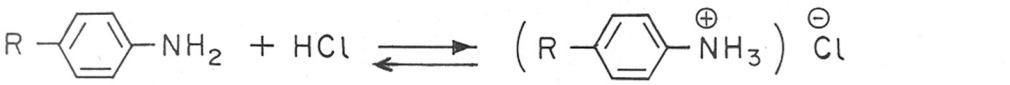
Step I

Synthesis of 2,6-dimethyl-4(p-tolylazo)phenol (Ic)

A solution of p-toluidine (0.05 mol) in hydrochloric acid (38 ml, 20%) was cooled (-10 to 0°C) and a solution of sodium nitrite (0.05 mole, 3.5 g) in water (40 ml) added to it with vigorous stirring at such a rate that the temperature of the reaction mixture did

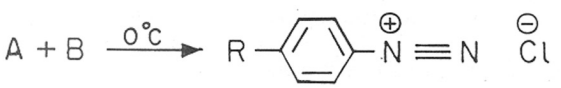
REACTION SCHEME

A

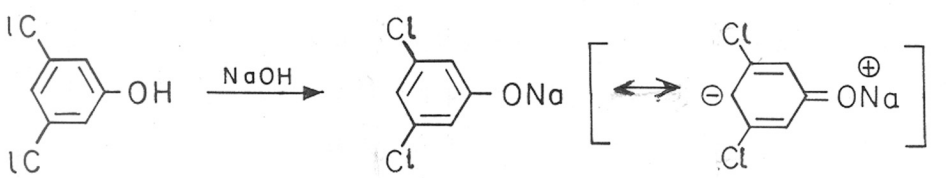


(p-Substituted aniline hydrochloride)

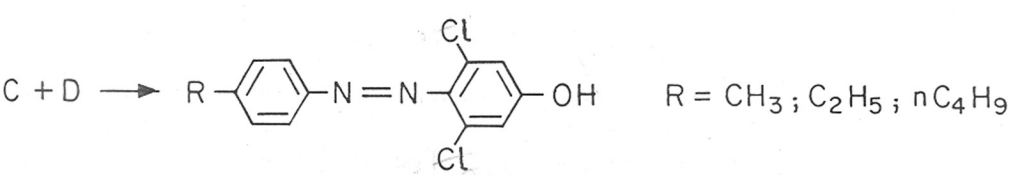
B



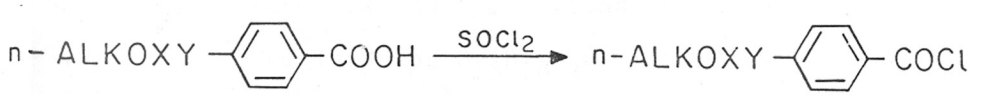
C



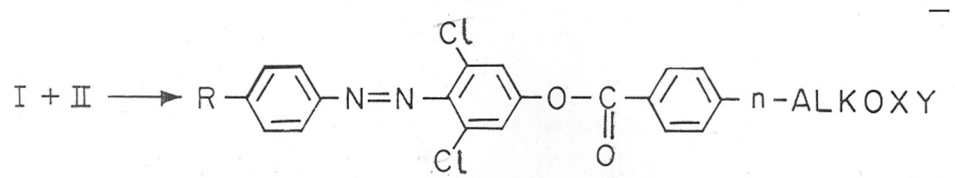
D



(I)



(II) n-ALKOXY – OCH_3
– OC_2H_5
– OC_4H_9
– OC_6H_{13}



not exceed 0°C. After keeping at this temperature for 30 min. the resultant diazonium solution was added into a solution of 2,5-dimethylphenol (0.05 mol.) in aq. sodium hydroxide (50 ml, 8%). The temperature of the reaction mixture was maintained below 5°. The resultant precipitate (3 g) was filtered, washed with water till neutral, dried and purified by column chromatography over silica gel (100 g) using pet.ether-benzene (1:1) and benzene as eluants to give TLC pure (Ic) Using this method following compounds have been synthesised.

Ia. 3,5-Dimethyl-4-(p-n-butyl phenyl azo)phenol

Yield 37%, m.p. 92°C.

Elemental analysis Found: C, 76.6; H, 7.9; N, 9.9

Required for $C_{18}H_{22}N_2O$: C, 76.5; H, 7.9; N, 9.9.

IR bands (cm^{-1}): 3333 (OH), 1613 and 1587 (-N=N); 1471 ($C-CH_3$); 1163 (aryl-OH), 854, 833 & 781, 724 (aromatic substituted). Fig. 3.

Ib 3,5-Dimethyl-4-(p-methyl phenyl azo) phenol

Yield: 40%, m.p. 85°C.

Elemental analysis Found: C, 75.0; H, 6.7; N, 11.7.

Required for $C_{15}H_{16}N_2O$: C, 75.0; H, 6.7; N, 11.6.

IR bands cm^{-1}: 3333 (OH), 1601 and 1590 (-N=N); 1460 ($C-CH_3$); 1156 (aryl-OH); 833, 724 (aromatic substituted).

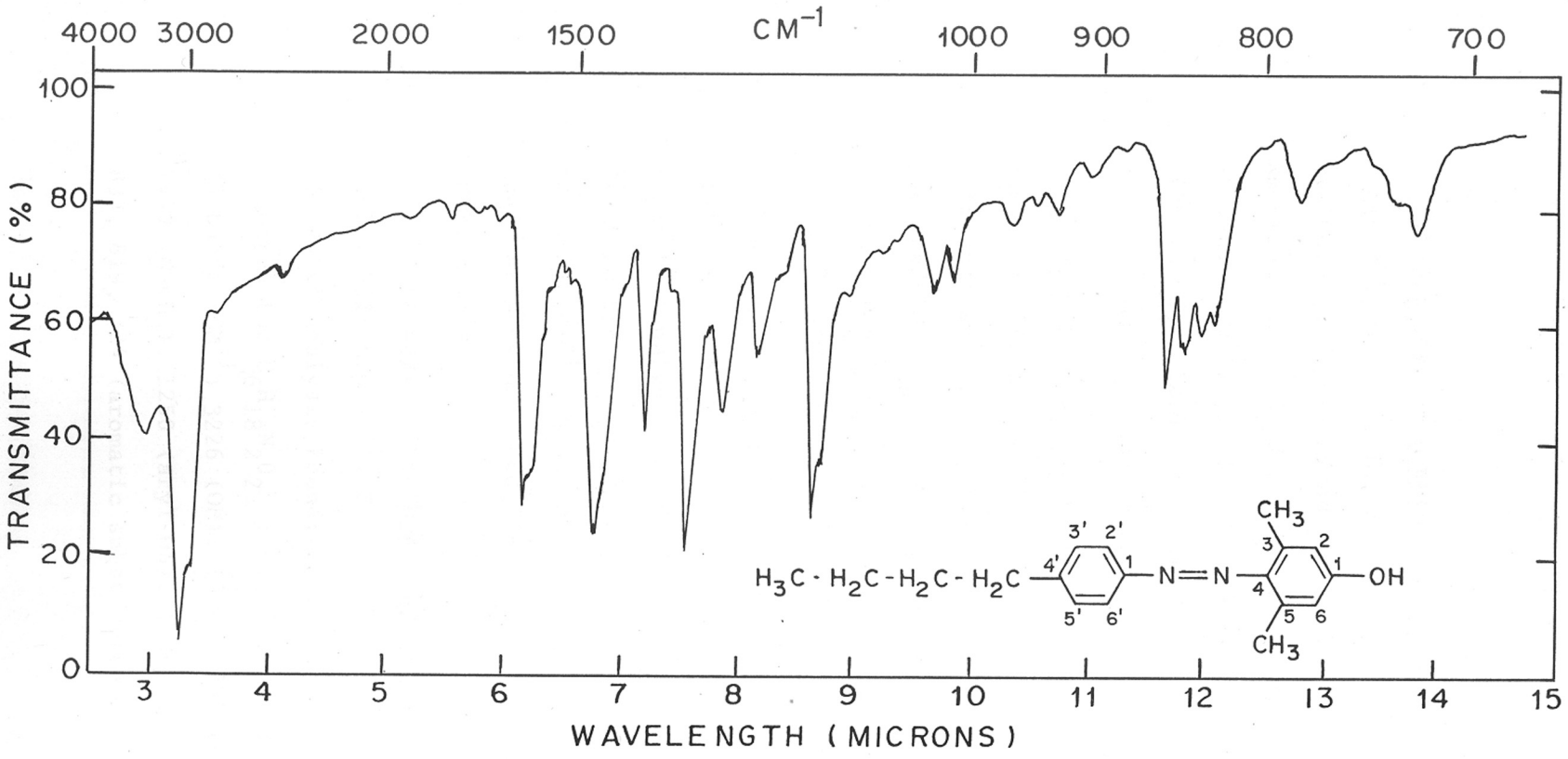


FIG. 3. IR SPECTRUM OF 3,5-DIMETHYL-4-(p-n-BUTYLPHENYLAZO) PHENOL

Ic 2,5-Dimethyl-4-(p-methyl phenyl azo) phenol

Yield 31%, m.p. 105°C.

Elemental analysis Found: C, 75.0; H, 6.7; N, 11.7

Required for $C_{15}H_{16}N_2O$ C, 75.0; H, 6.7; N, 11.7.

IR bands (cm^{-1})- 3333 (OH): 1613, 1587 (-N=N-); 1460 (C-CH_3); 1256 (aryl -OH); 900, 854, 826 (strong sharp) (aromatic substituted).

Id 2,6-Dimethyl-4-(p-n-butyl phenyl azo) phenol

Yield: 30.5%, m.p. 65°C.

Elemental analysis Found: C, 76.6; H, 7.9; N, 9.9

Required for $C_{18}H_{22}N_2O$ C, 76.6; H, 7.8; N, 9.9.

IR bands (cm^{-1})3448(OH),1587 (broad) (-N=N-), 1250 (aryl-OH), 833, 730 (aromatic substituted).

Ie 2,6-Dimethyl-4-(p-ethoxy phenyl azo) phenol

Yield 39%, m.p. 90°C.

Elemental analysis found: C, 71.1; H, 6.7; N, 10.4.

Required for $C_{16}H_{18}N_2O_2$: C, 71.1; H, 6.8; N, 10.3

IR bands (cm^{-1}) - 3333 (OH) ; 1471 (C-CH_3), 1250 (aryl- OH), 1042 (aryl-O-CH_2), 840, 769, 730 (aromatic substituted (C-H). Fig. 4 .

If 3,5-Dimethyl-4-(p-ethoxy-phenyl azo) phenol

Yield: 35%, m.p = 117°C.

Elemental analysis Found: C, 71.1; H, 6.7; N, 10.4.

Required for $C_{16}H_{18}N_2O_2$: C, 71.1; H, 6.7; N, 10.4.

IR bands (CM^{-1}) 3226 (OH); 1613, 1587 (-N=N-), 1449 (C-CH_3), 1250 (aryl-OH), 1136, 1031 (aryl-O-CH_2), 833, 819, 724 (aromatic substituted).

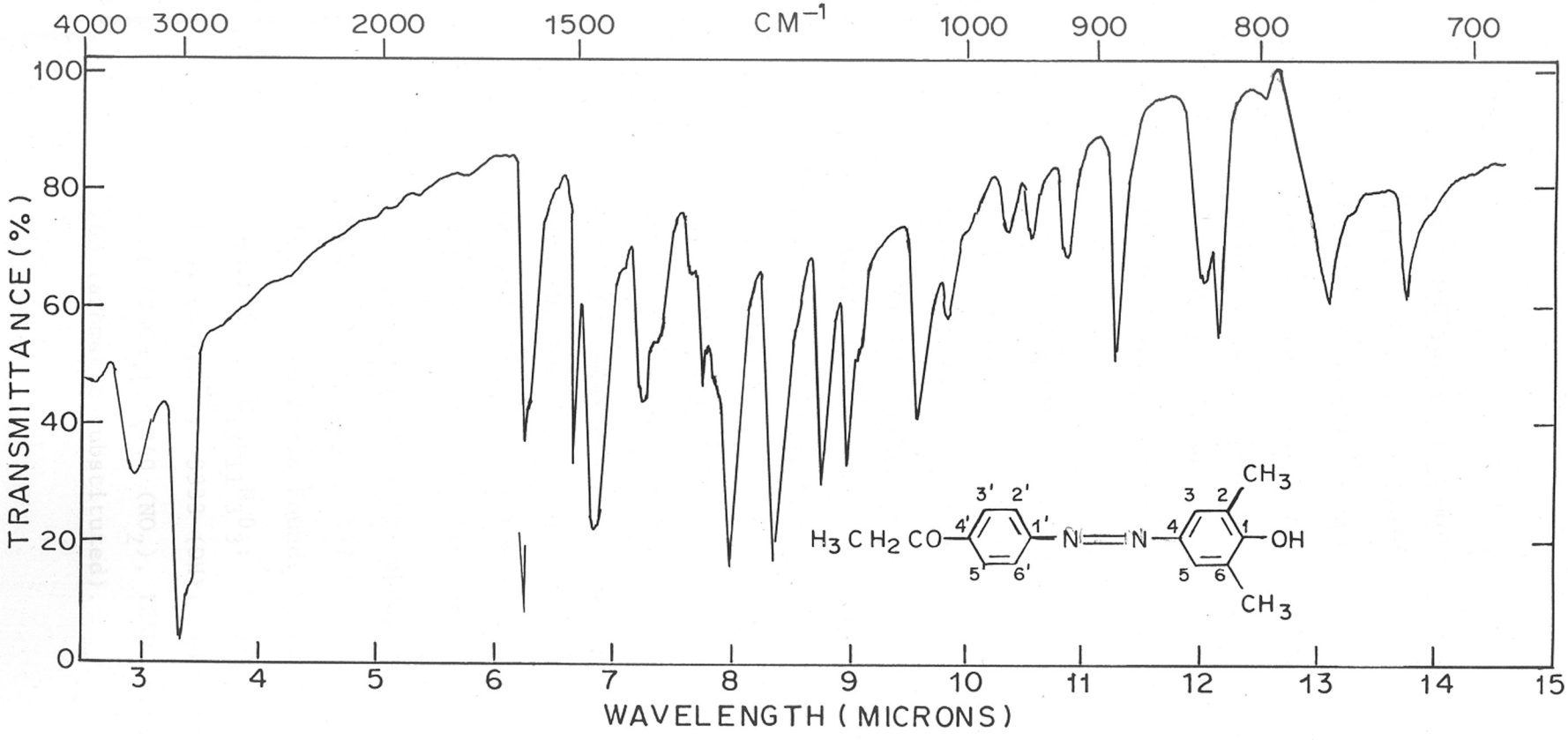


FIG. 4. IR SPECTRUM OF 2,6-DIMETHYL-4-(p-ETHOXY PHENYLAZO) PHENOL

Ig 2,3-Dimethyl-4-(p-methoxy-phenyl azo) phenol

Yield: 35%, m.p. = 150°C.

Elemental analysis Found: C, 70.3; H, 6.3; N, 10.9.

Required for $C_{15}H_{16}N_2O_2$: C, 70.2; H, 6.4; N, 11.0.

IR bands (cm^{-1}) 3448 (-OH), 1613, 1587 (-N=N)-, 1460 (C-CH_3), 1250 (aryl- OH), 1140, 1031 (aryl-O-C- ether linkage), 840(s), 819, 740 (sharp) (aromatic substituted).

Ih 2,3-Diethyl-4-(p-ethoxy-phenyl azo) phenol

Yield: 41%, m.p. 137°C.

Elemental analysis Found: C, 71.1; H, 6.7; N, 10.4.

Required for $C_{16}H_{18}N_2O_2$: C, 71.1; H, 6.8; N, 10.3.

IR bands (cm^{-1}) 3333 (OH), 1613, 1590 (-N=N-), 1299 (aryl-O-CH_2), 1250 (aryl -OH), 819, 757 (aromatic substituted).

Ii 2,3-Dimethyl-4-(p-methyl-phenyl azo) phenol

Yield: 40%, m.p. = 160°C.

Elemental analysis Found: C, 75.0; H, 6.7; N, 11.7.

Required for $C_{15}H_{16}N_2O$: C, 75.0; H, 6.7; N, 11.6.

IR bands (cm^{-1}) 3322 (OH); 1613 (broad -N=N-), 1250 (aryl- OH), 826 (aromatic substituted).

Ij 2-Nitro-4-(p-methyl-phenyl azo) phenol

Yield: 32.5% , m.p. = 147°C.

Elemental analysis Found: C, 60.7; H, 4.3; N, 16.3

Required for $C_{13}H_{11}N_3O_3$: C, 60.6; H, 4.3; N, 16.4

IR bands (cm^{-1}) 3333 (OH), 1613, 1587 (-N=N-), 1515, 1471 (C-CH_3), 1340 (NO_2), 1250 (aryl -OH), 826, 763 (aromatic substituted).

Ik 2,5-Dichloro-4-(p-methyl-phenyl azo) phenol

Yield: 30%, m.p. = 92°C.

Elemental analysis Found: C, 55.7; H, 3.6; N, 10.0;Cl,25.1,

Required for $C_{13}H_{10}Cl_2N_2O$:C, 55.7; H, 3.6; N, 10.0.Cl,25.01

IR bands (cm^{-1}):3448 (OH), 1613, 1587 (-N=N-),

1460, 1370 (c-CH_3); 1250 (aryl- OH); 1070 (C-Cl),

847, 820, 763, 719 (sharp strong) (aromatic substituted).

Il 3,5-Dichloro-4-(p-methyl-phenyl azo) phenol

Yield: 29%, m.p. 95°C.

Elemental analysis Found: C, 55.7; H, 3.57; N, 10.0,Cl,25.1.

Required for $C_{13}H_{10}Cl_2N_2O$: C, 55.8;H, 3.6; N, 10.0, Cl,25.1.

IR bands (cm^{-1}) 3600 (OH); 1600, 1562 (-N=N-),

1150 (s) (C-OH), 1050 (aryl-Cl); 820, 708 (aromatic substituted).

All the above mentioned phenols were crystallized from pet.ether-benzene mixture.

Synthesis of p-alkoxy benzoyl chlorides[153,154]

a) Synthesis of p-alkoxy benzoic acids

A mixture of p-hydroxy benzoic acid (0.25 mol), alkyl bromide (0.275 mol) and potassium hydroxide (0.5 mol in 120 ml of water) was refluxed for 10 hrs. Then additional potassium hydroxide (0.25 mol in 140 ml of water) was added and mixture was refluxed further for 3 hrs. The solution was cooled and acidified. The precipitate obtained was filtered and the solid product was washed with water. It was dried and

crystallized from glacial acetic acid.

(p-Anisic acid and p-ethoxy benzoic acid were prepared by using dimethyl sulphate and diethyl sulphate respectively).

p Anisic acid - m.p. 184°C

p-Ethoxy benzoic acid - m.p. 196°C.

p- n-Butoxybenzoic acid - C-N-147°C, N-I-160°C.

p-n-Hexyloxy benzoic acid-C-N-115°C; N-I-153°C.

(b) p-Alkoxy benzoic acid chloride was prepared by refluxing p-alkoxy benzoic acid with thionyl chloride. Then excess thionyl chloride was distilled off and the residue was distilled under vacuum.

p-Methoxy benzoyl chloride b.p.142°/25 mm

p-Ethoxy benzoyl chloride b.p. 140°/20 mm

p-n-Butoxy benzoyl chloride b.p.162°/25 mm

p-n-Hexyloxy benzoyl chloride b.p.180°/5 mm.

Step II: Synthesis of disubstituted -4'-substituted -4-(alkoxy benzoyloxy) azo benzenes

To a mixture of 3,6-dimethyl-4-(p-methyl phenyl azo) phenol (0.01 mol) and dry pyridine (10 ml) was added a solution of p-methoxy benzoyl chloride (0.015 mol) in dry pyridine (10 ml) and the reaction mixture refluxed in an oil bath for 6 hr, cooled to room temperature and water (20 ml) was added to it. The solid material, thus separated, was filtered, washed

successively with water and methanol and crystallized from pet.ether (60-80°C)-benzene mixture to give 2,4',6-trimethyl-4-(p-methoxy benzoyloxy) azobenzene as orange coloured needles.

Using this method following compounds have been synthesised.

II 1 2,6-Dimethyl-4'-n-butyl-4-(p-methoxy benzoyloxy)-azobenzene

Yield 55%.

Transition temperature: °C	C-N	N-I	Nematic range
	118	155	37

Elemental analysis Found: C, 75.0; H, 6.8; N, 6.7.

Required for $C_{26}H_{28}N_2O_3$: C, 74.9; H, 6.8; N, 6.8.

IR bands (cm^{-1}): 1724 (-C=O); 1613, 1537 (-N=N), 1266, 1075 (strong, sharp) for aryl-O-CH_2), 847 (sharp s), 763 (aromatic substituted). Fig. 5.

II 2. 2,6-Dimethyl-4'-n-butyl-4-(p-n-butoxy benzoyloxy) azobenzene

Yield: 53%

Transition temperature: °C	C-N	N-I	Nematic range
	98	122	24

Elemental analysis Found: C, 76.0; H, 7.5; N, 6.1.

Required for $C_{29}H_{34}N_2O_3$: C, 75.9; H, 7.5; N, 6.1.

IR bands (cm^{-1}) 1727 (-C=O); 1613, 1587 (-N=N-); 1460 (C-CH_3), 1250, 1053 (aryl-O-CH_2); 847, 763, 694 (aromatic substituted).

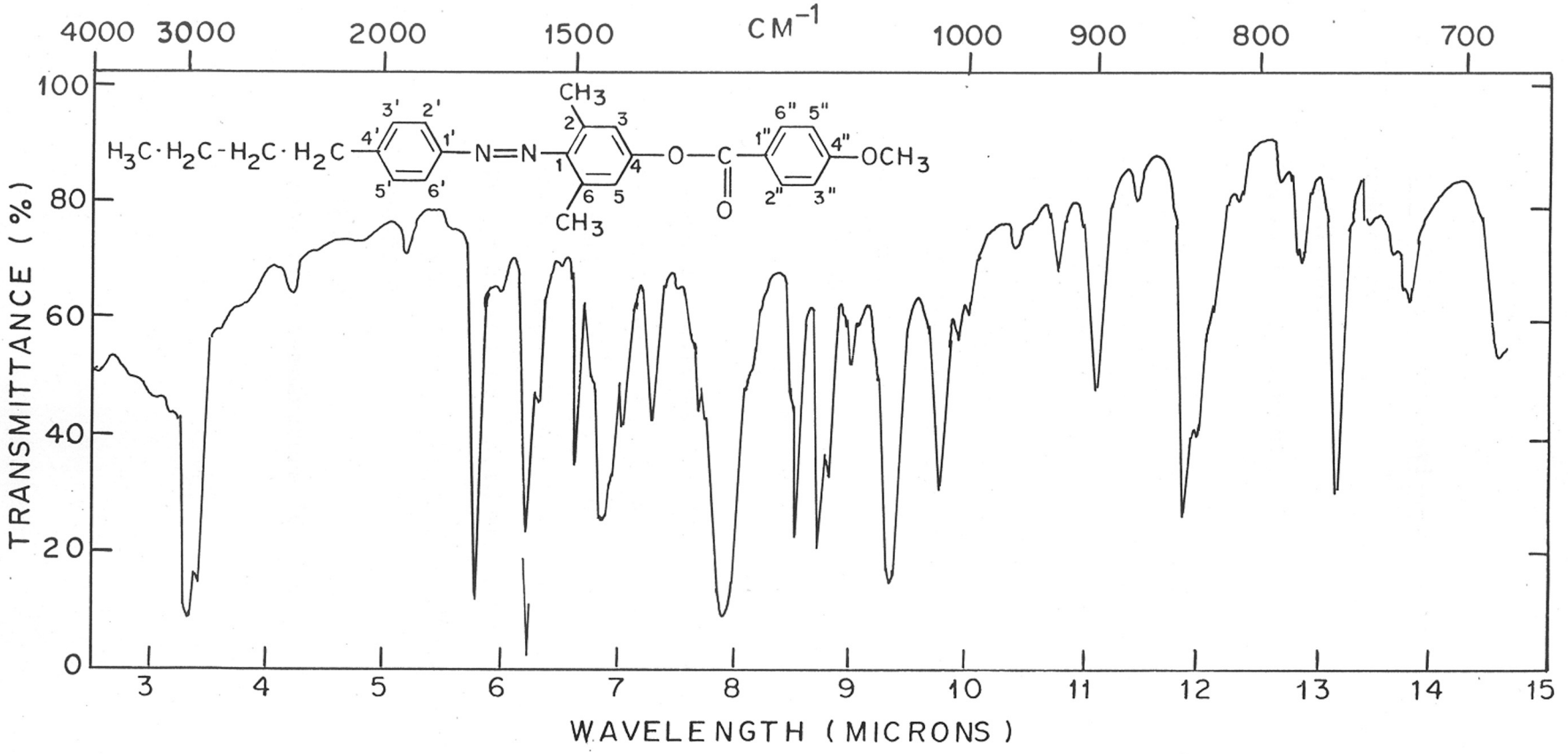


FIG. 5. IR SPECTRUM OF 2,6-DIMETHYL-4′-n-BUTYL-4-(p-METHOXY BENZOYLOXY)-AZOBENZENE

II 3. 2,4',6-Trimethyl-4-(p-methoxy benzoyloxy) azobenzene.

Yield: 48%.

Transition temperature: °C	C-N	N-I	Nematic range
	125	170	45

Elemental analysis Found: C, 73.8; H, 5.9; N, 7.5.

Required for $C_{23}H_{22}N_2O_3$: C, 73.8; H, 5.9; N, 7.5.

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1587 (-N=N-); 1470 (-C-CH_3), 1250, 1136, 1075 (aryl-O-C); 877, 840, 757, 724 (aromatic substituted). Fig. 6 .

II 4 2,4'6-Trimethyl-4-(p-ethoxy benzoyloxy)-azobenzene.

Yield: 50%.

Transition temperature °C	C-N	N-I	Nematic range
	123	180	57

Elemental analysis Found: C, 74.2; H, 6.2; N, 7.2.

Required for $C_{24}H_{24}N_2O_3$: C, 74.2; H, 6.3; N, 7.2.

IR bands (cm^{-1}) 1739 (-C=O); 1613, 1587 (N=N-); 1460 (C-CH_3); 1266, 1176, 1149, 1076 (aryl -O-C), 917, 885, 840, 763 (aromatic substituted).

II 5 2,4',6-Trimethyl-4-(p-n-butoxy benzoyloxy)-azobenzene.

Yield: 48%

Transition temperature °C;	C-N	N-I	Nematic range
	105	150	45

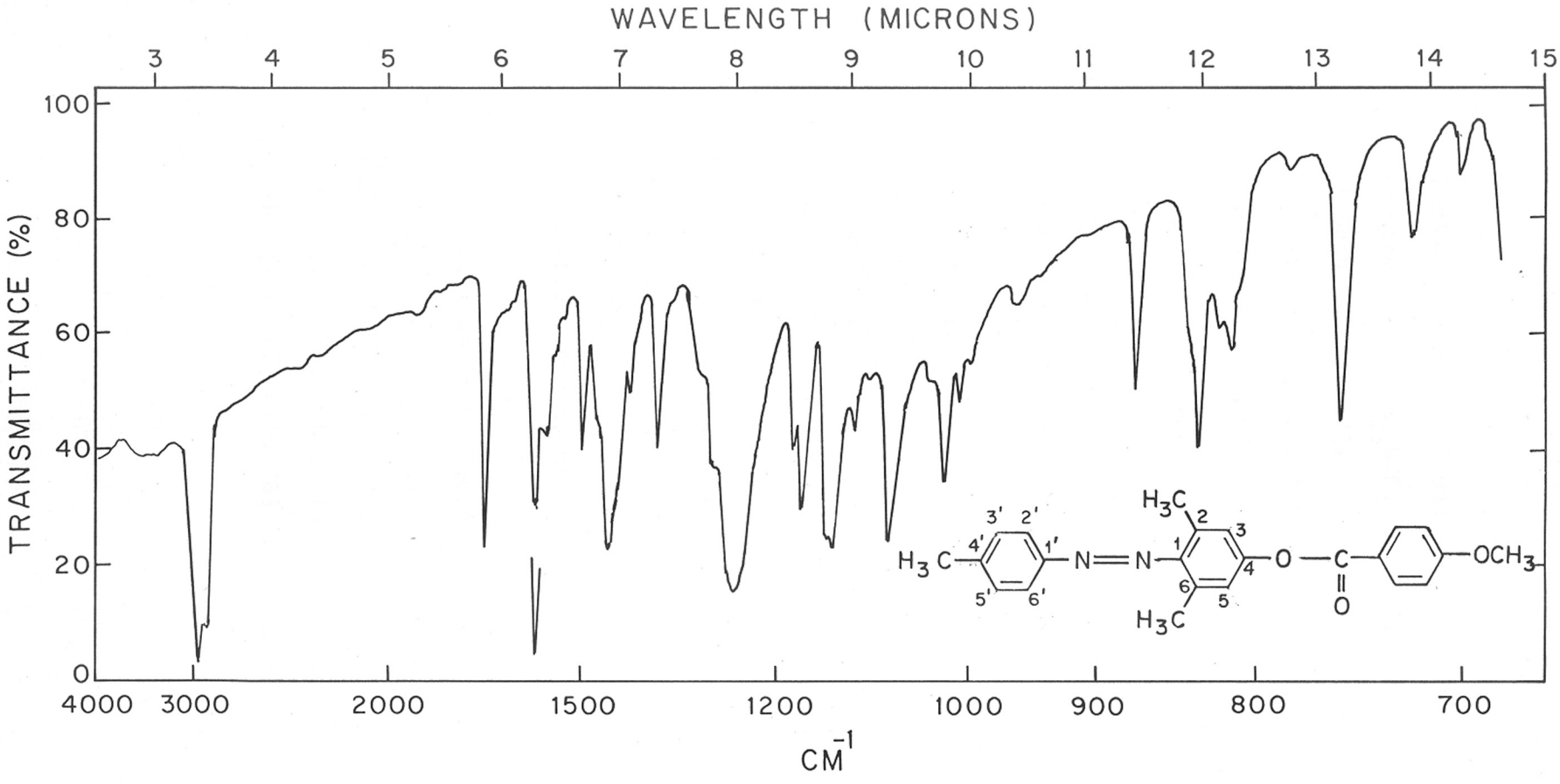


FIG. 6 . IR SPECTRUM OF 2,4',6-TRIMETHYL-4-(p-METHOXY BENZOYLOXY) AZOBENZENE

Elemental analysis Found: C, 75.0; H, 6.8; N, 6.7.

Required for $C_{26}H_{28}N_2O_3$: C, 75.0; H, 6.7; N, 6.8.

IR bands (cm^{-1}) 1730 (-C=O); 1613, 1587 (-N=N-); 1460 (C-CH_3 strong), 1250, 1166, 1064 (aryl-O-C ether linkage); 854, 826, 763 (aromatic substituted). Fig. 7.

II 6 2,4',6-Trimethyl-4-(p-n-hexyloxy benzoyloxy) azobenzene.

Yield: 45%

Transition temperature °C	C-N	N-I	Nematic range
	97	134	37

Elemental analysis Found: C, 75.7; H, 7.3; N, 6.3

Required for $C_{28}H_{32}N_2O_3$: C, 75.5; H, 7.3; N, 6.4.

IR bands (cm^{-1}) 1739 (-C=O); 1613, 1587 (-N=N-); 1460 (C-CH_3); 1250, 1163, 1059 (aryl-O-C); 854, 826, 763 (strong) (aromatic substituted).

II 7 3,4',6-Trimethyl-4-(p-methoxy benzoyloxy) azobenzene.

Yield: 49%

Transition temperature °C	C-N	N-I	Nematic range
	125	145	20

Elemental analysis Found: C, 73.9; H, 5.75; N, 7.6.

Required for $C_{23}H_{22}N_2O_3$: C, 73.7; H, 5.9; N, 7.5

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1587 (-N=N-), 1460 (C-CH_3), 1250, 1163, 1143, 1081 (aryl -O-C) (ether linkage); 847, 819, 763 (s) (aromatic substituted).

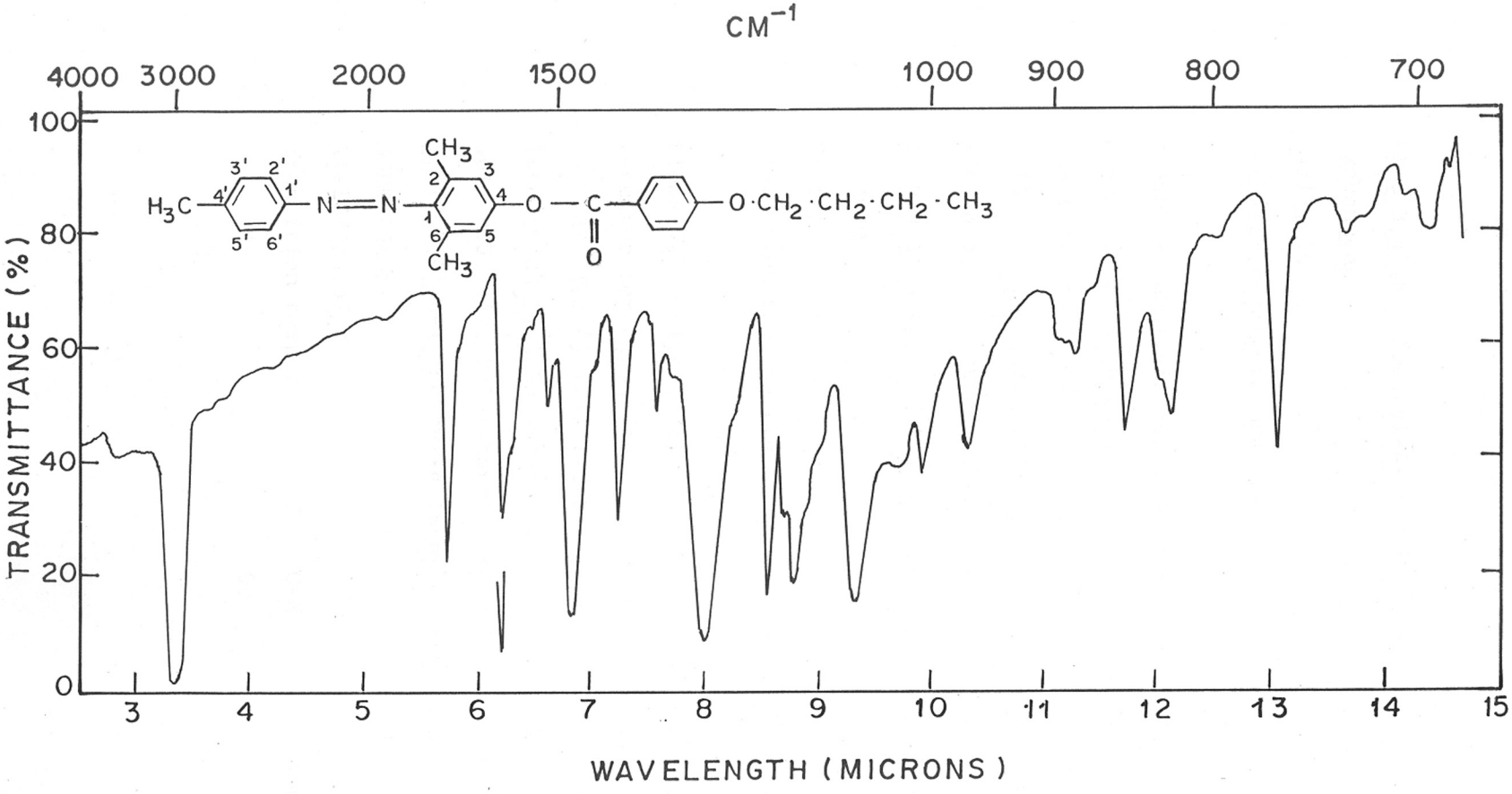


FIG. 7. IR SPECTRUM OF 2,4',6-TRIMETHYL-4-(p-nBUTOXYBENZOYLOXY) AZOBENZENE

II 8 3,4',6-Trimethyl-4-(p-ethoxy benzoyloxy) azobenzene.

Yield: 50.5%.

Transition temperature °C:	C-N	N-I	Nematic range
	130	160	30

Elemental analysis Found: C, 74.1; H, 6.35; N, 7.1.

Required for $C_{24}H_{24}N_2O_3$: C, 74.2; H, 6.2; N, 7.2.

IR bands (cm^{-1}) 1739 (-C=0), 1613, 1587 (-N=N-);
1460 ($C-CH_3$); 1274, 1176, 1149, 1099 (aryl -0-C);
909, 833, 763 (strong sharp) (aromatic substituted).

II 9 3,4',6-Trimethyl-4-(p-n-butoxy benzoyloxy)azobenzene.

Yield: 60%.

Transition temperature: °C	C-N	N-I	Nematic range
	110	130	20

Elemental analysis Found: C, 75.12; H, 6.8; N, 6.95.

Required for $C_{26}H_{28}N_2O_3$: C, 75.0; H, 6.8; N, 6.8.

IR bands (cm^{-1}) 1730 (-C=0); 1601, 1587 (-N=N-);
1460 ($C-CH_3$); 1250, 1163, 1136, 1064 (aryl-0-C);
961, 900, 847, 826 (sharp) (aromatic substituted).

II 10 3,4',6-Trimethyl-4-(p-n-hexyloxy benzoyloxy) azobenzene.

Yield: 55.5%.

Transition temperature: °C	C-N	N-I	Nematic range
	90	118	28

Elemental analysis Found: C, 75.8; H, 7.3; N, 6.1.

Required for $C_{28}H_{32}N_2O_3$: C, 75.7; H, 7.2; N, 6.2.

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1587 (-N=N-); 1460 ($C-CH_3$), 1266, 1081 (aryl -O-C); 909, 826, 769 (aromatic substituted). Fig. 8 .

II 11 3,5-Dimethyl 4'-n'butyl-4-(p-n-butoxy benzoyloxy) azobenzene.

Yield: 47%.

Transition temperature °C	C-N	N-I	Nematic range
	110	125	15

Elemental analysis Found: C, 75.9; H, 7.4; N, 6.1.

Required for $C_{29}H_{34}N_2O_3$: C, 76.0; H, 7.5; N, 6.1.

IR bands (cm^{-1}) 1724 (C=O),1600, 1575 (N=N); 1460 ($C-CH_3$), 1266, 1050 (aryl-O-CH_2); 769, 719 (aromatic substituted). Fig. 9 .

II 12 3,5-Dimethyl,4'-ethoxy-4-(p-methoxy-benzoyloxy) azobenzene.

Yield: 55%.

Transition temperature °C	C-N	N-I	Nematic range
	182	205	23

Elemental analysis Found: C, 71.3; H, 6.0; N, 6.9.

Required for $C_{24}H_{24}N_2O_4$: C, 71.3; H, 5.9; N, 7.0.

IR bands (cm^{-1}) 1724 (C=O); 1613, 1587 (N=N); 1460 ($C-CH_3$), 1250, 1163, 1064 (aryl -O-C); 900, 854, 763 (s)(aromatic substituted). Fig. 10.

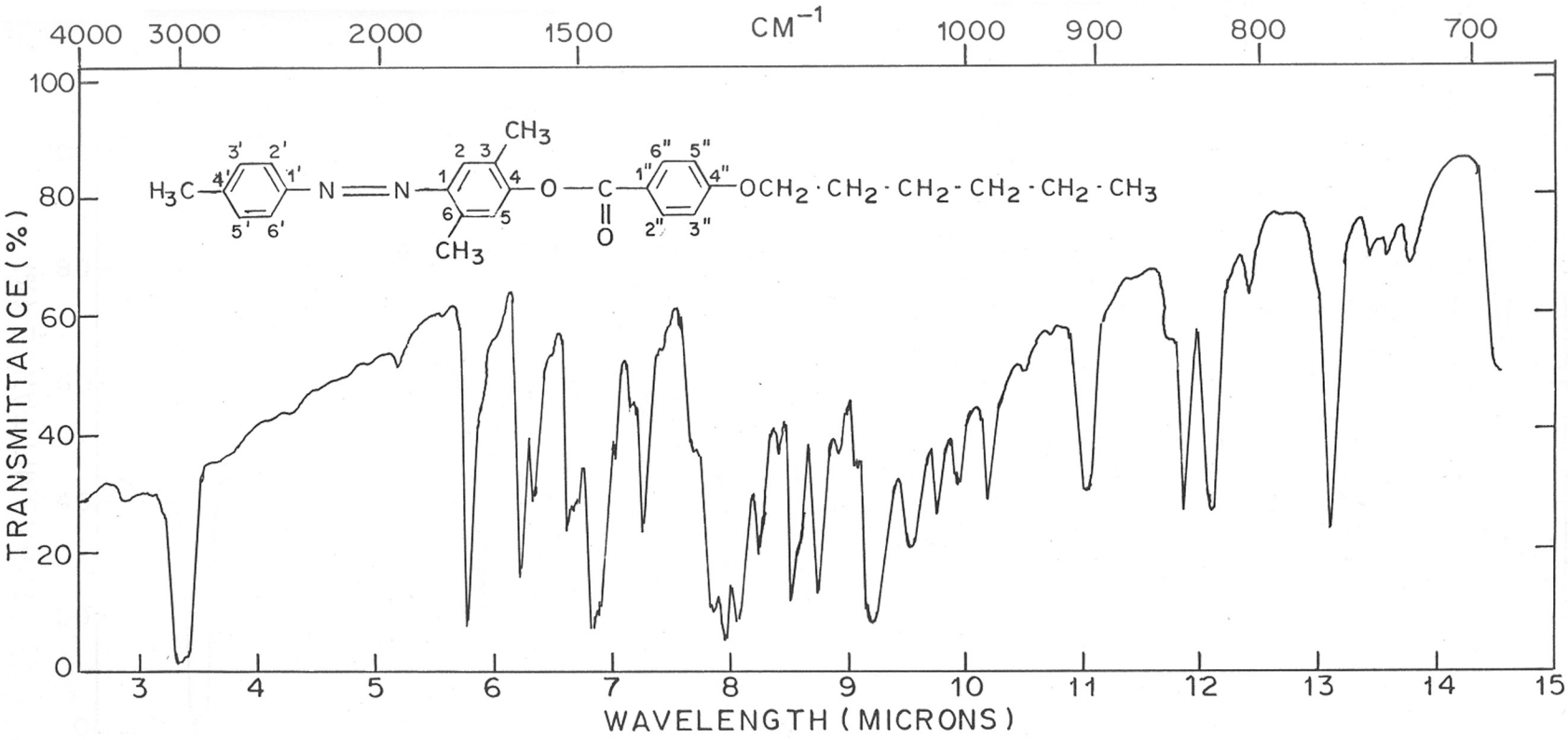


FIG. 8. IR SPECTRUM OF 3,4',6-TRIMETHYL-4-(p-n HEXYLOXY BENZOYLOXY) AZOBENZENE

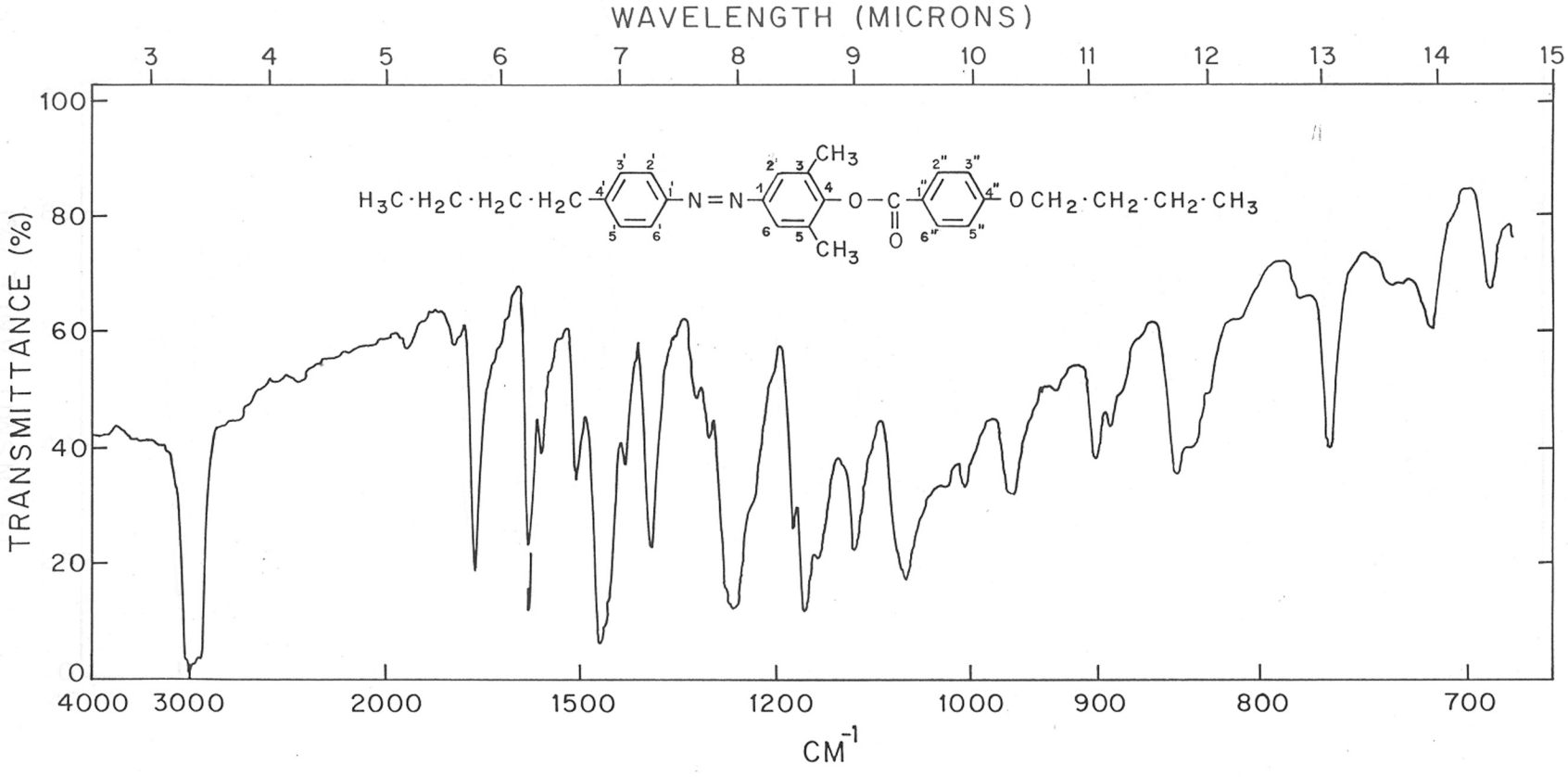


FIG. 9 : IR SPECTRUM OF 3,5-DIMETHYL, 4'-n BUTYL-4-(P-n BUTOXY BENZOYLOXY) AZOBENZENE.

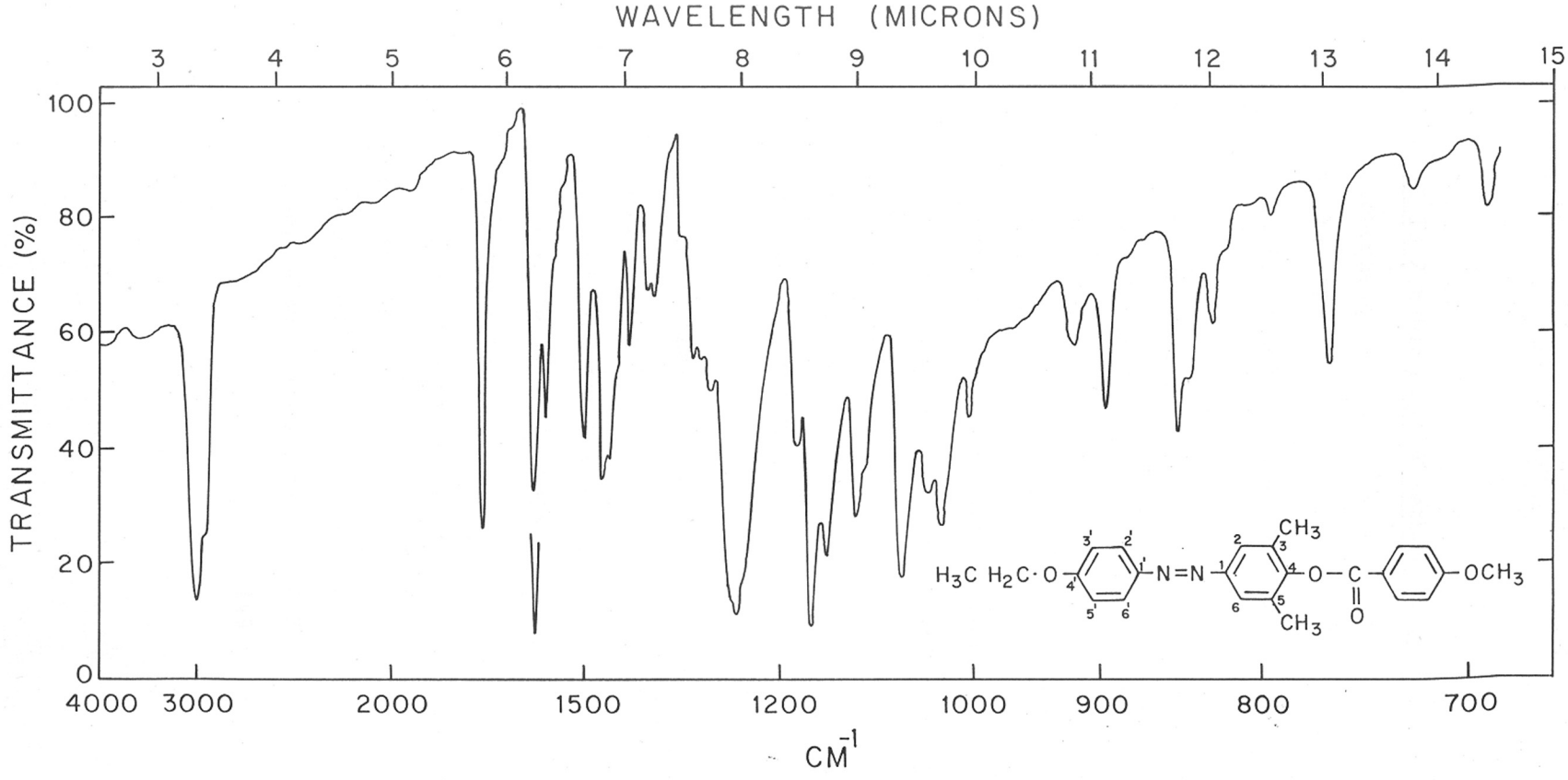


FIG. 10: IR SPECTRUM OF 3,5 DIMETHYL, 4' ETHOXY - 4 - (p-METHOXY BENZOYLOXY) AZOBENZENE.

II 13 2,6-Dimethyl-4'-ethoxy-4-(p-methoxy-benzoyloxy) azobenzene.

Yield: 58%.

Transition temperature °C	C-N	N-I	Nematic range
	140	210	70

Elemental analysis Found: C, 71.2; H, 6.0; N, 6.9.

Required for $C_{24}H_{24}N_2O_4$: C, 71.3; H, 5.9; N, 6.9.

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1587 (-N=N-); 1450 ($C-CH_3$), 1250, 1064 (aryl -O-C); 847, 769, 689 (aromatic substituted sharp bands).

II 14 2,3-Dimethyl, 4'methoxy-4-(p-methoxy benzoyloxy) azobenzene.

Yield: 50%.

Transition temperature °C	C-N	N-I	Nematic range
	200	270	70

Elemental analysis Found: C, 70.8; H, 5.7; N, 7.2

Required for $C_{23}H_{22}N_2O_4$: C, 70.7; H, 5.7; N, 7.1.

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1587 (-N=N-); 1460 ($C-CH_3$); 1250, 1075 (aryl -O-C); 840, 763 (aromatic substituted).

II 15 2,3-Dimethyl-4'ethoxy-4-(p-methoxy-benzoyloxy) azobenzene.

Yield: 60%.

Transition temperature °C	C-N	N-I	Nematic range
	149	255	106

Elemental analysis Found: C, 71.15; H, 6.0; N, 6.9.

Required for $C_{24}H_{24}N_2O_4$: C, 71.3; H, 5.9; N, 7.0.

IR bands (cm^{-1}) 1724 (-C=O); 1601, 1590 (N=N-); 1460 ($C-CH_3$), 1310, 1075 (aryl -O-C); 847, 765 (aromatic substituted).

II 16 2,3,4'-Trimethyl-4-(p,n-hexyloxy-benzoyloxy) azobenzene.

Yield: 63%.

Transition temperature °C	C-N	N-I	Nematic range
	120	200	80

Elemental analysis Found: C, 75.7; H, 7.3; N, 6.1.

Required for $C_{28}H_{32}N_2O_3$: C, 75.6; H, 7.3; N, 6.3.

IR bands (cm^{-1}) 1739 (-C=O),1613, 1587 (-N=N-), 1460 ($C-CH_3$); 1282, 1087 (aryl -O-C); 763, 735 (aromatic substituted). Fig. 11.

II 17 3-Nitro, 4'methyl-4-(p-methoxy-benzoyloxy) azobenzene.

Yield: 54%.

Transition temperature °C	C-N	N-I	Nematic range
	121	190	69

Elemental analysis Found: C, 64.4; H, 4.4; N, 10.7.

Required for $C_{21}H_{17}N_3O_5$: C, 64.4; H, 4.4; N, 10.8.

IR bands (cm^{-1}) 1724 (-C=O-); 1613, 1587 (-N=N-); 1504, 1333 (s) (aryl NO_2); 1250, 1163, 1042 (s) (aryl -O-C), 869, 847, 819, 757 (s) (aromatic substituted). Fig. 12 .

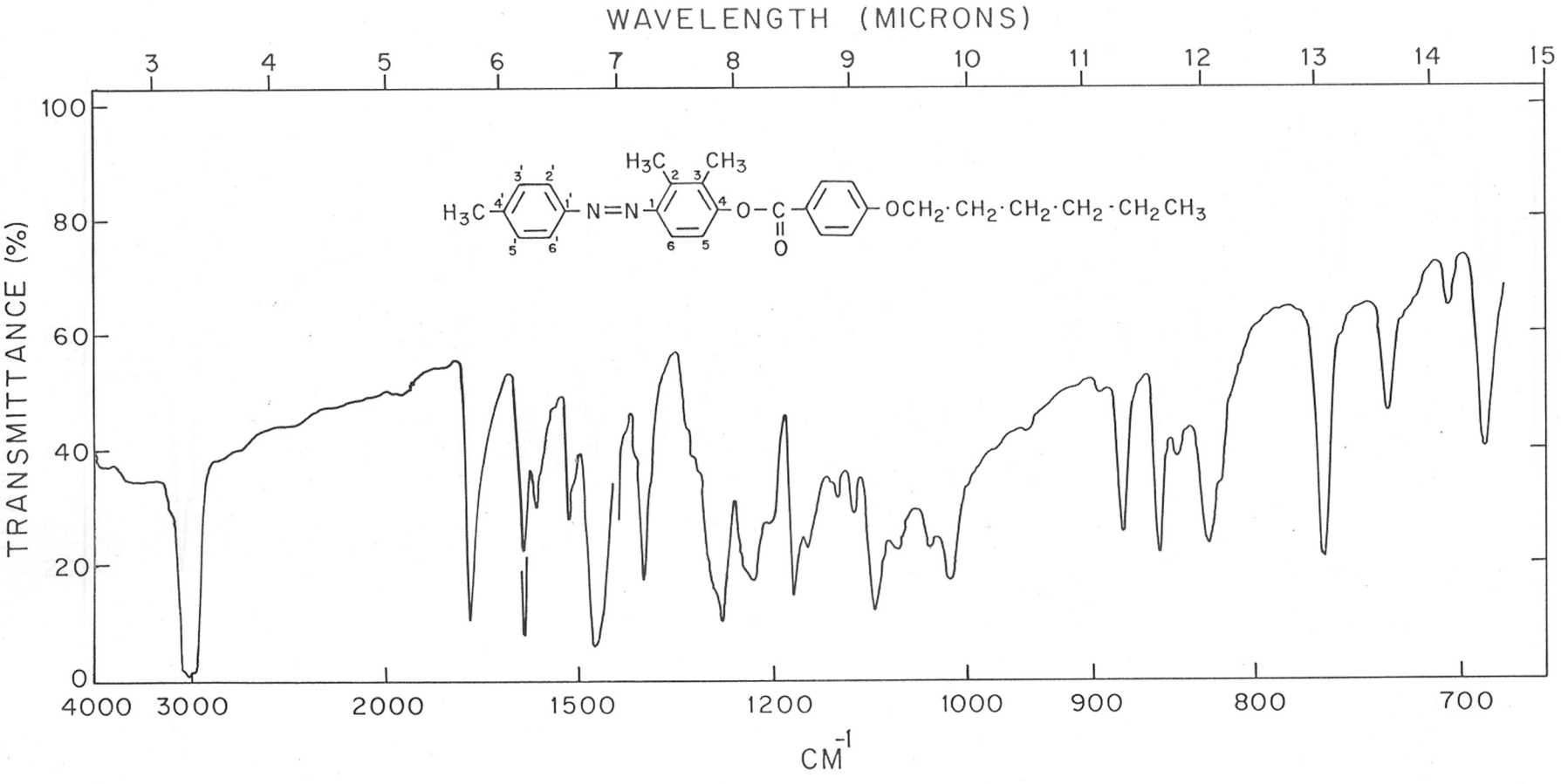


FIG. 11 : IR SPECTRUM OF 2,3,4'-TRIMETHYL-4-(p-HEXYLOXY BENZOYLOXY) AZOBENZENE.

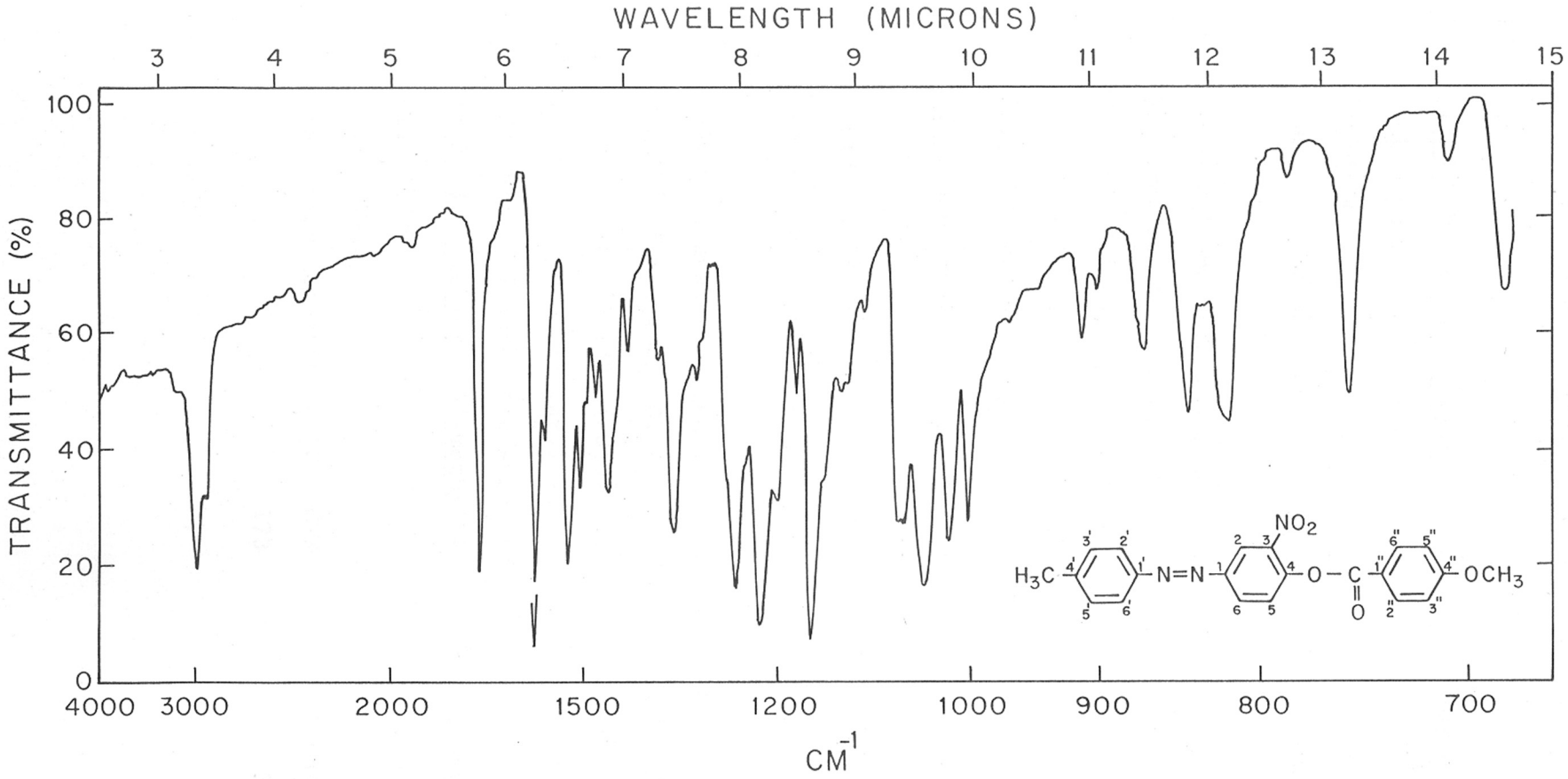


FIG.12: IR SPECTRUM OF 3 NITRO, 4'-METHYL-4-(p-METHOXY BENZOYLOXY) AZOBENZENE.

II 18 3-Nitro, 4'-methyl-4(p-n-butoxy-benzoyloxy) azobenzene.

Yield: 43%.

Transition temperature °C	C-N	N-I	Nematic range
	90	126	36

Elemental analysis Found: C, 66.5; H, 5.4; N, 9.7.

Required for $C_{24}H_{23}N_3O_5$: C, 66.6; H, 5.3; N, 9.8.

IR bands (cm^{-1}) 1724 (-C=O); 1600, 1575 (N=N-); 1460 (-C-CH_3); 1504, 1333 (NO_2); 1260, 1051 (aryl -O-C); 819, 757 (aromatic substituted).

II 19 3,6-Dichloro, 4'-methyl-4-(p-methoxy benzoyloxy) azobenzene.

Yield: 50.5%.

Transition temperature °C	C-N	N-I	Nematic range
	157	160	3

Elemental analysis Found: C, 60.7; H, 3.9; N, 6.7; Cl, 17.0.

Required for $C_{21}H_{16}N_2Cl_2O_3$: C, 60.7; H, 3.8; N, 6.8; Cl, 17.1.

IR bands (cm^{-1}) 1754 (-C=O); 1613, 1587 (-N=N-); 1460 (C-CH_3); 1250, 1176 (aryl -O-C); 1064 (aryl -C-Cl); 892, 826, 757 (aromatic substituted).

II 20 3,6-Dichloro, 4'-methyl-4-(p-ethoxy-benzoyloxy) azobenzene.

Yield: 49%.

Transition temperature °C	C-N	N-I	Nematic range
	173	176	3

Elemental analysis Found: C, 61.5; H, 4.2; N, 6.5; Cl, 16.6

Required for $C_{22}H_{18}N_2Cl_2O_3$: C, 61.6; H, 4.2; N, 6.5; Cl, 16.5

IR bands (cm^{-1}) 1754 (-C=O); 1613, 1587 (-N=N-); 1460 (C-CH_3); 1235, 1168 (aryl -O-C); 1053 (aryl -Cl); 892, 819, 757 (aromatic substituted).

II 21 3,6-Dichloro, 4'-methyl-4-(p-n-butoxy-benzoyloxy) azobenzene.

Yield: 48%.

Transition temperature °C	C-N	N-I	Nematic range
	120	130	10

Elemental analysis Found: C, 63.0; H, 4.8; N, 6.1; Cl, 15.3

Required for $C_{24}H_{22}N_2Cl_2O_3$: C, 63.1; H, 4.8; N, 6.1; Cl, 15.4.

IR bands (cm^{-1}) 1739 (-C=O); 1613, 1587 (-N=N-); 1460 (C-CH_3); 1266, 1235, 1010 (aryl-O-C); 1050 (aryl -C-Cl); 850, 819, 769 (aromatic substituted).

II 22 3,6-Dichloro, 4'-methyl-4-(p-n-hexyloxy benzoyloxy) azobenzene.

Yield: 53%.

Transition temperature °C	C-N	N-I	Nematic range
	107	115	8

Elemental analysis Found: C, 64.3; H, 5.4; N, 5.8; Cl, 14.6

Required for $C_{26}H_{26}N_2Cl_2O_3$: C, 64.4; H, 5.4; N, 5.7; Cl, 14.7.

IR bands (cm^{-1}) 1739 (-C=O); 1601, 1587 (-N=N-); 1266, 1250, 1163 (aryl -O-C); 1053 (aryl -C-Cl); 893, 840, 826, 763 (strong sharp) (aromatic substituted). Fig. 13.

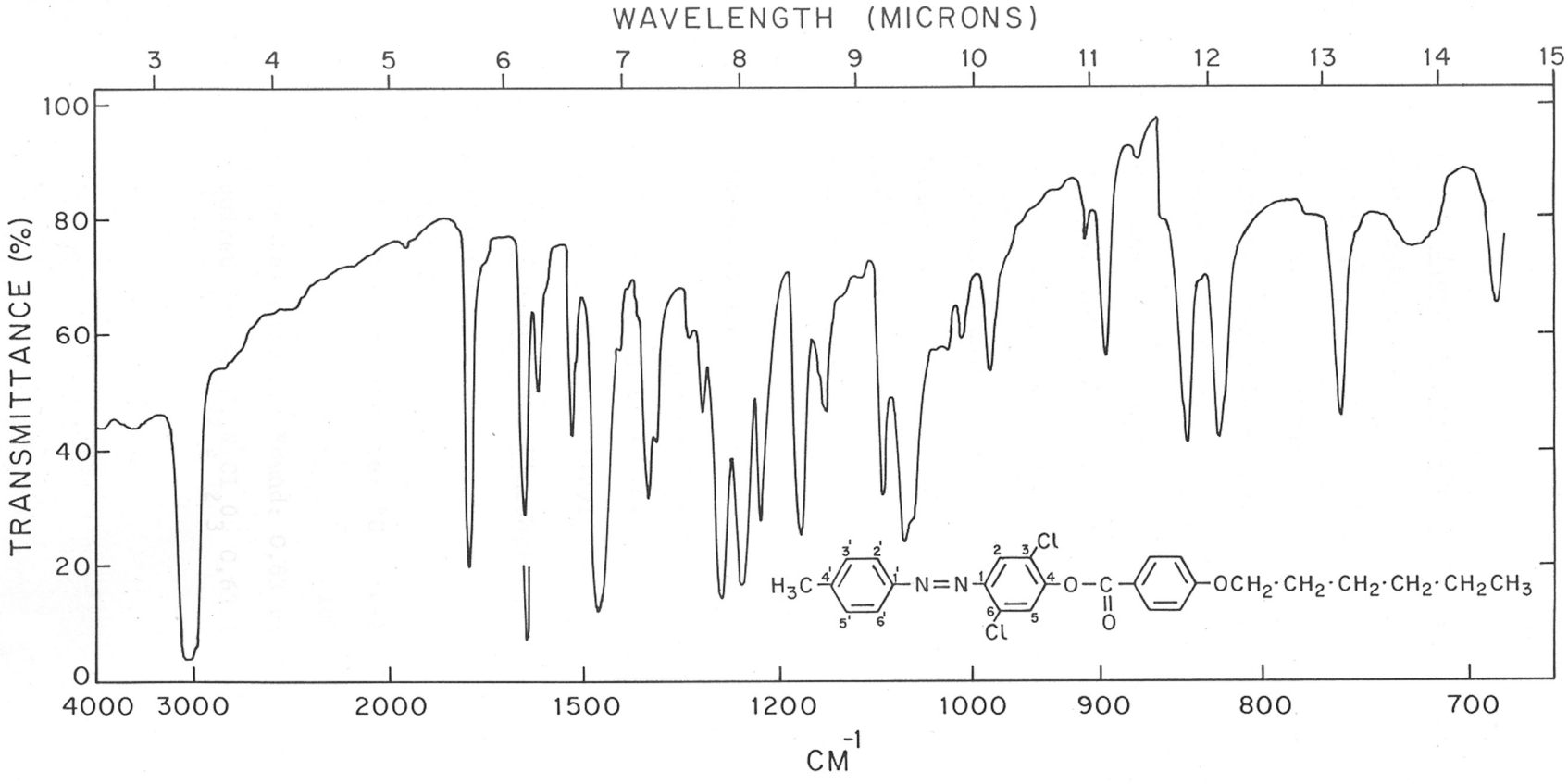


FIG.13: IR SPECTRUM OF 3,6-DICHLORO,4'-METHYL-4-(p-n HEXYLOXY BENZOYLOXY) AZOBENZENE.

II 23 2,6-Dichloro, 4'methyl-4-(p-methoxy benzoyloxy) azobenzene.

Yield: 49%.

Transition temperature °C C-N-I
160

Elemental analysis Found: C, 60.8; H, 3.9; N, 6.7; Cl,17.1.

Required for $C_{21}H_{16}N_2Cl_2O_3$:C,60.8; H, 3.8; N, 6.7; Cl,17.1.

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1575 (-N=N-); 1471 ($C-CH_3$); 1282, 1258, 1149 (aryl -O-C); 1087 (aryl -C-Cl); 847 (s, sharp), 763 (aromatic susbtituted).

II 24 2,6-Dichloro, 4'-methyl-4-(p-ethoxybenzoyloxy) azobenzene.

Yield: 48%.

Transition temperature °C	C-N	N-I	Nematic range
	145	162	17

Elemental analysis Found: C, 61.5; H, 4.2; N,6.5;Cl,16.8.

Required for $C_{22}H_{18}N_2Cl_2O_3$ C,61.3; H, 4.2; N,6.5;Cl,16.6.

IR bands (cm^{-1}) 1724 (-C=O),1613, 1575 (-N=N-); 1471 ($C-CH_3$); 1282, 1010 (aryl -O-C); 1064 (aryl -C-Cl).

II 25 2,6-Dichloro-4'methyl-4(p-n-butoxybenzoyloxy) azobenzene.

Yield: 50%.

Transition temperature: °C	C-N	N-I	Nematic range
	105	125	20

Elemental analysis Found: C,63.0; H,4.7;N,6.25;Cl,15.2.

Required for $C_{24}H_{22}N_2Cl_2O_3$ C,63.1;H,4.8;N,6.1; Cl, 15.3.

IR bands (cm^{-1}) 1724 (-C=O); 1613, 1575 (-N=N-); 1471 ($C-CH_3$); 1266, 1010 (aryl -O-C); 1087 (aryl -C-Cl); 826, 763 (aromatic substituted). Fig. 14.

II 26 2,6-Dichloro 4'-methyl-4-(p-n-hexyloxy benzoyloxy) azobenzene.

Yield: 51%.

Transition temperature °C	C-N	N-I	Nematic range
	90	110	20

Elemental analysis Found: C, 64.3; H, 5.4; N, 5.8; Cl,14.4.
Required for $C_{26}H_{26}N_2Cl_2O_3$: C,64.4; H . 5.3; N, 5.8; Cl,14.6.
IR bands (cm^{-1}) 1724 (-C=O); 1613, 1575(-N=N-); 1471 ($C-CH_3$); 1250, 1059 (s, sharp). (aryl -O-C); 1075 (aryl -C-Cl); 854, 833, 763 (aromatic substituted).

All the compounds described above have been crystallized from pet.ether (60-80)-benzene. Fig. 15.

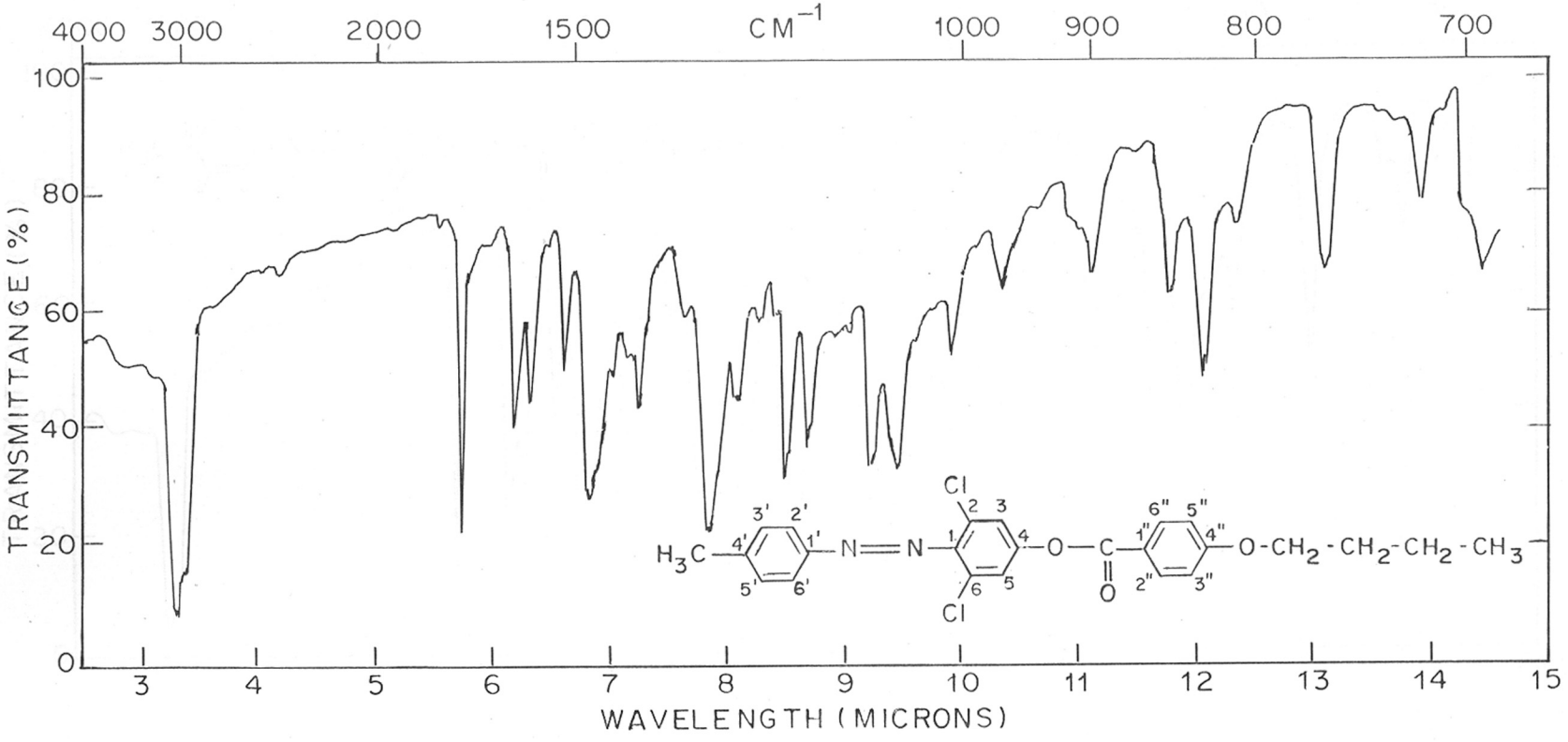


FIG. 14. IR SPECTRUM OF 2,6-DICHLORO 4'-METHYL-4-(p-n BUTOXY BENZOYLOXY) AZOBENZENE

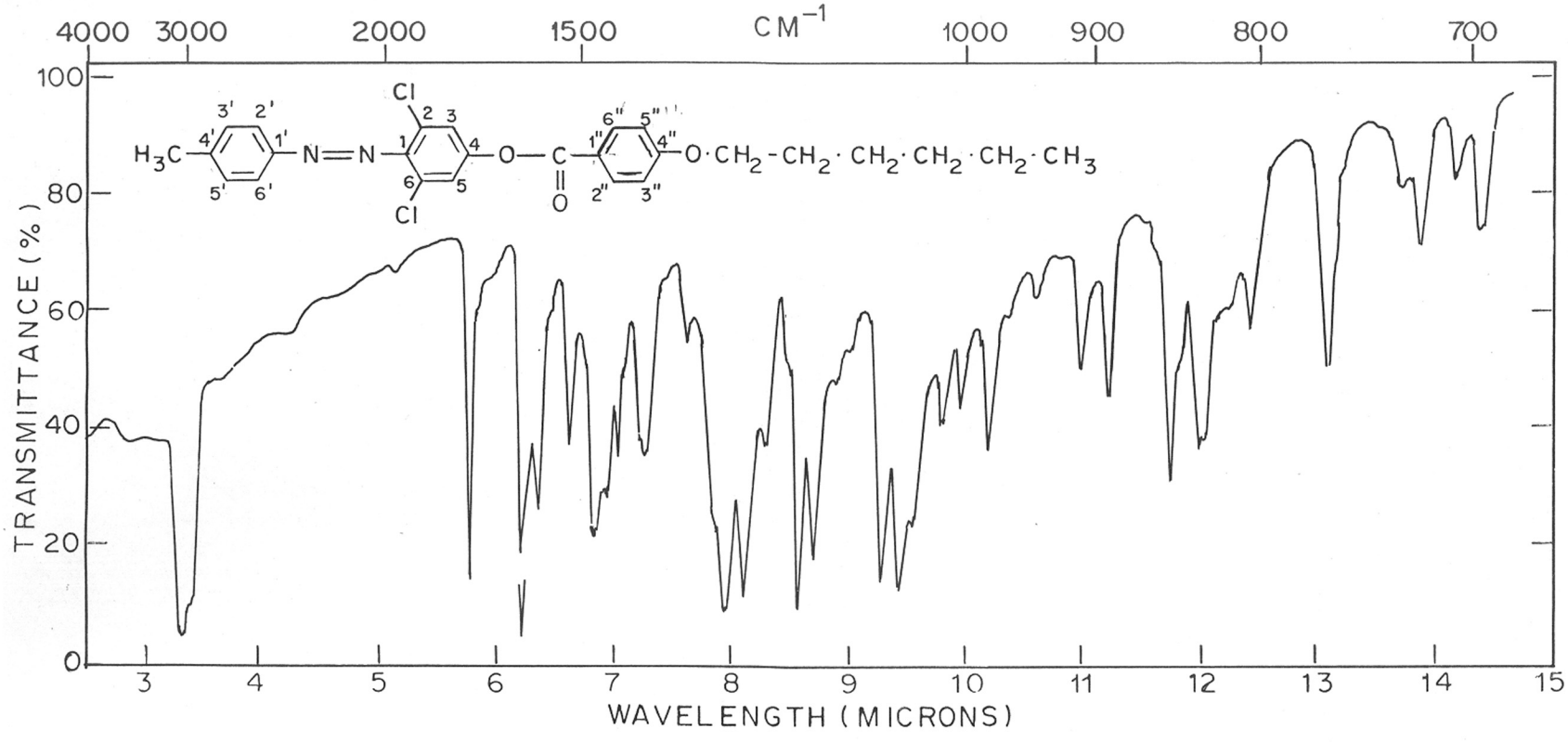


FIG. 15. IR SPECTRUM OF 2,6-DICHLORO-4'-METHYL-4-(p-n HEXYLOXY BENZOYLOXY) AZOBENZENE

CHAPTER I B

PMR data of laterally disubstituted and nitro-substituted liquid crystalline compounds.

PMR STUDY OF LIQUID CRYSTALLINE COMPOUNDS

The proton magnetic resonance spectroscopy (PMR) is a more powerful tool than any other physical method in terms of structural information derived from the spectrum. When it is used in combination with other spectroscopic methods for organic structural determination a great deal of structural information can be obtained. Nuclei of certain isotopes possess a mechanical spin or angular momentum. The total angular momentum depends on the nuclear spin or spin number, I, which may have values of 0, ½, 3/2---- depending on the particular nucleus. In nuclear magnetic resonance studies, the behaviour of nuclei having odd spin numbers (for e.g. ^{1}H , ^{19}F , ^{13}C, ^{31}P) when placed in a strong magnetic field and irradiated by radio frequency corresponds to characteristic signals attributed to flipping of protons under specific chemical environment present in molecule. Since an electric charge is associated with an atomic nucleus, the spinning nucleus gives rise to a magnetic field whose axis is coincident with the axis of spin. In the present chapter we are going to deal with PMR studies of series of liquid crystalline compounds which has been described in Chapter 1A. All the PMR spectra were recorded on T-60 (10% conc.soln.)

FT-80A spectrometers, in CCl_4 and $CDCl_3$ respectively using TMS as an internal standard.

The chemical shift of protons is influenced by the inductive, mesomeric and hyper conjugative effects of different substituents present in the molecule. An attempt has been made to correlate the observed chemical shifts of different protons with the total structure of the molecule. The chemical shifts of different phenols and corresponding liquid crystalline compounds are presented along with the structure. In case of Ia phenol, the C_2,C_6-H have appeared upfield because of the presence of 'OH' group on neighbouring C_1. The methyl groups at C_3, C_5-positions of the aromatic ring have shown down-field chemical shift corresponding to normal aromatic-CH_3. This may be attributed to the fact that adjacent electron withdrawing (-N=N-) moiety has deshielded the methyl groups. This effect is further shown by C_2, and C_6, H also. C_3,C_5, H and C_4,-CH_3 have shown normal chemical shift C_4,-ϕ-CH_2 protons have appeared at low field because of the delocalization effect of neighbouring phenyl ring.

I_b has shown almost same chemical shifts as I_a, according to the similarity of the structure. When compound I_c is considered C_2-CH_3 has appeared at upfield because of the influence of the neighbouring

carbon carrying 'OH' group. C_3-H which is flanked by (C-CH_3) and (-N=N-) shows the dominating ortho effect of (-N=N-) group over (C-CH_3) group when additive effect is considered. C_5-CH_3 has shown down-field chemical shift because of the neighbouring (-N=N-) group. C_6-H shows the upfield chemical shift as a result of combined ortho effects of hyper-conjugative methyl and mesomeric hydroxy groups.

In case of I_d C_2,C_6-CH_3 show upfield shift because of the shielding ortho effect of hydroxy group. C_3, C_5 H show down-field chemical shift as expected. $C_{2'}$,$C_{6'}$-H have shown further downfield shift as only deshielding effect of (-N=N-) group is acting. $C_{3'}$, $C_{5'}$-H have shown normal chemical shift. All the protons at $C_{4'}$ position have absorbed at expected δ value. The PMR spectrum of I_e compound shows theoretically expected results and the chemical shifts of respective protons are shifted upfield because of shielding effect of oxygen in conjugation with two phenyl rings connected with (-N=N-) when compared with the δ values of the compound I_d. This change may be explained on the basis of structural change at $C_{4'}$ position [R_1 is replaced by O-R_1]. $C_{4'}$-CH_2 and CH_3 protons show down-field shift because of deshielding effect due to direct attachment to oxygen atom.

In I_f the change in the position of the methyl substituents has reduced the shielding effect of oxygen at C_4, position on C_2, C_6 protons and C_3, C_5 methyls.

I_g gives the PMR spectrum where the chemical shift of proton at position C_5 shows the additive effect due to hyper conjugation by C_2-methyl group at para position and deshielding effect due to the proximity of (-N=N-) group. C_6-H shows the upfield chemical shift due to neighbouring hydroxy group and para hyperconjugative effect of C_3-methyl.

PMR spectrum of I_h compound shows almost identical chemical shift as I_g compound. In this case replacement of C_4,-OCH_3 by -OC_2H_5 is the only structural change. I_i spectrum shows more or less same chemical shifts as I_g and I_h.

The PMR data of I_j shows the additive influence of electron withdrawing nitro substituent and the (-N=N-) moiety in the molecule. The chemical shfits of C_3 and C_5 protons are deshielded and show down-field values. The C_6-$\underline{H}$ shows the chemical shift equivalent to C_3,-$\underline{H}$ and C_5,-$\underline{H}$ although it is in the vicinity of the hydroxyl function.

In PMR spectrum of I_k the C_3-$\underline{H}$ shows additive deshielding effect of C_2-Cl and C_4 (-N=N-) hence downfield chemical shift is seen. In case of C_6-$\underline{H}$ which

is flanked by C_5-Cl and C_1-OH the deshielding effect is reduced due to C_1-OH and upfield chemical shift is observed. The expected chemical shifts are observed for $C_{2'}$, $C_{6'}$, $C_{3'}$ and $C_{5'}$ protons.

When the PMR spectrum of I_1 is studied the additive shielding effect on C_2 and C_6 protons is observed due to C_1-OH, C_3-Cl and C_5-Cl.

From the above mentioned phenols series of liquid crystalline compounds was synthesized. In compound II (1) the chemical shifts of C_3-H and C_5-H show shielding effect by C_2-CH_3, C_6-CH_3 and C_4-O-C showing upfield chemical shift. $C_{2'}$,$C_{6'}$ protons show downfield shift due to electron withdrawing effect by C_4(-N=N-) moiety. The chemical shifts of $C_{2''}$ and $C_{6''}$ protons show the influence of electron withdrawing (deshielding) C_1-$\overset{O}{\overset{\|}{C}}$ group and the low field values are observed.

When the PMR spectra of remaining compounds (II2 onwards) are studied it is observed that the different protons have shown the chemical shifts as expected theoretically. The dominent influence of methyl and chloro substituents at A, B, C, D positions of the central phenyl ring in the liquid crystalline molecule is seen (similar to respective phenols). Change in -OR_2 group (methoxy, ethoxy, n-butoxy, n-hexyloxy) has not shown any particular effect on the chemical shifts.

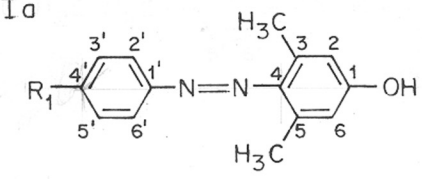
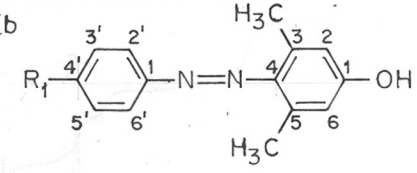
Compound Number	Structure	δ-Chemical shifts with respect to internal standard TMS				
Ia		1-OH	2,6-H	3,5-CH_3	3',5'-H	2',6'-H
		5.8(broad exchanges with D_2O)	6.3(broad s)	2.3(s)	7.2(d)	7.6(d)
		1H	2H	6H	2H	2H
		4'-CH_3	4'-CH_2-CH_2(CH_3)		4', $\emptyset CH_2$	
	$R_1 = n CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	1.0(broad t)	1.1 to 2 (m)		2.2 to 2.8 (m)	
		3H	4H		2H	
Ib		1-OH	2,6-H	3,5,4'-CH_3	2',6'-H	3',5'-H
		5.1(broad) (Exchanges with D_2O)	6.4(s)	2.4(s)	7.5(d)	7.2(d)
	$R_1 = CH_3$	1H	2H	9H	2H	2H

FIG. 16.

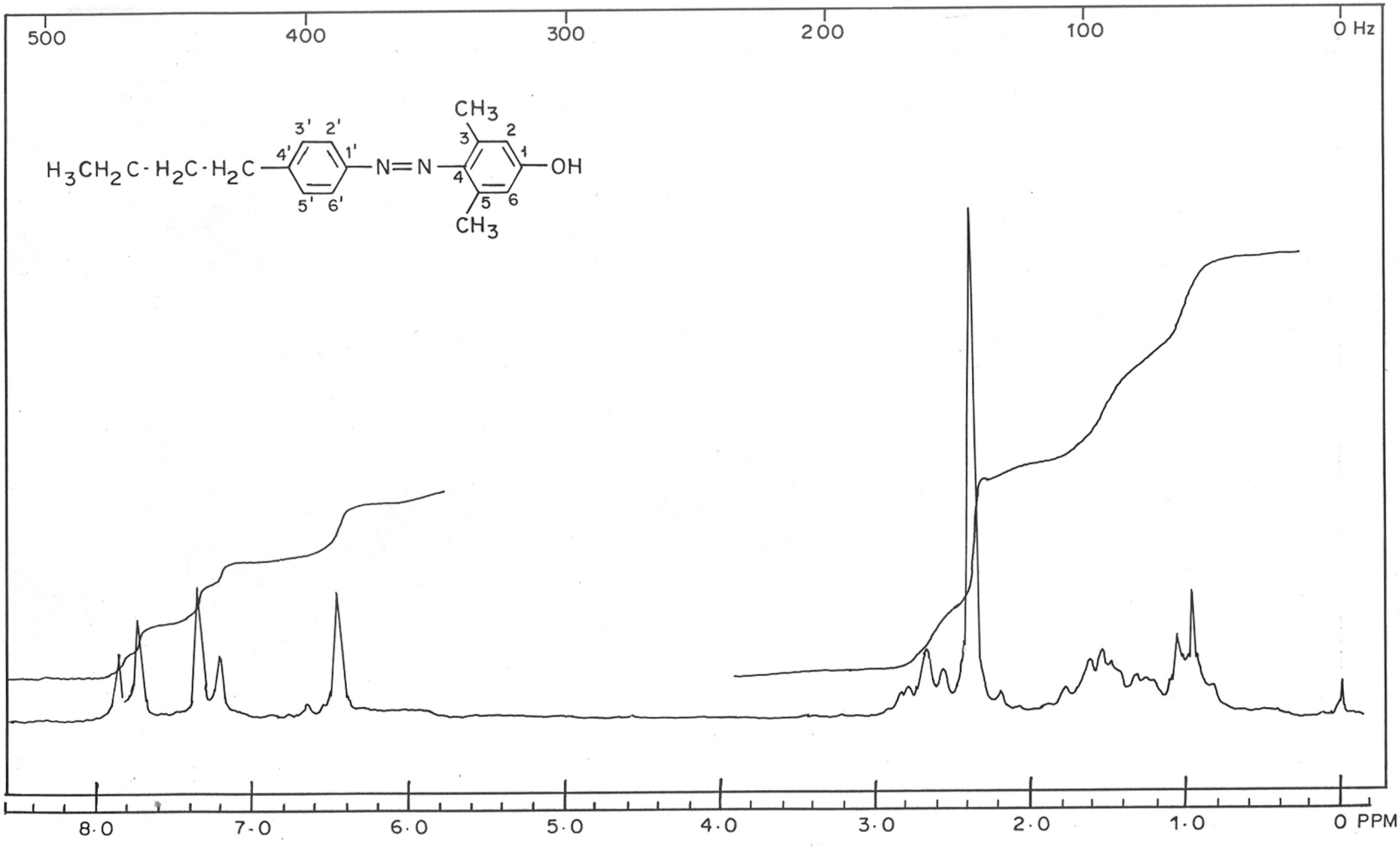
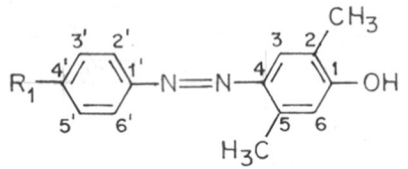
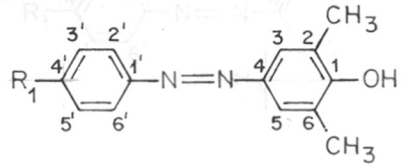


FIG. 16. PMR SPECTRUM OF 3-5-DIMETHYL-4-(p-n-BUTYLPHENYLAZO) PHENOL

Compound Number	Structure	δ- Chemical shifts with respect to internal standard TMS				
Ic		1-OH	2-CH_3	3-H	5-CH_3	6-H
		5.4 (broad exchange with D_2O)	2.26(s)	7.5(s)	2.6(s)	6.6(broad s)
		1H	3H	1H	3H	1H
		2',6'-H	3',5'-H	4'-CH_3		
	$R_1 = CH_3$	7.8(d)	7.3(d)	2.4(s)		
		2H	2H	3H		
Id		1-OH	2,6-CH_3	3,5 - H	2',6'-H	3',5'-H
		5.2(broad) exchanges with D_2O	2.2(s)	7.5(s)	7.8(d)	7.2(d)
		1H	6H	2H	2H	2H
	$R_1 = n CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	4'-CH_3	4'-CH_2-CH_2-(CH_3)		4'-Ø-CH_2	
		1.0 (unresolved triplet)	1.1 to 1.8 (m)		2.7(t)	
		3H	4H		2H	

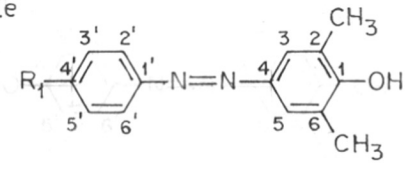
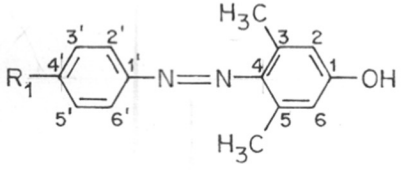
Compound Number	Structure	δ - Chemical shifts with respect to internal standard TMS				
Ie		1-OH	2',6'-H	2,6-CH_3	3,5-H	3',5'-H
		3.6(broad exchanges with D_2O)	7.2(d)	2.0(m)	6.4(s)	6.0(d)
		1H		6H	2H	2H
	$R_1 = -O \cdot CH_2 \cdot CH_3$	4'-O-CH_2	4'-CH_3			
		4.1(q)	1.4(t)			
		2H	3H			
If		1-OH	2,6-H	3,5-CH_3	2',6'-H	3',5'-H
		4.6(broad exchanges with D_2O)	6.5(s)	2.4(s)	7.8(d)	6.9(d)
		1H	2H	6H	2H	2H
	$R_1 = -O \cdot CH_2 \cdot CH_3$	4'-$OCH_2(CH_3)$	4'-CH_3			
		4.0(q)	0.9(t)			
		2H	3H			

FIG. 17.

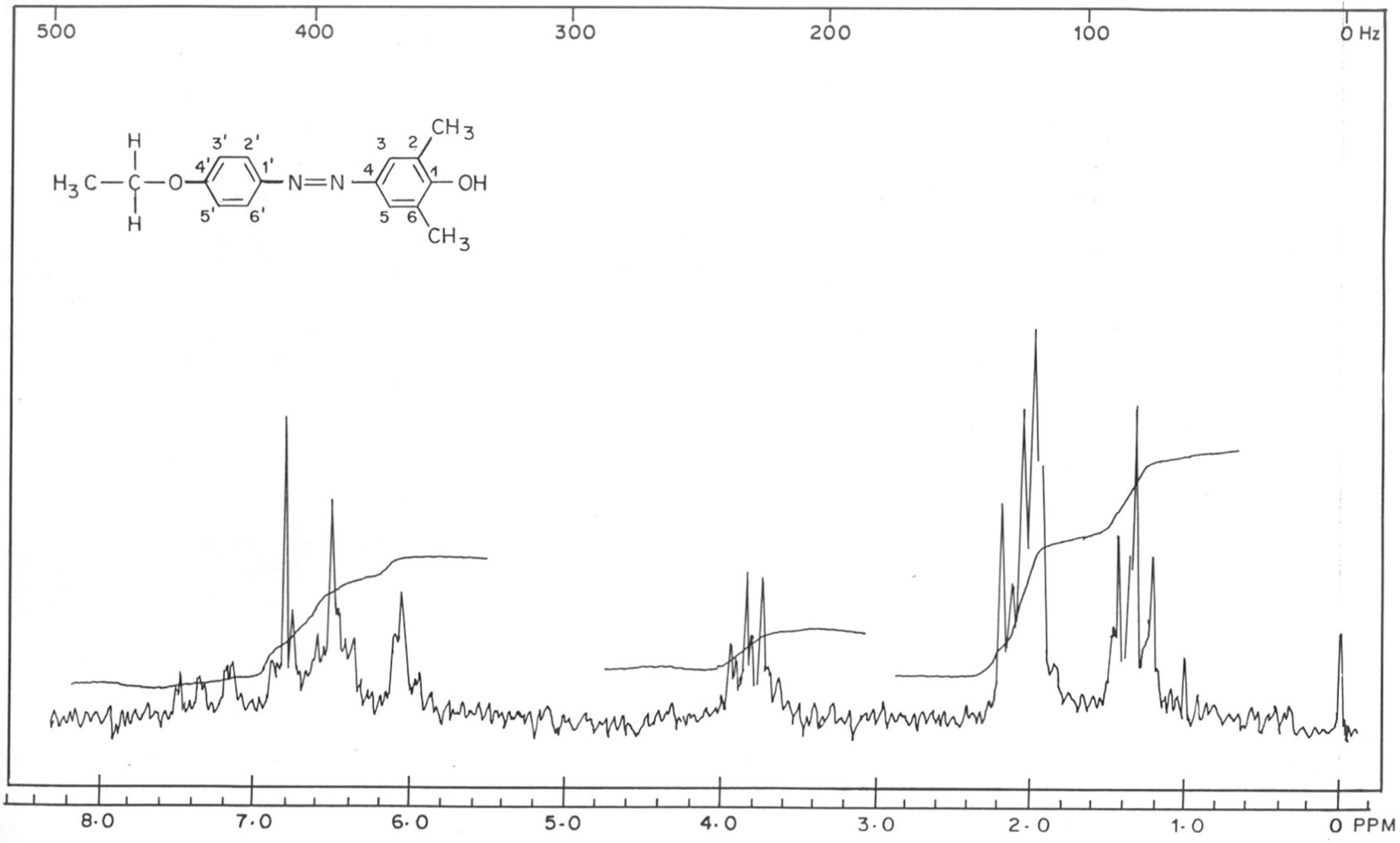
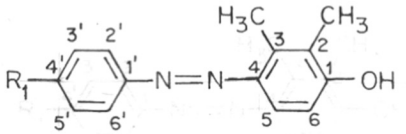
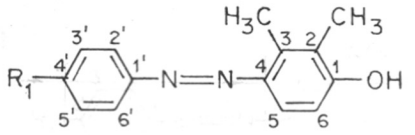
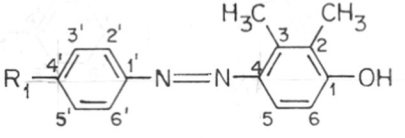
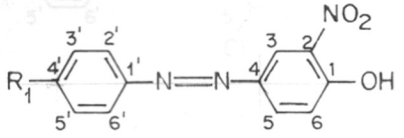
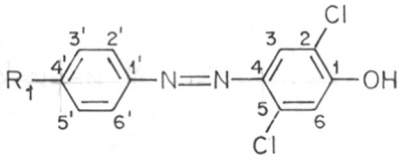
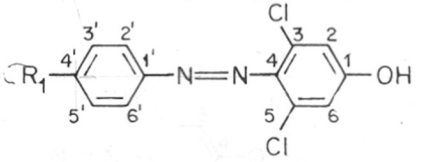
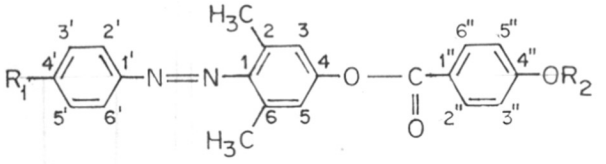
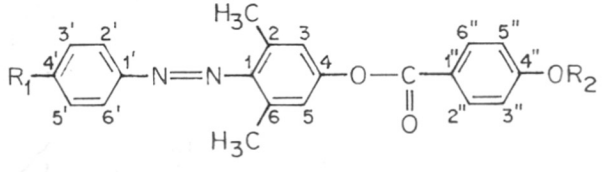


FIG. 17. PMR SPECTRUM OF 2,6-DIMETHYL-4-(p-ETHOXY PHENYLAZO) PHENOL

Compound Number	Structure	δ-Chemical shifts with respect to inernal standard TMS				
Ig		1-OH	2,-CH_3	3,-CH_3	5,-H	6,-H
		5.0 (broad exchanges with D_2O)	2.3(s)	2.7(s)	7.5(d)	6.6 (d)
		1H	3H	3H	1H	1H
	$R_1 = -OCH_3$	2',6'-H	3'5'-H	4'-O-CH_3		
		7.8(d)	7.0(d)	3.9(s)		
		2H	2H	3H		
Ih		1.0H	2,-CH_3	3,-CH_3	5,-H	6,-H
		3.8(s)	2.25(s)	2.36(s)	7.8(d)	6.7(d)
		1H	3H	3H	1H	1H
	$R_1 = O \cdot CH_2 \cdot CH_3$	2'6'-H	3'',5'-H	4'-OCH_2	4'-CH_3	
		7.9(dd)	6.9(dd)	4.0(q)	1.4(t)	
		2H	2H	2H	3H	

Compound Number	Structure	δ- Chemical shifts with respect to internal standard TMS				
Ii		1-OH	2,-CH_3	3,-CH_3	5,-H	6-H
		4.2(broad exchanges with D_2O)	2.2(s)	2.6(s)	7.5(d)	6.6(d)
		1H	3H	3H	1H	1H
	$R_1 = CH_3$	2',6',-H	3',5'-H	4'-CH_3		
		7.7(d)	7.2(d)	2.4(s)		
		2H	2H	3H		
Ij		1,-OH	3,-H	5,-H	2'6',-H	6,3',5',-H
		10.0(broad)	8.6(s)	7.6(d)	7.8(dd)	7.3(m)
		1H	1H	1H	2H	3H
	$R_1 = CH_3$	4'-CH_3				
		2.4(s)				
		3H				

Compound Number	Structure	δ- Chemical shifts with respect to internal standard TMS			
Ik		1,-OH	3,2',6'-H	6,3',5'-H	4',-CH_3
		5.0(broad exchanges with D_2O	7.7(d)	7.1(d)	2.5(s)
		1H	3H	3H	3H
	$R_1 = -CH_3$				
Il		1,-OH	2,6,-H	2',6'-H	3',5'-H
		5.1(broad)	6.6(s)	7.6'(d)	7.1 (d)
		exchanges with D_2O			
		1H	2H	2H	2H
	$R_1 = CH_3$	4',-CH_3			
		2.4(s)			
		3H			

Compound Number	Structure	δ-Chemical shifts with respect to internal standard TMS
II 1		2,6-CH_3 3,5-H 2',6'-H 3',5'-H 2'',6''-H 2.5(s) 7.0(s) 7.7(d) 7.2(d) 8.1(d) 6H 3H 2H 2H 2H 3'',5''-H 4''-OCH_3 4'-CH_2-CH_2- 4'Ø-CH_2 6.8(d) 3.9(s) 1.1 to 2.0(m) 2.3 to 2.9(t) 2H 3H 4H 2H 4'-CH_3- 1.0(unresolved triplet) 3H
	R_1 = n-$CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ R_2 = n-CH_3	FIG. 18.
II 2		2.6-CH_3 3,5-H 2',6'-H 3',5'-H 2.2(s) 7.4(s) 7.5(d) 7.0 (d) 6H 2H 2H 2H 4'4'',-CH_2-CH_2-(CH_3) 4'-Ø-CH_2 2'',6''-H 3'',5''-H 1.1 to 1.8(m) 2.6(t) 7.9(d) 6.7(d) 8H 2H 2H 2H 4''-OCH_2 4',4''-OCH_3 3.9(t) 1.0(m) 2H 6H
	R_1 = n-$CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ R_2 = n-$CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	

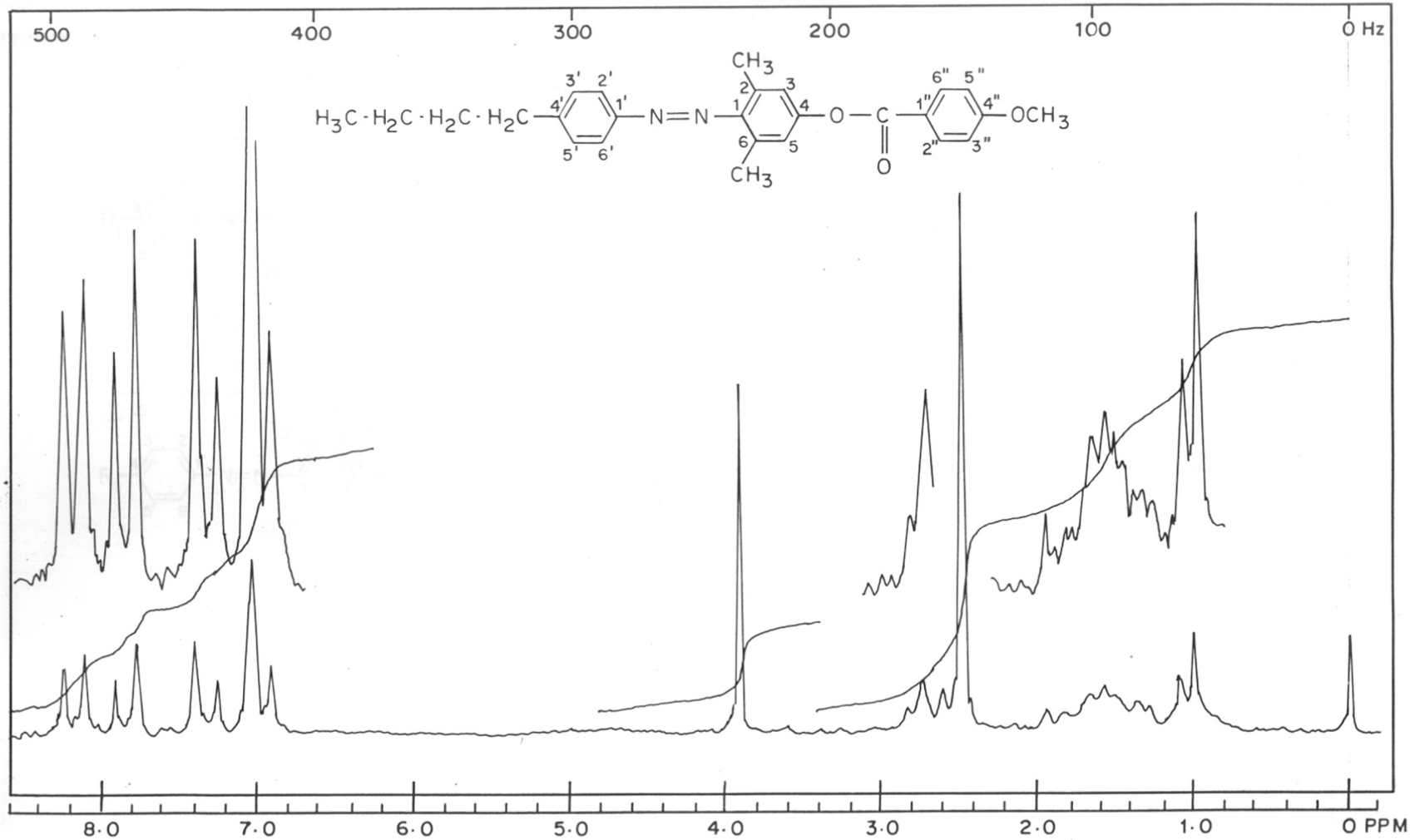


FIG. 18. PMR SPECTRUM OF 2,6-DIMETHYL 4'-n BUTYL-4-(p-METHOXY BENZOYLOXY)-AZOBENZENE

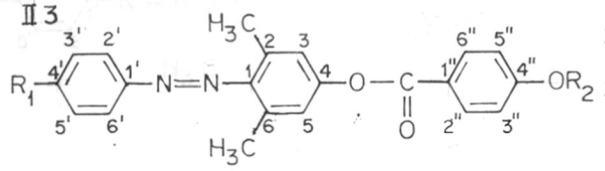
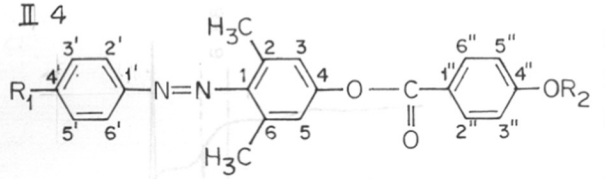
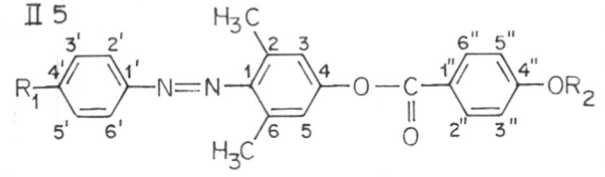
Compound No.	Structure	δ-Chemical shifts with respect to internal standard TMS					
II 3		2,6,CH_3	3,5, H	2',6'H	4'CH_3	2",6"H	4" O-CH_3
		2-4(s)	7(s)	7.3(d)	2.46(s)	8.2(d)	3.9(s)
		6H	2H	2H	3H	2H	3H
		3",5"H					
	$R_1 = CH_3$	7(d)					
	$R_2 = CH_3$	2H					
II 4		2,6,CH_3	3,5,H	2',6'H	3',5'H	4'CH_3	3",5"H
		2.4(s)	6.8(s)	7.7(d)	7.2(d)	2.4(s)	6.7(d)
		6H	2H	2H	2H	3H	2H
		2",6"H	4"CH_2 - CH_3				
	$R_1 = CH_3$	8(d)	4.0(q)	1.4(t)			
	$R_2 = CH_2 \cdot CH_3$	2H	2H	3H			
II 5		2.6,CH_3	3,5,H	2',6',H	3',5'H	4'CH_3	3",5"H
		2.4(s)	6.8(s)	7.7(d)	6.8(d)	2.37(s)	7.3(d)
		6H	2H	2H	2H	3H	2H
		2",6"H	4" CH_2-CH_2-CH_2-CH_3				
	$R_1 = CH_3$	8(d)	4.3(t)	2.0 to 1.1 (m)	1(t)		
	$R_2 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2H	2H	4H	3H		

FIG. 19.

FIG. 20.

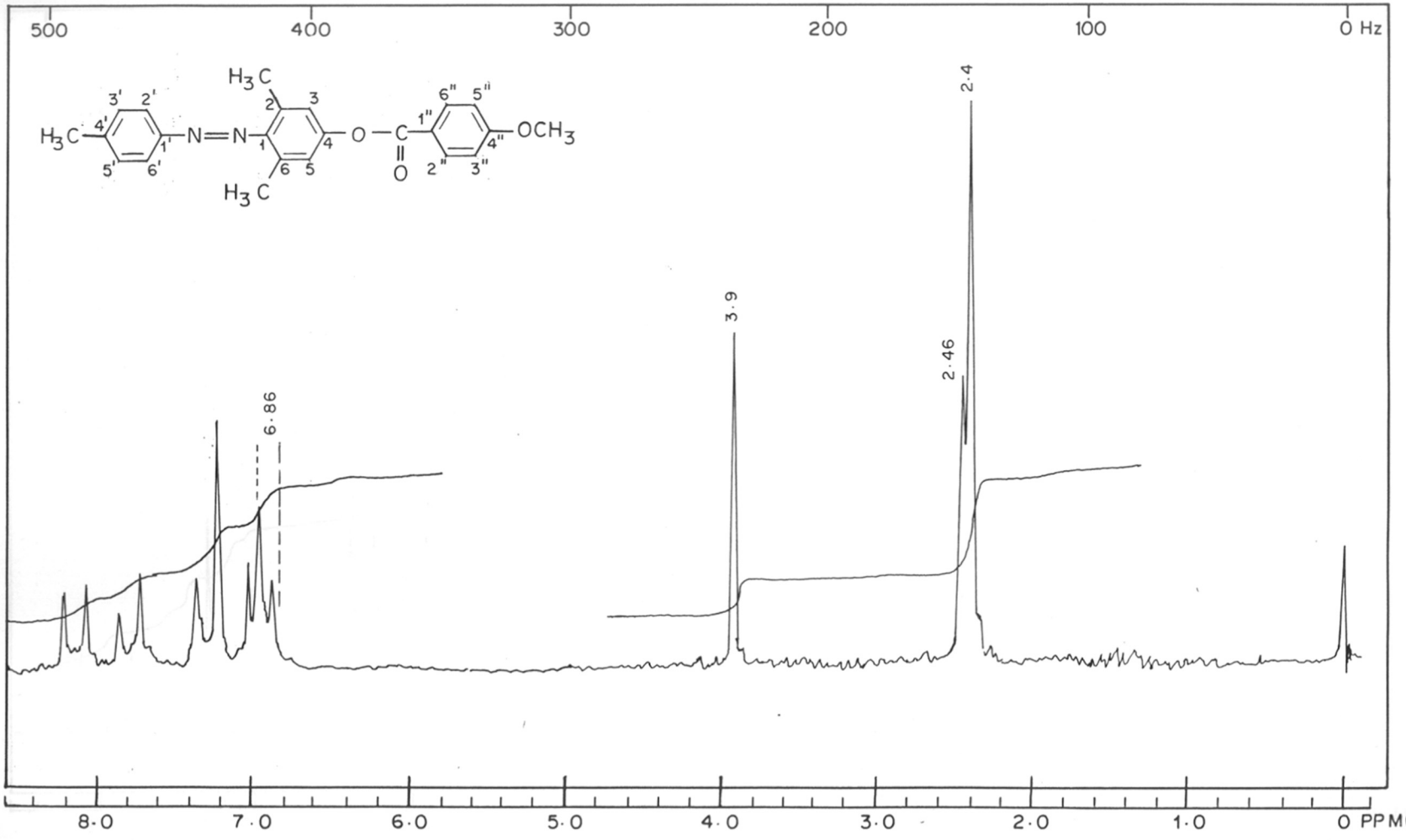


FIG. 19 . PMR SPECTRUM OF 2,4',6-TRIMETHYL-4-(p-METHOXY BENZOYLOXY) AZOBENZENE

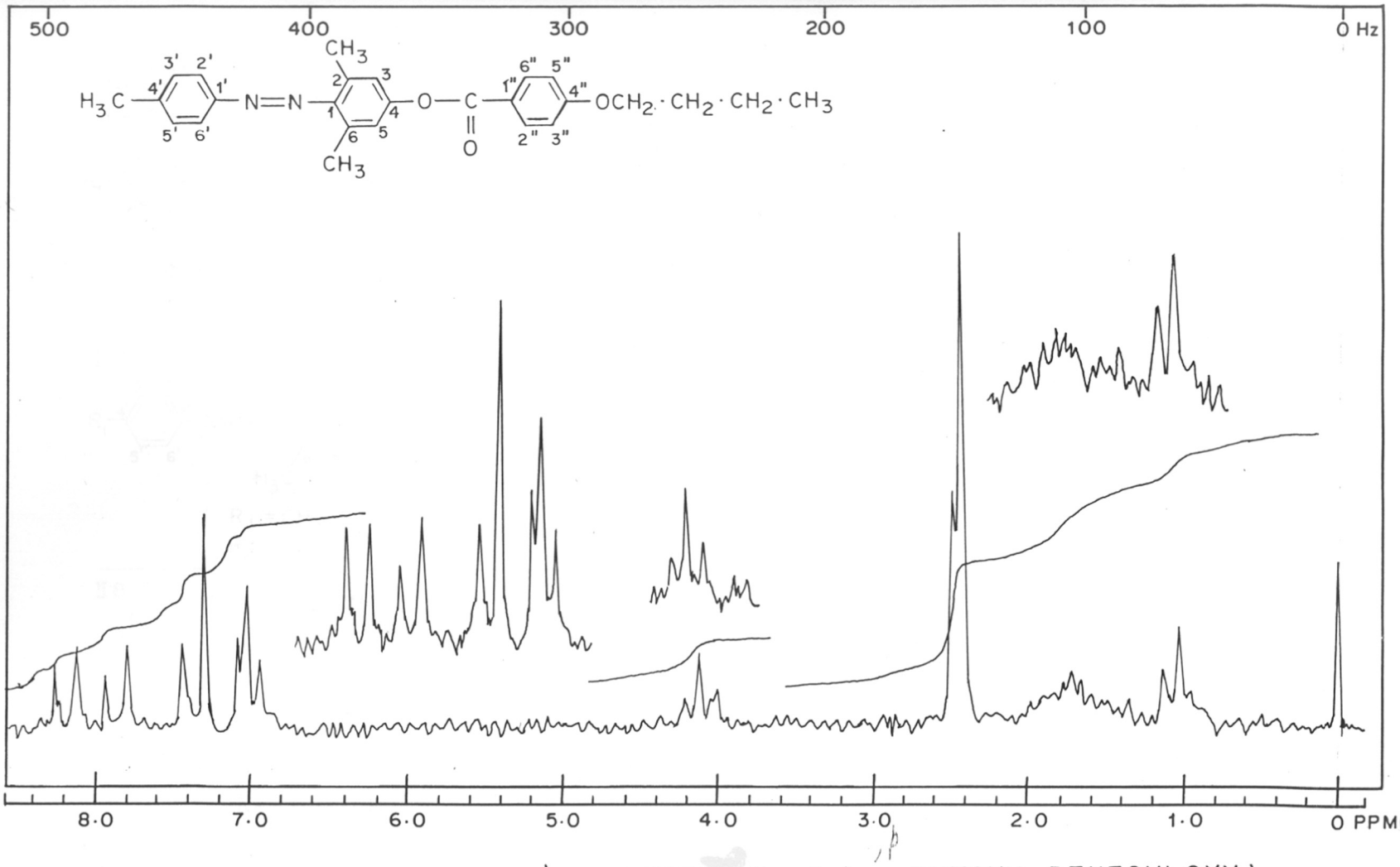
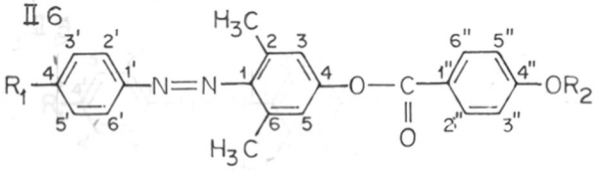
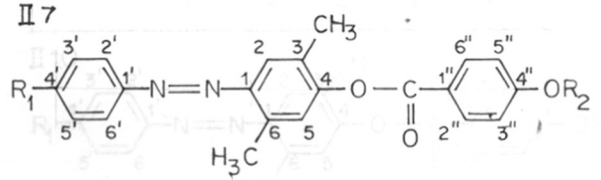
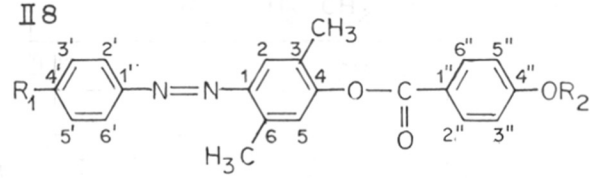


FIG. 20. PMR SPECTRUM OF 2,4',6-TRIMETHYL-4-(p-n-BUTOXY BENZOYLOXY) AZOBENZENE

Compound Number	Structure	δ- Chemical shifts with respect to internal standard TMS
II 6	 $R_1 = CH_3$ $R_2 = n CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2,6,CH_3 2.3(s) 6H; 3,5H 6.7(s) 2H; 2',6'H 7.5(d) 2H; 3',5'H 6.6(d) 2H; 4'CH_3 2.3(s) 3H; 3'',5''H 7.0(d) 2H; 2'',6''H 7.9(d) 2H; 4'' CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 3.9(t) 2H; 1 to 1.9(m) 8H; 0.9(t) 3H
II 7	 $R_1 = CH_3$ $R_2 = CH_3$	2,H 7.8(s) 1H; 3,CH_3 2.2(s) 3H; 5,H 7.1(s) 1H; 6,CH_3 2.7(s) 3H; 2',6'H 7.6(d) 2H; 3',5'H 7.2(d) 2H; 4',CH_3 2.4(s) 3H; 3'',5'',H 6.9(d) 2H; 2'',6''H 8(d) 2H; 4''-CH_3 3.8(s) 3H
II 8	 $R_1 = CH_3$ $R_2 = CH_2 \cdot CH_3$	2,H 7.9(s) 1H; 3,CH_3 2.2(s) 3H; 5,H 7(s) 1H; 6,CH_3 2.7(s) 3H; 2',6'H 7.7(d) 2H; 3',5'H 7.3(d) 2H; 4,CH_3 2.4(s) 3H; 2'',6'' 8.2(d) 2H; 3'',5''H 7(d) 2H (q); 4'', $-CH_2-$ CH_3 4.1(d), 1.46(t) 2H 3H

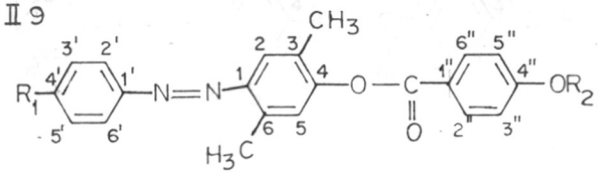
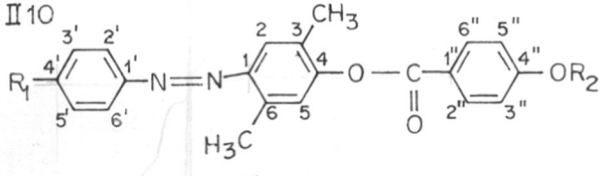
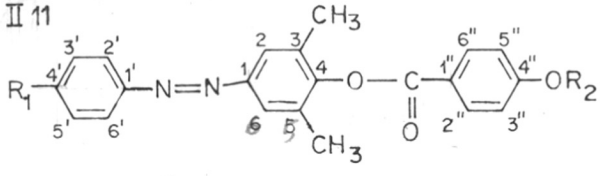
Compound Number	Structure	δ-Chemical shifts with respect to internal standard TMS
II 9	 $R_1 = CH_3$ $R_2 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2.H: 7.7(s) 1H; 3,CH_3: 2.1(s) 3H; 5,H: 7.1(s) 1H; 2',6'H: 7.7(d) 2H; 3',5',H: 7.2(d) 3H; 4',CH_3: 2.3(s) 3H; 3'',5'',H: 6.9(d) 2H; 2'',6'',H: 8(d) 2H; 4'' 0-CH_2-: 4(t) 2H; CH_2 -CH_2: 1.9 to 1.1 (m) 4H; -CH_3: 1(t) 3H
II 10	 $R_1 = CH_3$ $R_2 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2,H: 7.5(s) 1H; 3,CH_3: 2.4(s) 3H; 5,H: 6.8(s) 1H; 6,CH_3: 2.6(s) 3H; 2',6'H: 7.3(d) 2H; 3',5'H: 7(d) 2H; 4',CH_3: 2.3(s) 3H; 3'',5''H: 6.6(d) 2H; 2'',6'',H: 7.8(d) 2H; 4'' -CH_2-: 3.8(t) 2H; CH_2-CH_2-CH_2-CH_2: 1 to 2 (m) 8H; -CH_3: 0.9 3H
II 11	 $R_1 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ $R_2 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2,6,H: 7.6(s) 2H; 3,5-CH_3: 2.2(s) 2H; 2',6'-H: 7.8(d) 2H; 3',5'-H: 7.3(d) 2H; 4',4'-CH_2-CH_2-(CH_3): 1.1 to 2.0(m) 8H; 4'4''-CH_3: 1.0(unresolved triplet) 6H; 4'-Ø-CH_2: 2.7(t) 2H; 2'',6''-H: 8.1(d) 2H; 3'',5''-H: 6.9(d) 2H; 4'',Ø-OCH_2: 4.0(t) 2H

FIG. 21.

FIG. 22.

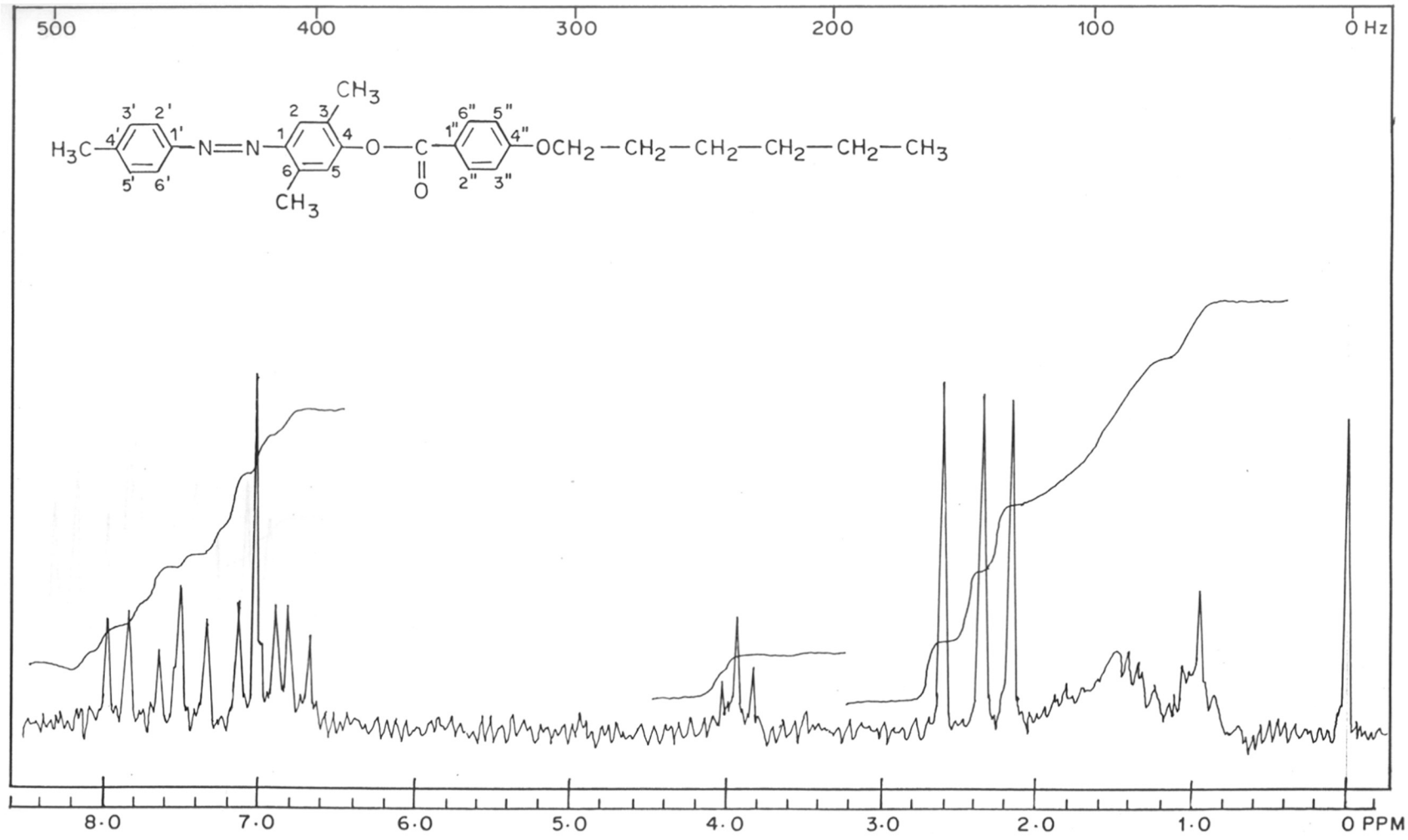


FIG. 21. PMR SPECTRUM OF 3,4',6-TRIMETHYL-4-(p-n-HEXYLOXY BENZOYLOXY) AZOBENZENE

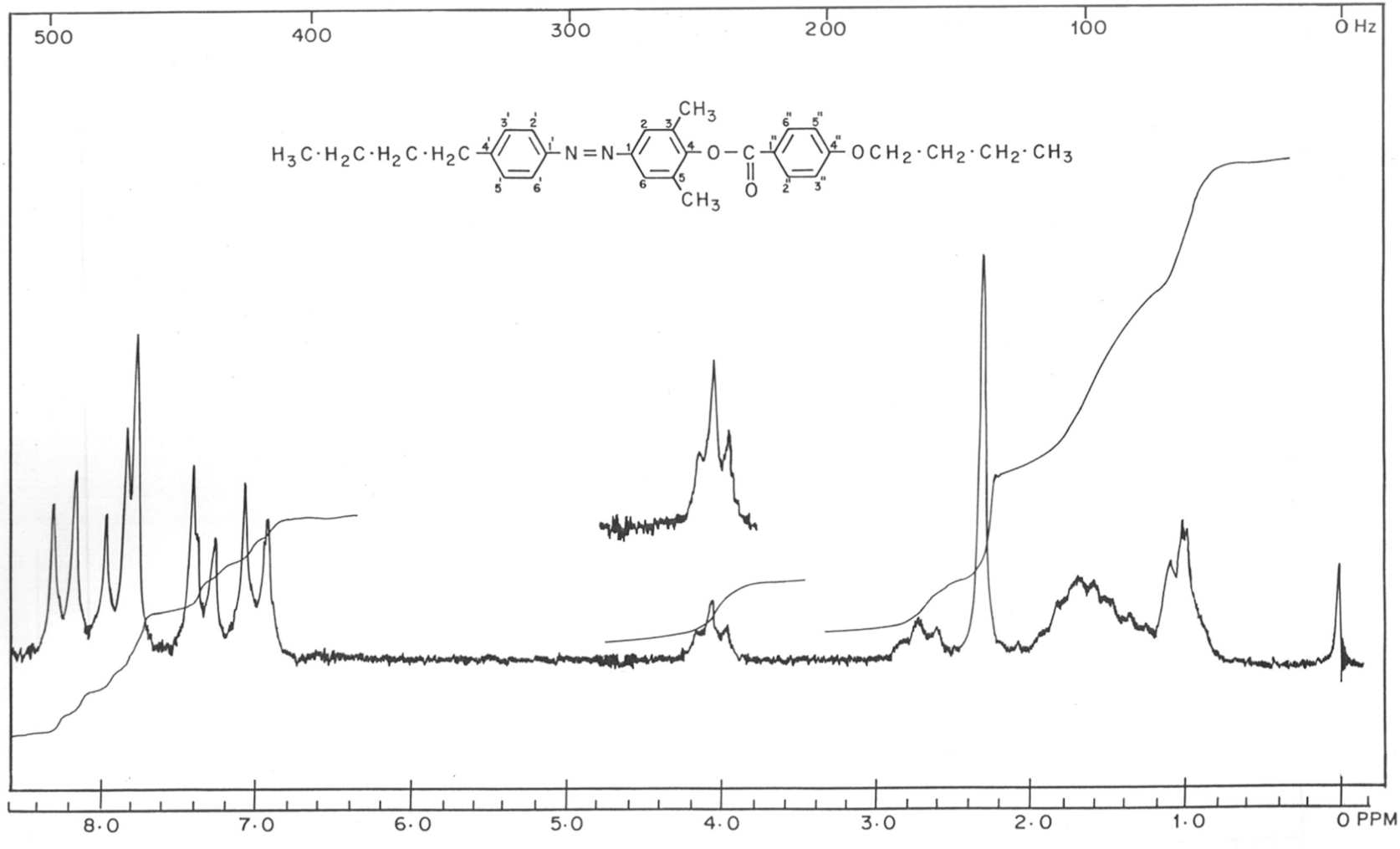


FIG.22: PMR SPECTRUM OF 3,5-DIMETHYL,4'-n-BUTYL-4-(p-n-BUTOXY BENZOYLOXY) AZOBENZENE.

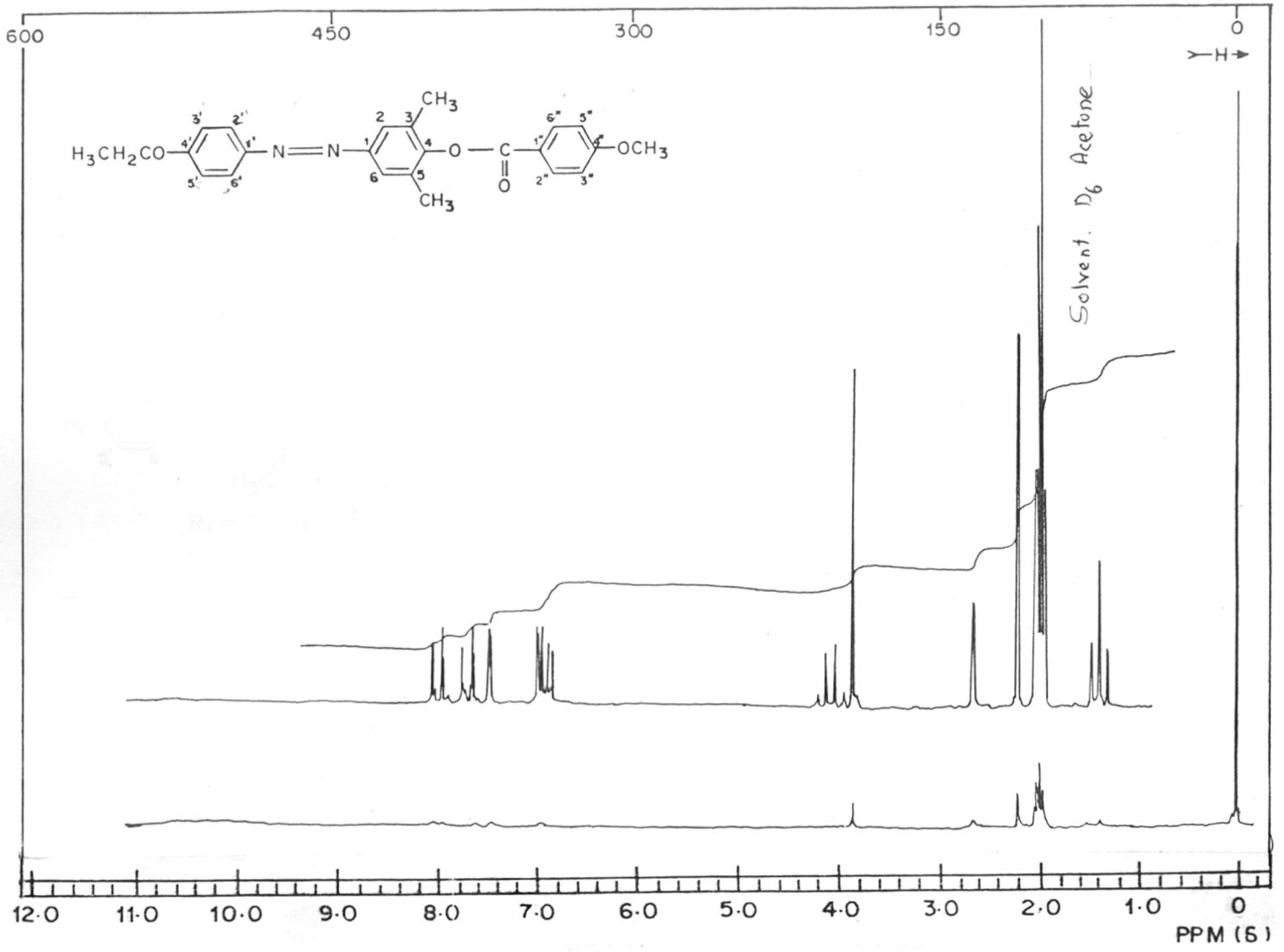


FIG. 23. PMR SPECTRUM OF 3,5-DIMETHYL 4'-ETHOXY-4-(p-METHOXY BENZOYLOXY) AZOBENZENE

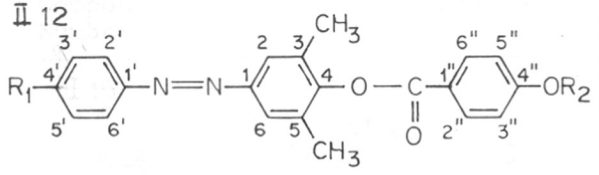
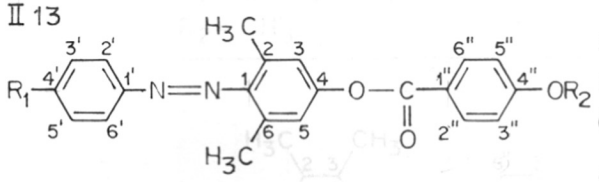
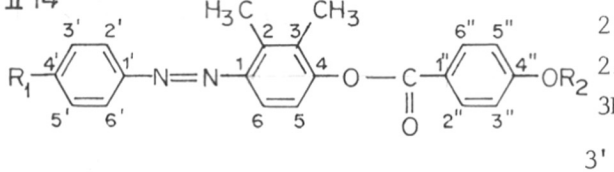
Compound No.	Structure	δ- Chemical shifts with respect to internal standard TMS					
II 12		2,6-H	3,5-CH_3	2',6'-H	3',5'-H	4'-OCH_2	4'-CH_3
		7.6(s)	2.3(s)	7.8(d)	7.1(d)	4.1(q)	1.4(t)
		2H	6H	2H	2H	2H	3H
		2'',6''-H	3'',5''-H	4''-OCH_3			
	$R_1 = O-CH_2 \cdot CH_3$	8.2(d)	7.0(d)	3.9(s)			
	$R_2 = CH_3$	2H	2H	3H			
II 13		2,6-CH_3	3,5-H	2',6'-H	3',5',3'',5''-H	4'-OCH_2	
		2.3(s)	6.7(s)	7.7(d)	7.0(d)	4.0(q)	
		6H	2H	2H	4H	2H	
		4'-CH_3	2'',6''-H	4''-OCH_3			
	$R_1 = O \cdot CH_2 \cdot CH_3$	0.9(s)	7.8(d)	2.7(s)			
	$R_2 = CH_3$	3H	2H	3H			
II 14		2,CH_3	3-CH_3	5-H	6-H	2',6'-H	
		2.7(s)	2.2(s)	7.0(d)	7.6(d)	7.9(d)	
		3H	3H	1H	1H	2H	
		3',5'-H	4'4''-OCH_3	2'',6''-H	3'',5''-H		
	$R_1 = O \cdot CH_3$	7.2(d)	3.9(s)	8.2(d)	7.5 (d)		
	$R_2 = CH_3$	2H	6H	2H	2H		

FIG. 23.

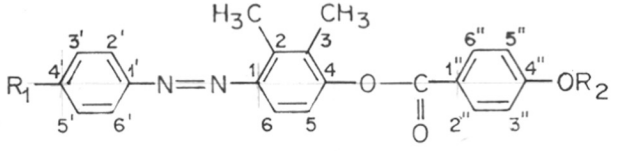
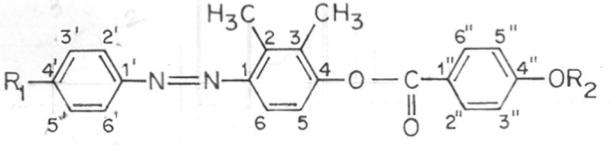
Compound Number	Structure	δ-Chemical shifts with respect to internal standard TMS
II 15	 $R_1 = O \cdot CH_2 \cdot CH_3$ $R_2 = CH_3$	2-CH_3 2.6(s) 3H; 3-CH_3 2.2(s) 3H; 5-H 6.9(d) 1H; 6-H 7.4(d) 1H; 2',6'-H 7.7(d) 2H; 3'5',3''',5''-H 6.8(d) 4H; 4'-OCH_2 4.0(q) 2H; 4'-CH_3 1.4(t) 3H; 2'',6''-H 8.0(d) 2H; 4''-OCH_3 3.8(s) 3H
II 16	 $R_1 = CH_3$ $R_2 = n CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2,CH_3 2.6(s) 3H; 3,CH_3 2.2(s) 3H; 6,H 7.5(d) 1H; 5,-H 7.0(d) 1H; 4'-CH_3 2.4(s) 3H; 2',6'-H 7.7(dd) 2H; 3'5'-H 7.2(d) 2H; 2'',6''-H 8.1(dd) 2H; 3'',5''-H 6.9(dd) 2H; 4''-O CH_2 4.0(t) 2H; 4''-$(CH_2)_4$- 1.1 to 2 (m, 8H; 4''-CH_3 0.95(t) 3H

FIG. 24.

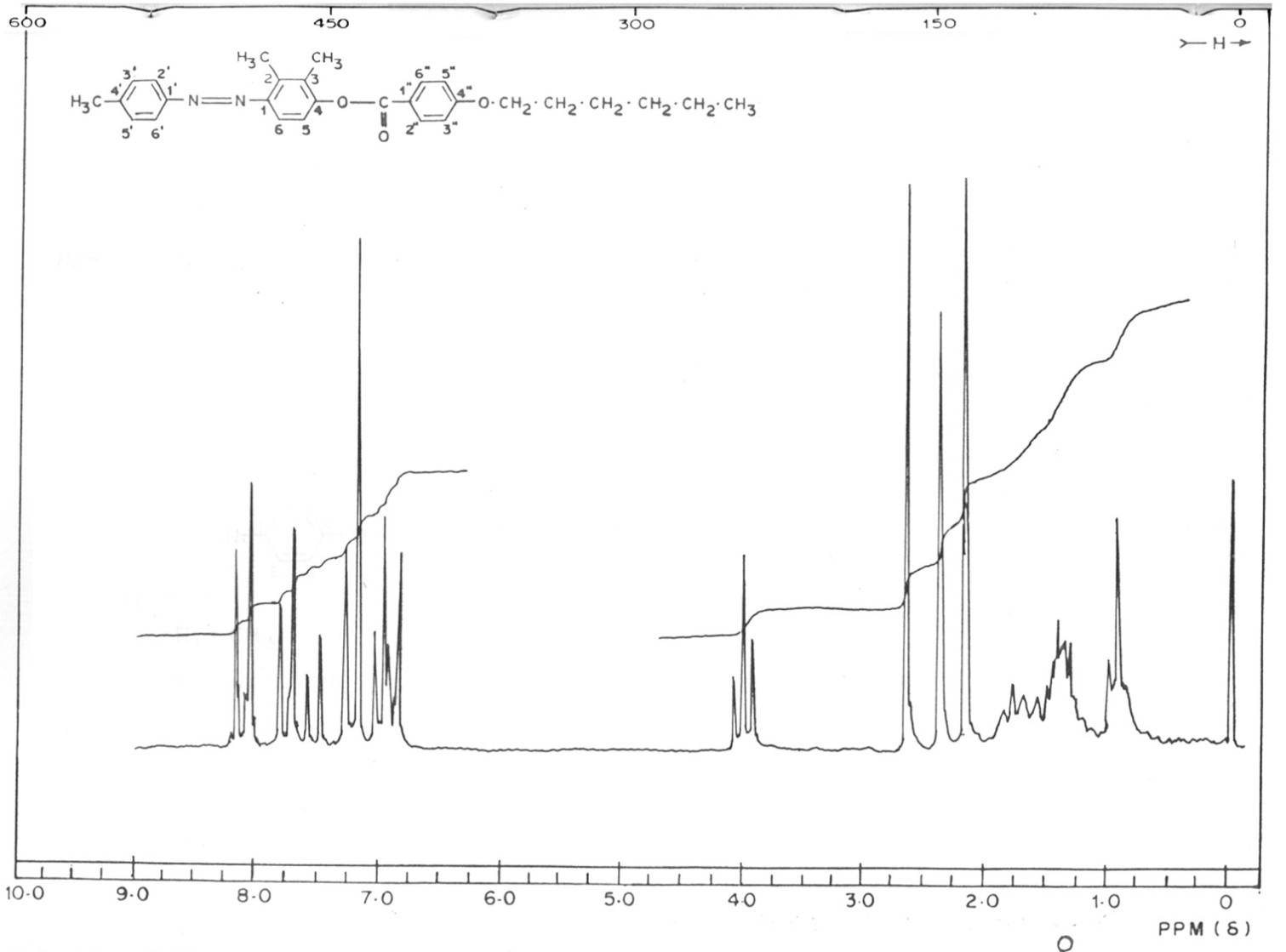
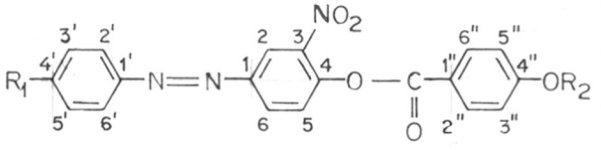
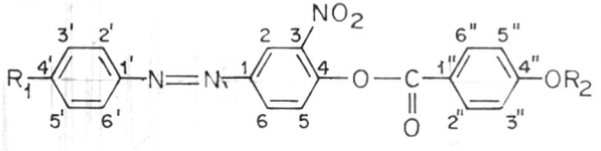


FIG. 24. PMR SPECTRUM OF 2,3,4'-TRIMETHYL-4-(p-n-HEXYLOXY BENZYLOXY) AZOBENZENE

Compound Number	Structure	δ - Chemical shifts with respect to internal standard TMS					
II 17		2.6-H	5,-H	2',6'-H	3',5' H	4'-CH_3	
		7.7(d)	7.5(dd)	7.6 (dd)	7.2(dd)	2.4(s)	
		2H	1H	2H	2H	3H	
		2'',6''-H	3'',5'' H	4''-OCH_3			
	$R_1 = CH_3$	8.1(dd)	6.9 (dd)	3.8(s)			
	$R_2 = CH_3$	2H	2H	3H			FIG. 25.
II 18		2,-H	5,-H	6,2',6'-H	3',5'-H	4',CH_3	2'',6''-H
		7.6(s)	7.2(d)	8.0(m)	7.4(d)	2.5(s)	8.5(d)
		1H	1H	3H	2H	3H	2H
		4''-OCH_2	4''-CH_3		3'',5''-H		
	$R_1 = CH_3$	4.0(t)	1.0(t.unresolved)		7.0(d)		
	$R_2 = n CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2H	3H		2H		

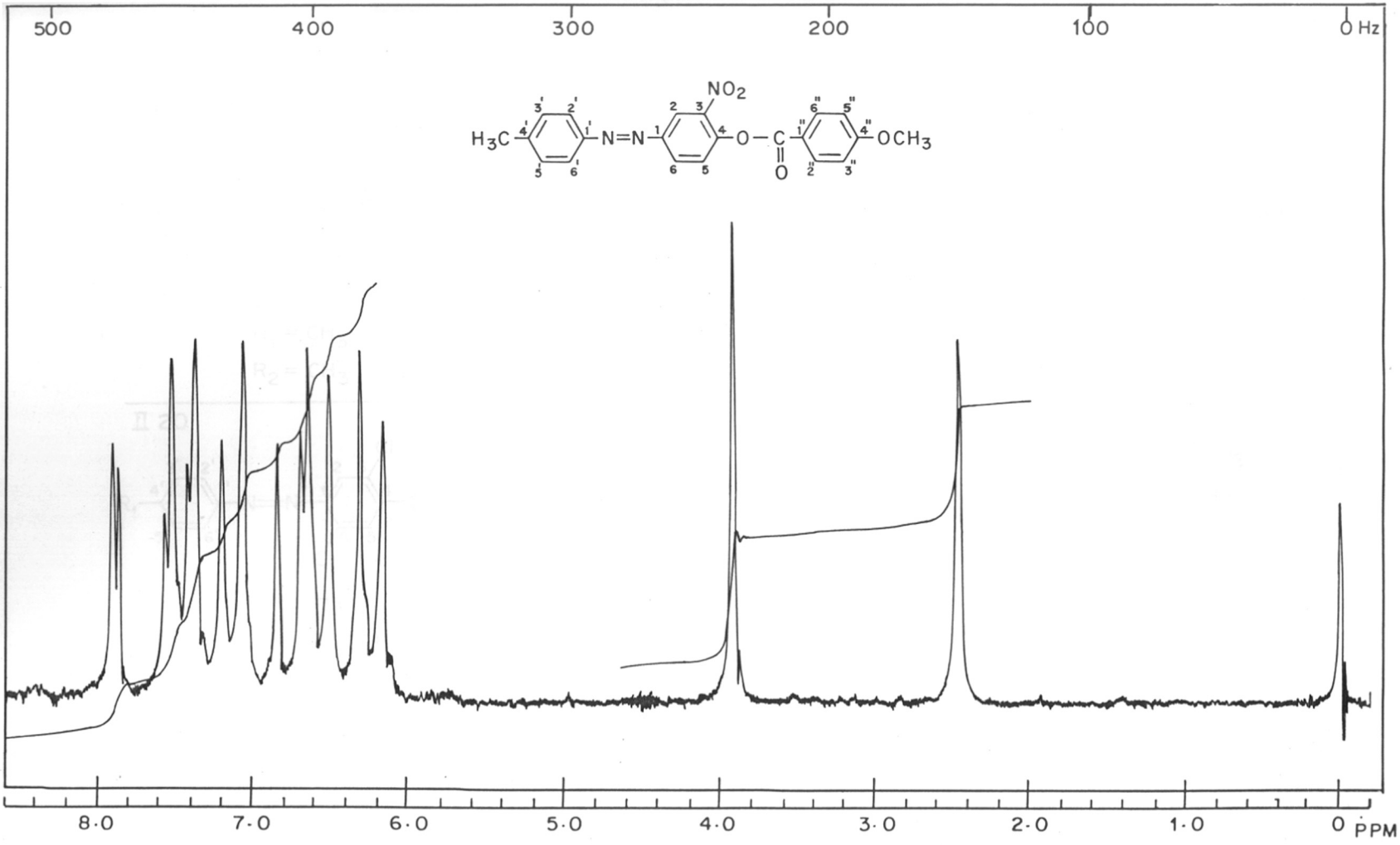
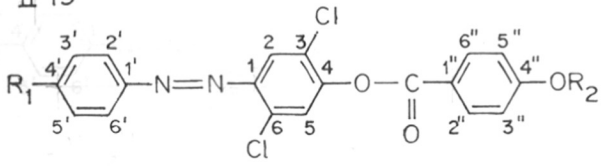
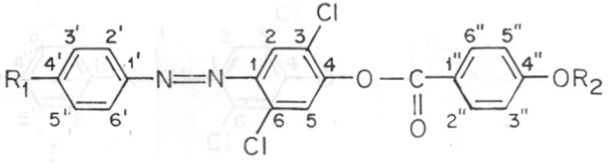


FIG. 25: PMR SPECTRUM OF 3 NITRO, 4'-METHYL-4-(p-METHOXY BENZOYLOXY) AZOBENZENE.

Compound Number	Structure	δ- Chemical shifts with respect to internal standard TMS					
II 19		2,H	5,H	2',6',H	3',5',H	4',CH_3	2'',6'',H
		7.5(s)	6.9(s)	7.5(d)	7(d)	2.6(s)	7.8(d)
		1H	1H	2H	2H	3H	2H
		3'',5'',H	4'',OCH_3				
		6.6(d)	3.76(s)				
		2H	3H				
	$R_1 = CH_3$						
	$R_2 = CH_3$						
II 20		2, H	5,H	2',6'H	3',5',H	4',CH_3	
		7.8(s)	7.5(s)	7.5(d)	7.3(s)	2.5(s)	
		1H	1H	2H	2H	3H	
		2'',6'',H	3'',5'',H	4''-CH_2- CH_3			
		8.1(d)	6.9(d)	4.19(q)	1.46(t)		
		2H	2H	2H	3H		
	$R_1 = CH_3$						
	$R_2 = CH_2 \cdot CH_3$						

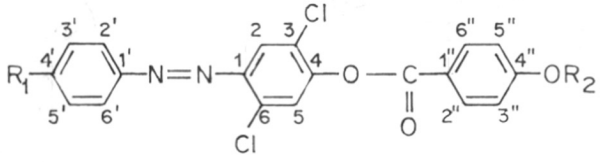
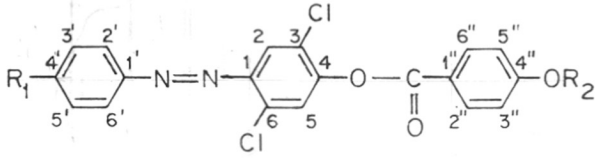
Compound No.	Structure	δ- Chemical shifts with respect to internal standards TMS					
II 21		2,H	5,H	2',6'H	3',5'H	4',CH_3	2'',6'',H
		7.8(s)	7.5(s)	7.8(d)	7.2(d)	2.43(s)	8.1(d)
		1H	1H	2H	2H	3H	2H
		3'',5'',H	4'' $-CH_2-CH_2-CH_2-CH_3$				
	$R_1 = CH_3$	6.8(d)	4(t)	2 to 1.2 (m)		0.93(t)	
	$R_2 = n\,CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2H	2H	4H		3H	
II 22		2,H	5,H	2',6',H	3',5',H	4,CH_3	2'',6'',H
		7.5(s)	7.2(s)	7.6(d)	7(d)	2.36(s)	7.8(d)
		1H	1H	2H	2H	3H	2H
		3'',5'',H	4'' $-CH_2-CH_2$	$-CH_2-CH_2-$	CH_2-CH_3-		
	$R_1 = CH_3$	6.6(d)	3.9(t)	1.9 to 1(m)	0.93(t)		
	$R_2 = n\,CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	2H	2H	8H	3H		

FIG. 26

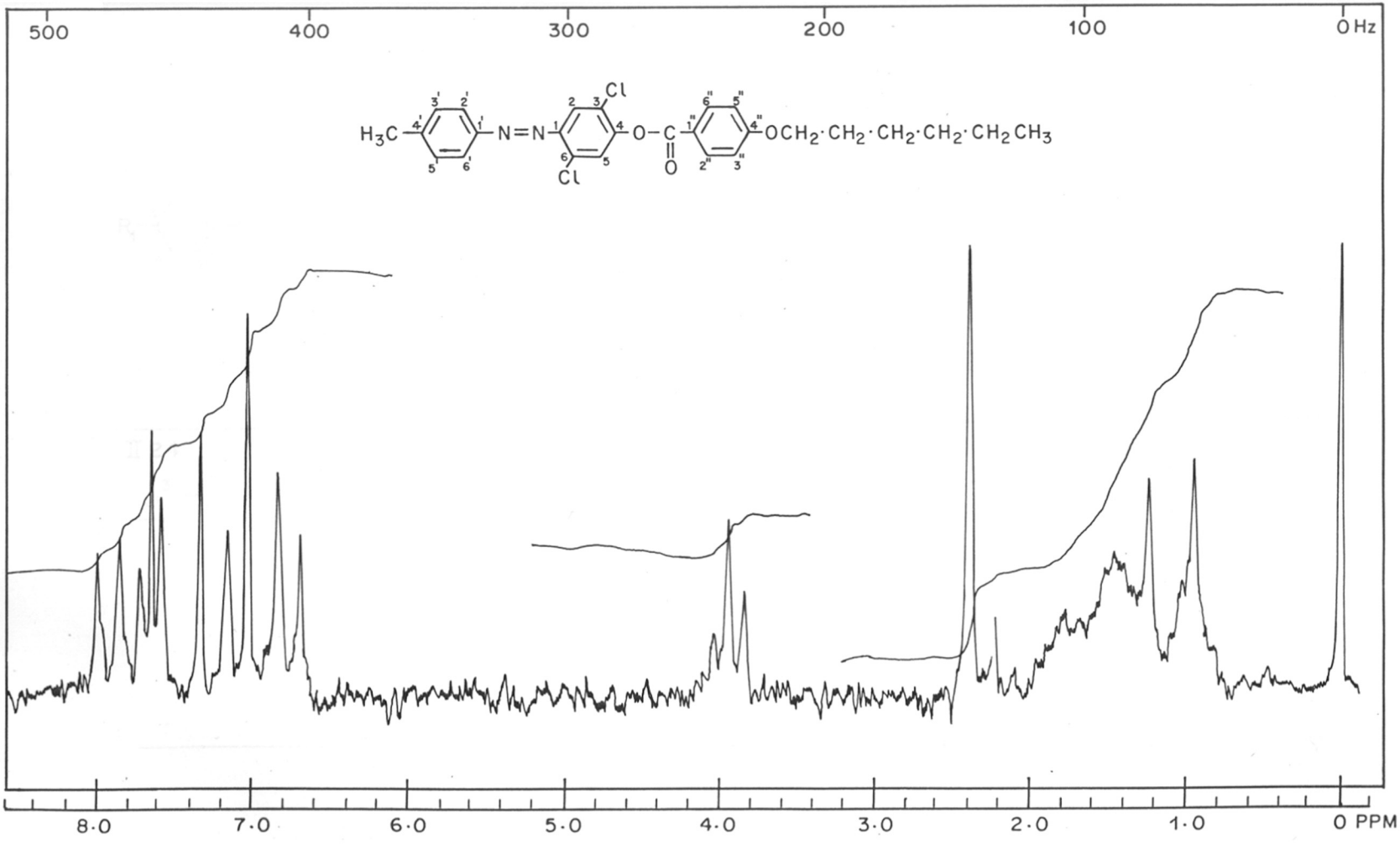
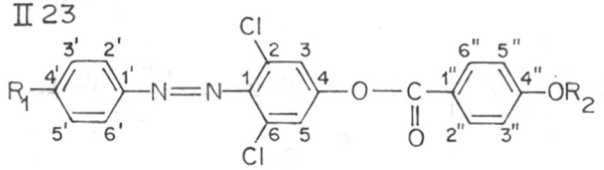
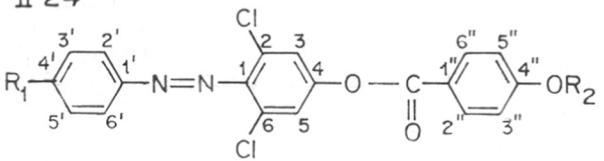


FIG.26: PMR SPECTRUM OF 3,6-DICHLORO,4'-METHYL-4-(p-n HEXYLOXY BENZOYLOXY) AZOBENZENE.

Compound Number	Structure	δ - Chemical shifts with respect to internal standard TMS
II 23		3,5,H: 7.2(s), 2H; 2'6'H: 7.8(d), 2H; 3',5',H: 7.2(d), 2H; 4',CH_3: 2.4(s), 3H; 2'',6''H: 8.2(d), 2H; 3'',5'',H: 6.8(d), 2H; 4'',OCH_3: 3.8(s), 3H
	$R_1 = CH_3$	
	$R_1 = CH_3$	
II 24		3,5,H: 6.8 to 7(s), (2H); 2',6'H: 7.5(d), 2H; 3',5',H: 7(d), 2H; 4',CH_3: 2.3(s), 3H; 2'',6'',H: 7.7(d), 2H; 3'',5'',H: 6.5(d), 2H; 4''-CH_2: 3.9(q), 2H; 4''-CH_3: 1.3(t), 3H
	$R_1 = CH_3$	
	$R_2 = CH_2 \cdot CH_3$	

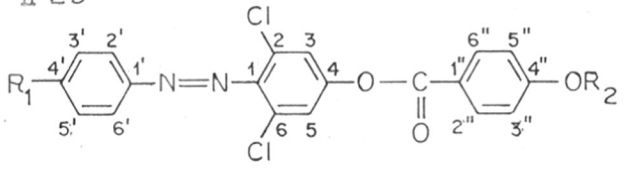
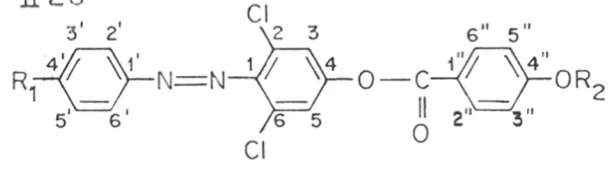
Compound Number	Structure	δ-Chemical shifts with respect to internal standard TMS
II 25	 $R_1 = CH_3$ $R_2 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	3,5,H: 7(s), 2H; 2',6'H: 7(d), 2H; 3',5',H: 7(d), 2H; 4',CH_3: 2.4(s), 3H; 2'',6'',H: 7.3(d), 2H; 3'',5'',H: 6.9(d), 2H; 4''-OCH_2: 4.3(t), 2H; 4'' CH_2-CH_2(-CH_3),4'',CH_3: 1.5 to 2 (m), 4H; 1(t), 3H
II 26	 $R_1 = CH_3$ $R_2 = nCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	3.5,H: 7.1(s), 2H; 2',6',H: 7.5(d), 2H; 3',5',H: 7.1(d), 2H; 4',CH_3: 2.4(s), 3H; 2'',6'',H: 8 (d), 2H; 3'',5'',H: 6.7(d), 2H; 4''-OCH_2: 4(t), 3H; 4'',CH_2-CH_2-CH_2-CH_2: 2.1 to 1.13, 8H; 4''-CH_3: 0.96(t), 3H

FIG. 27.

FIG. 28.

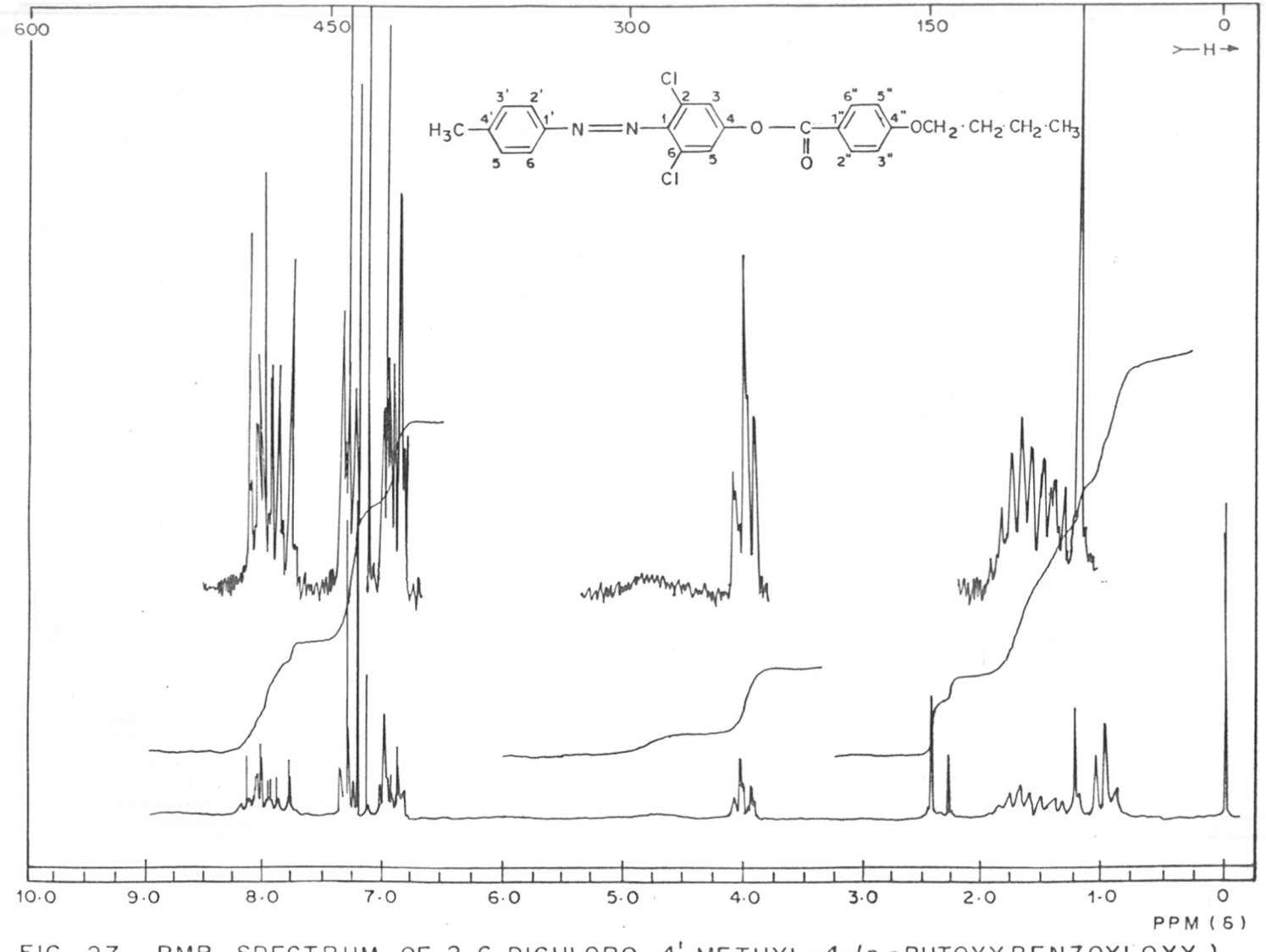


FIG. 27. PMR SPECTRUM OF 2,6 DICHLORO 4'-METHYL-4-(p-n BUTOXY BENZOYLOXY) AZOBENENE

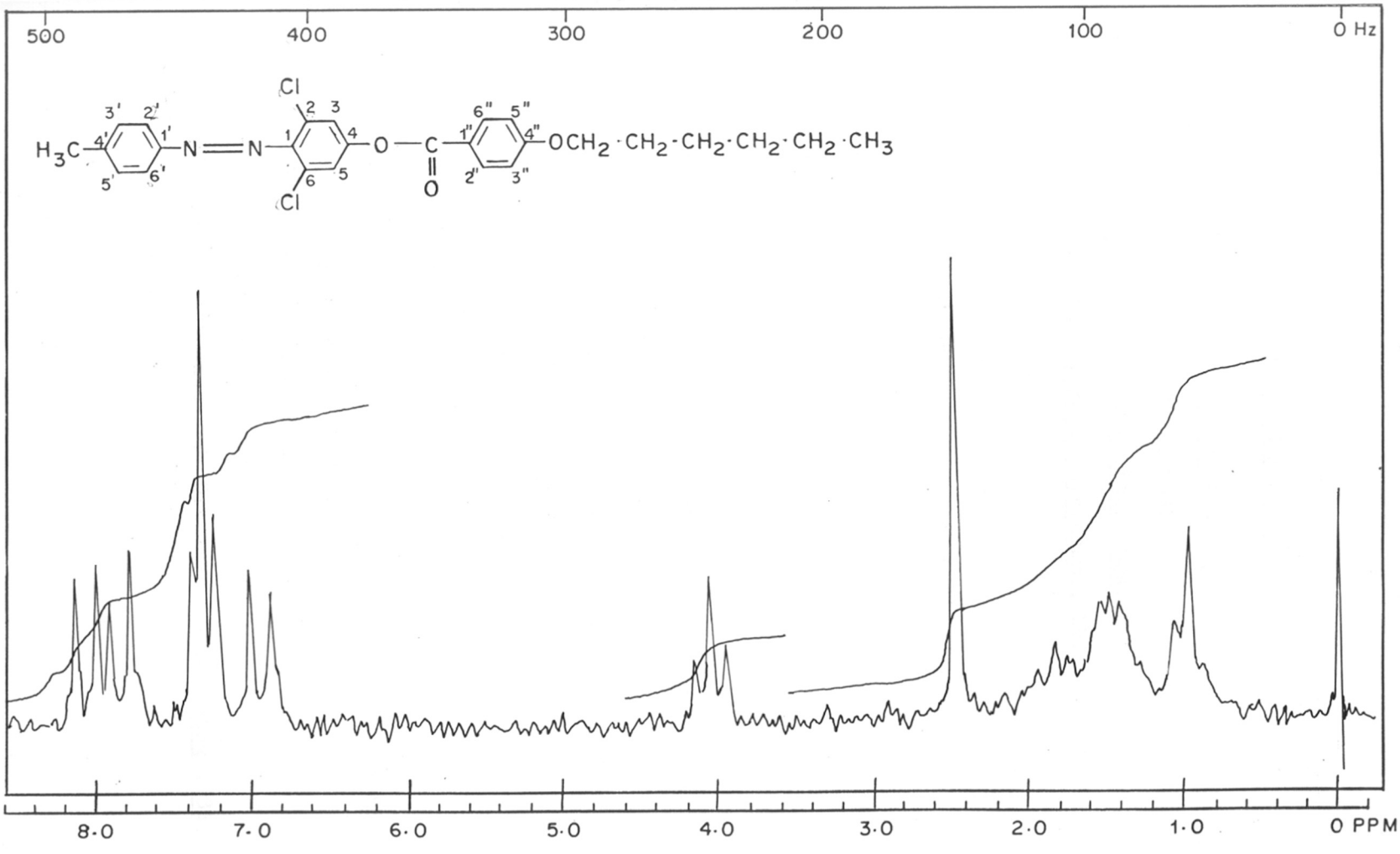


FIG. 28. PMR SPECTRUM OF 2,6-DICHLORO 4'-METHYL 4-(p-n-HEXYLOXY BENZOYLOXY) AZOBENZENE

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CHAPTER II

Study of liquid crystalline compounds as stationary substrates in Gas-Chromatography

S U M M A R Y

Gas Liquid Chromatography (GLC) is the most elegent and useful technique for the separation and analysis of volatile compounds that was, hitherto, regarded as tedious, difficult and even impossible. Complex mixtures of volatile substances with wide range of boiling points (-200° to 400°C) and in very small quantities can be separated by this technique. It is a highly efficient and rapid method and can be used for both qualitative and quantitative analyses.

Importance of liquid substrates

With the introduction of Gas Liquid Chromatography (GLC) as a tool for the separation of fatty acid esters, it has now been used almost in all the branches of chemistry and a number of new stationary phases have been developed for the effective separation of intricate mixture of volatile compounds. The appropriate choice of a stationary phase for the analysis of a required separation is very important. The main factors to be considered are (i) chemical nature of the sample to be analysed and (ii) upper and lower temperature limits at which the column is to be operated.

Liquid Crystals Substrates

Liquid crystals are categorised as "specific stationary phases". The liquid crystalline compounds having nematic mesomorphic state have been found to be effective for the separation of positional isomers as these phases separate the solute molecules according to their shape.

Unlike other conventional stationary phases separation of isomeric compounds depends not only on the boiling points and polarity of components but also on shapes of the solute molecules.

In order to establish a correlation between nematic range and selectivity, stationary phases of laterally mono- and disubstituted liquid crystalline compounds have been synthesised.

It was felt that the introduction of different bulkier groups such as chlorine, methyl, nitro group on the central phenyl ring of the liquid crystalline substrate may be quite interesting to investigate and therefore a new series of liquid crystalline compounds was synthesised. The effect of lateral disubstituion on both the sides of central phenyl ring of the structural unit of liquid crystalline compounds has been studied and their utility as liquid substrates for the separation of various substituted benzene and

naphthalene isomers is tested. Some of the liquid crystalline stationary phases have given promising results and they are presented in this chapter.

Results and behaviour pattern of different solutes on liquid crystalline stationary phases

Previous work on liquid crystalline stationary phases in this laboratory

As pointed out earlier nematogenic compounds have been used in GLC to achieve the separation on the basis of molecular shapes of solutes. Previous attempts to find out the correlation of the nematic transition range and the selectivity of the liquid crystalline stationary phases in GLC have shown that wider the nematic range, higher is the selectivity. To study the relationship between nematic range and selectivity laterally mono- and disubstituted liquid crystalline compounds have been synthesised in our laboratory[1-6]. These compounds, as stationary phases in GLC, have shown very interesting results for the separation of different positional isomers of benzene.

Present Approach

To study the effect of lateral substitution in detail it was felt necessary to systematically synthesise liquid crystalline phases where the central phenyl ring of the molecule is substituted at different positions. The lateral monosubstitution of CH_3 (Electron donating) group earlier reported[3] was also

replaced by $-NO_2$ (Electron withdrawing) group to observe any particular change in nematic range and/or selectivity of the stationary phases.

Simultaneously new series of laterally disubstituted liquid crystalline compounds having substitution at 2,6, 3,5, 3,6-positions of the central phenyl ring have been synthesised and used as stationary phases to study their effects for the separation of various isomeric compounds.

The detection and separation of isomeric alkyl naphthalenes has gained importance due to their toxic properties and relatively higher water solubility. These compounds are harmful even at µg/kg concentration.

The separation of monomethyl naphthalene isomeric mixture was achieved successfully on some of the columns while a few stationary phases were useful for the separation of dimethyl naphthalene (DMN) isomers. Retention behaviour and relative retentions for the disubstituted benzene isomers were also studied on these liquid crystalline stationary phases.

EXPERIMENTAL

New laterally mono- and disubstituted liquid crystalline compounds were synthesised[7] and their behaviour as stationary phases in GLC has been examined. Their structure, transition temperatures and nematic ranges are tabulated in Table No.I

Solid support

Celite (BDH, England 80-120 mesh) was used as a solid support for all the columns. Celite was heated in an oven at 150°C for 5 hrs and cooled in desicator before use.

Impregnation

The requisite quantity of liquid crystalline compound was taken in chloroform and the weighed quantity of solid support was added to the solution. Chloroform was gradually removed on water-bath at 60°C. The coated celite was then dried in an oven at 70° to 80°C for two hrs. The free flowing impregnated material was then packed into the washed and dried aluminium columns. The column parameters are given in Table No.2

Solutes

Commercially available (GC analysed) compounds which are used as the standard samples were of 96-98%

purity. The reported boiling points of these compounds are given in Table No.3.

Apparatus

An AIMIL (India) dual column gas chromatograph having thermal conductivity detector [TCD] was employed. Hydrogen was used as carrier gas.

Column conditioning

It is necessary to stabilize the column before taking actual readings. For this purpose all the columns were conditioned at 10°C below the nematic to isotropic transition temperatures of the phase used in that particular column for 5 hr. Injector block temperature was kept at 150°C for oven temperature upto 100°C and at 200°C for oven temperatures above 150°C. Similarly detector temperature was kept at 150°C for oven temperature upto 100°C and at 240°C for oven temperatures above 100°C. Retention time t_R' was measured from solvent peak maxima to sample peak maxima. The flow rate of carrier gas was measured using a soap film flow meter. Samples were injected with a syringe using the smallest detectable sample volume.

RESULTS AND DISCUSSION

Conventional stationary phases show their selectivity towards solute molecules according to their boiling points and /or polarity. The solute retention mechanism in case of liquid crystalline stationary phases involves in part fitting of the solute molecules in the lattice structure of substrate.

Kelker et al.[8,9] have introduced the use of liquid crystalline phases in GLC. The shape of the solute molecule plays the major role in case of liquid crystalline stationary phases. The linear solute molecules are expected to fit between the molecular layers of a nematic mesophase more readily than the non-linear ones. Thus elongated p-isomer is eluted later than m-isomer irrespective of their boiling points. The selective affinity of the gas chromatographic column towards the separation of two components can be shown by relative retention of one component with respect to other component. When the relative retention (α) value is 1.1, separation of those two components is possible under normal conditions.

Retention behaviour of mono- and dimethyl naphthalenes (DMNS) on liquid crystal columns

Tables 4 and 6 give the account of retention times of mono and dimethyl naphthalene isomers and their relative retention values (α factor) are given in Tables 5 and 7.

Literature survey[10-18] shows that the separation mechanism of mono- and DMN isomers is complex. The elution order may follow either boiling point pattern or length to breadth ratios of the solute molecules. The elution order of DMNs on the basis of breadth to length (b/l, a shape parameter)[16] is as follows:

(1) 1,4 and 1,5-DMN (2) 1,7-; 1,3- and 1,6-DMN (3) 2,6-DMN. Positions of 1,2- and 2,3-DMN have not been predicted in the above pattern as the ortho effect (present in these two isomers) which certainly affects the retention values. Patrykiejew et al.[18] have tried to separate the DMN isomers by using glass capillary column (21 m x 0.3 mm). They have found the elution order for DMNs as follows:

(1) 1,7-DMN (2) 1,3-DMN (3) 1,4-DMN (4) 1,6-DMN (5) 1,5-DMN (6) 2,6-DMN (7) 2,3-DMN (8) 1,2-DMN

The present retention time data (Tables 4 and 6) reveals the fact that the behaviour of all methyl naphthalene isomers is more or less the same on all the liquid crystalline stationary phases studied.

2,6-DMN having b/l ratio 0.57 (lowest among all DMN isomers) has eluted out first whereas 1,2-DMN shows maximum retention times on all columns though its b/l ratio, 0.76 is not the highest among all isomers. In case of monomethyl naphthalene isomers the 2-methyl naphthalene having higher boiling point has been eluted out first while the lower boiling 1-methyl naphthalene is retained for longer time on the column. This elution pattern clearly indicates the predominance of b/l ratio on the separation capacity in case of liquid crystalline stationary phases. The b/l ratios for 1-methyl naphthalene and 2-methyl naphthalene are 0.90 and 0.65 respectively. DMNs have followed more or less the boiling points order for their elution. 2,3- and 1,2-DMNs have been retained for longer time which shows that the ortho effect of the isomer also plays important role in determining the elution order. The main factor determining the retention of isomeric is the symmetry of substitution[18] (the mutual arrangement of methyl groups relative to each other and to the aromatic skeleton) when both methyl groups are located on the same side of the aromatic skeleton as in case of 1,3-dimethyl naphthalene, the presence of methyl groups prevents a solute molecule from penetrating

deeply into the ordered phase of liquid crystal. On the other hand when the methyl groups are located on opposite sides of aromatic skeleton as in case of 1,4-dimethyl naphthalene, both methyl groups are assumed to act as 'hooks' that impede the movement of solute molecules from the stationary phase. Two methyl groups on same side are too large on obstacle for a molecule to overcome, so that only part of aromatic skeleton can penetrate the liquid crystalline phase. The methyl groups separated by aromatic ring (on opposite side) act separately and the interaction between the solute and solvent may force the substance being chromatographed into the stationary phase despite the presence of methyl groups Fig. I If substitution is on both the rings then penetration in liquid crystalline phase becomes difficult and those iosmers are eluted out first (1,7-DMN). This is all hypotehtical explanation for the behaviour of DMNs on liquid crystalline stationary phases.

Effect of the various lateral substituents of the liquid crystalline stationary phases on selectivity and elution sequence of mono-and dimethyl naphthalene isomers

[I] Results obtained on methyl substituted liquid crystalline stationary phases

Disubstitution of methyl groups at A & D positions (Table 5) of central phenyl ring of the substrate molecule proves to be useful for the separation of

1-methyl and 2-methyl naphthalenes. Column Nos.II3, II4 and II13 give separation factor for these two isomers as 1.14 1.14 and 1.12 respectively (Table 5). Column No.II4 gave the separation of following isomeric pairs of DMN (chromatogram No. I)

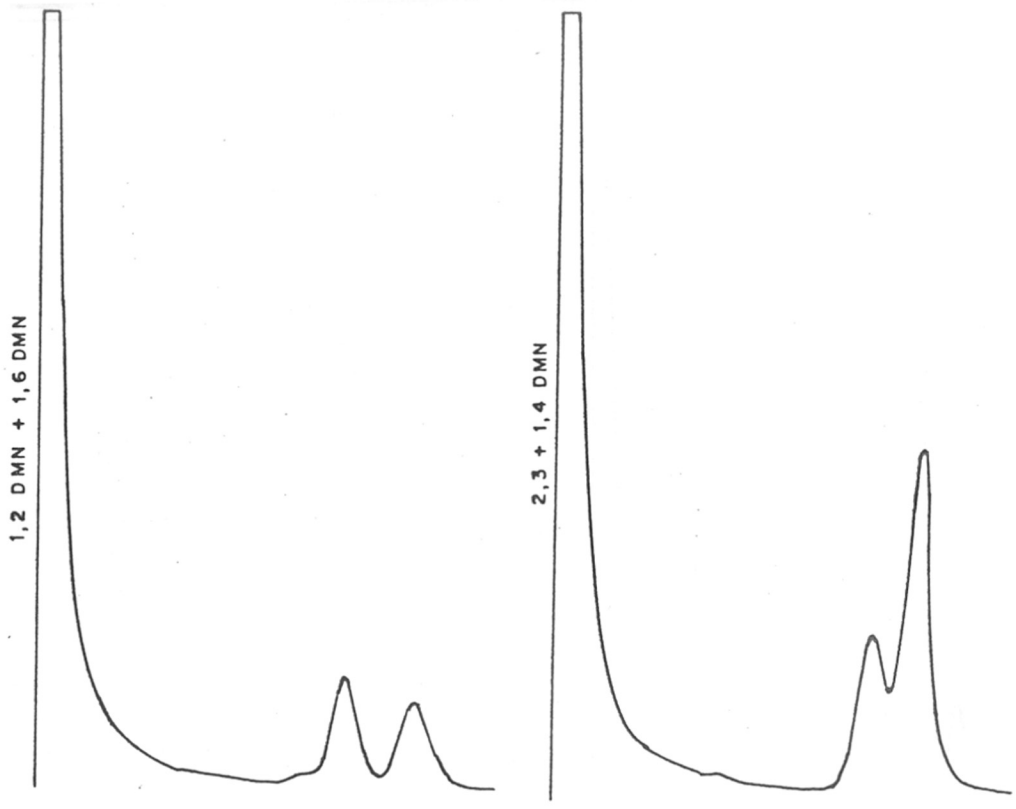
(1) 1,2- and 1,3-DMN (2) 2,3- and 1,3-DMN

(3) 2,3- and 1,6-DMN (4) 2,3-and 1,4-DMN-

(5) 2,3- and 2,6-DMN (6) 1,2- and 1,6-DMN

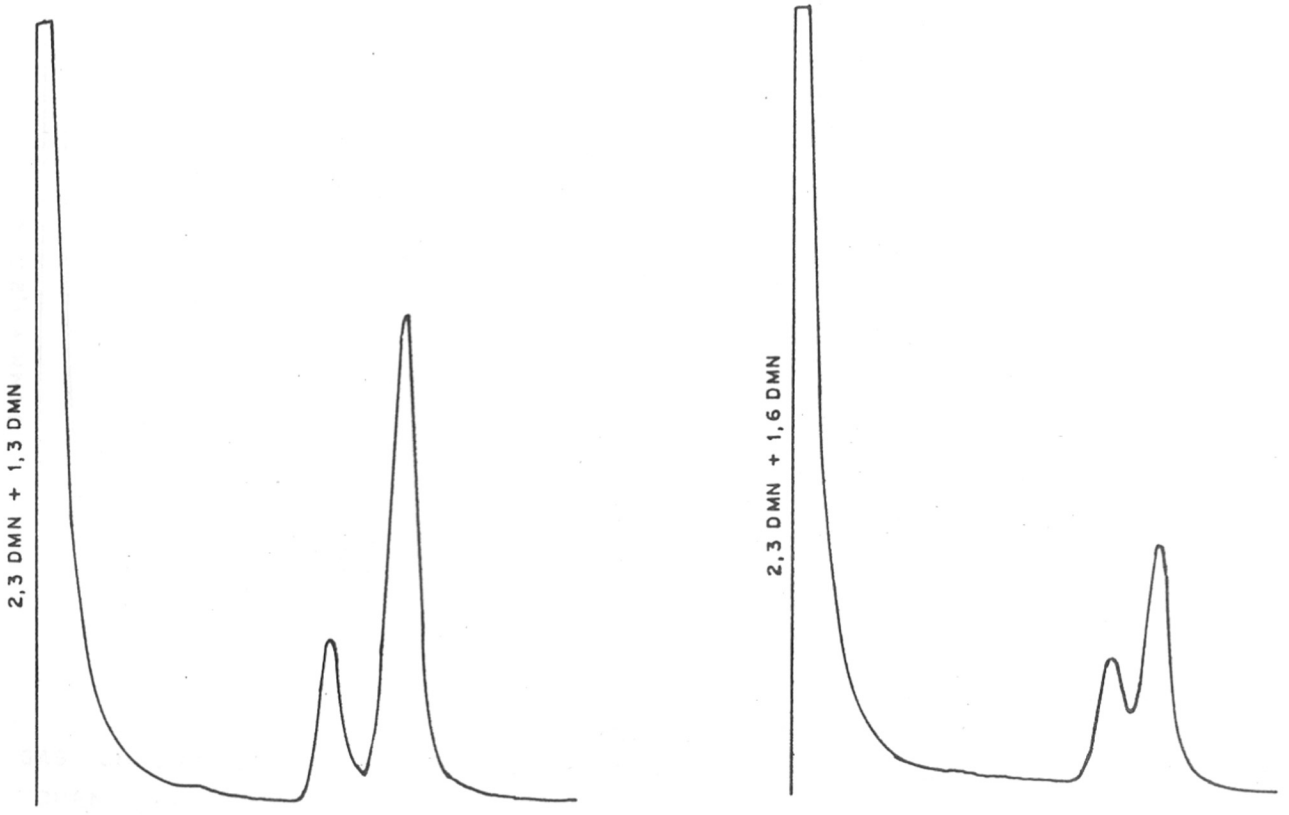
(7) 1,2- and 1,4-DMN.

When the two methyl groups are at the B & C positions (Table 5) Column No.II12 shows less selectivity towards all solutes from this category. In the case of methyl substitution at the A & D positions it can be seen that they are adjacent to (-N=N-) moiety which due to the presence of a double bond may help to retain the planarity of substrate molecule intact whereas for the (0-C-) group adjacent to B & C positions in which the single bond is involved probably the free rotation of the single bond causes the interaction of two bulky methyl groups. The separation mechanism in case of liquid crystalline stationary phases depends on the interaction of solute and solvent molecules according to shape parameter. Thus it is quite likely that lateral substitution at different positions causing



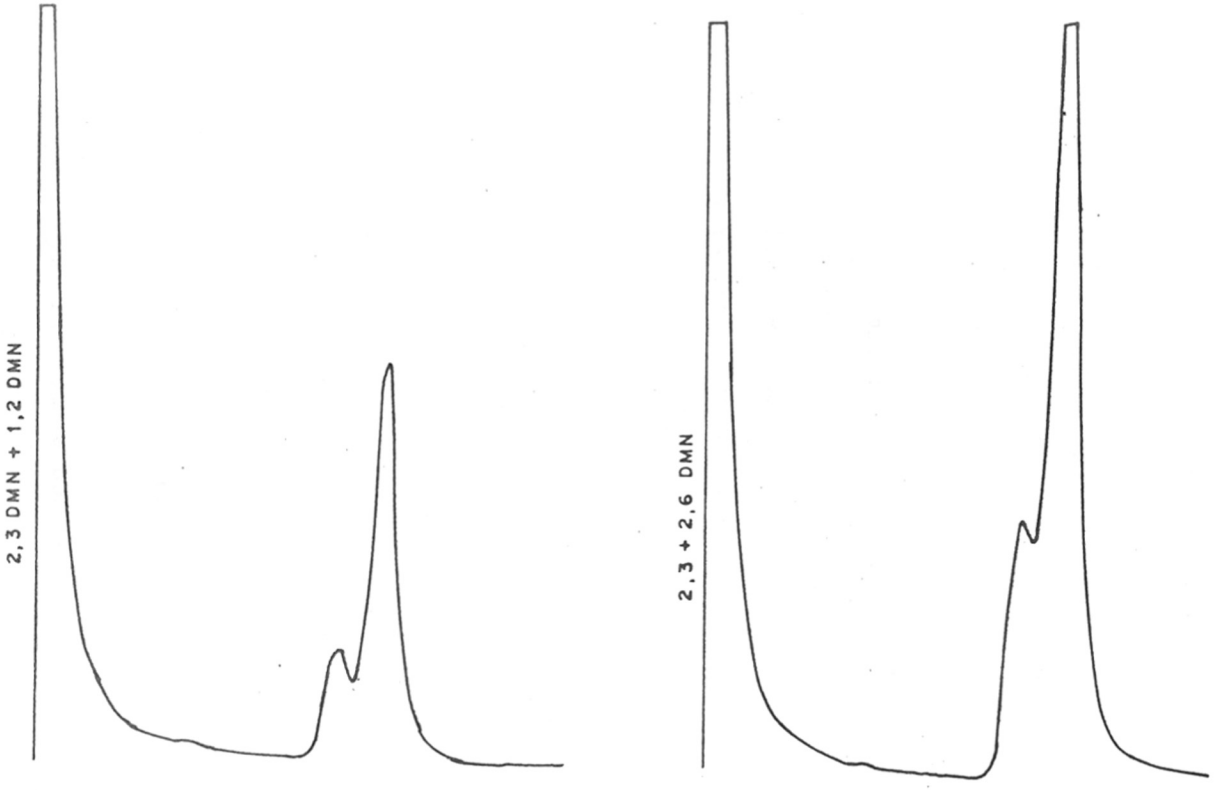
CHROMATOGRAM NO. 1.

GAS CHROMATOGRAM OF ISOMERIC PAIRS OF DMN ON COLUMN NO. II 4. (OVEN TEMP., 162°C, INJECTION TEMP. 150°C, DETECTOR TEMP., 240°C, DETECTOR TYPE, FID) CHROMATOGRAM RECORDED ON HEWLETT PACKAD, 5730.



CHROMATOGRAM NO. 1.

GAS CHROMATOGRAM OF ISOMERIC PAIRS OF DMN ON COLUMN NO. II 4 (OVEN TEMP., 162°C, INJECTION TEMP., 150°C, DETECTOR TEMP., 240°C AND DETECTOR TYPE FID)
CHROMATOGRAM RECORDED ON HEWLETT PACKARD-5730



CHROMATOGRAM NO. 1.

GAS CHROMATOGRAM OF ISOMERIC PAIRS OF DMN ON COLUMN NO. II 4. (OVEN TEMP., 162°C, INJECTION TEMP., 150°C, DETECTOR TEMP., 240°C DETECTOR TYPE, FID). CHROMATOGRAM RECORDED ON HEWLETT PACKARD - 5730

change in linearity or mainly planarity of the substrate molecule must be influencing the elution sequence of isomeric solutes. Column No.X_1 (one of the specially prepared high temperature columns) having two methyl substituents at A & B positions (on same side of aromatic skeleton) showed separation factor 1.14 for monomethyl naphthalenes and around 1.1 for DMNs. This is in agreement with the hypothesis which has been discussed earlier. Two methyl groups on same side may be leading to the formation of a gap of appropriate size for the separation of monomethyl naphthalene isomers from each other. Column No.X_2 (prepared for comparison) wherein the monomethyl substitution was at position A does not show any selectivity towards monomethyl naphthalene isomers but some of the pairs of DMNS can be separated.

The comparison of the results on column No.II15 and X_3, having nearly same nematic range, shows that the increase in terminal alkoxy chain-length has shown incrase in selectivity in case of DMN isomers (Table 5).

The stationary phase in column No.II3 has shown maximum retention times for all solutes (Table 4). Two lateral methyl substituents are at A & D positions of the substrate molecule adjacent to rigid (-N=N-) moiety. The double bond must be helping to retain

the planarity (rigidity) of the total substrate molecule. The two bulky methyl groups occupying more space probably help to form the gap of appropriate size and thus maximum solubility towards these solutes must be the total result.

[II] The effect of NO_2 substitution on selectivity of liquid crystalline phases

A column with the electron withdrawing $-NO_2$ group being substituted on the central phenyl ring of the substrate molecule at 'B' position (Column No.II,17) has shown a wide nematic range and accordingly the separation capability is increased. It shows selectivity towards mono- as well as DMNs.

The separation of following pairs of DMNs is achieved on this column (Chromatogram No.2).

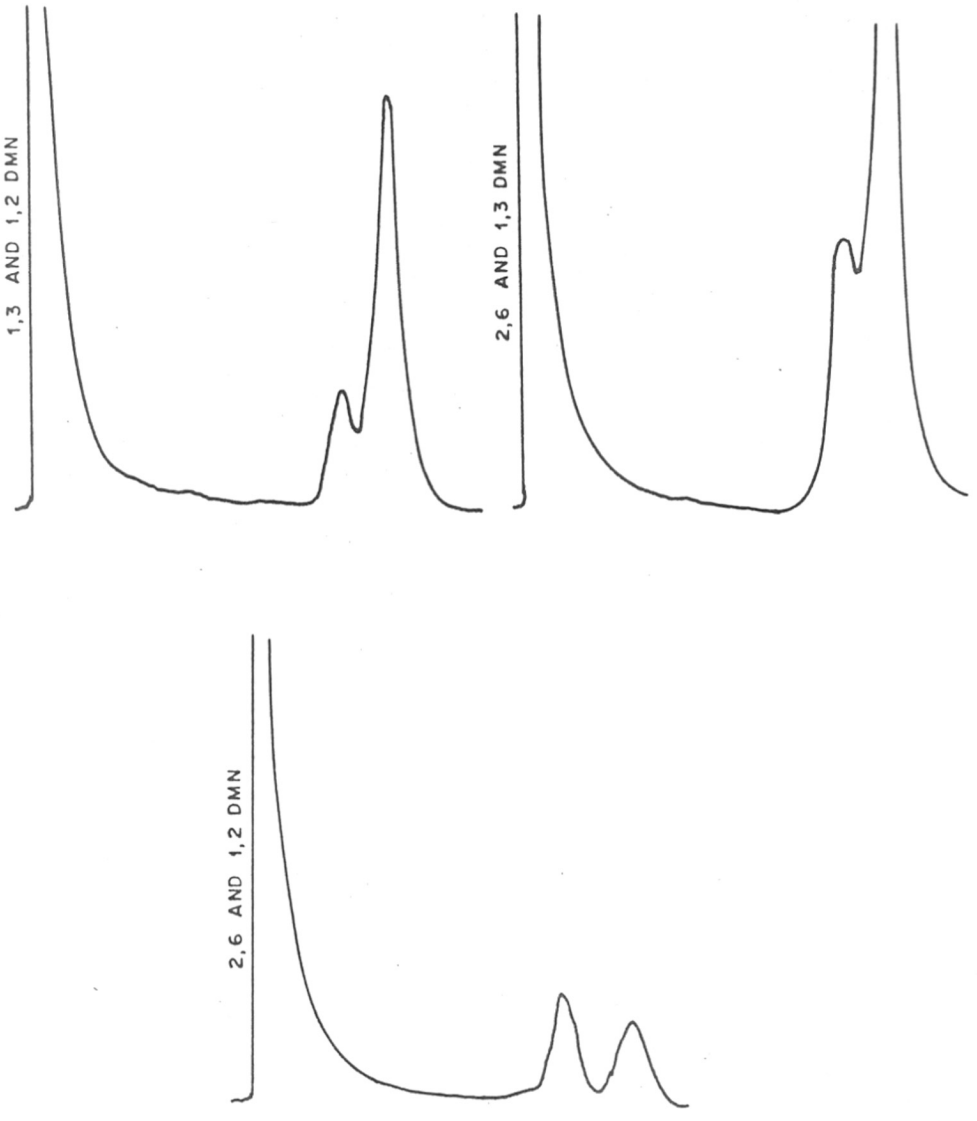
(1) 2,6- and 1,3-DMNs (2) 2,3-and 2,6-DMN

(3) 1,2- and 2,3-DMN (4) 1,2 and 1,3-DMN

(5) 1,2- and 2,6-DMN

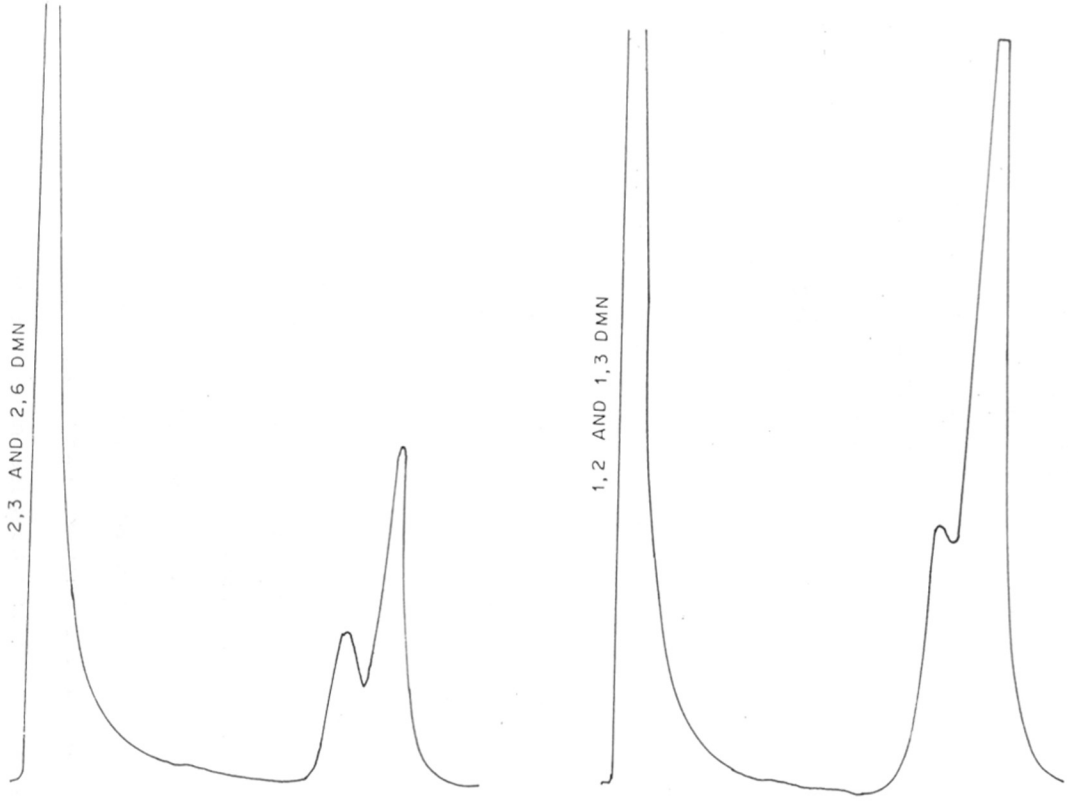
[III] Selectivity of chloro substituted Liquid Crystals

The introduction of mono as well as dichloro lateral substituents in the substrate has increased the separation factor for mono and DMNs equally (observation in contrast to mono- and dimethyl lateral substituents) (Table 7). The dichloro substitution at A and D positions of the central phenyl ring has been effective for baseline



CHROMATOGRAM NO. 2.

GAS CHROMATOGRAM OF ISOMERIC PAIRS OF DMN ON COLUMN NO. II 17. (OVEN TEMP. 170°C, INJECTION TEMP., 150°C, DETECTOR TEMP., 240°C AND DETECTOR TYPE FID)



CHROMATOGRAM NO. 2.

GAS CHROMATOGRAM OF ISOMERIC PAIRS OF DMN ON COLUMN NO. II 17. (OVEN TEMP., 170°C, INJECTION TEMP., 150°C, DETECTOR TEMP., 240°C, AND DETECTOR TYPE, FID).

separation of monomethyl naphthalene isomers (Chromatogram No.3) (Column No.II 23). Separation of following pairs of DMN isomers has been achieved.

(1) 1,3- and 2,6-DMN (2) 2,6-and 1,2-DMN.

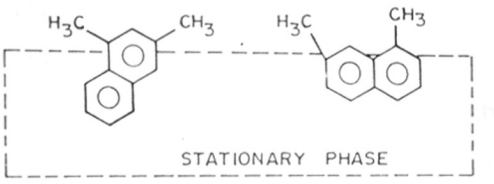
(3) 2,3- and 2,6-DMN (4) 1,4- and 2,6-DMN

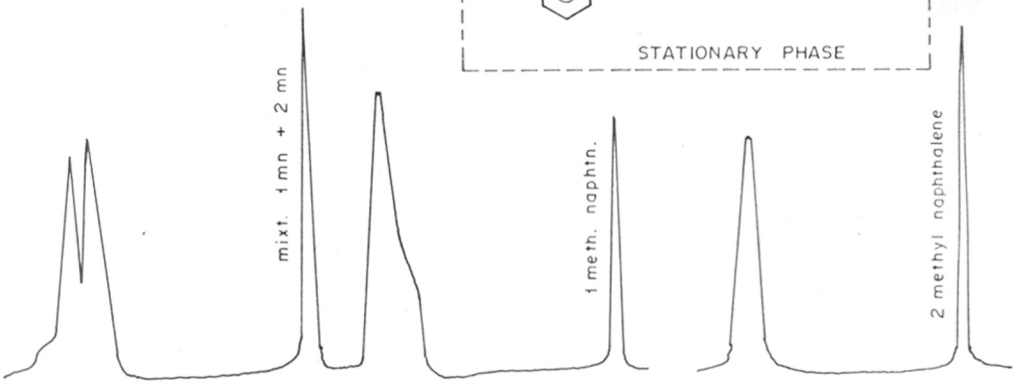
(5) 1,2- and 1,6-DMN.

The solubility of substituted naphthalenes is highest on above said column. As the lateral dichloro substitution is at A and D position and adjacent to (-N=N-) group in the substrate molecule the planarity/ linearity/rigidity may be remaining intact and probably must be causing the highest solubility for these solutes.

The comparison of Column No.II4 having two methyl substituents at A & D positions in the substrate with column No.II23 where two chloro substituents are at A & D positions on central phenyl ring of the substrate molecule (the remaining structure is exactly same) shows that dichloro substitution has been advantageous over methyl substitution when separation factors for all isomeric pairs of mono- and DMN are considered (Tables 5,7). This may be explained on the basis of difference in space occupation by methyl and chloro groups. Methyl group occupies more space because of inclusion of three single bonds although its weight is much more less than heavier-chloro atom. The inter-molecular gap in between methyl substituted substrate

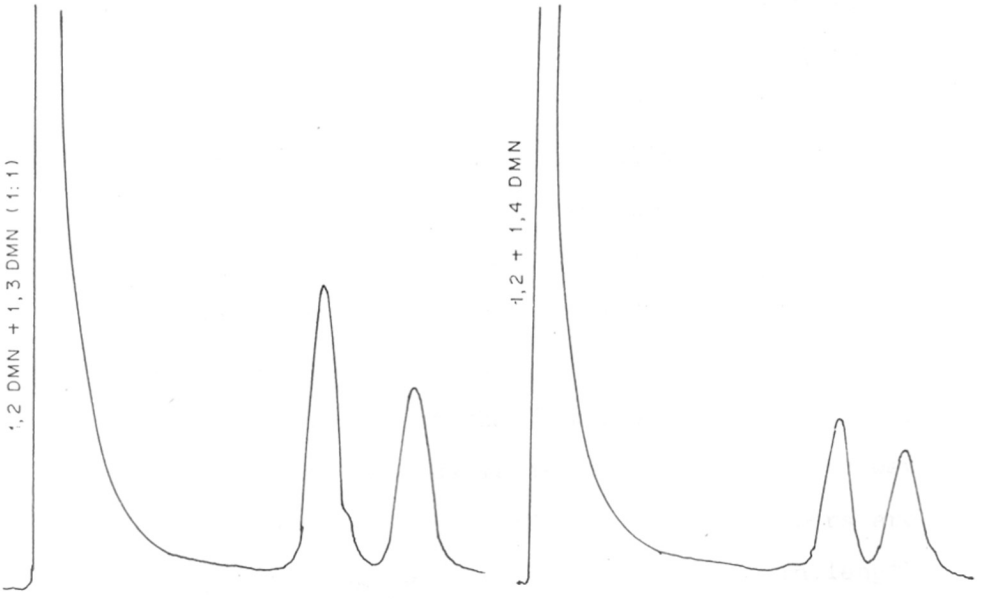
FIG. I





CHROMATOGRAM NO. 3

GAS CHROMATOGRAM OF MIXTURE OF MONOMETHYL NAPHTHALENE ISOMERS ON COLUMN NO. II 23 (OVEN TEMP. 170 °C, INJECTION TEMP. 150°C; DETECTOR TEMP., 240°C AND DETECTOR TYPE, FID)



CHROMATOGRAM NO. 1.

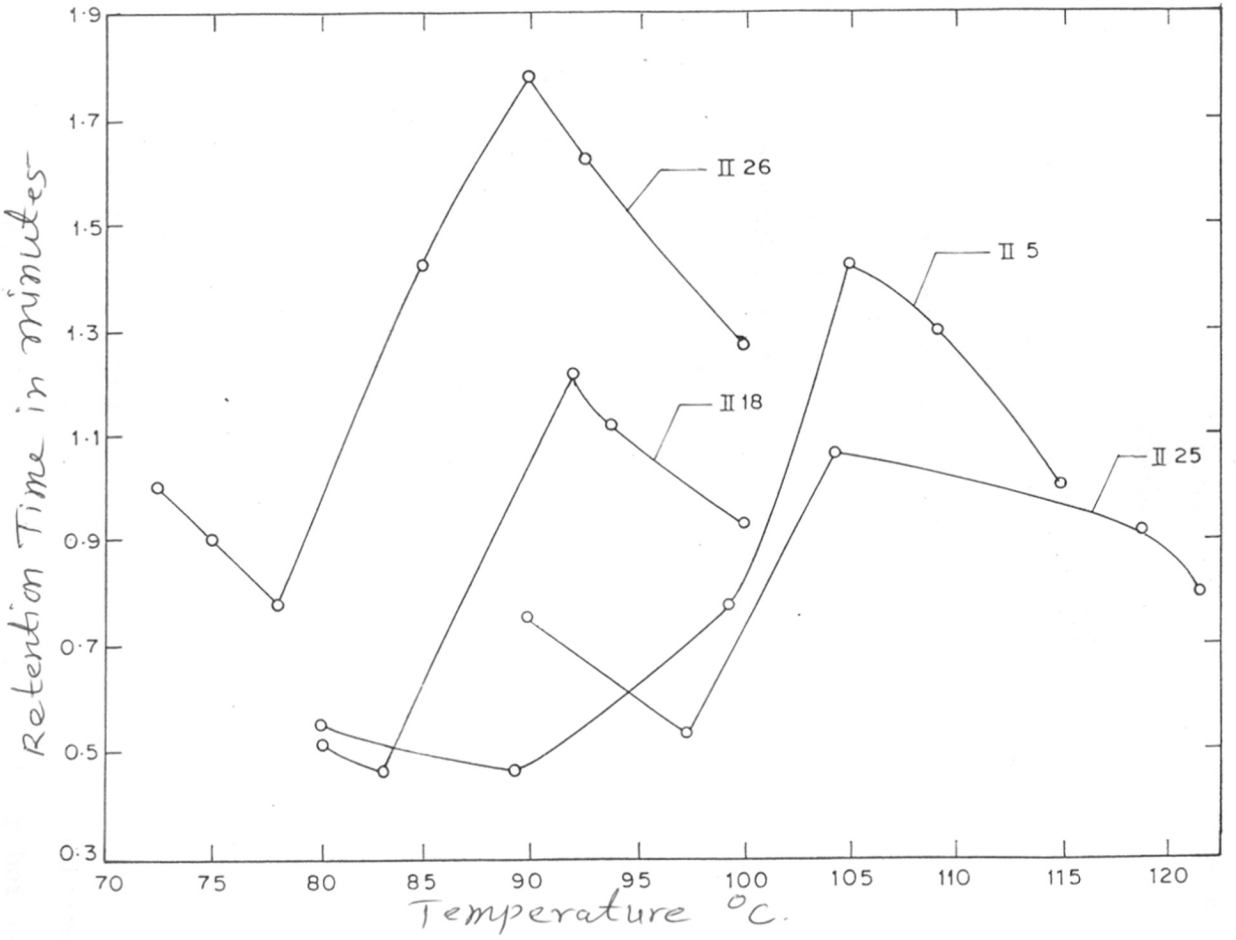
GAS CHROMATOGRAM OF ISOMERIC PAIRS OF DMN ON COLUMN NO. II 4 (OVEN TEMP., 162°C, INJECTION TEMP., 150°C, DETECTOR TEMP., 240°C, AND DETECTOR TYPE, FID) CHROMATOGRAM RECORDED ON HEWLETT PACKARD. 5730.

molecules must be smaller compared to chloro substituted substrate molecules. Probably this fact may be causing the difference in the separation factors. Thus higher α values are obtained on the chloro substituted phases (column No.II23) than on the methyl substituted stationary phases (column No.II4), (Tables 5,7).

Different positional isomers of benzene also were studied on these liquid crystalline stationary phases

[A] XYLENES

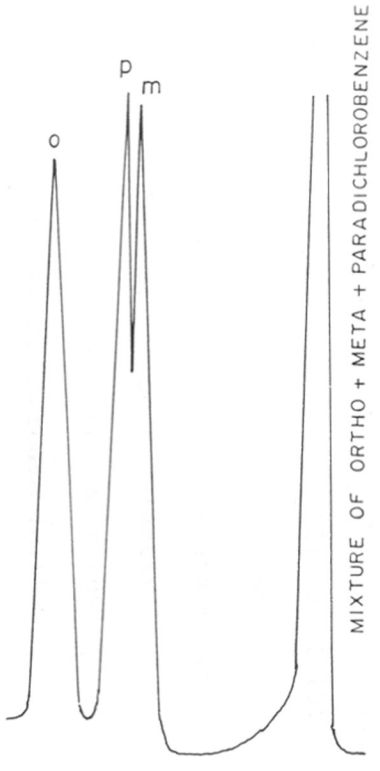
On the conventional columns usually separation of ortho and meta isomers takes place according to their boiling points however the meta and para isomers which are close boiling elute together. The liquid crystalline stationary phases, where the separation is achieved according to the shape parameter, are useful for meta-para isomeric separations. Laterally dimethyl substituted column No.X_1 has been able to separate the three xylene isomers where both methyl substituents are at A and B positions of the central phenyl ring. With substitution at A & D position increase in the alkoxy chain-length of the terminal group has reduced the selectivity towards meta-para separation. However, the ortho-meta and ortho-para separation factors are not showing any change with the increase in chain-length. (Column Nos. II5 and II6), (Table 9).



GRAPH SHOWING THE BEHAVIOR OF P-XYLENE ON COLUMN NOS. II·18, II·5, II·25, II·26

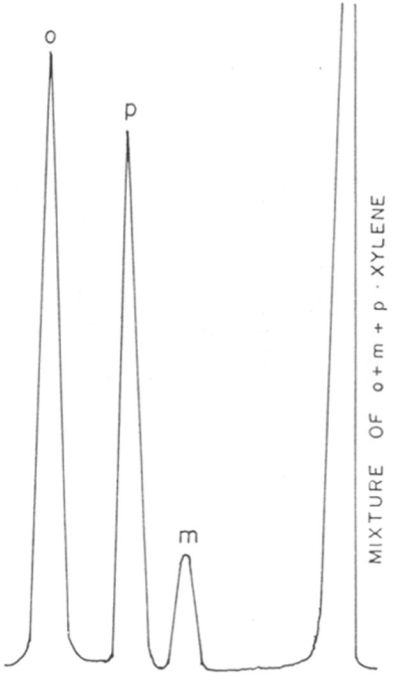
Dichloro substitution at A and D positions of the central phenyl ring of the substrate has shown best separation of all the three isomers [Column No.II26 (Table 11) and Chromatogram No.4]. This result may be explained on the basis of formation of intermolecular gap of appropriate size because of the dichloro substitution at positions A and D on the central phenyl ring adjacent to (-N=N-) moiety on the liquid crystalline substrate. Increase in the number of carbon atoms in the terminal alkoxy chain from ethyl to n-butyl has no effect on the meta, para separation factor (column No.II24 and II25) but when the carbon number is further increased to n-hexyl (column No.26) tremendous influence on selectivity towards the separation of ortho, meta and para isomers is observed although there is not much change in nematic range Table 1). This observation may be attributed to the fact that there is a change in conformation of liquid crystalline molecule because of the spacial arrangement of n-hexyl chain. Thus there is an increase in selectivity of the substrate towards the isomeric solute pair in contact.

Dichloro substitution at B & D positions in the substrate has not shown any special effect. Ortho-meta and ortho-para pairs separate on the basis of boiling points but meta-para separation is not possible.



CHROMATOGRAM NO. 5.

GAS CHROMATOGRAM OF MIXTURE OF DI-CHLOROBENZENE ISOMERS ON COLUMN NO. II 18. (OVEN TEMP., 105°C, INJECTOR TEMP. 130°C., DETECTOR TEMP., 150°C AND DETECTOR TYPE, TCD).



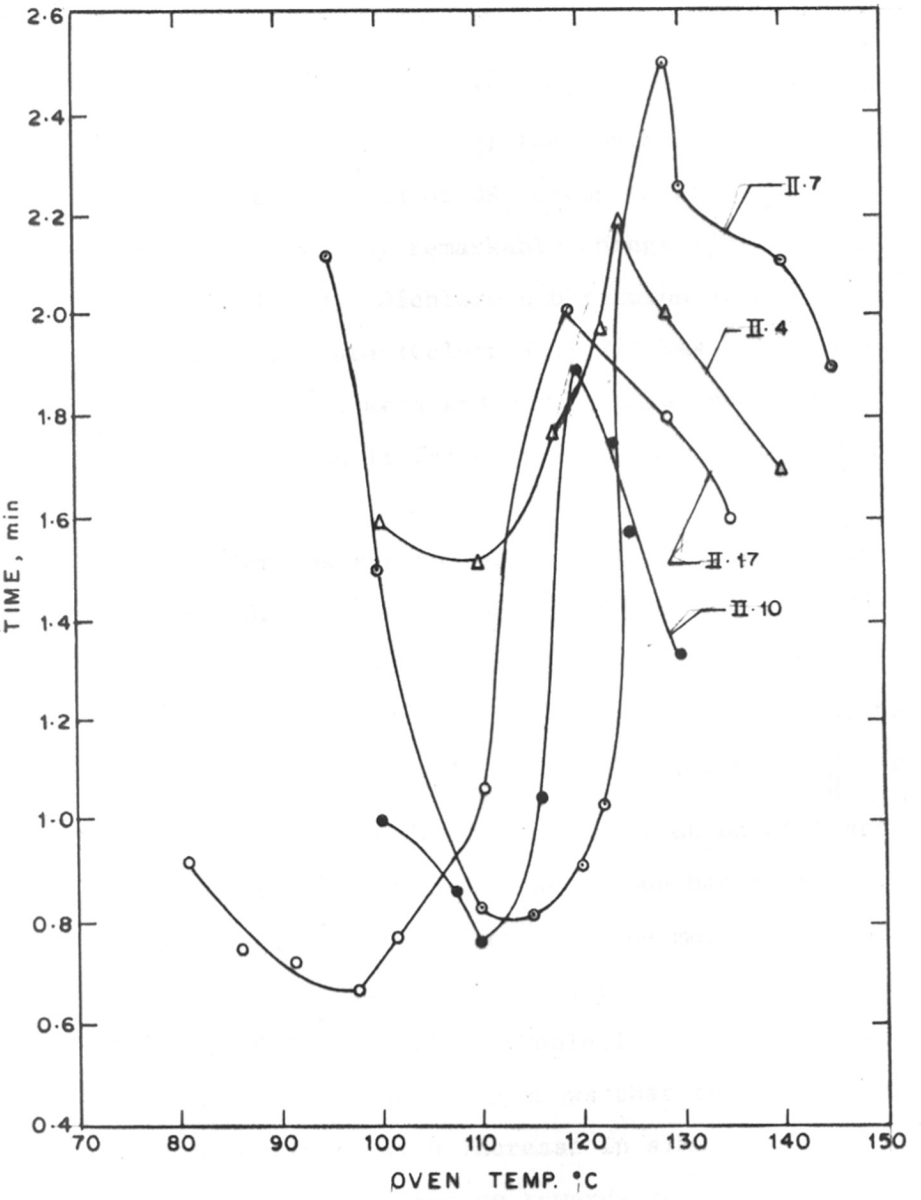
CHROMATOGRAM NO. 4.

GAS CHROMATOGRAM OF MIXTURE OF XYLENE ISOMERS ON COLUMN NO. II 26. (OVEN TEMP., 90°C, INJECTOR TEMP., 120°C, DETECTOR TEMP., 150°C, AND DETECTOR TYPE, TCD).

Mononitro moiety laterally substituted is very promising in case of xylene isomers as all the three isomers are separated (Column No.II17). In this case increase in chain-length of terminal alkoxy group reduces the selectivity towards meta-para separation along with the decrease in nematic range (Column No.II18) (Table 11).

[B] DICHLOROBENZENES

Dimethyl substitution at A and D positions on the central phenyl ring of the substrate (Column Nos. II4, II5, II6) (Table 9) shows that the separation factor for meta-para isomers increases with increase in the terminal alkoxy chain-length when the ethoxy group is substituted by butoxy group. When the terminal alkoxy chain-length is increased to n-hexyloxy a further decrease in selectivity is observed (Table 7) although there is not much change in the ortho-meta and ortho-para ratios. If the same dimethyl substituions are at B & D positions (Column Nos.II8 and II10) with an increase in carbon number in terminal alkoxy group selectivity decreases towards meta-para separation. Column No.II5 has shown the best selectivity towards these three isomers. When the two methyl groups are at A and B positions an increase in the alkoxy chainlength has



GRAPH SHOWING RETENTION BEHAVIOUR OF PDCB ON COLUMN NOS. II·7, II·17, II·10, II·4

increased the separation factor for the isomeric pairs (Column Nos.II16 and X_1) (Column Nos.II13 and X3).

Introduction of OR_1 group in place of R_1 group has not shown any remarkable change (Column Nos.II14 and X_1) (Table 11). Dichloro substituion at B & D positions in the substrate (Column No.II22) has shown selectivity towards ortho, meta and ortho, para isomeric pair separation but it failed to separate meta-para isomeric mixture.

Our observation about the substitution at B & D positions in case of methyl substituents also is the same as chloro substituents. The planarity of the liquid crystalline molecule must be getting disturbed because of the free rotation of adjacent (- C - O-) single bond. The dichloro substitution at A and D position adjacent to (-N=N-) group has been successful in retaining the planarity of the molecule intact and all the three isomers are separated from each other (Column No.II26) (Table 11). Bheaviour of Column No.II24 and II25 shows that there is decrease in selectivity with increase in alkoxy chain-length from ethoxy to n-butoxy towards meta-para separation especially. But as the chain-length increases further to n-hexyloxy (Column No.II26) the separation factor for all the three isomes is increased (Table 11). In case of electron withdrawing nitro substitution

interesting results are achieved when the behaviour of these two columns is observed towards dichlorobenzene isomers (Column Nos.II17, II18). Increase in alkoxy chain-length from methoxy to n-butoxy has increased the separation factors for all the three pairs (Table 11) (Chromatogram No.5). P131. Earlier observations about the relationship between nematic range and selectivity are not applicable in this case as Column No.II18 shows higher separation factors when compared to column No.II17 for all the three isomeric pairs of dichlorobenzene although its nematic range is almost half the nematic range of the column No.II17 (Table 1).

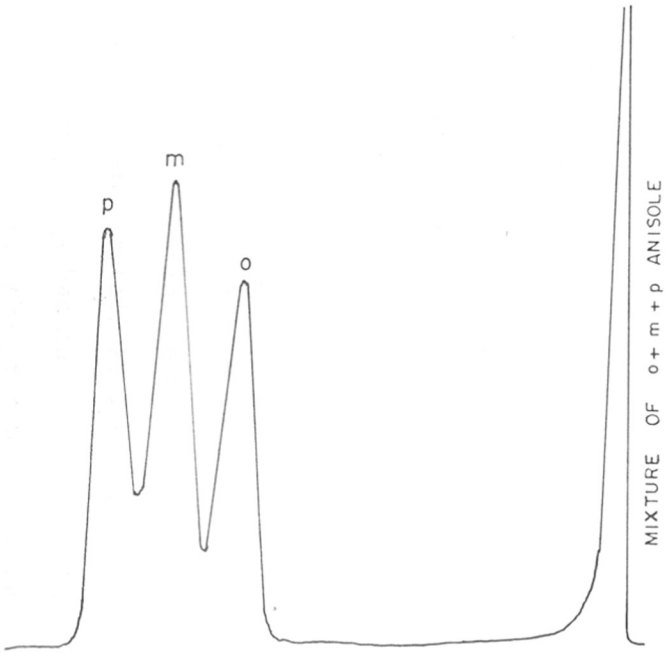
[C] BROMOTOLUENES

Column No.II16, where ~~to~~ two methyl groups are at A & B positions of the central phenyl ring of the substrate and n-hexyloxy acts as terminal alkoxy group shows the maximum separation factor for all the three pairs (Chromatogram No.6). The nematic range of this column is 80°C. With the interchange of both the terminal R_1 and R_2 groups of the liquid crystal stationary phase profound influence on the separation factors of meta, para and ortho, para-isomeric pairs is observed (Column No.II1 and II5) (Table 9). When the two methyl groups are at B & D positions the increase

in number of carbon in alkoxy chain has decreased the selectivity towards all the isomeric pairs (Column Nos.II7, II8, II10). Column No.II11, where two methyl groups are at B and C positions has given the separation of all isomers. Substitution of equal groups at both the ortho positions of the (-C-O-) linkages must have helped in retaining the liquid Crystalline molecule planar inspite of the possibility of the rotation of single bond. The intact rodlike structure of stationary phase must be helping for the observed separation phenomenon. Column No.II16, II24 and II11 are the columns in this group which could show the ortho to meta ratio $>$ 1.1 (Table 11).

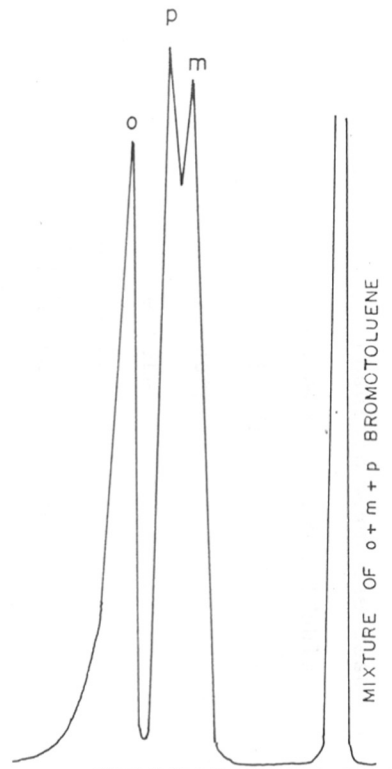
The dichloro substitution has not shown any selectivity towards the separation of bromotoluene isomers.

The electron withdrawing - NO_2 substitution which has shown effective selectivity in case of other isomeric solutes did not give separation factor $>$ 1.1 for meta-para and ortho-para pairs (Column No.II17). Introduction of OR_1 group instead of R_1- has shown effectiveness towards the meta-para and ortho-para pairs separation irrespective of the positions of dimethyl groups in the central phenyl ring of the substrate.



CHROMATOGRAM NO. 7.

GAS CHROMATOGRAM OF MIXTURE OF METHYL ANISOLE ON COLUMN NO. II 16 (OVEN TEMPERATURE, 127°C, INJECTOR TEMPERATURE 150°C, DETECTOR TEMP. 240°C AND DETECTOR TYPE, TCD)



CHROMATOGRAM NO. 6

GAS CHROMATOGRAM OF MIXTURE OF BROMOTOLUENS ON COLUMN NO. II 16 (OVEN TEMPERATURE, 127°C, INJECTOR TEMPERATURE 150°C, DETECTOR TEMP. 240°C AND DETECTOR TYPE, TCD)

[D] METHYL ANISOLES

On column Nos. II4, II5 and II6 with lateral disubstitution at A & D positions a sharp decline in separation factors for ortho, meta, para methyl anisoles is observed when the results of these three columns are compared (Table 9). The conformational effect by the introduction of n-hexyloxy group may be the cause for the observed fact. The total result is always an effect of solute solvent interaction.

When the alkyl terminal group (R_1) is replaced by an alkoxy moiety in the substrate molecule no substantial change is observed in selectivity. Substitution of two methyl groups at A & B positions has played the important role in achieving the separation of all the three isomeric pairs of methyl anisole (Column No.II16) (Chroamtogram No.7). Dimethyl substituents at B & D positions in the substrate has not given any remarkable separation factors for all the three isomers. The separation factor data of Column Nos.II24, II25, II26 where dichloro substitution is at A & D positions, shows a continuous increase in meta, para separation factor with increase in the alkoxy chain length (Table 11).

Substitution at B & D positions by two chloro groups has failed to separate the meta, para-pair even with the presence of long alkoxy chain in

the substrate molecule (Column No.II22). The inclusion of $-NO_2$ group in the substrate molecule has not helped in meta-para separation although ortho-meta and ortho-para separation is achieved.

When R_1 is replaced by OR_1 in the substrate molecule better selectivities are observed (Column Nos. II13 and X3) where dimethyl substitution is at A & D and A & B positions in the substrate respecstively. As dimethyl substitution at A & D and at A & B has shown good selectivity even with R_1 group (without the presence of $-OR_1$) one cannot say exactly about the utility of extra oxygen in the molecule.

[E] PICOLINES

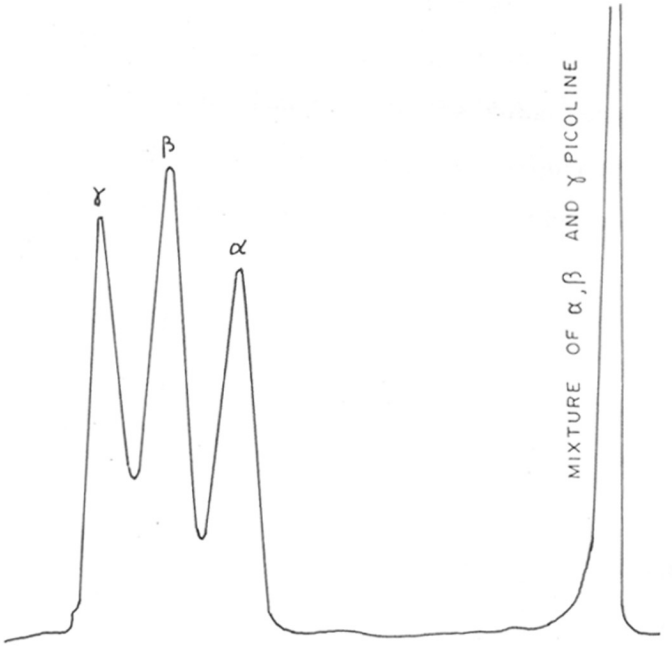
Picolines could be separated on all the columns. Dimethyl substituents at A & D positions in the substrate molecule has not shown any special selectivity towards picoline isomers.

The separation factor for close boiling isomers is important in case of picolines. Column Nos.II3, II4, II5 show increase in separation factor for BP pair along with the alkoxy chain-length. When methoxy is replaced by ethoxy group there is gradual increase in separation factor but when it is further substituted by n-butoxy group tremendous

increase is observed (Table 9), column II 5 (Chromatogram No.8). This may be due to spacial arrangement of n-butyl group in the substrate molecule. In case of column Nos.II7 and II8 where dimethyl substitution is at B & D positions in the substrate molecule when methoxy group is replaced by ethoxy group sudden increase in separation factor for βγ pair is observed although the nematic range is increased by only 10°C (Table 9).

When behaviour of picolines is considered on column Nos.II6, II10, II16, where terminal alkoxy group is same (n-hexyloxy) it is observed that dimethyl substitution at B & D positions fails to show any selectivity towards γβ pair while dimethyl substitution at A & B and A & D positions has shown equal increase in selectivity and inspite of the vast difference in their nematic ranges (Table 1, 9 and 11).

Dichloro substitution at B & D positions in the substrate has helped to achieved remarkable separation factor for αβ isomeric pair (Column Nos. II24, II25, II26) (Table 11). In case of dichloro substituion at A & D positions on the central phenyl ring of the substrate it is seen that terminal ethoxy and butoxy groups show same selectivity towards βγ pair but there is sudden



CHROMATOGRAM NO. 8.

GAS CHROMATOGRAM OF MIXTURE OF PICOLINES (OVEN TEMP., 105°C, INJECTOR TEMP., 130°C, DETECTOR TEMP., 240°C. AND DETECTOR TYPE TCD) COLUMN II 5.

drop in the separation factor when n-butoxy group is replaced by n-hexyloxy group although the nematic ranges are nearly same for these three columns. (Column Nos.II24, II25, II26) (Table 1, 11). In case of nitro substitution in the substrate replacement of terminal methoxy group by n-butoxy group has incrased the separation factor substantially for $\alpha\beta$ isomers (1.34 to 1.8).

[F] TOLUIDINES

Separation of toluidine isomers was a challenging problem a few years ago and many research workers have found out solutions for the same. Separation of all the three isomers has been achieved on column No.II3 where R_1 group in the substrate molecule has been replaced by OR_1 group and dimethyl substituents are at A & B positions of the central phenyl ring of the liquid crystalline molecule (Table 9).

Baseline separation of these three isomers is possible by using [illegible] column chromatograph [illegible] column Nos.II7 and II12 are used in combination with each other. Ortho-para, and ortho-meta isomers can be separated on column No.II7 while meta-para pair is comfortably separated on Column No.II12 (Tables 9,13).

[G] CRESOLS

All the columns have shown the separation of ortho, meta and ortho, para pairs. Dimethyl substituents at A & B positions of the substrate have shown increase in the separation factor of meta, para pair (Column Nos.II14, II16). Introduction of OR_1 group in place of $-R_1$ group in the liquid crystalline molecule has shown further advantage for the separation of all the three isomeric pairs of cresol (Column No.II14) (Table 11,13).

[H] CHLOROANILINES

Column No.II17 (Table 11) has shown the best selectivity towards chloroanilines. The lateral electron withdrawing $-NO_2$ substitution has shown its influence on these solutes.

Dimethyl substitution at A & B positions of the central phenyl ring has shown good selectivity towards chloroaniline isomers (Column Nos. , ., II15, II16,X_3) (Tables 11,13) Introduction of OR_1 in place of $-R_1$ group and n-hexyl group in terminal alkoxy chain has shown special effectiveness when the results are observed carefully.

[G] NITROTOLUENES

All the columns could separate the three isomeric pairs (Column Nos.II16, II17, X_3) (Table 11). (Column Nos. X_1, II 12, II14, II25) (Table 13).

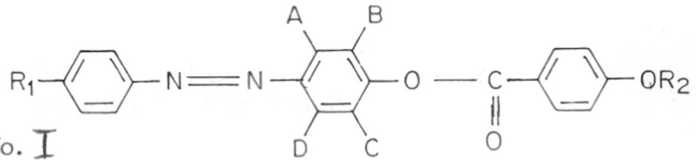


Table No. I

Compd. No.	R_1	R_2	A	B	C	D	Transition temp. °C C - N	N - I	Nematic range °C
II 1	n-C_4H_9	-CH_3	CH_3	H	H	CH_3	118	155	37
II 2	n-C_4H_9	-C_4H_9	CH_3	H	H	CH_3	98	122	24
II 3	CH_3	-CH_3	CH_3	H	H	CH_3	125	170	45
II 4	CH_3	C_2H_5	CH_3	H	H	CH_3	123	180	57
II 5	CH_3	n-C_4H_9	CH_3	H	H	CH_3	105	150	45
II 6	CH_3	n-C_6H_{13}	CH_3	H	H	CH_3	97	134	37
II 7	CH_3	CH_3	H	CH_3	H	CH_3	125	145	20
II 8	CH_3	C_2H_5	H	CH_3	H	CH_3	130	160	30
II 9	CH_3	C_4H_9	H	CH_3	H	CH_3	110	130	20
II 10	CH_3	n-C_6H_{13}	H	CH_3	H	CH_3	90	118	28
II 11	n-C_4H_9	n-C_4H_9	H	CH_3	CH_3	H	110	125	15
II 12	-OC_2H_5	-CH_3	H	CH_3	CH_3	H	182	205	23
II 13	-OC_2H_5	-CH_3	CH_3	H	H	CH_3	140	210	70
II 14	OCH_3	-CH_3	CH_3	CH_3	H	H	200	270	70
II 15	-OC_2H_5	CH_3	CH_3	CH_3	H	H	198	275	77
II 16	CH_3	n-C_6H_{13}	CH_3	CH_3	H	H	120	200	80
II 17	CH_3	CH_3	H	NO_2	H	H	121	190	69
II 18	CH_3	n-C_4H_9	H	NO_2	H	H	90	126	36
II 19	CH_3	CH_3	H	Cl	H	Cl	157	160	3
II 20	CH_3	C_2H_5	H	Cl	H	Cl	173	176	3
II 21	CH_3	n-C_4H_9	H	Cl	H	Cl	120	130	10

Table No. 1 (continued)

Compd. No.	R_1	R_2	A	B	C	D	Transition temp. °C C - N	N - I	Nematic range
II 22	CH_3	n-C_6H_{13}	H	Cl	H	Cl	107	115	8
II 23	CH_3	CH_3	Cl	H	H	Cl	160		-
II 24	CH_3	C_2H_5	Cl	H	H	Cl	145	162	17
II 25	CH_3	n-C_4H_9	Cl	H	H	Cl	105	125	20
II 26	CH_3	n-C_6H_{13}	Cl	H	H	Cl	90	110	20
X_1	CH_3	CH_3	CH_3	CH_3	H	H	168	236	68
X_2	CH_3	CH_3	CH_3	H	H	H	140	207	67
X_3	OC_2H_5	n-C_4H_9	CH_3	CH_3	H	H	140	240	100
Y_1	CH_3	CH_3	Cl	H	H	H	180	230	50
Y_2	CH_3	C_2H_5	Cl	H	H	H	128	185	57

C-N Crystal to Nematic

N-I Nematic to Isoptropic

Table No.2 Column Parameters

Compd./ Column No.	Total wt. at packing in gms	Length of the column meters	Amount of stationary phase (wt. %)
1	2	3	4
1	14.12	1.8	All the stationary phases are 5% w/w
2	14.00	1.75	
3	13.5	1.91	
4	13.5	1.85	
5	12.25	1.75	
6	13.00	1.91	
7	13.00	1.8	
8	13.5	1.81	
9	13.2	1.8	
10	13.0	1.94	
11	13.82	2.00	
12	14.00	2.00	
13	13.00	1.91	
14	13.00	1.94	
15	12.75	1.91	
16	12.25	1.91	
17	12.23	2.00	
18	13.65	1.94	
19	13.00	1.80	
20	12.5	1.8	
21	13.0	1.91	
22	13.5	1.91	
23	13.25	1.91	
24	13.5	1.91	
25	13.6	2.00	
26	13.12	1.91	
X1	13.0	2.00	
X2	12.7	1.85	
X3	12.67	1.90	
Y1	13.5	2.00	
Y2	12.5	1.75	

Table No.3

Positional Isomers studied

S.No.	Name of the compound	B.p./m.p.°C
1	Ethyl benzene	136
2	o-Xylene	142
3	m-Xylene	137
4	p-Xylene	139
5	o-Dichlorobenzene	180
6	m-Dichlorobenzene	172
7	p-Dichlorobenzene	174/53
8	o-Bromotoluene	181
9	m-Bromotoluene	183
10	p-Bromotoluene	185/28
11	o-Methyl anisole	171.3
12	m-Methyl anisole	177.2
13	p-Methyl anisole	176.5
14	o-Nitrotoluene	222.3
15	m-Nitrotoluene	227.5
16	p-Nitrotoluene	237.7/54.5
17	α-Picoline	129
18	β-Picoline	143.8
19	γ-Picoline	143.1
20	o-Cresol	191/31
21	m-Cresol	202
22	p-Cresol	202.5/34
23	o-Chloroaniline	288.8
24	m-Chloroaniline	230.5
25	p-Chloroaniline	232/70
26	o-Toluidine	200.6
27	m-Toluidine	203
28	p-Toluidine	200.3/42

continued..

Table No.3 (continued)

S.No.	Name of the compound	B.p./m.p.°C
	Terpene hydrocarbons	
29	Longifolene	254.6/70.6 mm
30	Isolongifolene	107-9/7 mm
31	Longicyclene	252/706 mm
	Mono and Disubstituted Naphthalene isomers	
32	Naphthalene	217.7 /760 mm
33	1-Methyl naphthalene	240-241/760 mm
34	2-Methyl naphthalene	241-242/760 mm
35	1,2-Dimethyl naphthalene	266/760 mm
36	1,3-Dimethyl naphthalene	263/760 mm
37	2,3-Dimethyl naphthalene	269/760 mm
38	1,4-Dimethyl naphthalene	268/760 mm
39	1,6-Dimethyl naphthalene	264/760 mm
40	1,5-Dimethyl naphthalene	265/760 mm
41	2,6-Dimethyl naphthalene	262/760 mm

Table No.4 Column Nos. and oven temperatures °C

Retention time data in minutes for naphthalene & substituted naphthalene on methyl substituted liquid crystalline stationary phases

Compounds	II3	II4	II12	II13	II14	II15	II16	X_1	X_2	X_3
	162	162	182	176	200	199	169	166	172	171
Naphthalene	2.15	1.73	1.83	0.93	0.97	0.92	1.47	0.73	1.5	1.2
2-Methyl naphthalene	3.83	3.00	3.12	1.27	1.43	1.45	2.52	1.23	3.33	2.6
1-Methyl naphthalene	4.35	3.35	3.38	1.42	1.52	1.53	2.75	1.4	3.53	2.68
2,6-Dimethyl naphthalene	6.5	5.00	5.02	2.07	2.37	2.28	4.63	2.1	5.5	4.47
1,3-Dimethyl naphthalene	7.32	5.6	5.4	2.27	2.27	2.42	4.7	2.22	6.13	4.15
1,6-Dimethyl naphthalen	7.27	5.73	5.78	2.25	2.45	2.45	4.77	2.4	6.5	4.58
1.5-Dimethyl naphthalene	7.9	6.23	6.17	2.58	2.67	2.62	5.15	2.48	6.38	4.8
1,4-Dimethyl naphthalene	8.17	6.42	6.32	2.47	2.65	2.6	5.12	2.23	6.67	4.5
2,3-Dimethyl naphthalene	8.47	6.45	6.38	2.68	2.7	2.78	5.28	2.38	6.28	5.08
1,2-Dimethyl naphthalene	8.92	6.92	6.57	2.73	2.92	2.95	5.75	2.55	7.37	5.53

Table No.5 α Factors for naphthalene and mono- and dimethyl naphthalenes on methyl substituted liquid crystalline phases

Column Numbers

Name of pair	II3	II4	II12	II13	II14	II15	II16	X_1	X_2	X_3
2-Methylnaph. / naphthalene	1.78	1.74	1.70	1.36	1.47	1.58	1.71	1.68	2.22	2.16
1-Meth.naph. / 2-meth.naph	1.14	1.116	1.08	1.12	1.06	1.05	1.09	1.14	1.06	1.03
1,3-dmn / 2,6-dmn	1.13	1.12	1.07	1.1	1.04	1.06	1.01	1.06	1.06	1.07
1,6-dmn / 1,3-dmn	1.01	1.02	1.07	1.0	1.07	1.01	1.01	1.08	1.06	1.1
1,5-dmn / 1,6-dmn	1.09	1.08	1.06	1.15	1.08	1.07	1.08	1.03	1.01	1.05
1,4-dmn / 1,5-dmn	1.03	1.03	1.02	1.04	1.09	1.0	1.0	1.1	1.04	1.06
2,3-dmn / 1,4-dmn	1.04	1.01	1.01	1.08	1.01	1.06	1.03	1.07	1.06	1.13
1,2-dmn / 2,3-dmn	1.05	1.07	1.03	1.07	1.08	1.06	1.09	1.07	1.17	1.08
1,2-dmn / 2,6-dmn	1.37	1.38	1.3	1.31	1.23	1.29	1.24	1.21	1.34	1.24

Table No.6 Retention time data of naphthalene and substituted naphthalenes on nitro- and chloro-substituted liquid crystalline stationary phases

	Column numbers and oven temperatures in °C				
	II 17	Y1	Y2	II20	II23
Compound	170	180	172	161	162
Naphthalene	1.37	1.00	1.88	1.78	2.52
2-meth. naphthalene	2.22	1.63	3.06	3.08	3.92
1-meth. naphthalene	2.45	1.88	3.37	3.55	4.95
2,6-dimeth. naphthalene	3.72	2.66	4.00	5.35	7.5
1,3-dimeth. naphthalene	4.52	3.00	4.12	6.18	8.33
1,6-dimeth. naphthalene	4.42	3.4	4.37	6.35	8.47
1,5-dimeth. naphthalene	4.83	3.35	4.55	6.8	9.17
1,4-dimeth. naphthalene	4.53	3.46	4.38	6.37	9.75
2,3-dimeth. naphthalene	4.83	3.28	4.97	7.37	9.55
1,2-dimeth. naphthalene	5.4	4.00	5.22	7.9	10.4

Table No.7 α factor for Naphthalene, Monomethyl naphthalenes and dimethyl naphthalenes on mono nitro and mono and dichloro substituted liquid crystalline phases

Column Numbers

Name of pair	II 17	Y1	Y2	II 20	II 23
2 meth.naphth. / Naphth.	1.6	1.63	1.6	1.7	1.5
1-meth.naphth. / 2-meth.naphth.	1.1	1.15	1.1	1.15	1.26
1,3-dmn / 2,6-dmn	1.21	1.13	1.03	1.15	1.11
1,6-dmn / 1,3-dmn	1.02	1.13	1.06	1.02	1.02
1,5-dmn / 1,6-dmn.	1.09	1.01	1.04	1.07	1.08
1,4-dmn / 1,5-dmn	1.06	1.03	1.04	1.06	1.06
2,3-dmn / 1,4-dmn	1.06	1.05	1.13	1.16	1.02
1,2-dmn / 2,3-dmn	1.11	1.22	1.05	1.07	1.09
1,2-dmn / 2,6-dmn	1.45	1.5	1.3	1.47	1.38

Table No.8. Retention time data for different positional isomers of substituted benzene in minutes

Solutes	Column Nos. and oven temperatures in °C							
	II 1	II 3	II 4	II 5	II 6	II 7	II 8	II 10
	120	135	124	105	101	130	137	90
o-Xylene	-	-	-	1.87	1.78	-	-	2.38
m-Xylene	0.92	-	-	1.46	1.38	-	-	1.9
p-Xylene	0.97	-	-	1.62	1.43	-	-	2.03
o-Dichloro-benzene	4.25	2.1	2.25	5.93	7.42	2.2	1.52	5.88
m-Dichloro-benzene	3.36	1.5	1.75	4.23	5.4	1.35	1.13	4.62
p-Dichloro-benzene	3.85	1.77	1.97	5.15	5.98	1.73	1.33	4.8
o-Bromo-toluene	4.33	1.62	2.0	5.37	3.13	2.78	1.3	5.32
m-Bromo-toluene	4.36	1.68	2.12	5.3	3.35	3.00	1.33	5.28
p-Bromo-toluene	4.8	1.8	2.38	6.4	3.52	3.55	1.58	5.85
o-Methyl anisole	3.2	1.2	1.62	3.67	2.32	2.18	0.95	3.83
m-Methyl anisole	3.82	1.42	1.87	4.42	2.72	2.725	1.12	4.68
p-Methyl anisole	4.3	1.58	2.05	5.1	2.85	2.79	1.23	5.5
α-Picoline	1.36	0.65	0.9	1.72	1.03	1.00	0.45	1.73
β-Picoline	2.32	1.10	1.48	2.65	1.62	1.66	0.67	2.12
γ-Picoline	2.87	1.25	1.73	3.55	1.75	1.83	1.00	2.17
o-Toluidine*	8.23	2.4	1.75	-	-	3.75	-	-
m-Toluidine	8.74	2.87	1.87	-	-	4.57	1.33	-
p-Toluidine	8.45	2.62	1.75	-	-	4.68	1.13	-
o-Cresol	-	2.64	2.28	-	-	4.37	2.91	-
m-Cresol	11.1	3.52	2.87	-	-	6.25	3.7	-
p-Cresol	11.87	3.37	2.97	-	-	6.00	3.95	-
o-Chloro-aniline	-	4.00	4.00	-	-	-	-	-
m- "	-	7.53	7.53	-	-	-	-	-
p- "	-	7.2	7.2	-	-	-	-	-
o-Nitrotoluene	-	4.8	-	-	-	-	-	-
m- "	-	6.5	-	-	-	-	-	-
p- "	-	8.2	-	-	-	-	-	-

* Injected at high temperature

Table 96 factors for different positional isomers of substituted benzene

Pairs of solutes	Column Nos. and oven temperatures in °C							
	II 1	II 3	II 4	II 5	II 6	II 7	II 8	II 10
	120	135	124	105	101	130	137	90
o-Xylene / m-xylene	-	-	-	1.28	1.29	-	-	1.25
p-Xylene / m-xylene	1.05	-	-	1.11	1.04	-	-	1.07
o-Xylene / p-Xylene	-	-	-	1.15	1.24	-	-	1.17
o-DCB * / m-DCB	1.26	1.4	1.28	1.4	1.37	1.6	1.34	1.27
p-DCB / m-DCB	1.14	1.18	1.13	1.22	1.1	1.28	1.18	1.04
o-DCB / p-DCB	1.1	1.2	1.14	1.15	1.24	1.2	1.14	1.22
o-BT ** / m-BT	1.0	1.03	1.06	1.01	1.07	1.08	1.02	1.01
p-BT / m-BT	1.1	1.07	1.12	1.2	1.05	1.18	1.19	1.1
p-BT / o-BT	1.1	1.1	1.2	1.2	1.12	1.28	1.21	1.1
o-meth.Anisole / m-meth.Anisole	1.19	1.21	1.15	1.2	1.17	1.25	1.2	1.22
p-meth.Anisde / m-meth.Anisole	1.12	1.11	1.1	1.15	1.05	1.02	1.1	1.04
p-meth.Anisole / o-meth.Anisole	1.34	1.35	1.5	1.4	1.23	1.28	1.29	1.17
β-Picoline / α-Picoline	1.27	1.69	1.64	1.54	1.57	1.66	1.49	1.22
γ-Picoline / β-Picoline	1.23	1.14	1.17	1.34	1.1	1.1	1.49	1.02
o-Toluidine / m-Toluidine	1.06	1.2	1.07	-	-	1.22	-	-
m-Toluidine / p-Toludine	1.03	1.1	1.06	-	-	1.02	1.18	-
p-Toluidine / o-Toludine	1.02	1.1	1.0	-	-	1.25	-	-
o-Cresol / m-Cresol	-	1.33	1.26	-	-	1.43	1.27	-
m-Cresol / p-Cresol	1.07	1.04	1.03	-	-	1.04	1.07	-
p-Cresol / o-Cresol	-	1.3	1.3	-	-	1.37	1.36	-
o-Chlo.Aniline / m-Chlo.Aniline	-	1.9	-	-	-	-	-	-
m-Chlo.Aniline / p.Chlo.Aniline	-	1.04	-	-	-	-	-	-
o-Chlo.Aniline / p-Chlo.Aniline	-	1.08	-	-	-	-	-	-

* DCB = Dichlorobenzene ** BT = Bromotoluene

Table 10 Retention time data for positional isomers of substituted benzene in minutes

	Column Nos. and oven temperatures °C									
	II 11	III3	III6	III7	III8	II22	II24	II25	II26	X3
Solute	103	135	I27	121	105	110	149	110	90	140
o-Xylene	-	-	-	0.73	1.42	1.3	0.52	1.2	2.38	-
m-Xylene	-	-	-	0.55	1.08	0.97	0.45	0.93	1.6	-
p-Xylene	-	-	-	0.62	1.13	1.00	0.42	1.00	1.87	-
o-Dichloro-benzene	2.18	0.95	1.97	2.48	4.93	4.7	1.67	4.43	10.0	1.7
m- "	1.7	0.75	1.43	1.83	3.43	3.5	1.23	3.47	7.32	1.28
p- "	1.88	0.83	1.75	2.08	3.95	3.67	1.4	3.5	8.22	1.5
o-Bromo Tolune	1.87	0.82	1.67	2.42	5.13	4.16	1.42	4.00	10.23	1.45
m- "	2.06	0.85	2.13	2.43	5.22	4.58	1.62	4.18	9.77	1.53
p- "	2.32	0.97	2.5	2.68	5.5	4.67	1.6	4.38	10.7	1.8
o-Methyl anisole	1.45	0.67	1.3	1.9	-	3.17	1.05	2.5	7.12	1.12
m - "	1.78	0.77	1.55	2.47	-	3.6	1.27	3.03	8.15	1.3
p- "	1.92	0.88	1.75	2.68	-	3.8	1.28	3.17	9.88	1.47
α-Picoline	0.47	0.5	0.58	1.17	1.23	2.06	0.62	2.78	5.25	0.53
β-Picoline	0.77	0.88	0.97	1.57	2.22	4.43	0.8	4.93	7.5	0.77
γ-Picoline	0.85	1.02	1.08	-	-	5.1	1.03	6.52	9.0	1.00
o-Toluidine	5.53	2.12	2.00	2.16	-	-	-	-	-	3.15
m-Toluidine	5.48	2.4	2.12	2.32	-	-	-	-	-	3.33
p-Toludine	5.43	2.2	2.18	2.23	-	-	-	-	-	3.28
o-Cresol	6.53	2.05	5.57	1.85	-	-	1.95	-	-	3.33
m-Cresol	6.79	2.88	3.97	2.33	-	-	2.55	-	-	4.43
p-Cresol	6.54	3.05	5.1	2.34	-	-	2.7	-	-	4.58
o-Chloro-aniline	-	-	3.13	3.72	-	-	-	-	-	1.82
m- "	-	-	5.75	2.17	-	-	-	-	-	2.28
p- "	-	-	6.42	4.32	-	-	-	-	-	2.55
o-Nitro-toluene	-	-	3.55	3.57	-	-	-	-	-	1.43
m- "	-	-	4.9	5.45	-	-	-	-	-	1.97
p- "	-	-	6.37	6.3	-	-	-	-	-	2.47

Table No.11 (α) factors for different positional isomers of substituted benzene

Pair of solutes	Column Nos. and oven temperatures °C									
	III1	III3	III6	III7	III8	II22	II24	II25	II26	X_3
	103	135	127	121	105	110	149	110	90	140
o-Xylene / m-xylene	-	-	-	1.32	1.3	1.34	1.15	1.29	1.48	-
m-Xylene / p-Xylene	-	-	-	1.13	1.05	1.03	1.07	1.07	1.17	-
p-Xylene / o-Xylene	-	-	-	1.18	1.26	1.3	1.24	1.2	1.27	-
o-DCB* / m-DCB	1.28	1.27	1.38	1.35	1.44	1.34	1.35	1.28	1.37	1.33
m-DCB / p-DCB	1.1	1.1	1.22	1.14	1.15	1.05	1.14	1.01	1.12	1.17
p-DCB / o-DCB	1.16	1.2	1.13	1.17	1.25	1.28	1.19	1.26	1.22	1.13
o-BT** / m-BT	1.1	1.0	1.27	1.0	1.02	1.1	1.14	1.04	1.04	1.05
p-BT / m-BT	1.12	1.14	1.17	1.1	1.05	1.02	1.01	1.05	1.14	1.17
p-BT / o-BT	1.24	1.18	1.5	1.1	1.07	1.12	1.13	1.1	1.04	1.24
o-Meth. Anisole / m-meth. Anisole	1.23	1.15	1.19	1.3	-	1.15	1.2	1.2	1.1	1.16
p-Meth. Anisole / m-meth. Anisole	1.08	1.14	1.13	1.08	-	1.04	1.00	1.05	1.21	1.13
p-Meth. Anisole / o-meth. Anisole	1.32	1.31	1.35	1.4	-	1.2	1.22	1.26	1.39	1.3
β-Picoline / α-Picoline	1.64	1.76	1.7	1.34	1.8	2.15	1.3	1.77	1.43	1.45
γ-Picoline / β-Picoline	1.1	1.16	1.1	-	-	1.15	1.3	1.32	1.2	1.3
o-Toluidine / m-toluidine	1.01	1.13	1.06	1.07	-	-	-	-	-	1.06
m-Toluidine / p-Toluidine	1.01	1.1	1.02	1.04	-	-	-	-	-	1.01
p-Toluidine / o-Toluidine	1.01	1.04	1.08	1.03	-	-	-	-	-	1.04
o-Cresol / m-Cresol	1.04	1.4	1.28	1.25	-	-	1.3	-	-	1.33
m-Cresol / p-Cresol	1.04	1.05	1.1	1.00	-	-	1.06	-	-	1.03
p-Cresol / o-Cresol	1.0	1.5	1.4	1.26	-	-	1.14	-	-	1.37
o-Chloro-Aniline / m-Chloro-Aniline	-	-	1.83	1.71	-	-	-	-	-	1.25
m-Chloro-Aniline / p-Chloro-Aniline	-	-	1.12	1.99	-	-	-	-	-	1.12
o-Chloro-Aniline / p--Chloro-Aniline	-	-	2.05	1.16	-	-	-	-	-	1.4
o-Nitro-tol. / m-Nitro-tol.	-	-	1.38	1.53	-	-	-	-	-	1.38
m-Nitro-tol. / p-Nitro-tol.	-	-	1.3	1.15	-	-	-	-	-	1.25
p-Nitro-tol. / o-Nitro-tol.	-	-	1.79	1.76	-	-	-	-	-	1.72

* DCB = Dichlorobenzene ** BT = Bromotoluene

Table No.12. Retention time data for positional isomers of substituted benzene in minutes

Solutes	Column Nos. and oven temperatures in °C			
	II 12 186	II 14 200	II 15 200	X_1 170
o-Toluidine	1.67	0.66	0.73	-
m-Toluidine	1.43	0.68	0.72	2.37
p-Toluidine	1.67	0.72	0.72	2.37
o-Cresol	1.23	0.66	0.73	1.73
m-Cresol	1.63	0.73	0.89	2.23
p-Cresol	1.62	0.80	0.89	2.35
o-Chloroaniline	1.87	0.95	0.9	3.22
m-Chloroaniline	3.32	1.58	1.57	6.23
p-Chloroaniline	3.32	1.77	1.87	6.63
o-Nitrotolune	1.42	1.02	1.00	3.63
m-Nitrotoluene	2.93	1.32	1.28	2.74
p-Nitroltoluene	3.67	1.72	1.65	6.55

Table No.13 (α) factor for positional isomers of substituted benzene

	Column Nos. and oven temperatures in °C			
	X_1	II 12	II 14	II 15
Pairs of solutes	170	186	200	200
o-Toluidine / m-Toluidine	-	1.17	1.03	1.0
m-Toluidine / p-Toluidine	1.0	1.17	1.05	1.0
p-Toluidine / o-Toluidine	-	1.00	1.09	1.0
o-Cresol / m-Cresol	1.29	1.32	1.1	1.22
m-Cresol / p-Cresol	1.05	1.0	1.1	1.00
p-Cresol / o-Cresol	1.36	1.32	1.2	1.22
o-Chloro-Aniline / m-Chloro-Aniline	1.93	1.77	1.7	1.74
m-Chloro-Aniline / p-Chloro-Aniline	1.06	1.0	1.1	1.19
p-Chloro-Aniline / o-Chloro-Aniline	2.05	1.77	1.9	2.08
o-Nitro-Toluene / m-Nitro-Toluene	1.32	2.06	1.29	1.28
m-Nitro-Toluene / p-Nitro-Toluene	2.39	1.25	1.3	1.29
p-Nitro-Toluene / o-Nitro-toluene	1.8	2.58	1.69	1.65

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CHAPTER III

Application of liquid crystalline substrates in gas chromatography for the study of reaction kinetics and identification of the products obtained in Friedel-Crafts reaction

SUMMARY

The results which are discussed in previous chapter reveal the fact that the liquid crystalline stationary phases are acting as good solvents for mono and dimethyl naphthalenes as well as for various disubstituted benzene isomers.

This finding was utilized in actual qualitative analysis of the products of Friedel-Crafts reaction. Alkylation of naphthalene and monomethyl naphthalene using alcohols in presence of catalyst has been carried out. The percentage composition of reaction mixtures was studied at different intervals of time by GLC using one of the presently synthesized liquid crystalline column. The results are described in this chapter.

Introduction to Friedel-Crafts reactions

The versatile Friedel-Crafts reaction took place for the first time with the reaction of benzene with amyl chlorides in the presence of aluminium chloride to produce amyl benzene by Charles Friedel and his American collaborator James-Mason Crafts in Paris on May 14, 1877[1]. They showed that "anhydrous aluminium chloride could be used as a condensing agent in a general synthetic method for furnishing an infinite number of hydrocarbons". The definition by C.C. Price in Encyclopaedia Britanicca reads as "The Friedel-Crafts reaction is commonly considered as a process of uniting two or more organic molecules through the formation of carbon-carbon bonds under the influence of certain strongly acidic metal halide catalysts". Friedel-Crafts found that besides $AlCl_3$ other metal halides, such as ferric chloride, zinc chloride and sodium aluminium chloride are also active catalysts. One should not restrict to any specific term under this name as it includes all sorts of reactions including substitution, isomerisation, elimination, cracking polymerization or addition reactions taking place under the catalytic effect of the Lewis acid type acidic halides (with or without co-catalysts)

or proton acids. It was restricted to Aromatic field until World War II. The use of aluminium chloride as catalyst for such condensations has been dealt in detail by Thomas[2].

Composition of reaction systems

a) The substance to be substituted.

b) A reagent that supplies the substituent for e.g. olefin, alkyl halide, alcohol, acid halide or anhydride etc.

c) A catalyst which may be a Lewis-acid type acidic halide or a proton acid in the Bronsted Lowry sense.

d) A solvent, the function of which is sometimes taken over over by the excess of the substrate or reagent. Solvents are generally non-ionizing type, e.g. CS_2, CCl_4, Ligroin etc. although solvents with higher dielectric constants are also employed, nitrobenzene, nitromethane etc.

e) The product formed in the reaction.

f) The byproduct conjugate acid Hx which originates from catalyst.

The most important reagents are alkyl halides olefins and alcohols. But many other types of reagents[3] such as ethers, mercaptans, sulfides, thiocyanates, sulfates, sulfonates or even alkanes and

cycloalkanes under conditions where they are converted to carbonium ion, have also been used. When alkyl halides are used as reagent, the reactivity is in the order F > Cl > Br > I.

Alcohols are more active than alkyl halides. But if Lewis acid catalyst is used, more amount of catalyst is required since the catalyst complexes with the hydroxyl group[4]. Proton acids are often used to catalyse alkyation with alcohols. Olefins are good alkylating agents. With respect to them the reaction is addition of ArH to a C=C bond.

When esters are used as reagents for alkylation there is competition between alkylation and acylation. That is why they are not widely employed in Friedel-Crafts reactions although the product can be controlled by choice of reagent, catalyst and reaction conditions.

Regardless of which reagent is used, a catalyst is always required. In general the catalysts can be arranged in the following order over their reactivity.

$AlBr_3 > AlCl_3 > GaCl_3 > FeCl_3 > SbCl_5 > ZnCl_4 > BCl_3 > BF_3 > SbCl_3$

The reactivity order may change depending upon the substrates, reagent and reaction conditions.

Aromatic hydrocarbons- Lewis acid halide complexes have received much experimental attention. They are covalent nonconducting compounds of relatively low

stability[5]. These are π complexes in which the π sextet as a whole acts as the electron donor[6]. Gustavson[7,8] announced the isolation of liquid complexes of aluminium halides with benzene and tolune of the approximate composition $Al_2X_6.6C_6H_6$ and $Al_2X_6.6C_6H_5$ from the red oil formed by passing dry hydrogen halide and aromatic hydrocarbon.

Friedel-Crafts Alkylation

$$ArH + RCl \xrightarrow{AlCl_3} ArR$$

This is a reaction of very broad scope. Most important reagents used are the alkyl halides, olefins and alcohols. Friedel-Crafts-alkylation is unusual among the principal aromatic substitutions. In that the entering group is activating so that di- and poly. alkylations are frequently observed. However, the activating effect of simple alkyl groups (e.g. ethyl, isopropyl) is such that the compounds with these groups as substituents are if attacked in Friedel-Crafts alkylations react only about 1.5 to 3 times as fast as benzene[9]. So it is often possible to obtain high yields of monoalkyl products. Actually, the fact that di- and polyalkyl derivatives are frequently obtained is not due to the small difference in reactivity but to the circumstance that alkylbenzenes are prefrentially soluble in the catalyst layer, where the reaction

actually takes place. This drawback may be removed by the use of suitable solvent, by high temperatures and by high speed stirring. The reported yields of alkylated products from Friedel-Crafts reaction of naphthalene were generally low[10] and the chemical structures of products were doubtful or uncertain. Many investigations were reported in the literature[11-13].

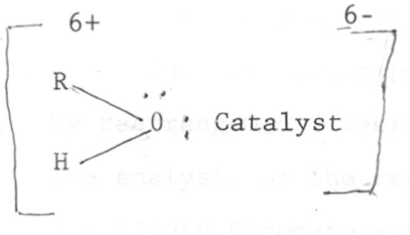
Naphthalene and other fused ring compounds generally give poor yields in Friedel-Crafts reactions because the fused ring compounds are so reactive that they react with the catalyst and so excess amount of catalyst is required. An important synthetic limitation of Friedel-Crafts alkylation is that rearrangement frequently takes place in the reagent. But by controlling the reaction conditions proper products can be obtained. Alkyl cations are most powerful electrophiles but in case of inactive substrates degradation and polymerization of the electrophile occurs before it can attack the ring. Thermodynamic stability of alkylbenzenes is primary $>$ secondary $>$ tertiary. Alkylation is less selective than acylation followed by reduction.

Mechanism

Friedel-Crafts alkylation is categorized under Electrophilic substitution. The electrophile in Friedel-Crafts alkylation is a carbo-cation atleast in most cases[14].

$$ROH + AlCl_3 \longrightarrow ROAlCl_2 \longrightarrow R^+ + OAlCl_2$$

The carbo-cation is formed from the attacking reagent and the catalyst. However, there is evidence that many Friedel-Crafts alkylations especially with primary reagents do not go through a completely free-carbocation. The ion may exist as tight ion pair with, say, $AlCl_4^{\ominus}$ as the counterion or as a complex. According to Olah[15] slow step in the reaction of an aromatic with an electrophilic reagent is the formation of an oriented π complex. Formation of highly polarised complex is the rate determining step.



The carbonium ion may be free ion held by a combination of electrostatic and covalent forces to form the Counter or 'Gegen' ion.

Reactivity and orientation of Naphthalene

In fused ring systems like naphthalene one ring is to have six electrons, the other will be having four electrons. The ring having six electrons acts as

aromatic ring while other acts as butadiene system[16]. The positions are not equivalent and there is usually a preferred orientation even in the unsubstituted hydrocarbons. The α position is the preferred site of attack. When the attack is at α position more cannonical forms are observed when compared with the attack at β position[17]. But if the reaction is reversible and the equilibrium is reached then thermodynamically β position is the preferred position for attack[18,19]. (thermodynamically stable product). Koike and Okawa[20] studied the orientation. They suggested that formation of β -isomer takes place by an abnormal orientation mechanism. Probably $AlCl_3$ combines with naphthalene thus blocking the α position of naphthalene nucleus.

The extensive delocalization of charges in the coresponding arenium ion in case of naphthalene when compared with benzene arenium ion causes more reactivity in case of naphthalene and thus substitution is faster.

The alkylation process is generally accompanied by rearrangement, reorientation or other side reactions. The analysis of the reaction product is very complex. Gas Liquid Chromatography is the best tool in the hands of organic chemists for the accurate and convenient analysis of such products. Zee Cheng[21] reported the different monoalkylated products and identified the

same by GLC using conventional long columns and by Infrared Spectroscopy. Liquid crystalline stationary phases have been found useful for the separation of close-boiling mono as well as dimethyl substituted naphthalene isomers. To show the applicability of liquid crystalline stationary phases some Friedel-Crafts-alkylation reactions were carried out and the products were identified using these stationary phases in gas chromatography.

EXPERIMENTAL

Reactions of naphthalene and 1-methyl naphthalene with t-butanol[12]

Naphthalene, 1-methyl naphthalene and anhydrous aluminium chloride (BDH) were used without further purification.

The t-butanol used in this reaction was distilled and dried before use.

Method of t-butylation of naphthalene and 1-methyl methyl naphthalene using t-butanol

In a three necked round bottom flask equipped with dropping funnel, a reflux condenser protected by guard tube and thermometer, was taken a mixture of 3.2 g (0.05 mole) naphthalene and 2 ml (0.05 mole) t-butanol in 10 ml of dry ligroin. The magnetically well stirred reaction mixture was cooled to 0°C and anhydrous aluminium chloride 2.2 g (0.035 mole) was added within two/three minutes into it in three portions. The reactants were stirred at 0°C for 15 minutes and then heated in oil bath at 80°C for 5 hrs. The reaction mixture was then cooled to room temperature and extracted with ether, washed with water, dried over Na_2SO_4. Similar conditions were observed when the substrate was changed to 1-methyl-naphthalene and reaction time was increased to 8 hrs, 12 hrs and

20 hrs. The ether extract was analysed by Gas Liquid Chromatography method. The analysis of samples was carried out on Hewlett Packard Gas Chromatograph using Flame Ionization Detector.

The column of 2 meter length having liquid crystalline stationary phase was used (column No.II17, Table 1, Chapter II) for the separation of t-butylated products.

Results and discussion

Table No.1 and Table No.2 show the amount of different product formed in t-butylation of naphthalene and 1-methyl naphthalene using aluminium chloride as catalyst.

Tsukevanik and Terenteva[12] claimed that naphthalene reacts with tertiary alcohols forming a mixture of equal parts of mono and dialkylnaphthalene when aluminium chloride is used as catalyst. They also found that excess of $AlCl_3$ and prolonged heating results in polyalkyl naphthalene. The monoalkyl isomer may be α or β or mixture of α and β while F.M. Rowe et al.[19] found out that the monoisomer must be β and two ditert butyl naphthalenes are either 2,6 or 2,7 ditertbutyl naphthalenes. α-isomer which is formed in the beginning of the reaction gets transformed to β isomer on heating. Lazurin et al.[22] proved that mono-t-butyl isomer will be only 2-t-butyl naphthalene

which enhances the further introduction of other groups.

The GLC data of ether extract of the product formed during the reaction of naphthalene with t-butanol after different reaction time intervals is presented in Table I. Time factor has not shown remarkable effect on the total pattern of formation of different products. The change in % of mono, di, tri or tetra-t-butyl naphthalene compounds is the only difference found.

First peak shows the presence of unreacted naphthalene which is almost negligible after 5 hr reaction. Second peak at 2.11 minutes show the presence of mono-tertbutyl naphthalene. It may be α or β-tertbutyl-naphthalene or the mixture of these close boiling isomers. The single peaks at 5.8 and 6.3 minutes are due to the presence of ditertbutyl naphthalene isomers which are forming the major portion (34 and 43%) of the total yield respectively. Further products may be polyalkylation products (tri, tetra, tertbutyl naphthalenes) which are formed in less amount. The reaction mixture although showed separate peaks for the different tert-butyl naphthalene isomers they could not be identified due to unavailability of standard samples.

Most probably the monotertbutyl isomer must be thermodynamically[22] stable β isomer as the reaction has been carried out at 80°C. The ditertbutyl naphthalene isomers (confirmed by GCMS) must be either 1,4- and

1,2-ditertbutyl or 2,6- and 2,7-ditertbutyl naphthalene isomers[19]. Sometimes β isomer can give rise to 1,2-ditertbutyl naphthalene and in such cases another ditertbutyl naphthalene isomer will be 1,4-ditertbutyl naphthalene isomer (favoured para substitution).

In case of the tert-butylation of 1-methyl naphthalene (Table 2) separation of many products is achieved.

The peak at 1.15 minutes shows the unreacted 1-methyl naphthalene. The first countable peak (16-20%) must be due to mono-tertbutyl methyl naphthalene (confirmed by GCMS). Mostly this isomer must be 1-methyl 4-tert butyl naphthalene (para position of methyl group in the ring) as attack by bulky tert-butyl group will be causing steric hindrance if it goes at 2-position (ortho to methyl). The peak at 8.16 minutes forming around 40-70% portion of the total yield (amount varying according to reaction time) is 1-methyl ditert-butyl naphthalene (confirmed by GCMS). The activating (electron donating) groups promote the further substitution in the same ring in case of fused ring systems[23,24]. The another incoming tertbutyl group might have attacked the available ortho position of methyl group and 1-methyl 2,4-ditertbutyl naphthalene must have formed. Remaining products must be 1-methyl, tri-tetratertbutyl naphthalene

compounds which are formed in smaller amounts.

The liquid crystalline stationary phase could show the clear cut separation of the reaction mixtures.

Table 1 GLC data of reaction products of naphthalene and t-butanol (Fig I)

Retention time in	Reaction time in hrs Amount of products formed %			
minutes	5	8	12	20
0.89	1.32	1.02	0.72	0.6
2.11	3.31	3.83	3.2	6.98
5.8	33.55	36.13	34.94	37.72
6.3	42.66	48.13	45.63	48.58
8.0	1.08	1.19	1.15	0.96
8.8	1.14	1.215	1.24	0.96
12.9	1.23	1.63	1.65	1.05
15.3	6.05	3.04	3.41	1.41
19.94	4.45	3.21	4.08	4.0

Table 2 GLC data of reaction products of 1-methyl naphthalene and t-butanol (Fig II)

Retention time in	Reaction time in hrs Amount of products formed %			
minutes	5	8	12	20
1.15	2.5	2.1	1.98	1.17
1.69	0.6	0.92	0.32	0.71
2.95	16.5	17.2	20.36	22.93
6.5	1.36	1.0	1.33	1.28
8.16	66.85	55.46	48.79	38.27
9.54	1.25	3.12	1.65	1.97
10.86	3.73	8.50	5.71	5.8
12.9	3.1	4.25	2.76	2.6
21.00	2.07	3.04	1.76	1.98
24.1	1.54	10.56	3.87	5.1

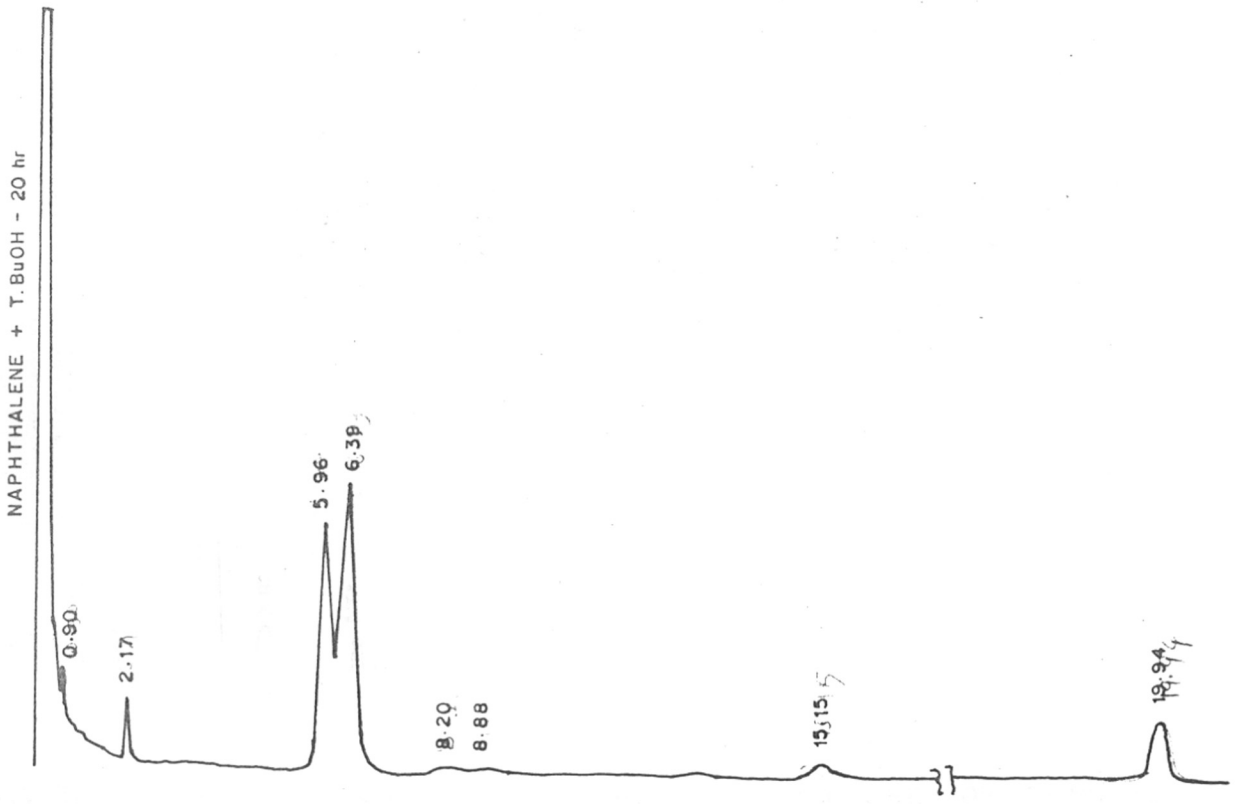


FIG I GLC ANALYSIS OF THE REACTION MIXTURE OF T-BUTYLATION OF NAPHTHALENE WITH T-BUTANOL IN PRESENCE OF ALUMINIUM CHLORIDE (Oven temp. 170, Injection temp. 150°C, Detector temp. 240°C and Detector type FID)

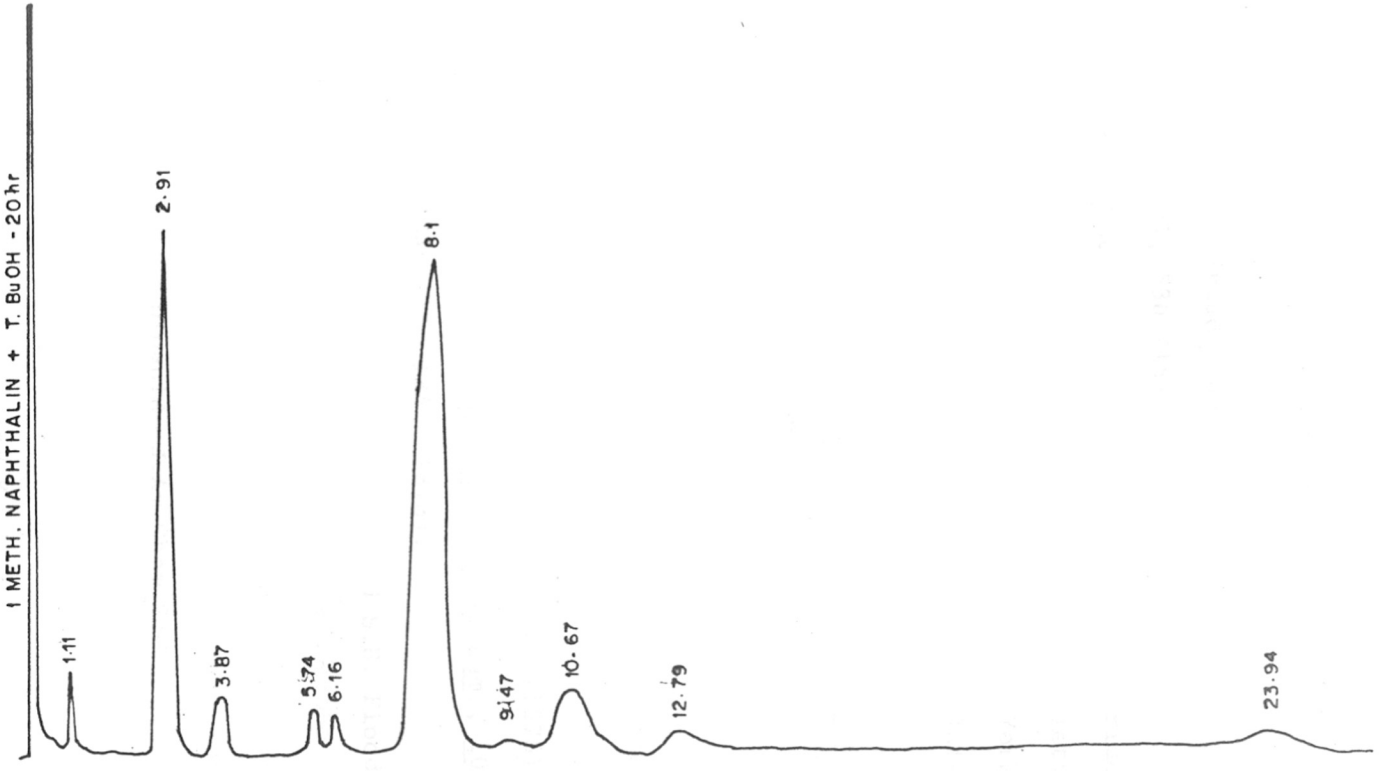


FIG II GLC ANALYSIS OF THE REACTION MIXTURE OF T-BUTYLATION OF 1-METHYL NAPHTHALENE WITH T-BUTANOL IN PRESENCE OF ALUMINIUM CHLORIDE (Oven temp. 180°C, Injector temp. 150°C, Detector temp. 240°C and Detector type FID)

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