COMPUTERISED

APPLICATION OF CHROMATOGRAPHY IN THE GAS-LIQUID CRYSTAL SYSTEM FOR THE SEPARATION OF ALKYL BENZENES COMPARED WITH CONVENTIONAL STATIONARY PHASES.

A Thesis Submitted to the

University of Poona

for the degree of

MASTER OF SCIENCE

(PARTLY BY PAPERS, PARTLY BY RESEARCH)

in Chemistry

NATIONAL CHEMICAL LABORATORY LIBRARY
No. TH-417
Date

547.53'021:543.544.25(043)
JAD

BY

MS. ANITA L. JADHAV
B. Sc. (Hons)

NATIONAL CHEMICAL LABORATORY
POONA 411 008 (INDIA)
MARCH 1983.

Dedicated

To My Mother

ACKNOWLEDGEMENTS

I would like to express sincerely my deep sense of gratitude to Dr. B.B. Ghatge, Scientist, NCL, under whose able guidance and encouragement the work presented in this thesis has been carried out.

I am thankful to Dr. R.B. Mitra, Dy.Director, for his keen interest throughout the progress of the work.

I would also like to express my gratitude towards Dr. L.K. Doraiswamy, Director, National Chemical Laboratory, for his kind permission to allow me to submit this work in the form of a thesis.

My sincere thanks are due to Drs. K.P. Naikwadi and B.V. Bapat for the invaluable help rendered by them throughout the course of the work.

I acknowledge with great pleasure the help rendered by all my colleagues, especially, Mrs. N.V. Bhalerao and Dr. D.G. Panse.

A Jadhav

(Ms. Anita L. Jadhav)

NCL, Poona-8

Date: 18th March 1983.

CONTENTS

Pages

CHAPTER – I

INTRODUCTION .. 1-41

References .. 42-51

CHAPTER - II

Experimental

(A) Synthesis of the laterally substituted liquid crystalline stationary phase .. 53-63

(B) Synthesis of some alkyl benzene positional isomers studied, using standard methods .. 64-80

(C) Experimental (GLC) .. 81-91

References .. 92

CHAPTER – III

Results and Discussion .. 93-133

References .. 134-136

CHAPTER I

INTRODUCTION

INTRODUCTION

The success of any scientific research depends largely on the rational choice and use of experimental methods. In chemistry, which is the science of structure and transformation of substances, the central experimental problem often consists in determining the composition of complex mixtures, trace impurities that contaminate the main substance and physicochemical characteristics of substances. The achievements in chemistry and the chemical industry during the past two decades are due in many respects to the vigourous development of gas chromatography, the wide use of which has led to revolutionary changes in the methods of organic and gas analysis and in many physicochemical methods. At present, gas chromatography is the most versatile and widespread method for the analysis of organic compounds. Most of the chemists and chemical technologists prefer gas chromatography as an analytical tool due to

1. Rapidity of analyses
2. High efficiency
3. Use of very small sample volume

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.

Historical Background

The development of gas chromatography began after James and the Nobel Laureate Martin published the first work on gas liquid chromatography[1,2].

Chromatography as a general method of separation, however, dates back to 1850 when F.F. Runge, a German chemist who described a process to separate certain dyes- known today as paper chromatography. W. Ramsay employed this technique around 1905 for separating mixtures of gas and vapours. The term 'chromatography' (meaning colour writing) was coined in 1906 by the Russian botanist Mikhail Semyonovich Tsvet (1872-1919) who proposed an adsoprtion chromatographic method of separation in the liquid phase and described its application to the analysis of chlorophyll in plants[3]. Carotenoids and related pigments were separated by Palmer[4] in 1922, while Kuhn et al. demonstrated the separation of the carotenes and xanthophylls in egg yolk[5].

Classification of the chromatographic methods

Chromatography can be defined as a physical process of separation in which the components to be separated are distributed between two phases- a stationary phase having large surface area (e.g. a porous solid) and a mobile phase

(a gas or a liquid) moving in contact with the stationary phase. The sample components are selectively retained by a stationary phase due to the difference in the equilibrium distribution of the sample components between the two immiscible mobile and stationary phases respectively.
Table I presents the classification of chromatographic methods depending upon the state of either stationary or mobile phase and the mechanism of retention involved. The present work is on gas liquid chromatography hence the other chromatographic methods are not discussed further.

Gas liquid chromatography (GLC)

The present wide-spread use of gas chromatography is associated with the implementation of gas-liquid chromatography. When working out the method of liquid-liquid partition chromatography, Martin and Synge[2] suggested the use of gas as the moving phase and the first paper on the application of gas liquid partition chromatography was published in 1952 by James and Martin[1].

Basic principles and the theory of gas liquid chromatography (GLC)

In the GLC method of analysis, the sample mixture is rapidly volatilized in the injection port at a suitable temperature. The sample vapour is introduced as a plug into

Table I

Stationary Phase	Nomenclature	Method of implementation	Interaction involved
A. Liquid Chromatography (mobile phase is liquid)			
I Solid			
a) Solid	Liquid-solid chromatography	Paper, TLC, Column	Absorption
b) Organo Gels	Gel-permeation chromatography	Column	Permeation
c) Ion-exchange resins	Ion-exchange chromatography	Paper, TLC, Column	Ion-exchange
II Liquid	Liquid-Liquid chromatography	Paper, TLC, Column	Partition
B. Gas Chromatography (mobilephase is a gas)			
I Solid			
a) Solid	Gas solid chromatography	Column	Adsorption
b) Liquid + solid adsorbent	Gas solid or adsorption layer chromatography	Column	Molecular sieving
II Liquid	Gas liquid Chromatography	Column	Partition

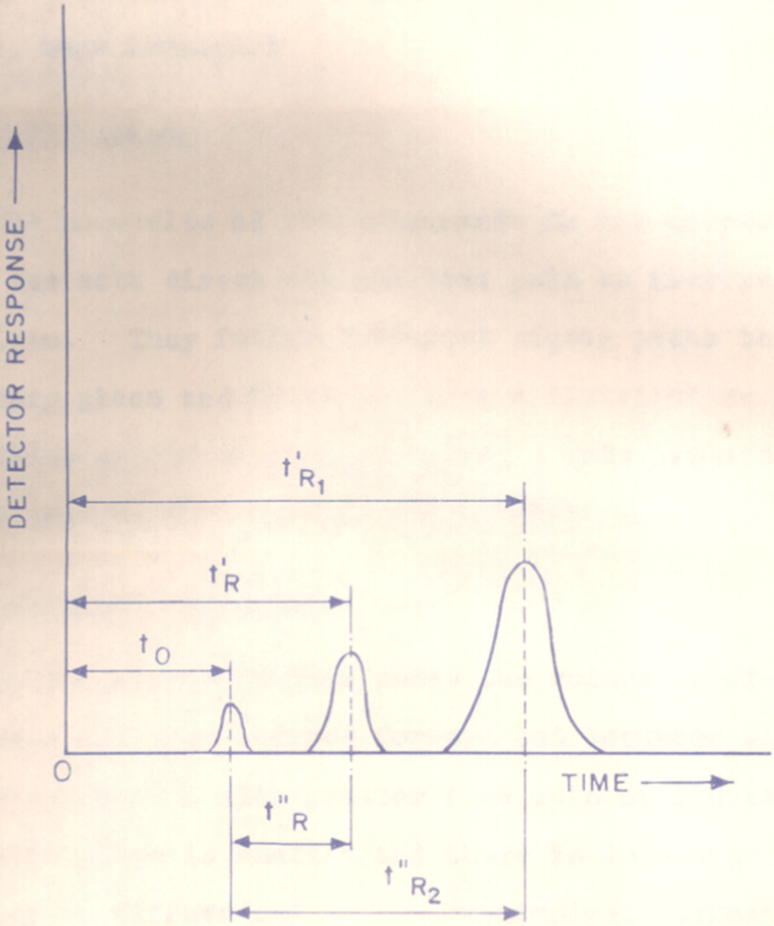
the carrier gas stream in a very thin, sharp and narrow zone at the inlet of the column. The carrier gas called the mobile phase flows through the column continuously and the sample components get distributed between the two heterogenous phases. As the carrier gas moves forward, the partitioning of the components between the two phases is followed by diffusion and mass transfer operations and finally the components emerge out of the column and are detected. The time required for the elution of each component is called the retention time ($t'R$). A component that is not retained by the stationary phase leaves the chromatographic column at time (t_o)- the so called dead time (the time needed by the front of the carrier gas to go through the column). A measure of the interaction of a component with the stationary phase is given by the value of the net retention time ($t''R$). (Figure 1).

$$t''R = t'R - t_o$$

The retention time is measured from the time of sample injection to the time at which peak height is maximum.

Initially, though the sample components are concentrated in a narrow zone at the injection end of the column, the zone widens as it moves with the carrier gas and becomes more diffuse. The three basic reasons for zone broadening are:-

FIGURE 1.



1. Eddy diffusion
2. Longitudinal diffusion
3. Mass transport

1. Eddy diffusion

The molecules of the components do not necessarily follow the most direct and shortest path as they pass through the column. They follow different zigzag paths through the stationary phase and therefore have a distribution of velocities around an average value. This process which leads to peak broadening is called eddy diffusion.

2. Longitudinal diffusion

In the gaseous mobile phase the molecules of the components can also diffuse forward and backward along with the carrier gas. With greater flow rate of the carrier gas the elution time is smaller and there is less time for the molecules to diffuse and hence longitudinal diffusion becomes less important at higher flow rates.

3. Mass transport

The repeated transfer of the molecules from the stationary phase to the mobile phase is diffusion controlled. The resistance to mass transfer in the column, which prevents instantaneous equilibration of the solute molecules between the two phases, is the main cause of peak broadening i.e., peak broadening is a measure of non-equilibrium due to resistance to mass transfer in the column.

The efficiency of the chromatographic column is thus related to peak broadening. The various factors that affect the GLC separation process are explained in the different theories of gas liquid chromatography.

1. Theory of the packed columns

a. Plate theory

b. Rate theory

a. Plate theory

The plate theory was introduced by Martin and Synge[6] and improved by Mayer, Tompkins[7] and Glueukauf[8]. The efficiency of the column can be calculated from the equation,

$$N = E = 16 \left(\frac{\text{retention distance to peak maxima}}{\text{peak width at the base}} \right)^2$$

where, N = number of theoretical plates.

The unit of efficiency is the 'theoretical plate' a term borrowed from the distillation terminology[9,10]. Theoretical plate is defined[11] as the length of the column required to establish an equilibrium between the vapour pressure of the solute in the gas phase to the vapour pressure of the solute in the liquid phase. When the number of theoretical plates and the length of the column L, are known, the value of the height equivalent to a theoretical plate (HETP) may be expressed as

$$\text{HETP} = \frac{L}{N} = \frac{L}{16}\left(\frac{\text{retention distance to peak maxima}}{\text{peak width at the base}}\right)^2$$

HETP is the peak broadening relative to retention time. Low values of HETP correspond to greater number of theoretical plates i.e. high column efficiency.

b. <u>The Rate theory</u>

The Van Deemter, Zuiderweg and Klinkenberg's[12] equation for rate theory was evolved from the deduction of Lapidus and Amundson[13] and by extention of Glueckauf's theory[13a]. The relationship between the efficiency and the various column parameters is equated.

$$H = 2\lambda d_p + \frac{2\,\gamma D_G}{\mu} + \frac{8}{\pi^2} \times \frac{K}{(1+K)^2} \times \frac{d_f^{\,2}\mu}{D_L}$$

where $H = \text{HETP} = \dfrac{\text{Column length}}{\text{Column efficiency}}$

λ, γ = constants

d_p = the support material particle size

d_f = stationary phase film thickness

D_G = Diffusion coefficient of sample in gas

D_L = Diffusion coefficient of sample in liquid

K = Partition coefficient

μ = the linear gas velocity through the column

The above equation can be simplified as follows:

$$H = A + \frac{B}{\mu} + C\mu$$

where, the constant A is called the eddy diffusion term and to minimise A i.e. to increase column efficiency, support material should have particles of smaller diameter. This term is zero in capillary columns, which have open cross sections without any packing support material. The term B/μ contributes to peak broadening due to longitudinal diffusion of the molecules in the carrier gas. High gas velocities reduce this term. $C\mu$ is a most significant factor and contributes to the plate height due to resistance to mass transfer.

2. Theory of open tubular columns

The invention of open tubular, or as they were first called capillary columns is linked with the name of Golay[14]. He described the performance of the capillary columns as

$$H = \frac{B}{\mu} + (C_L + C_G)\mu$$

where, C_L = diffusion resistance in the liquid phase

C_G = diffusion resistance in the gas phase

The eddy diffusion term is absent as there is no packing.

Resolution

Optimum effective separation of sample components can be achieved depending upon column efficiency and column selectivity. Column or stationary phase selectivity is defined as the difference between the retention times of two components. The greater the difference in retention times of the two components the greater the column selectivity. The separation factor of components A and B having retention times $T'R_A$ and $T'R_B$ respectively is given as

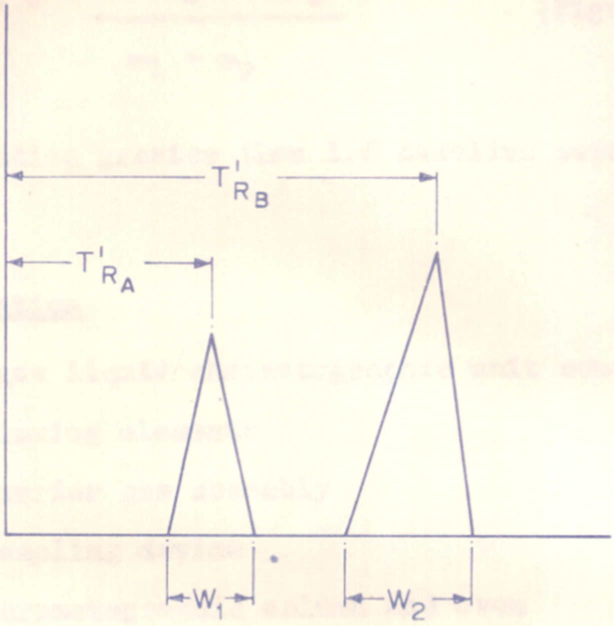
$$\text{Separation factor } (\alpha) = \frac{T'R_B}{T'R_A} \qquad \text{(Figure 2)}$$

A high separation factor is obtained for A and B when the distance between the peak maxima is greater than the combined half width of the two peaks at the base

$$\text{i.e. } T'R_B - T'R_A \geq \frac{\omega_1}{2} + \frac{\omega_2}{2}$$

The resolution (R) of the column is the extent of separation of the two components, it depends on the sharpness of each peak and the separation between two peaks i.e. it combines both efficiency and the separation factor.

FIGURE 2.



$$\text{SEPARATION FACTOR } (\alpha) = \frac{T'_{R_B}}{T'_{R_A}}$$

$$\text{RESOLUTION } (R) = \frac{2\,(T'_{R_B} - T'_{R_A})}{w_1 + w_2}$$

$$R = \frac{2(T'R_B - T'R_A)}{\omega_1 + \omega_2} \qquad \text{(Figure 2)}$$

With resolution greater than 1.5 baseline separation is achieved.

Instrumentation

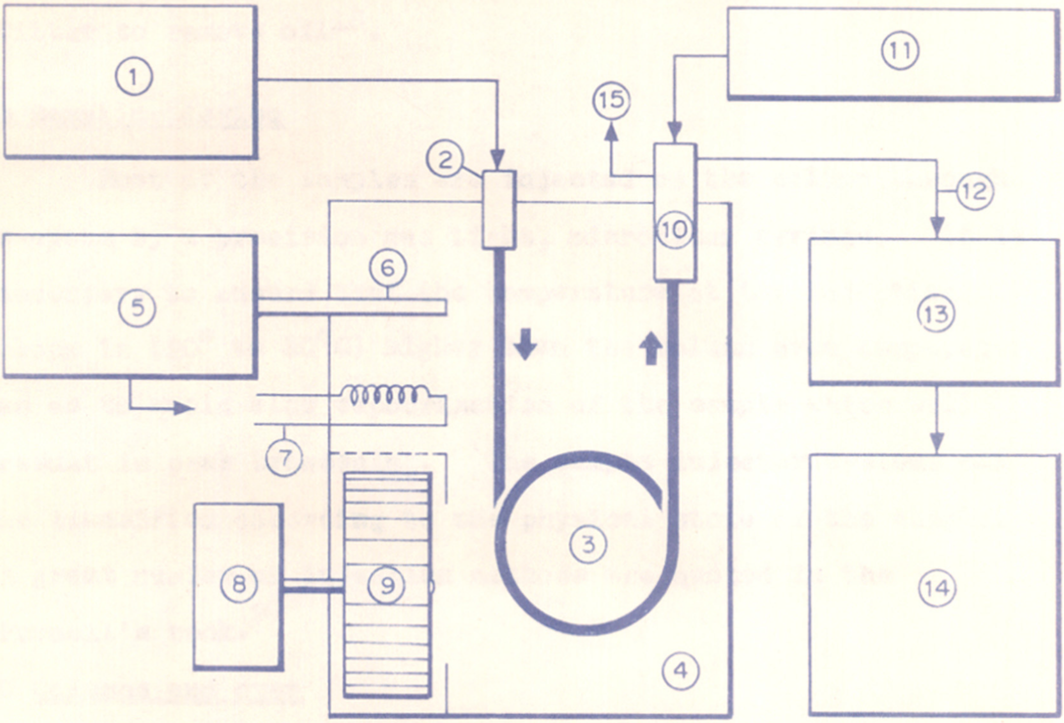
The gas liquid chromatographic unit consists basically of the following elements

A. Carrier gas assembly
B. Sampling device
C. Chromatographic column and oven
D. Detectors
E. Recording and evaluating system

Block diagram of the GLC apparatus is shown in (Figure 3).

A. Carrier gas

Carrier gas is usually supplied from a cylinder fitted with a double stage regulator. The most commonly used carrier gases are helium, argon, nitrogen and hydrogen. The choice of a carrier gas depends upon the detector system being utilised (e.g. TCD detector- hydrogen helium are used) The carrier gas should be inert to the system employed. To avoid impurities such as water, oxygen, oil vapours etc. which can affect the liquid phase or the detector, it is



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 GASES OUTLET

FIG. 3. CHROMATOGAPHIC APPARATUS SHOWN SCHEMATICALLY

purified by passing through a molecular sieve and fine filter to remove oil[15].

B Sampling device

Most of the samples are injected on the column through a septum by a precision gas tight, microliter syringe. It is necessary to ensure that the temperature at the injection block is (20° to 50°C) higher than the column oven temperature so as to avoid slow vapourization of the sample which will result in peak broadening. The sample injector systems can be classified according to the physical state of the sample. A great number of injection methods are quoted in the Purnell's book.[9]

C Columns and oven

Columns made from copper aluminium, stainless steel[16] and glass tubings are generally used in GLC analysis. They are usually coiled for compactness. There are basically three types of columns: packed, capillary and preparative. Packed columns used for routine analytical work are three to 10 ft long with internal diameter 2 to 4 mm. Capillary columns are used for separations of complex mixtures and may be 50 to 100 feet long or more with internal diameter between 0.25 and 0.5 mm. Preparative GLC column tubings have about 9 to 12 mm diameter. The GLC column is enclosed in an oven made of metal block. The temperature of the oven can be controlled to atleast ± 1°C.

D. Detectors

An efficient detector can detect continuously, rapidly and with high sensitivity the components which appear in the carrier gas as it emerges from the column. The detector senses the changes in a certain physical or chemical property of the effluent gas stream on the appearance of the components. A number of books[17,18] and review articles[19,20,21] that treat the theory, operation mode and detector characteristics in detail, have appeared recently. The thermal conductivity and flame ionisation detectors have been in use for a long time.

Thermal conductivity detector (TCD)

The thermal conductivity detector remains to be a 'universal' detector today and cannot be replaced by the more sensitive and/or more specific detectors because of its simplicity, stability, versatility and low cost.

Thermal conductivity is the transfer of kinetic energy due to a temperature gradient. The use of this principle in a gas chromatographic detector necessitates that the column effluent to be measured, flow through a cavity. The cavity is generally contained in a metal block which is heated to constant temperature. Within the cavity is contained a hot element whose heat losses to the heated block occur at a rate dependant upon the thermal conductivity of the detector. Thus, with a constant current passing through the filament, the heat transfer is constant under equilibrium conditions. When a vapour component enters the cavity, the different thermal conductivity of the gas changes the heat transfer mechanism within the cavity, this changes the temperature of the hot element. A change in temperature of the filament is accompanied by a change in its resistance, which causes an imbalance in a bridge circuit, and results in an analogy signal being sent to the recorder. The extent of imbalance is proportional to the vapour component causing the change. A Wheatstone's bridge circuit with four elements (for high sensitivity, stability and dual column operation) forms the thermal conductivity detector and it measures the difference in thermal conductivity between a carrier gas and component. These elements can be thermistors, hot wires or transistors. The TCD has a very extensive literature including several general reviews[10,22,23].

Flame ionisation detector (FID)

The flame ionisation detector (FID) was introduced in 1958[24,25]. It possesses several outstanding features.

1. It responds to virtually all organic compounds with high sensitivity.

NATIONAL ... L... No TH-417
Date
547.53'021:543.544.25(043)
JAD

2. It does not respond to common carrier gas impurities such as water or CO_2.

3. It has minimal effects from flow, pressure or temperature changes.

4. In the absence of sample, it has virtually no response. This gives a stable baseline.

5. Linearity is good for a range as high as 10^8. The detector consists of a small hydrogen- air diffusion flame burning at the end of a jet- the tip of a length of capillary tubing. When organic compounds are introduced into the flame from the column, electrically charged species are formed. These are collected by applying a voltage across the flame. The resulting current is amplified by an electrometer and recorded as a signal. The lack of response to air and water makes this detector suitable for the analysis of pollutants, aqueous samples, biological materials etc. It does not respond to carbondisulphide which make CS_2 a convenient solvent used for diluting the component mixtures.

The other commonly used detectors are hydrogen flame detector, electron capture detector, flame photometric detector, mass spectrometer[26,27], helium ionisation detector and several others.

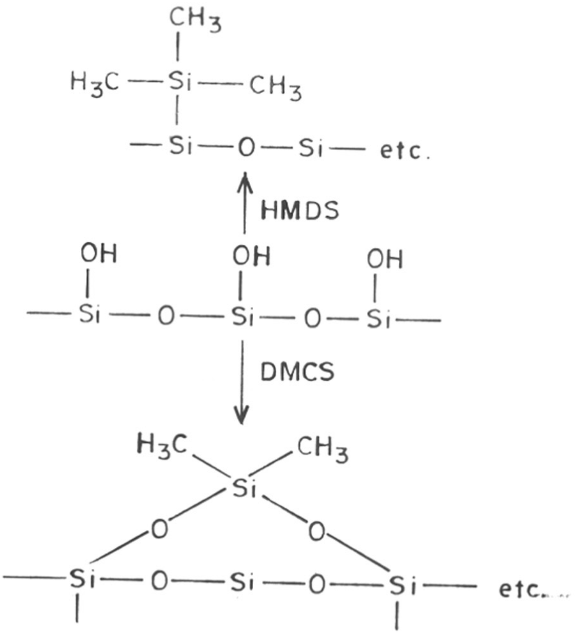
E. Recorders and integrators (evaluating systems)

The response of the detector is plotted by the recorder which furnishes the chromatogram, the result of the analysis. 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. Integrators are coupled to the detector or recorder to give an output which is proportional to the total mass of substance eluted from the column. A two pen recorder to trace both peak and time integral was developed by Doolen[28].

Computers are now a days used to process GLC data. Measurement of peak areas and retention time with high accuracy, correction for baseline drift and analysis of partially resolved peaks by a curve-fitting procedure to obtain percentage of each component are some of the operations carried out using computers.

Solid supports

Solid supports are employed primarily to hold the liquid phase well distributed while allowing the gas to pass over the liquid phase. The support material should be porous, it should be inert towards both the stationary phase and sample and the particles should be of uniform size. The diatomite skeletons form basically the support material. The trade name for this diatomaceous silica is celite. An extensive study by Baker and coworkers[29] of pore size distribution and other characteristics of celite showed that most of the liquid phase is located in the fine pores with a thin layer over the remainder of the support. The celite surface is covered by hydroxyl groups. Hence peak tailing is observed for samples having free hydroxyl or acidic groups. The peak tailing can be reduced by treating celite with a silylating reagent such as hexamethyldisilazine (HMDS) or dimethyldichlorosilane (DMCS)[30,31].



Alkali treated solid support is suitable for separating strongly basic nitrogen compounds. The tailing observed for free acid samples is minimized by treating celite with phosphoric acid.

The Stationary Phase

The selection of a proper stationary phase to get good separation of the components of a mixture is always very critical.

The principal factors in selecting appropriate liquid phase are summarized below.

1. Low vapour pressure at operating temperature.
2. Chemical stability and low viscocity at operating temperature.
3. Selectivity for the components to be separated.
4. Reasonable solubility in some common solvent.

Although at the very beginning of GLC it was clear that the solute-stationary phase chemical interactions play a most important role in the separation processes[32,33,34] the choice of stationary phase has been mainly emperical.

The relatively recent necessity to separate isomers with very similar physical and chemical properties has stimulated increased attention to the principles that are fundamental to the selectivity of stationary phases.

Liquid phases are primarily distinguished by their polarity and it is related to the ratio of the polarizable groups to the non-polar groups in the solvent molecules. Rohrschneider[35] investigated the relative polarity of various liquid phases on the basis of their retention of different types of hydrocarbons. Maier and Kárpáthy have carried out a similar classification[36]. These types of graphic representations provides means for the selection of a liquid phase with appropriate polarity for the separation of the components of a sample. The selectivity of a stationary phase is altered by change in temperature[36a]. 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[37], molecular weights[38], number of carbon atoms in the molecule[39], or vapour pressures[40]. Taking into account the huge number of compounds suggested for use as stationary phases in GLC, their classification is rendered difficult due to their different structures and properties. Littlewood[10] has suggested the following four groups of stationary phases.

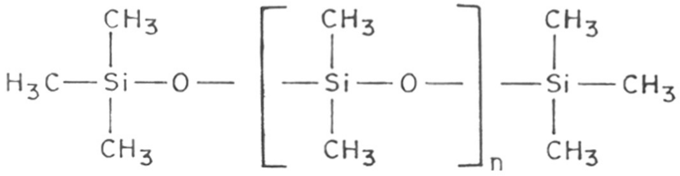
I <u>Non polar stationary phases (paraffinic)</u>

These include all alkanes and mixtures of alkanes and alkyl silicones. The paraffinic stationary phases are a very good medium for solubilization of hydrocarbons that generally elute in the order of increasing boiling point. The hydrocarbons are much more soluble in these stationary phases than any polar solute with a similar boiling point. Because non-polar stationary phases do not interact specifically with the solutes to be separated, they can be used in gas chromatography as reference stationary phases. The commonly used stationary phases of this group are

1. Methyl silicones
2. Squalane
3. Apiezon greases

1. Methyl silicones

These are among the most widely used non-polar stationary phases. Some papers dealing with the chemistry and their use as stationary phases in GLC have been published[42,43,31]. The methyl silicones are practically inert, being attacked only by halogens, halogenated acids and a few strong bases. Their general formula is



$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\left[-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\right]_n-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-CH_3$$

Their relative low viscocity and high thermal stability allows the use of silicone oils over wide temperature ranges

(-50 to 300°C). These stationary phases are generally loaded in a low proportion on a solid support. Treatment of hexamethyldisilazone or dimethyldichlorosilane is given to the solid support to overcome undesired effects at the surface of the solid support[31,44,45].

Methyl silicone stationary phases are marketed under various commercial names egs:- General electric supplies methyl silicones under the names: SE-30; SF-96; E-301, VISCASIL. Dow Corning under the names: DC-200; DC-11; DC-220. Applied sciences under the names: JXR; OV-1, OV-101. New a days silicones are chemically bonded to solid support (celite, silica gel, glass beads) by polymerisations. Karasek[46] has reviewed the nature and uses of chemically bonded phases.

2. Squalane (2, 6,10,15,19-23- hexa methyl tetra cosane)

Squalane is used for the separation of C_5-C_8 hydrocarbons[47,48], some mercaptans[49] and anaesthetics[50].

3. Apiezon greases

Apiezon greases are widely used as liquid phases for the separation of many classes of compounds Apiezons are obtained by subjecting selected lubricating oils to a high temperature treatment.

According to the temperature of the heat treatment, the Apiezons are classified alphabetically: C, E, H, J, K, L, M, T. Apiezon L is the most widely used as it has low vapour pressure and allows higher operating temperatures.

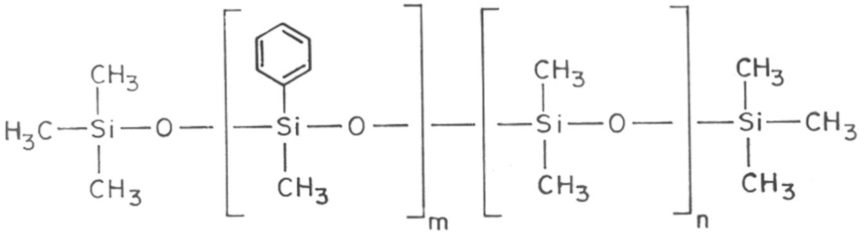
II Dilute stationary phases

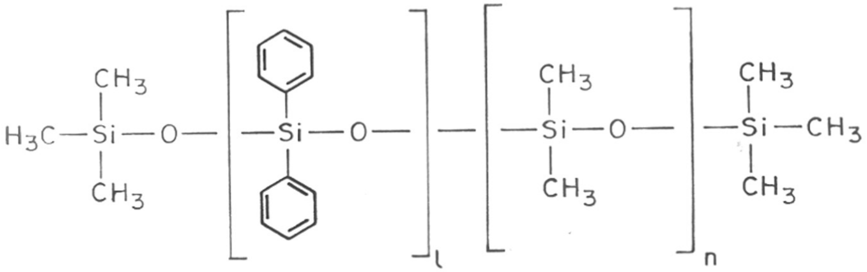
The main characteristic of this class is that its members readily dissolve the polar solutes as well as those that are non-polar thus being of universal use as stationary phases in GLC. Their retention characteristics are determined by the fact that they have polar groups with which polar solutes can interact, but not so many as to make a strongly cross-linked solvent lattice, the internal pressure of which is such as to exclude non-polar molecules.

Phenyl silicones

Substitution of phenyl groups into methyl silicones increase the solubility parameter to something approaching that of benzene. The phenyl groups improve the oxidation stability and lubricating properties. They are among the most heat resistant. Among the phenyl silicones there are:

(a) Phenyl silicones with a small content of phenyl groups.





Some of the commercial names are

DC-701, MS 510, OV-3 (10% phenyl, 90% methyl)

OV-7 (20% phenyl, 80% methyl),etc.

(b) Phenyl silicones with a medium content of phenyl groups.

examples: OV-17 (35% phenyl, 65% methyl)

OV-61, DC-703, etc.

(c) Phenyl silicones with a high content of phenyl groups

examples: OV-25 (75% phenyl, 25% methyl)

DC 710, OE 4011, etc.

The other methyl phenyl silicones include, methyl chlorophenyl, methyl phenyl vinyl, methyl cyanopropyl phenyl silicones respectively.

Some aromatic compounds like benzyl diphenyl, alkylnapthalene, phenyl acetonitrile, dibenzyl ether and several others may also be classed as dilute stationary phases.

III Concentrated stationary phases

These stationary phases contain polar groups. The polar part may be the 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. Many stationary phases from this class interact with solutes to be separated, forming hydrogen bonds. They are generally unsuitable for hydrocarbon analysis. Polar solutes have considerable retentions in these stationary phases and it is for these that they are principally used. A few examples of concentrated stationary phases are given below.

1. <u>Water</u>: Karger et al.[51,52] have reported the use of water as a liquid stationary phase in GLC. Separation of octane isomers on 10% w/w water porasil C column was obtained.
2. Among the nitrile stationary phases the most widely used is 1,2,3-tris (2 cyanoethoxy)-propane[53].
3. Stationary phases that contain nitro groups are used for the separation of aromatic hydrocarbons from alkanes, substituted aromatic hydrocarbons and low boiling halogenated hydrocarbons.[54,55]

4. Poly(ethylene glycols) obtained by polymerisation of ethylene oxide are the commonly used stationary phases in GLC. The principal factors determining the retention characteristics of these phases are the presence of moisture, the concentration of the hydroxyl end groups and to a very much smaller degree the molecular weight distribution of the liquid phase[56]. Some of the polymeric stationary phases are poly(ethylene glycol), poly(styrene oxide), poly(vinyl formyl propionitrile) etc.

5. The linear polyesters stationary phases can be synthesised from a number of dibasic acids and glycols. Polyesters are generally recommended as stationary phases for the separation of fatty acids, methyl esters, essential oils, steroids, etc.

6. Fused inorganic salts are used as stationary phases for the separation of metal halides[57].

IV Specific stationary phases

These stationary phases react specifically with a particular class of solutes. The interactions between the stationary phases and solutes must, on one hand be strong enough to provide the specificity and on the other hand, be sufficiently labile to remove the components to be analysed from the stationary phase.

The transition metal complexes form a group of specific stationary phases. Separation of olefins has been obtained by using dicarbonyl-rhodium (I) trifluoro acetyl camphorate[58]. Bradford et al. reported high selectivity of silver nitrate-ethylene glycol as a stationary phase for the separation of butenes[59]. The analytical potential of silver nitrate ethylene glycol columns was evaluated by Smith and Ohlson[60]. Recently, Wasik and Tsang[61] used aqueous silver nitrate as stationary phase. Instability of silver nitrate columns at higher temperatures restricts its application to low boiling compounds. Thallium (I) nitrate in diethylene glycol as a stationary phase improves the stability of silver nitrate columns at high temperatures without loss of selectivity[62].

A very selective phase for the separation of isomeric xylenes is Bentone-34. It is obtained by treating bentonite (a clay, $Al_2O_3(SiO_2)_4H_2O$) with dimethyldioctadecyl ammonium salts. This material was first used for GLC by White and Cowan[63]. The organo-clay compound is so selective in its retention of the m-isomer that the elution order of xylenes is para, ortho, meta, respectively. The selectivity of Bentone-34 can be attributed to its layer structure; the adsorption of the solute between the layers of the expanded clay depends upon its geometrical shape.

Mortimer and Gent[64] found that the peak symmetry is improved by using Bentone-34 modified with a conventional stationary phase. The most used modifying solvent for Bentone-34 is silicone oil[65,66].

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

Liquid crystals as stationary phases

A. Introduction to liquid crystals

Liquid crystal compounds have been known for about 100 years, but their application in GLC began recently[67]. 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 chromatography[68-73].

The recent upto date literature reveals the popularity of the use of liquid crystal stationary phases. K. Watabe and co-workers[74,75,76] have made a detailed study of the influence of an electrical field on the nematic phase. They[77] have also carried out the determination of peak overlapping with a liquid crystal stationary phases Witkiewicz et al.[78] have developed new liquid crystalline phases containing napthalene fragments in their molecules. The effect of solid support on the properties of liquid crystalline stationary phases has been investigated by Janini et al.[79] An upto date review on liquid crystal stationary phases for GLC has appeared in the December volume of Journal of Chromatography (Chromatographic reviews) 1982 by Z. Witkiewicz[80].

B. History

It is generally accepted that matter exists in three states: solid, liquid and gas. However, this is not quite correct, in particular, certain organic materials do not show a single transition from solid to liquid, but rather a cascade of transitions involving new phases; the mechanical properties and the symmetry properties are intermediates between those of a liquid and those of a crystal. For this reason they have been called 'Liquid Crystals'.

Recognition of the liquid crystal phase was made in 1818 by Reinitzer[81] a botanist, who synthesized cholesteryl benzoate and found that it had two melting points. The solid melted at 145°C to give a turbid liquid, which changed sharply to a clear liquid at 179°C. O. Lehmann[82] showed that the turbid liquid was birefringent and hence anisotropic and he therefore classified it as liquid crystalline. Friedel[83,84] proposed the name mesophases because they lie between the solid and liquid phases.

C. Classification of liquid crystals

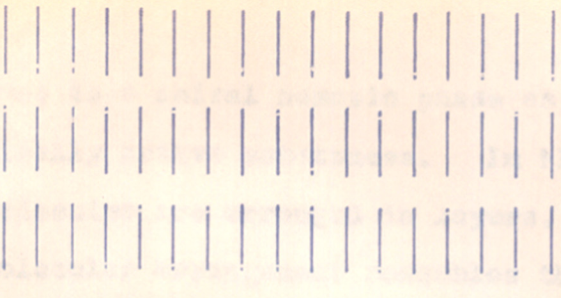
Liquid crystals can be divided into two main groups. Those in one group are classified as *thermotropic liquid crystals;* compounds in this class are obtained by heating a solid and exist only in a specific temperature range. *Lyotropic liquid crystals* constitute the second group and are obtained by mixing two or several components, an amphiphile being usually one of the components.

Only thermotropic liquid crystals are at present being used in chromatography. Most compounds that exhibit thermotropic mesomorphism can be classified by two structures (A) Smectic, (B) Nematic. (Figure 4 a,b). In the smectic structure the molecules are not only arranged parallel to one another but also are fixed in layers (Figure 4a). According to Demus[85] atleast seven different types of smectic phases can be observed.

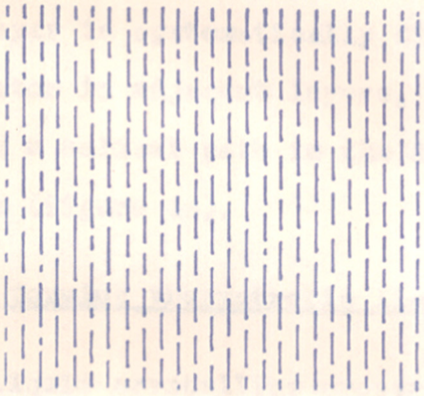
The nematic[86] phase owes its name to its microscopic thread like appearance. The molecules in the nematic structure are aligned preferentially along one direction. They are positionally disordered but orientationally ordered (Figure 4b). At higher temperatures they undergo a transition to a conventional (isotropic) liquid phase (Figure 4d). The cholesteric phase is assumed to be a variety of the nematic

FIGURE 4.

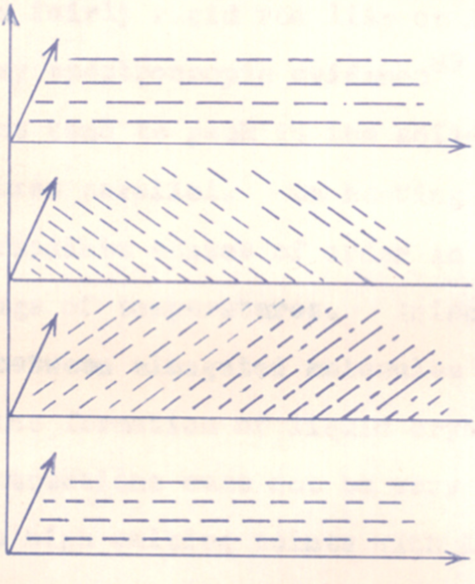
a. SMECTIC



b. NEMATIC



c. CHOLESTERIC



d ISOTROPIC

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 director in adjacent layers, with the overall displacement tracing a helical path in the direction normal to the molecular planes (Figure 4c).

D. Requirements for forming thermotropic liquid crystals

Thermotropic liquid crystalline property is shown only by elongated fairly rigid rod like or lath like molecules. X-ray spectroscopic evidence[87] indicates that rod-like molecules tend to pack in the solid crystal state with their long axes parallel. On heating they pass through one or more intermediate states of order in a stepwise manner over a range of temperatures. Anisotropy of the cohesive forces between elongated molecules is therefore a requirement for the formation of liquid crystals. The intermolecular attractions 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 for a liquid crystal to be formed, the cohesive forces operating between the elongated molecules must be anisotropic and of suitable magnitude.

E. Compounds forming thermotropic liquid crystals

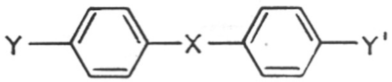
Mesomorphism is found in aromatic, aliphatic, multi-ring and polymeric compounds. Compounds forming liquid crystals have been described in a series of reviews and monographs[70,71,87-91]. Aromatic compounds form the largest group of known compounds exhibiting mesomorphism. Bernal and Crowfoot[92] proposed 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 $-\underset{\overset{\|}{O}}{C}-O-$ towards the extremities of the molecule.

A summary of 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 the relative flexibility of the long chains in compounds of the paraffinic series. It has generally been well established that the nematic phase is superior to smectic and cholesteric phases for GLC separations of positional isomers[70,93]. Liquid crystal compounds with a nematic mesophase have been most thoroughly investigated[94].

F. Analysis of structural and positional isomers

The interaction forces in the sorbate-liquid crystal melt system, due to the ordered arrangement of molecules in the temperature range of the mesophase, promote the separation of aromatic meta- and para- isomers with similar boiling points. This effect, first observed by Kelker[69,95] and Dewar and Schroeder[96] using p,p'-azoxyanisole, proved to be characteristic of many liquid crystals; it is associated with the fact that the more closely linear form of the molecule of the para-isomer compared with the meta-isomer enables the former to penetrate more readily into the lattice of the liquid crystal and is accordingly more strongly retained.

Above the clarification point the order of elution of isomers is usually determined by their boiling points[73]. The results of the above investigations led to extensive analytical use of liquid crystal sorbents. Several reports on the separation of alkyl napthalenes[97] polycyclic aromatic hydrocarbons and their derivatives[98-101], disubstituted benzenes[102-104], phenol ethers[105], high boiling hydrocarbons[106], polychlorinated biphenyl[107], methyl esters of methoxy benzanthracene[108] and benoxaprofen[109] have appeared in literature. Cholesteric stationary phases have also been used in GLC, but these phases are non-selective towards meta- and para-isomer separations while steroid epimers have been separated using nematic liquid crystals[110]. M.S. Vigdergauz et al. have reviewed the analytical and physicochemical aspects of GLC using liquid crystal sorbents, up-to-date[111].

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[112-115].

A number of polyesters were synthesised from different aliphatic dicarboxylic acids and diols and it was found out that the number of methylene groups between two carboxylic groups of the acidic fragment of the polyester has a profound influence on the degree of separation. Ghatge et al.[116,117] have synthesised different alkyl phthalates as well as aromatic and substituted aromatic polyesters stationary phases. It was specially observed that the introduction of amino group in phthalic acid and preparing polyester with 1,3-propanediol has shown selectivity for isomeric chlorinated compounds.

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 selective 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[118-120] several new laterally substituted liquid crystalline stationary phases and has studied the applications[121-123] of these phases for the separations of various positional isomers.

Introduction to Present Work

The importance of nematic liquid crystals in gas liquid chromatography (GLC) depends on their ability to separate positional isomers irrespective of their boiling points. The topic was first reviewed by Kelker and Schivizhoffen[68], subsequently by Schroeder[93], Janini[94] and more recently by Vidgergauz et al.[111], with up-to-date uses of liquid crystals for the separation of different classes of compounds.

The separation and identification of structural and positional isomers of mono-, di- and trisubstituted alkyl benzenes has industrial importance. Retention indices[124,125], Kovats retention indices[126] and a linear free energy relationship[127] have been used for structural determinations of alkyl benzenes. Several workers have attempted to separate alkyl benzenes using different commercially available stationary phases, with columns of varying lengths[128-132] and material. The separation of benzene, toluene, ethyl benzene and o-, m- and p-xylenes using a polar solid stationary phase was carried out by Belyakova et al.[133] A. di Corcia et al.[134] used Carbopack C modified with 2,4,5,7-tetranitrofluorenone (TeNF) as a stationary phase to separate alkyl benzenes. There are several references[65,135-137] for the use of Bentone-34 in a modified form as a stationary phase giving improved resolution and separation, but here too, the columns used are of considerable length[136] and the analyses time is long. Bentone-34 (dimethyloctadecyl ammonium bentonite) is a technical product consisting of bentonite clay treated with an ammonium base. The characteristics of the clay vary from batch to batch, giving rise to difficulties in the exchange reaction with the ammonium base, whence follows the poor reproducibility of the retention characteristics. The non-uniformity of the distribution of isomeric xylenes requires the modification of bentone with a silicone or dinonyl phthalate in appropriate proportions. As a consequence of the non-reproducibility of the results, this ratio also varies from batch to batch. Compared with bentones, liquid crystals have the following advantage: being individual organic compounds and being fairly pure, they ensure the reproducibility of the selective properties. Vernon and Khakoo[104] found liquid crystalline stationary phases to be superior to Bentone-34. Maidachenko et al.[138] have patented the use of liquid crystals as a stationary phase for alkyl benzene separations.

The major energy project in our laboratory is concerned with isomerisation of xylenes, ethylation and isopropylation of benzene and aromatization of ethylene which gives rise to different alkyl benzenes. This prompted us to investigate the suitability of the liquid crystal phases developed by us[119,121] for the separation and identification of alkyl benzenes using gas liquid chromatography and to compare the application of a liquid crystalline stationary phase with the conventional stationary phases such as SE-30 and OV-17.

REFERENCES

1. A.T. James and A.J.P. Martin, Biochem.J., 50, 679 (1952).
2. A.J.P. Martin and R.L. Synge, Biochem.J., 35, 91 (1941).
3. M.S. Tsvet, Proc.Warsaw Soc.Nat.Sci.Biol., Sec. 14, No.6 (1903).
4. L.S. Palmer, 'Carotenoids and related pigments' Chemical Catalogue Co., New York (1922).
5. R. Kuhn, A. Winterstein, E. Lederer, Hoppe Seyler's Z. Physisol.Chem., 197, 141 (1931).
6. A.J.P. Martin and R.L. Synge, Biochem. J., 35, 1358 (1941).
7. S.W. Mayer and E.R. Tompkins, J.A.C.S., 69, 2866 (1947).
8. E. Glueckauf, Trans.Farad.Soc., 51, 34 (1955).
9. J.H. Purnell, 'Gas Chromatography', J. Wiley, New York (1962).
10. A.B. Littlewood, 'Gas chromatography: Principles, Techniques and Applications', Academic Press, London (1962).
11. A.I.M. Keulemans, 'Gas Chromatography', Reinhold, New York (1959).
12. J.J. Van Deemter, F.J. Zuiderweg and A. Klinkenberg, Chem.Eng.Sci., 5, 271 (1956).
13. L. Lapidus and N.R. Ammundson, J.Phys.Chem., 56, 984 (1952).

13a. E. Glueckauf, 'Principles of Operation of Ion Exchange Columns', Soc. of Chem.Ind., London (1955).

14. M.J.E. Golay, 'Gas Chromatography 1960', Butterworths, London, (1960).

15. E. Gruska, M.N. Meyers, P.D. Scheltler and J.C. Giddings, Anal.Chem., 41, 889 (1969).

16. R.D. Condon, Anal.Chem., 31, 1717 (1959).

17. J.J. Kirkland, 'Modern Practice of Liquid Chromatography', Wiley, New York (1971).

18. L.R. Snyder and J.J. Kirkland, 'Introduction to Modern Liquid Chromatography', Wiley, Interscience, New York (1974).

19. J.J. Kirkland, Analyst, 99, 859 (1974).

20. A. Janik, J. Chromatogr.Sci., 13, 93 (1975).

21. D.L. Sounders, Anal.Chem., 46, 470 (1976).

22. R. Kaiser, 'Gas Phase Chromatography', Butterworths, London (1963).

23. A.E. Lawson and J.M. Miller, J.Gas Chromatogr., 4, 273 (1966).

24. J.N.W.Harley, V. Pretorius, Nature, 181, 177 (1958).

25. I.G. William, R.A. Dewar, Nature, 181, 760 (1958).

26. W. McFadden, 'Techniques of combined Gas Chrom/Mass Spectrometry- Applications in Organic Analysis', Wiley, New York (1973).

27. B.J. Gudzinowicz, M.J. Gudzinowicz and H.F. Martin, 'Fundamentals of Integrated GC-MS. Marcel Dekker, New York (1977).

28. O.K. Doolen, ISA Symposium on Gas Chromatography, Michigan State University, June 10-12 (1959).

29. W.J. Baker, E.H. Lee, R.T. Wall, ISA Symposium on Gas Chromatography, Michigan State University, June 10-12 (1959).

30. D.T. Sawger, J.K. Barr, Anal.Chem., 34, 1518 (1962).

31. J. Bohemen, J.C.S., 2444 (1960).

32. A.T. James, Biochem. J., 52, 252 (1952).

33. A.T. James and A.J.P. Martin, Analyst, London, 77, 915 (1952).

34. A.T. James, A.J.P. Martin and G.H. Smith, Biochem. J., 52, 238 (1952).

35. L. Rohrschneider, Z. Anal.Chem., 170, 256 (1959).

36. H.J. Maier and O.C. Kárpáthy, J.Chromatogr., 8, 308 (1962).

36a. A.G. Polgar, J.J. Holst, S. Groennings, Anal.Chem., 34, 1226 (1962).

37. H.M. Tenney, Analyt.Chem., 30, 2 (1958).

38. M.B. Evans and J.F. Smith, Nature, 190, 905 (1961).

39. R.P.W. Scott and C.S.G. Phillips in A.B. Littlewood's A. Goldup, E.D., Gas Chromatography (1964), Inst. of Petroleum, London (1965) p.266.

40. D. Jentzsch and G. Bergmann, Z. Analyt.Chem., 170, 239 (1959).

41. M. Riedmann, Z.Anal.Chem., 260, 341 (1972).

42. C.R. Trash, J.Chromatogr.Sci., 11, 196 (1973).

43. A.E. Coleman, ibid., p.198.

44. W.R. Supina, R.S. Henly, R.F. Kruppa, J.Am.Oil Chem.Soc., 43, 202A (1966).

45. D.M. Ottenstein, J.Gas Chromatogr. 6, 129 (1968).

46. F.W. Karasek, Res.Develop., 22(6), 34 (1971).

47. F.T. Eggertsen, S. Groennings, Analyt.Chem., 30,20 (1958).

48. K.H. Nelson, W.J. Hines, M.D. Grimes and D.E. Smith, ibid., 32, 10 (1960).

49. J.H. Sullivan, J.T. Walsh and C. Merritt Jr., ibid., 31, 1826 (1959).

50. M. Cheneau and G. Guiochon, Bull.Soc.Chim.Fr.,2601 (1963).

51. B.L. Karger, A. Hartkopf and H. Posmanter, J.Chromatogr.Sci. 7, 315 (1969).

52. B.L. Karger, J.Chem.Educ., 43, 47 (1966).

53. C.A. Clemons, P.W. Leach, A.P. Altshuller, Analyt.Chem., 35, 1548 (1963).

54. R.O.C. Norman, Proc.Chem.Soc., 151 (1958).

55. F.A. Fabrizio, R.W. King, C.C. Cerato and J.W.Loveland, Analyt.Chem., 31, 2060 (1959).

56. M.B. Evans, J.F. Smith, J.Chromatogr., 36, 489 (1968).

57. J. Tadmor, Anal.Chem., 36, 1565 (1964).

58. E. Gil-Av, V. Schurig, Analyt.Chem., 43, 2030 (1971).
59. B.W. Bradford, D. Harvey, D.E. Chakley, J.Inst.Petrol., 41, 80 (1955).
60. B. Smith and R. Ohlson, Acta.Chem.Scand., 16, 351 (1942).
61. S.P. Wasik and W. Tsang, J.Phys.Chem., 74, 2970 (1970).
62. D.V. Banthorpe, C. Gatford and B.R. Hollebone, J.Gas.Chromatogr., 6, 61 (1968).
63. D. White and C.T. Cowan, Trans.Faraday Soc., 55, 557 (1958).
64. J.V. Mortimer, P.L. Gent, Analyt.Chem., 36, 754 (1964).
65. J.V. Mortimer, P.L. Gent, Nature, 197, 789 (1963).
66. J.M. Vergnaud, J.Chromatogr., 27, 54 (1967).
67. H. Kelker, Ber. Bunsenges., Phys.Chem., 67, 698 (1963).
68. H. Kelker and E. Schivizhoffen, In 'Advances in Chromatography', J.C. Giddings, R.A. Keller Eds., Vol. 6, p.247 (1968).
69. G.H. Brown, Anal.Chem., 41, 26 (1969).
70. I. Illy, Anal.Chem., 29, 216 (1974).
71. M.S. Vigdergauz and R.V. Vigalok, Uspekhi Gazovoi Khromatografii (Adv.in Gas Chromatogr.) Kazan, 4, 27 (1975).
72. H. Kelker, 'Advances in Liquid Crystals', Acad. Press, New York, Sanfrancisco, London, 3, 237 (1978).
73. Z. Witkiewicz, Wiad. Chem., 1, 19, (1977).

74. K. Watabe, J.Chromatogr., 192, 89 (1980).

75. K. Watabe, J.Chromatogr., 206, 223 (1981).

76. K. Watabe, T. Hobo, and S. Suzuki, J.Chromatogr., 239, 499 (1982).

77. K. Watabe, T. Hobo, S. Suzuki, J.Chromatogr., 249, (2), 209 (1982).

78. Z. Witkiewicz, J.Szulc, A. Ziòlek, R. Dabrowski, J. Dziaduszek, J.Chromatogr., 246 (1), (1982).

79. G.M. Janini, M.T. Ubeid, J.Chromatogr., 248 (2), 217 (1982).

80. Z. Witkiewicz, J.Chromatogr., 251 (3), 311 (1982).

81. F. Reinitzer, Monatsh, 9, 421 (1888).

82. O. Lehmann, Z. Physik.Chem., 4, 462 (1889).

83. G. Friedel, in 'Colloid Chemistry', Edited by, J. Alexander, Vol. I, p. 102 (1926).

84. G. Friedel and E. Friedel, Z. Krist, 79, 1 (1931).

85. D. Demus, M. Klapperstuck, V. Link, H. Zaschke, Mol.Cryst. Liq. Cryst., 15, 161 (1971).

86. G. Friedel, Ann.Phys., 18, 273 (1922).

87. G.H. Brown, W.G. Shaw, Chem.Rev., 57, 1049 (1957).

88. V.A. Usoi'tseva and I.G. Chistyakov, Uspekhi Khim, 32, 1124 (1963) [Russian Chem.Rev. No.9, (1963)].

89. D. Vorlander, Ber., 41, 2033 (1908).

90. G.W. Gray,'Molecular Structure and the Properties of Liquid Crystals', Acad.Press, London-N.Y. (1962).

91. I.G. Chistyakov, 'Zhidkie Kristally' (Liquid Crystals) IZD.Nauka, Moscow (1966).

92. J.D. Bernal, D. Crowfoot, Trans.Faraday Soc., 29, 1032 (1933).

93. J.P. Schroeder, in 'Liquid Crystals and Plastic Crystals', G.M. Gray and P.A. Winsor Eds., Vol. I, p.356 Ellis Horwood, Chichester, England (1974).

94. G.M. Janini, in 'Advances in Chromatography', Vol. 17, p.231, J.C. Giddings, E. Grushka, J. Cazes and P.R. Brown, Eds., New York (1979).

95. H. Kelker, Z. Analyt.Chem., 198, 254 (1963).

96. M.J.S. Dewar and J.P. Schroeder, J.A.C.S., 86, 5235 (1964).

97. S. Wasik and S. Chesler, J.Chromatogr., 122, 451 (1976).

98. G.M. Janini, K. Johnsten, W.L. Zielinski Jr., Anal.Chem., 47, 670 (1975).

99. G.M. Janini, G.M. Muschik, J.A. Schroer and W.L. Zielinski, Anal.Chem., 48, 1879 (1976).

100. G.M. Janini, G.M. Muschik and W. Zielinski Jr., Anal.Chem., 48, 800 (1976).

101. G.M. Janini, B. Sheikh, W. Zielinski Jr., J.Chromatogr., 132, 136 (1977).

102. Z. Witkiewicz, J. Szulic, R. Dabrowski and Sadowski, J.Chromatogr., 200, 68 (1980).

103. G. Kraus, H. Zaschke, J.Prakt.Chem., 323, 199 (1981).

104. J.F. Vernon and A.N. Khakoo, J.Chromatogr., 157, 412 (1978).

105. L.E. Cook and R.C. Spangled, Anal.Chem., 46, 122 (1974).

106. Z. Wtikiewicz, A. Wadawczyk, J.Chromatogr., 173, 43 (1979).

107. Analabs Tech.Bull., North Haven, Conn, p.117 (1976).

108. G.M. Muschik, T. Kelly and W.B. Manning, J.Chromatogr. 202, 75 (1980).

109. M. Hall, D.M.B. Mallen, J.Chromatogr., 118, 268 (1976).

110. W.L. Zielinski Jr., K. Johnsten, G.M. Muschik, Anal.Chem., 48, 907 (1976).

111. M.S. Vigdergauz, R.V. Vigalok and G.V. Dmitrieva, Russian Chem.Rev., 50 (5), 498 (1981).

112. B.V. Bapat, B.B. Ghatge, S.C. Bhattacharyya, J.Chromatogr., 18, 308 (1965).

113. B.V. Bapat, B.B. Ghatge, S.C. Bhattacharyya, J.Chromatogr., 23, 363, 227 (1966).

114. B.V. Bapat, T.K. Sankpal, B.B. Ghatge and S.C. Bhattacharyya, J.Chromatogr., 29, 33 (1967).

115. K.S. Uppal, D.G. Panse, B.V. Bapat and B.B. Ghatge, Ind.J.Tech., 18, 248 (1980).

116. K.S. Uppal, D.G. Panse, B.V. Bapat and B.B. Ghatge, Ind.J.Tech., 18, 246 (1980).

117. K.S. Uppal, D.G. Panse, B.V. Bapat, B.B. Ghatge, Ind.J.Tech., 19, 195 (1981).

118. K.P. Naikwadi, B.V. Bapat and B.B. Ghatge, Ind.J.Chem., Sec. B, 20, 165 (1981).

119. K.P. Naikwadi, B.V. Bapat, B.B. Ghatge, J.Chromatogr., 195, 309 (1980).

120. D.G. Panse, B.V. Bapat, B.B. Ghatge, Ind.J.Chem., Sec. B 21, 66 (1982).

121. K.P. Naikwadi, D.G. Panse, B.V. Bapat, B.B. Ghatge, J.Chromatogr. 206, 361 (1981).

122. K.P. Naikwadi, P.P. Powar, B.V. Bapat, B.B. Ghatge, Ind.J.Tech. (Communicated).

123. D.G. Panse, K.P. Naikwadi, B.V. Bapat and B.B. Ghatge, Ind.J.Tech., 19, 518 (1981).

124. C.E. Doering, D. Estel and R. Fischer, J.Prakt.Chem., 316 (a) (1974).

125. R.K. Kuchhal, P. Kumar, P.L. Gupta, K.L. Mallick, Chromatographia, 9, 540 (1976).

126. V. Švob, D. Deur-Šiftar, J.Chromatogr., 91, 677 (1974).

127. N. Dimov, T. Petkova, D. Shopov, J.Chromatogr., 91, 691 (1974).

128. T.M. Nagiev, R.A. Iskenderov, N.D. Medzhidov, Z.M. Nagieva and Z. Yu. Ramazanova, Azerb.Neft Khoz, 12, 41 (1970) Anal.Abstr., 22, 1637 (1972).

129. V.A. Panova, Z.V. Nikolaeva and Yu Yu Lur'e, Ochistka Proizvod, Stochnykh. Vod, 5, 158 (1973).

130. L. Soják, J. Janák and J.A. Rijks, J.Chromatogr., 138, 119 (1977).

131. V.M. Nabivach, P. Bur'yan and I. Matsak,
Vopr.Khim, Tekhnol, 53, 64 (1978).

132. C.A. Clemons, P.W. Leach and A.P. Altschuller,
Anal.Chem., 35, 1546 (1963).

133. L.D. Belyakova, A.V. Kiselev, G.A. Soloyan,
Chromatographia, 3, 254 (1970).

134. A. Di. Corcia, A. Liberti and R. Samperi,
J.Chromatogr, 122, 459 (1976).

135. F. Matoušek, Z. Anal.Chem., 236, 201 (1968).

136. H.W. Dürbeck, Z. Anal.Chem., 251, 108 (1970).

137. D.M. Ottenstein, D.A. Bartley, W.R. Supina,
Anal.Chem., 46, 2225 (1974).

138. G.G. Maidachenko, R.V. Vigalok and M.S. Vigdergaud,
USSR. Pat., 455, 276 (1974); C.A., 83: 53009_e (1972).

CHAPTER II

EXPERIMENTAL

GENERAL REMARKS

1. All the starting materials were commercial products and checked for purity before use.
2. Benzene, toluene, ethylbenzene and the xylene isomers were distilled before use.
3. Acetyl chloride, acetic anhydride were distilled before use.
4. Ethyl formate (G.C. pure), $AlCl_3$, both (BDH, India) used without further purification.
5. KOH and hydrazine hydrate used were of AR grade.
6. The infra red and PMR spectra were obtained on a Perkin-Elmer 137B, and Varian T 60 Spectrometer respectively.

   The IR frequencies are given in reciprocal centimeters and the PMR chemical shifts are reported in p.p.m. on the δ scale relative to an internal standard TMS.
7. IR spectra of isopropyl and n-propyl benzene were obtained on a Perkin-Elmer 599B Spectrophotometer.

EXPERIMENTAL

(A) Synthesis of the laterally substituted liquid crystalline stationary phase[1]

General method of synthesis

p-Substituted aniline was diazotized and subsequent phenyl diazonium chloride was coupled with m-cresol by following the method of Bolotin et al.[2] The purity was checked by IR, TLC and elemental analysis.

p-Alkoxy benzoic acid and its acid chloride was synthesised by a known method[3,4]. The azo compound was then condensed with distilled acid chloride to get the final liquid crystalline compound.

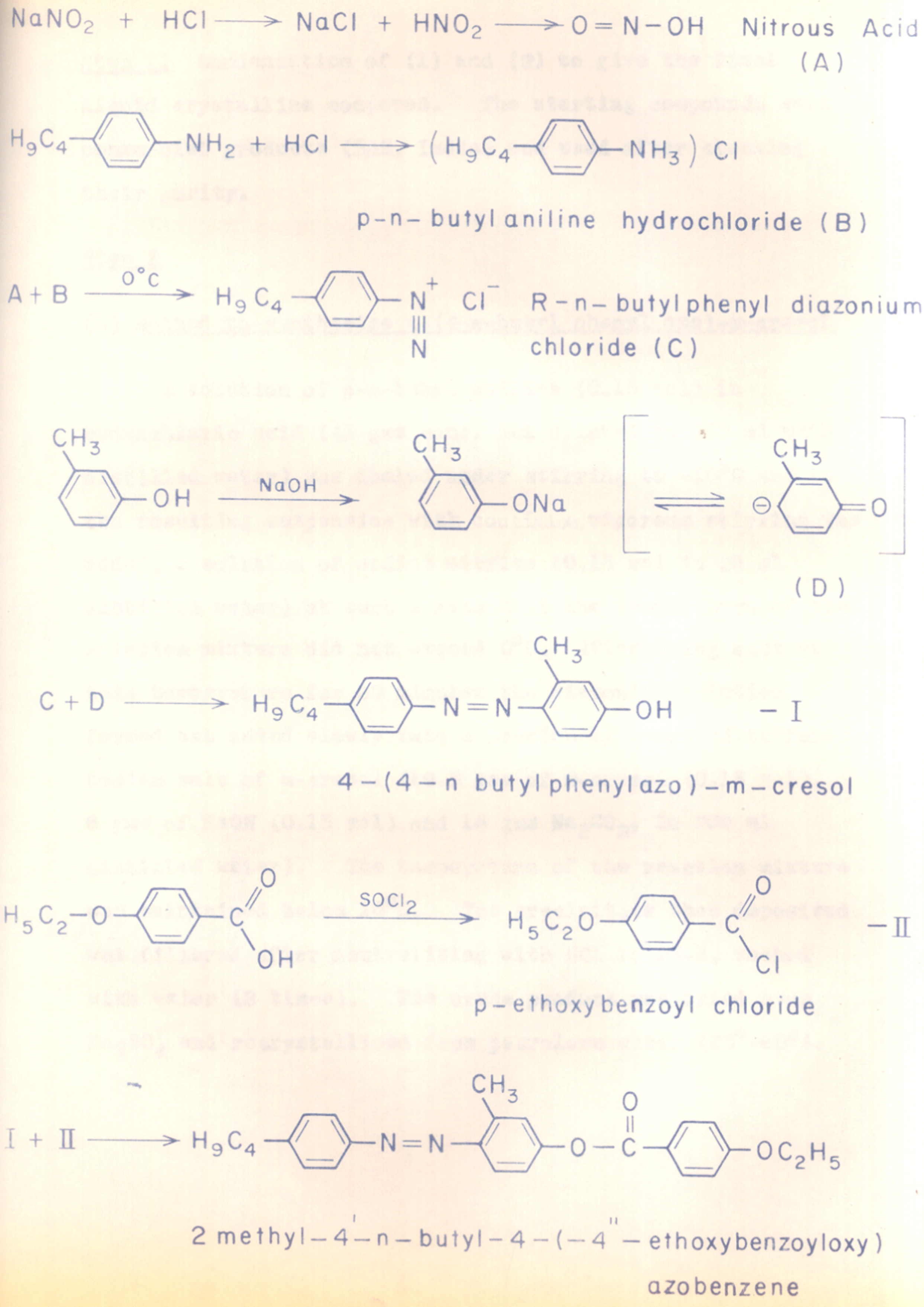
The total synthesis is of two steps.

Step I Synthesis of

(1) 4-(4-n-butyl phenyl azo)-m-cresol

(2) p-ethoxy benzoyl chloride

REACTION SCHEME



Step II Condensation of (1) and (2) to give the final liquid crystalline compound. The starting compounds were commercial products (BDH, India) and used after checking their purity.

Step I

(1) Method to synthesize 4-(4-n-butyl phenyl azo)-m-cresol

A solution of p-n-butyl aniline (0.15 mol) in hydrochloric acid (45 gms conc. HCl diluted to 150 ml with distilled water) was cooled under stirring to -10°C and to the resulting suspension with continuous vigorous stirring was added, a solution of sodium nitrite (0.15 mol in 25 ml distilled water) at such a rate that the temperature of the reaction mixture did not exceed 0°C. After being kept at this temperature for 30 minutes the diazonium solution formed was added slowly into a previously prepared buffered sodium salt of m-cresol (16.2 gms of m-cresol (0.15 mol), 6 gms of NaOH (0.15 mol) and 18 gms Na_2CO_3, in 200 ml distilled water). The temperature of the reaction mixture was maintained below 10°C. The precipitate that deposited was filtered after neutralising with HCl to PH-8, washed with water (3 times). The crude product was dried over Na_2SO_4 and recrystallised from petroleum ether (60°-80°).

The product was characterised as the expected
4-(4-n-butylphenyl azo)-m-cresol.
m.p. = 67°C, yield = 40%

Elemental analysis Found: C, 75.88; H, 7.23; N, 10.73.
Required for $C_{17}H_{20}N_2O$: C, 76.08; H, 7.51; N, 10.44%
IR bands (cm^{-1}) : 3600, 1350 (-OH), 1590 (-N=N-)
(Fig. No. 1)
PMR signals (δ) : 0.8 δ - 1.8 δ (m, 7H, $Ar-CH_2-C\underline{H}_2-C\underline{H}_2-C\underline{H}_3$)
2.6 δ (q, 5H, $Ar-C\underline{H}_3$, $-C\underline{H}_2-CH_2-CH_2-CH_3$)
6.1 δ (s, 1H, $O\underline{H}$ D_2O exchange)
6.7 δ - 7.9 δ (m, 7H, $Ar-\underline{H}$)
(Fig. No. 2)

(2) Synthesis of p-ethoxy benzoyl chloride[3,4]

a. Synthesis of p-ethoxy benzoic acid

A mixture of p-hydroxy benzoic acid (0.25 mol), diethylsulphate (0.275 mol) and potassium hydroxide (0.5 mol in 120 ml of water) was refluxed for 10 hours. Then additional potassium hydroxide (0.25 mol in 140 ml of water) was added and the mixture was refluxed further for 3 hours. The solution was cooled and acidified. The precipitated acid was filtered and the solid product was washed with water. It was then dried and crystallised from glacial acetic acid. m.p. = 196°C; (lit. = 196°C).

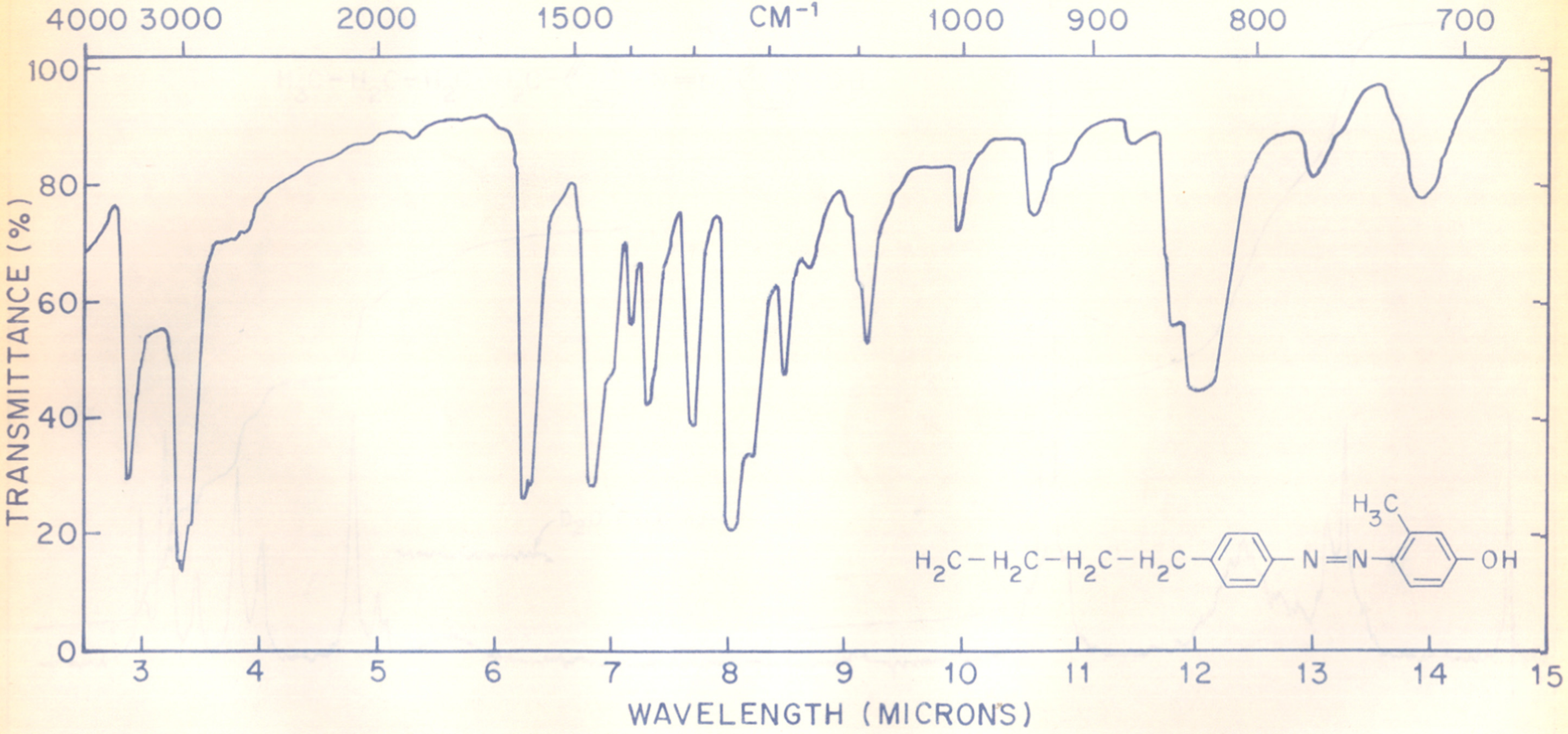


FIG. 1. IR SPECTRUM OF 4-[4-n-BUTYL PHENYLAZO]-m-CRESOL

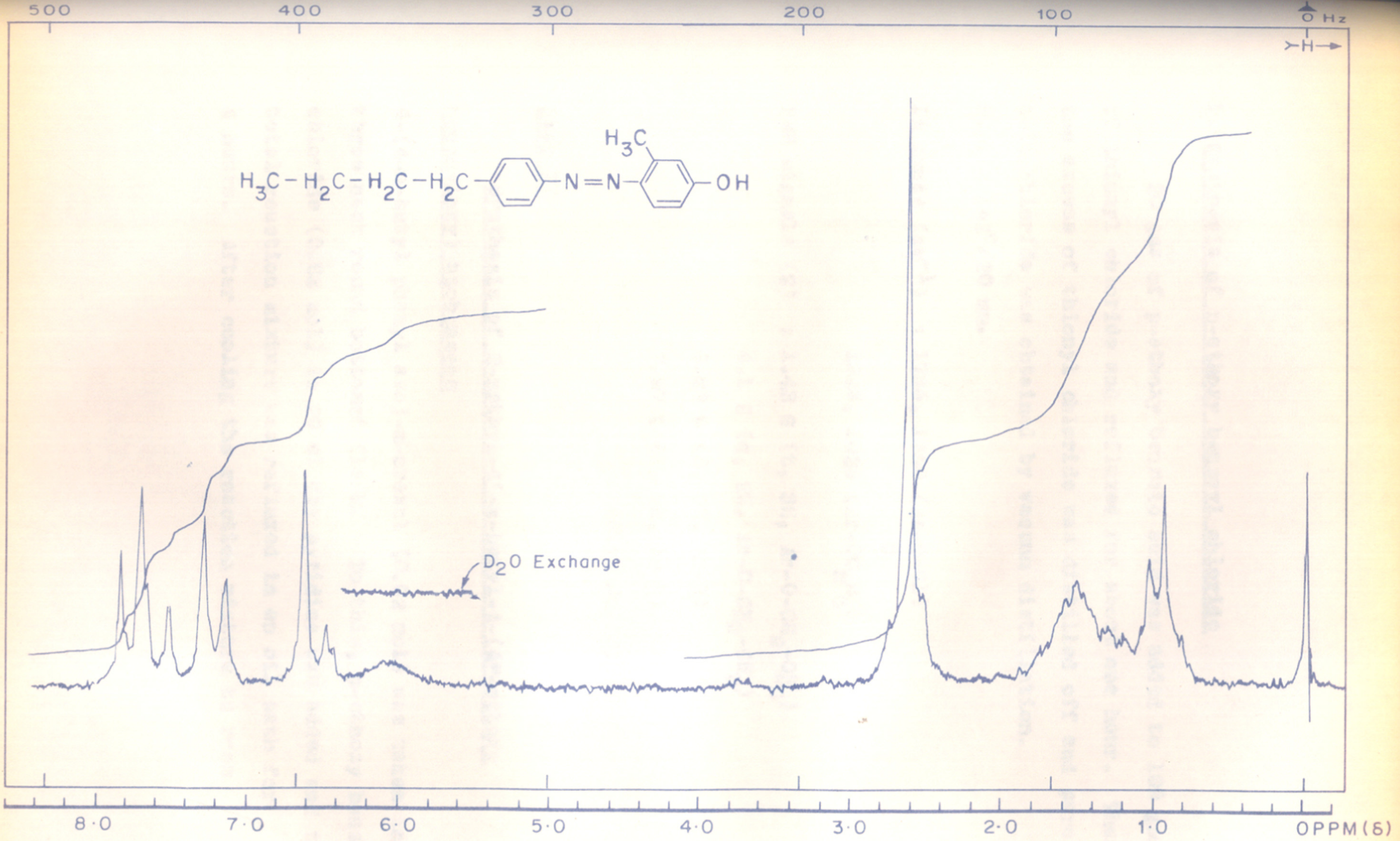
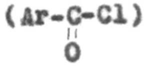


FIG. 2. PMR SPECTRUM OF 4-[4-n BUTYL PHENYLAZO]-m-CRESOL

b. Synthesis of p-ethoxy benzoyl chloride

20 gms of p-ethoxy benzoic acid was added to 100 gms of thionyl chloride and refluxed for about one hour. Then the excess of thionyl chloride was distilled off and pure acid chloride was obtained by vacuum distillation.
B.p. = 142^{o}/20 mm.

IR bands (cm^{-1}) : 1785, 1750



$(Ar-\underset{\overset{\|}{O}}{C}-Cl)$

1325, 1025 ($Ar-OC_2H_5$)

PMR signals (δ) : 1.43 δ (t, 3H, $Ar-O-CH_2-C\underline{H}_3$)
4.1 δ (q, 2H, $Ar-O-C\underline{H}_2-CH_3$)
6.83 δ (d, 2H, $Ar-\underline{H}$)
7.97 δ (d, 2H, $Ar-\underline{H}$)
(Fig. No. 3)

Step II

Synthesis of 2-methyl-4'-n-butyl-4-(4"-ethoxy benzoyloxy) azobenzene

4-(4-n-butyl phenyl azo)-m-cresol (0.02 mol) was taken in a three neck round bottomed flask. To this, p-ethoxy benzoyl chloride (0.03 mol) in 20 ml dry pyridine was added and the total reaction mixture was refluxed in an oil bath for 4 hours. After cooling the reaction mixture to room

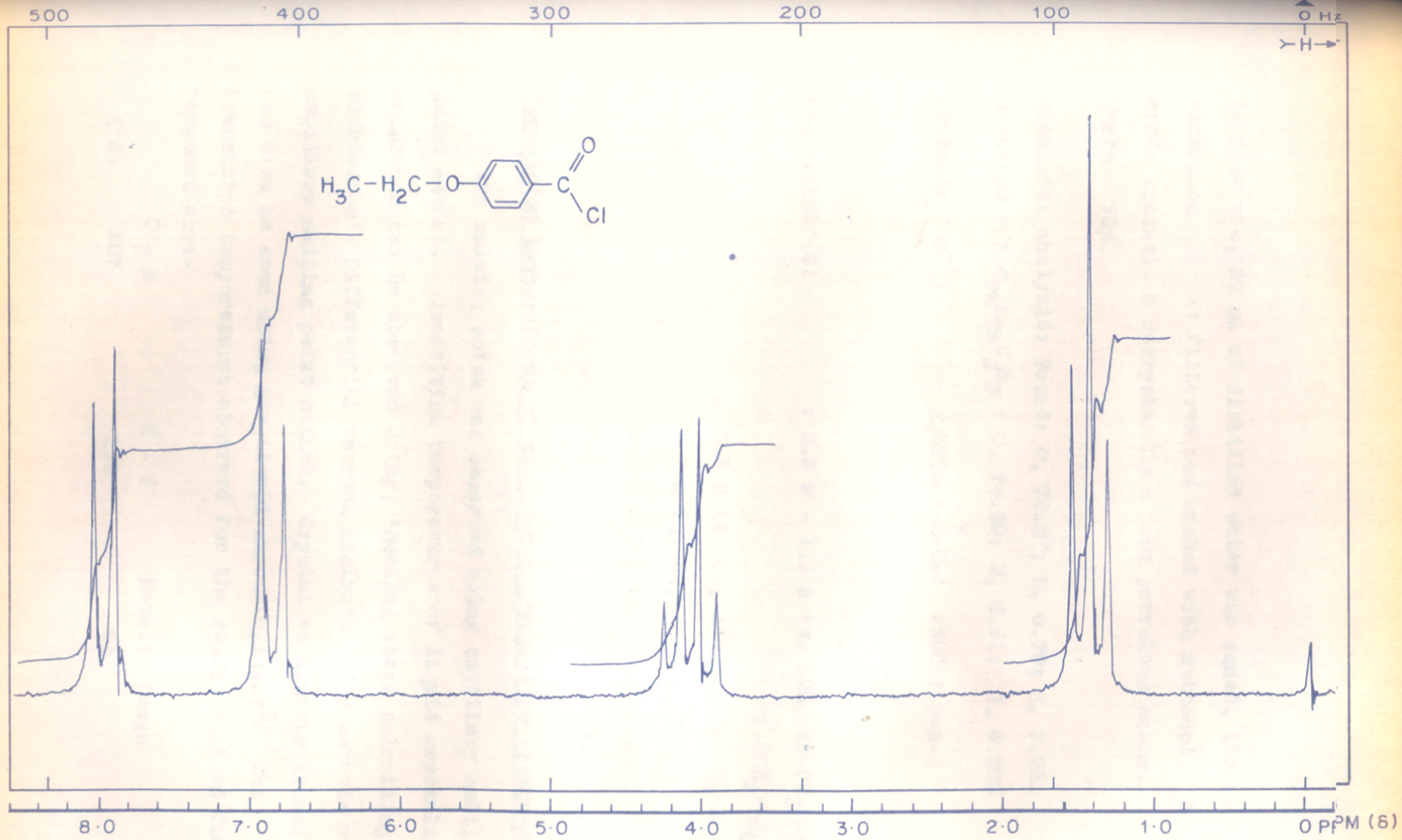


FIG. 3. PMR SPECTRUM OF p-ETHOXY BENZOYL CHLORIDE

temperature, 50 ml of distilled water was added, the solid separated out was filtered and washed with methanol. The crude product was recrystallised from petroleum ether. Yield = 70%.

Elemental analysis: Found: C, 74.27; H, 6.79; N, 7.03.
Required for $C_{26}H_{28}N_2O_3$: C, 74.60; H, 6.51; N, 6.96%

IR bands (cm^{-1}) : 1735 ($-\overset{O}{\overset{\|}{C}}-O-$), 1590 ($-N=N-$)
1250, 1050 ($Ar-O-CH_2-$)
(Fig. No.4)

PMR signals (δ) : 0.8 δ - 1.9 δ (m, 10H, $Ar-CH_2-C\underline{H}_2-C\underline{H}_2-C\underline{H}_3$, $Ar-OCH_2-C\underline{H}_3$)
2.8 δ (t, 5H, $Ar-C\underline{H}_3$, $Ar-C\underline{H}_2-CH_2-CH_2-CH_3$)
4.1 δ (q, 2H, $Ar-O-C\underline{H}_2-CH_3$)
6.9 - 8.2 δ (m, 11H, $Ar-\underline{H}$)
(Fig. No.5)

Transition temperatures of the liquid crystalline compound

The melting point was observed using capillary melting point method. Transition temperatures of liquid crystalline compounds can be observed using, 'Heating stage polarizing microscope'; Differential thermal analysis (DTA) method; and capillary melting point method. Crystal to Nematic transition can also be seen using gas liquid chromatography[5]. The transition temperatures observed for the recrystallised final compound are:-

	C - N	N - I	Nematic Range
(°C)	107	199	92

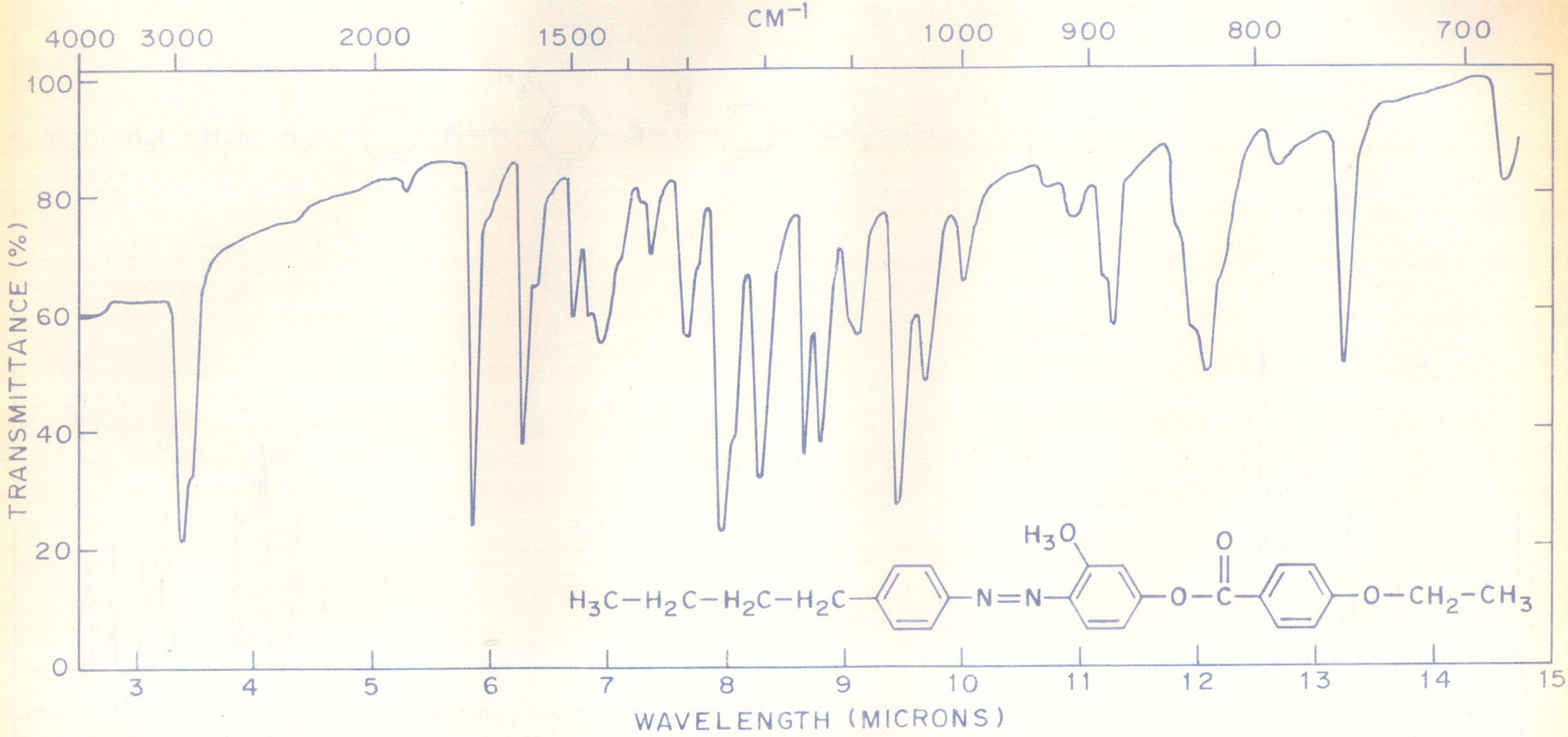


FIG. 4. IR SPECTRUM OF 2-METHYL-4'-n-BUTYL-4-(4"-ETHOXY BENZOYLOXY) AZOBENZENE

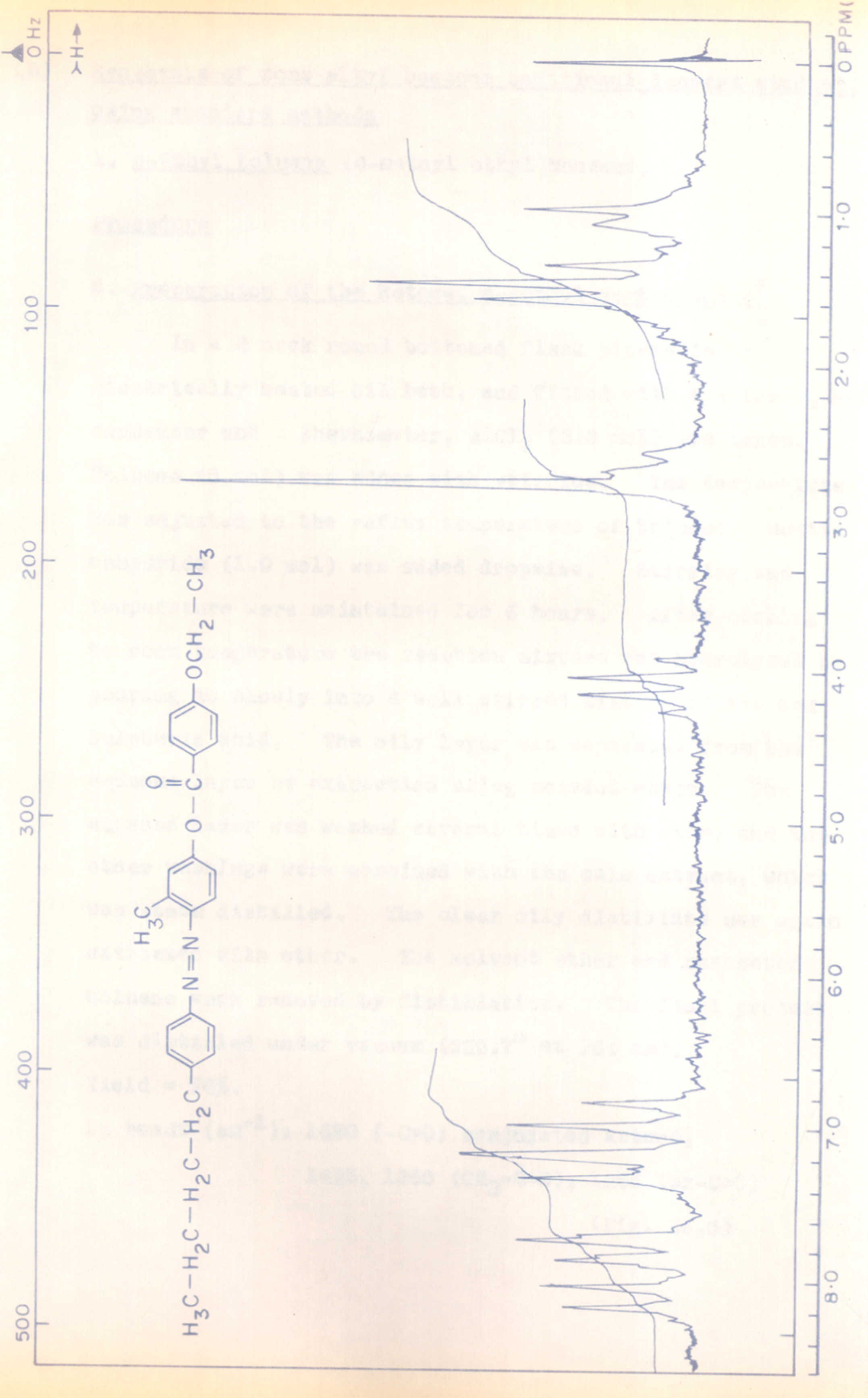


FIG. 5. PMR SPECTRUM OF 2-METHYL-4′-n-BUTYL-4-[4″-ETHOXY BENZOYLOXY] AZOBENZENE

(B) Synthesis of some alkyl benzene positional isomers studied, using standard methods

1. p-Ethyl toluene (4-methyl ethyl benzene)

Procedure

a. Preparation of the ketone, 4-methyl acetophenone[6]

In a 3 neck round bottomed flask placed in an electrically heated oil bath, and fitted with a stirrer, reflux condenser and a thermometer, $AlCl_3$ (3.3 mol) was taken. Toluene (5 mol) was added with stirring. The temperature was adjusted to the reflux temperature of toluene. Acetic anhydride (1.0 mol) was added dropwise. Stirring and temperature were maintained for 6 hours. After cooling to room temperature the reaction mixture was hydrolysed by pouring it slowly into a well stirred mixture of ice and sulphuric acid. The oily layer was separated from the aqueous layer by extraction using solvent ether. The aqueous layer was washed several times with ether and the ether washings were combined with the main extract, which was steam distilled. The clear oily distillate was again extracted with ether. The solvent ether and unreacted toluene were removed by distillation. The final product was distilled under vacuum (226.7° at 764 mm).

Yield = 74%.

IR bands (cm^{-1}): 1680 (-C=O) conjugated ketone,

1425, 1360 (CH_3-C=O), 1265 (Ar-C=O)

(Fig. No.6)

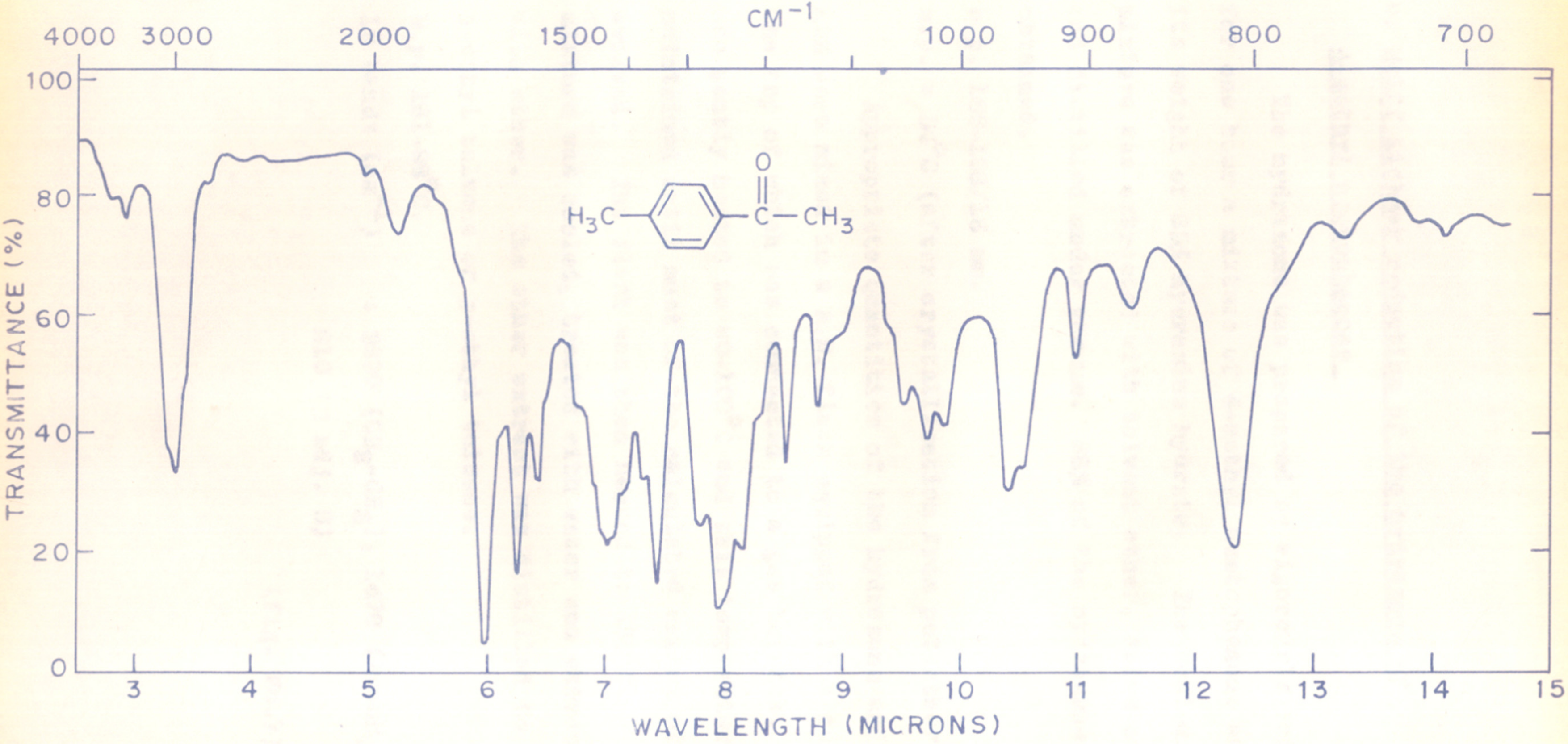


FIG. 6. IR SPECTRUM OF 4-METHYL ACETOPHENONE

b. Wolff Kishner reduction of the hydrazone of 4-methyl acetophenone

The hydrazone was prepared by vigorously refluxing for one hour a mixture of 4-methyl acetophenone and twice its weight of 85% hydrazine hydrate. The cooled reaction mixture was extracted with solvent ether, dried over KOH and distilled under vacuum. 88% of the hydrazone was obtained.

b.p. 166-168/16 mm.

m.p. = 34°C (after crystallisation from pet.ether)

Appropriate quantities of the hydrazone and powdered KOH were mixed in a R.B. flask equipped with a reflux condenser, the top of which was connected to a gas burette. The flask was gently heated to 90-100°C and this temperature was maintained until most of the calculated amount of N_2 had evolved. The flask was then heated to 150°C. The reaction mixture was cooled, treated with water and extracted with ether. The ether extract was distilled to give 80% of 4-ethyl toluene or p-ethyl toluene.

B.p. 161-98°C.

IR bands (cm^{-1}) : 2800 (CH_2-CH_3), 1470 ($Ar-CH_2$),
810 (2 adj. H)

(Fig. No.7)

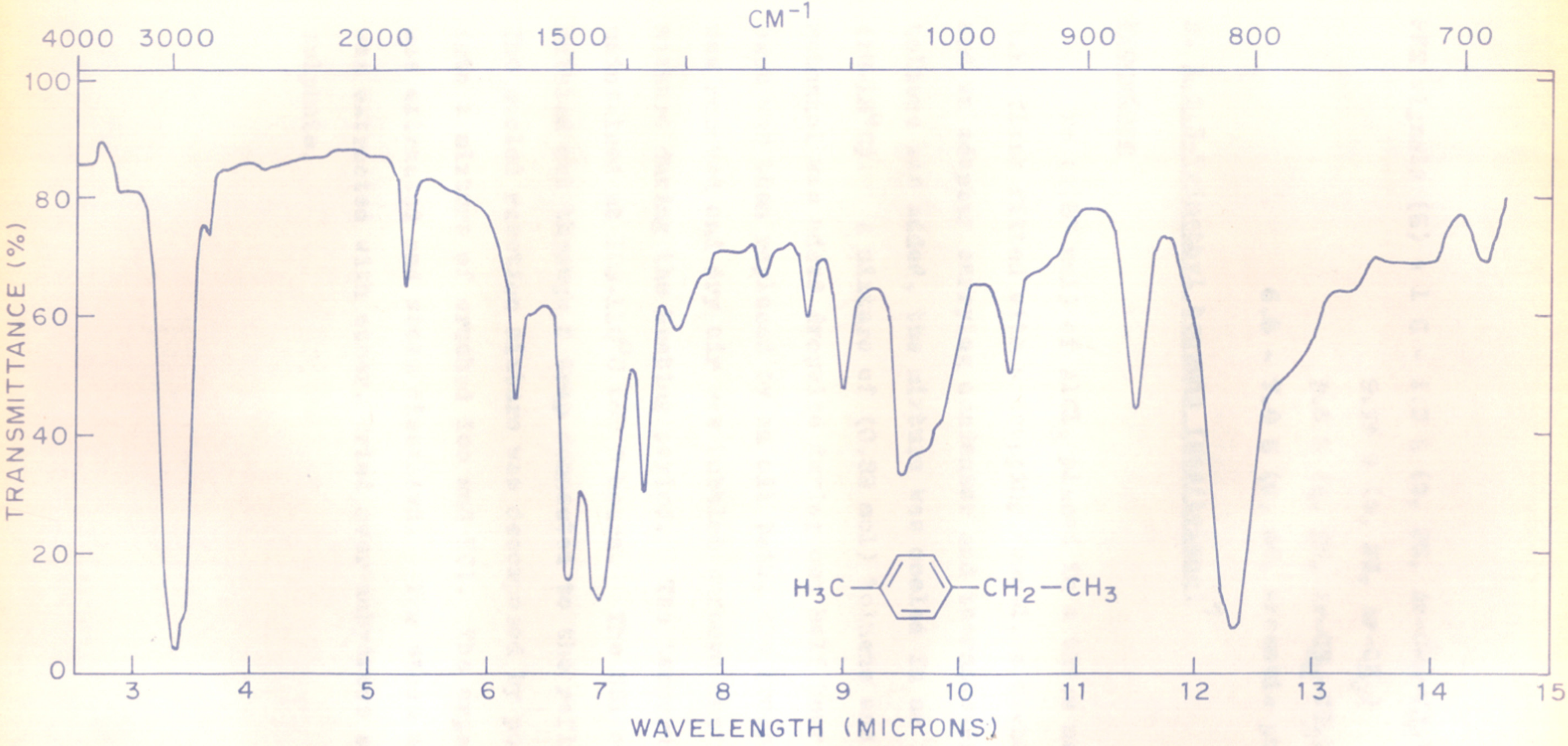


FIG. 7. IR SPECTRUM OF P-ETHYL TOLUENE (4-METHYL ETHYL BENZENE)

PMR signals (δ) : 1 δ - 1.3 δ (t, 3H, Ar-CH_2-$C\underline{H}_3$)
2.25 δ (s, 3H, Ar-$C\underline{H}_3$)
2.5 δ (q, 2H, Ar-$C\underline{H}_2$-CH_3)
6.8 - 7.0 δ (d, 4H, aromatic protons)

2. <u>1,3,5-Trimethyl benzene (Mesitylene)</u>[7]

<u>Procedure</u>

To (2.66 mol) of $AlCl_3$ placed in a three neck R.B. flask fitted with a dropping funnel, a mechanical stirrer and an adapter carrying condenser and thermometer, (0.33 mol) toluene was added, the mixture was cooled in an icebath (10-15°C). A mixture of (0.33 mol) toluene and (1.3 mol) methanol was added dropwise during one half hour. The ice-bath was then replaced by an oil bath, the dropping funnel was removed and dry air was bubbled through the reaction mixture during the heating period. The temperature was maintained at 108-110°C for 3 hours. The HCl evolved was bubbled out through a trap connected to the reflux condenser. The cooled reaction mixture was decomposed by pouring it into a mixture of crushed ice and HCl. The organic layer was extracted and steam distilled. The steam distillate was extracted with ether, dried over anhydrous sodium sulphate.

Pure mesitylene was obtained after distillation under vacuum.

B.p. = 164.71°C

Yield = 80%

IR bands (cm^{-1}) : 3020 (Ar-CH), 2971, 2860 (Ar-CH$_3$), 762, 706 (Ar-CH meta)

PMR signals (δ) : 2.25 δ (s, 9H, Ar-C$\underline{H}_3$)
6.78 δ (s, 4H, Ar-$\underline{H}$)

3. Isopropyl benzene (cumene)[8]

Procedure

A mixture of benzene (10 mol), isopropanol (1 mol) and H_2SO_4 (9 mol) was taken in a 3 neck R.B. flask fitted with a reflux condenser, a mechanical stirrer and a thermometer. The apparatus was set up on a water bath at 80°C, refluxing temperature of benzene. The stirring and temperature was maintained for 4 hours. After cooling to room temperature, the reaction mixture was poured into cold water, saturated with brine to obtain clear separation. The organic layer was extracted with ether, washed with bicarbomate to remove acid and then with water till neutral. The ether extract was dried over anhydrous sodium sulphate and then distilled to remove ether and unreacted benzene.

Pure isopropyl benzene was obtained after distillation.

B.p. = 152-153°C

Yield = 88%

IR and NMR data agreed with the literature values.

IR bands (cm^{-1}) : 758, 738, 695, 562, 534 (aromatic ring puckering)

(Fig. No.8)

PMR signals (δ) : 0.90 δ $\left(d, 6H, -CH\begin{matrix} C\underline{H}_3 \\ C\underline{H}_3 \end{matrix}\right)$

2.47 δ $\left(m, 1H, Ar-C\underline{H}\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right)$

6.60 δ (s, 5H, Ar-$\underline{H}$)

4. <u>n-Propyl benzene</u>[8]

<u>Procedure</u>

A mixture of benzene (10 mol) and n-propanol (1 mol) was taken in a 3 neck R.B. flask equipped with a stirrer, reflux condenser connected to a trap, and thermometer. $AlCl_3$ (1.1 mol) was added, 0.5 g to 1.0 g at a time, with stirring. After the addition was complete, the reaction mixture was heated at 80°C for 4 hours. The reaction mixture was cooled to room temperature and poured over crushed ice acidified with HCl. The organic layer was separated, washed with bicarbonate and then with water till washings were neutral. The ether extract was dried and distilled to remove ether and unreacted benzene. n-Propyl benzene was obtained in 40% yield after fractional

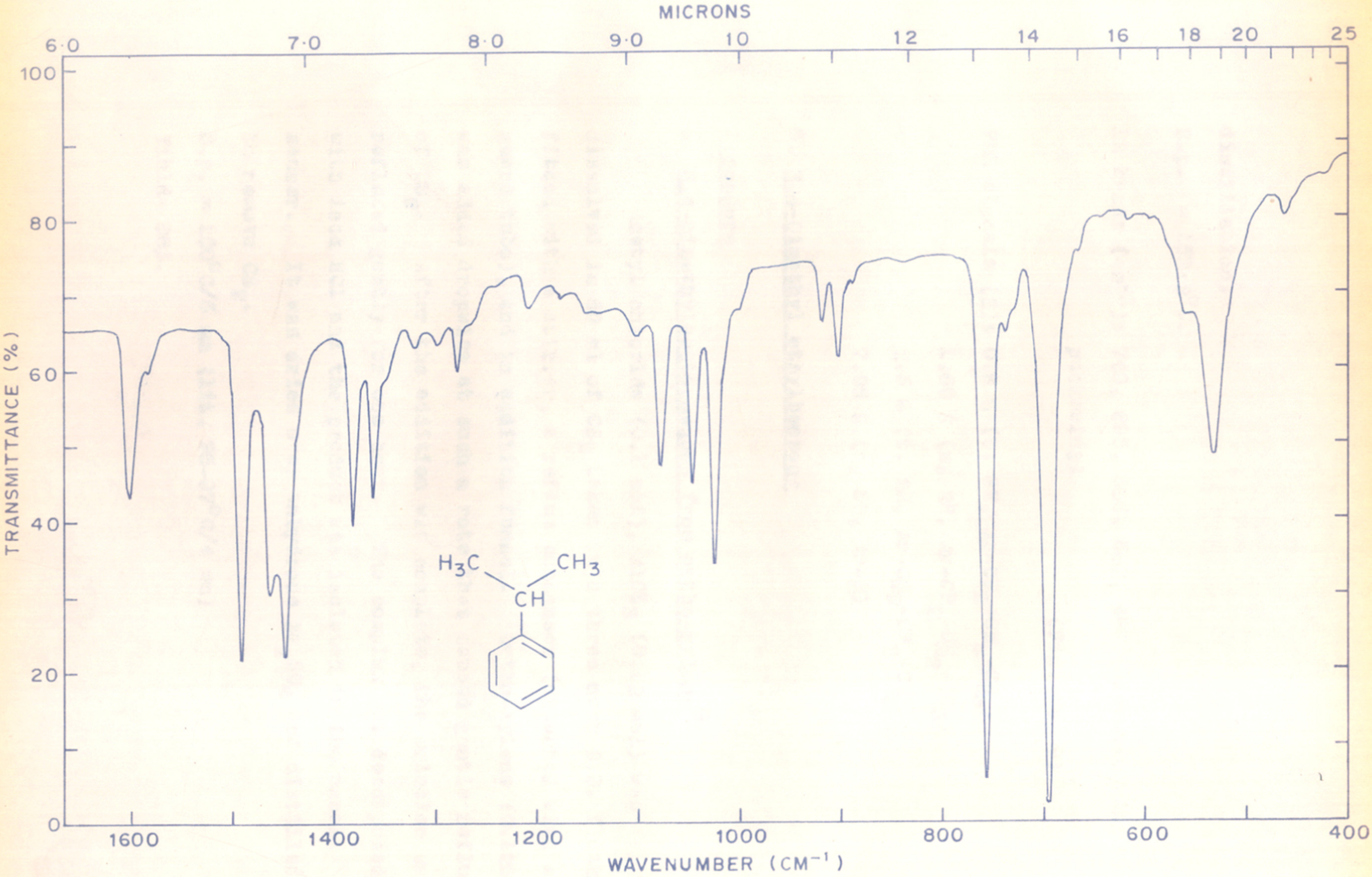


FIG. 8. IR SPECTRUM OF ISOPROPYL BENZENE

distillation.

B.p. = 159·2°C.

IR bands (cm^{-1}): 740, 695, 586, 563, 488 (aromatic ring puckering)

(Fig. No. 9)

PMR signals (δ): 0.9 δ (t, 3H, $Ar-CH_2-CH_2-C\underline{H}_3$)
1.60 δ (m, 2H, $Ar-CH_2-C\underline{H}_2-CH_3$)
2.5 δ (t, 2H, $Ar-C\underline{H}_2-CH_2-CH_3$)
7.05 δ (s, 5H, $Ar-\underline{H}$)

5. 3,4-Dimethyl ethylbenzene

Procedure

a. 3,4-Dimethylacetophenone from ortho-xylene[9]

Acetyl chloride (0.1 mol), $AlCl_3$ (0.12 mol) was dissolved in 50 ml of CS_2 taken in a three neck R.B. flask fitted with a stirrer, a reflux condenser (attached with a guard tube), and an addition funnel. Ortho-xylene (0.125 mol) was added dropwise at such a rate that caused gentle refluxing of CS_2. After the addition was complete, the solution was refluxed gently for one hour. The complex was decomposed with iced HCl and the product was isolated in the usual manner. It was dried over anhydrous Na_2SO_4 and distilled to remove CS_2.

B.p. = 100°C/5 mm (lit. 95-97°C/4 mm)

Yield= 86%.

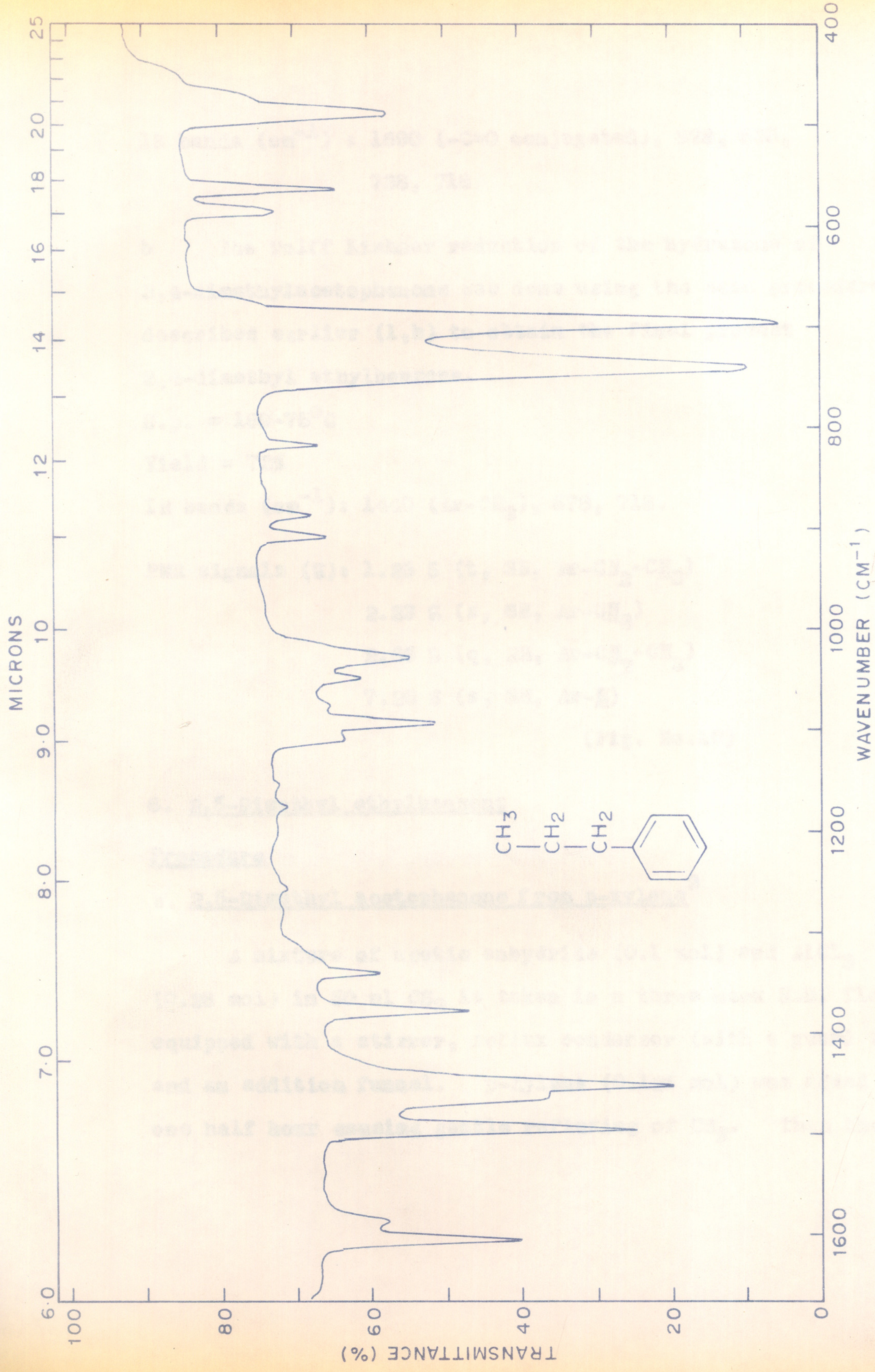


FIG. 9. IR SPECTRUM OF n-PROPYL BENZENE

IR bands (cm^{-1}) : 1690 (-C=O conjugated), 878, 835,
738, 718.

b The Wolff Kishner reduction of the hydrazone of 3,4-dimethylacetophenone was done using the same procedure described earlier (1,b) to obtain the final product 3,4-dimethyl ethylbenzene.

B.p. = 189-75°C

Yield = 73%

IR bands (cm^{-1}): 1440 ($Ar-CH_2$), 878, 718.

PMR signals (δ): 1.23 δ (t, 3H, $Ar-CH_2-C\underline{H}_3$)
2.23 δ (s, 6H, $Ar-C\underline{H}_3$)
2.66 δ (q, 2H, $Ar-C\underline{H}_2-CH_3$)
7.26 δ (s, 3H, $Ar-\underline{H}$)
(Fig. No.10)

6. 2,5-Dimethyl ethylbenzene

Procedure

a. 2,5-Dimethyl acetophenone from p-xylene[9]

A mixture of acetic anhydride (0.1 mol) and $AlCl_3$ (0.28 mol) in 50 ml CS_2 is taken in a three neck R.B. flask equipped with a stirrer, reflux condenser (with a guard tube) and an addition funnel. p-Xylene (0.125 mol) was added in one half hour causing gentle refluxing of CS_2. Then the

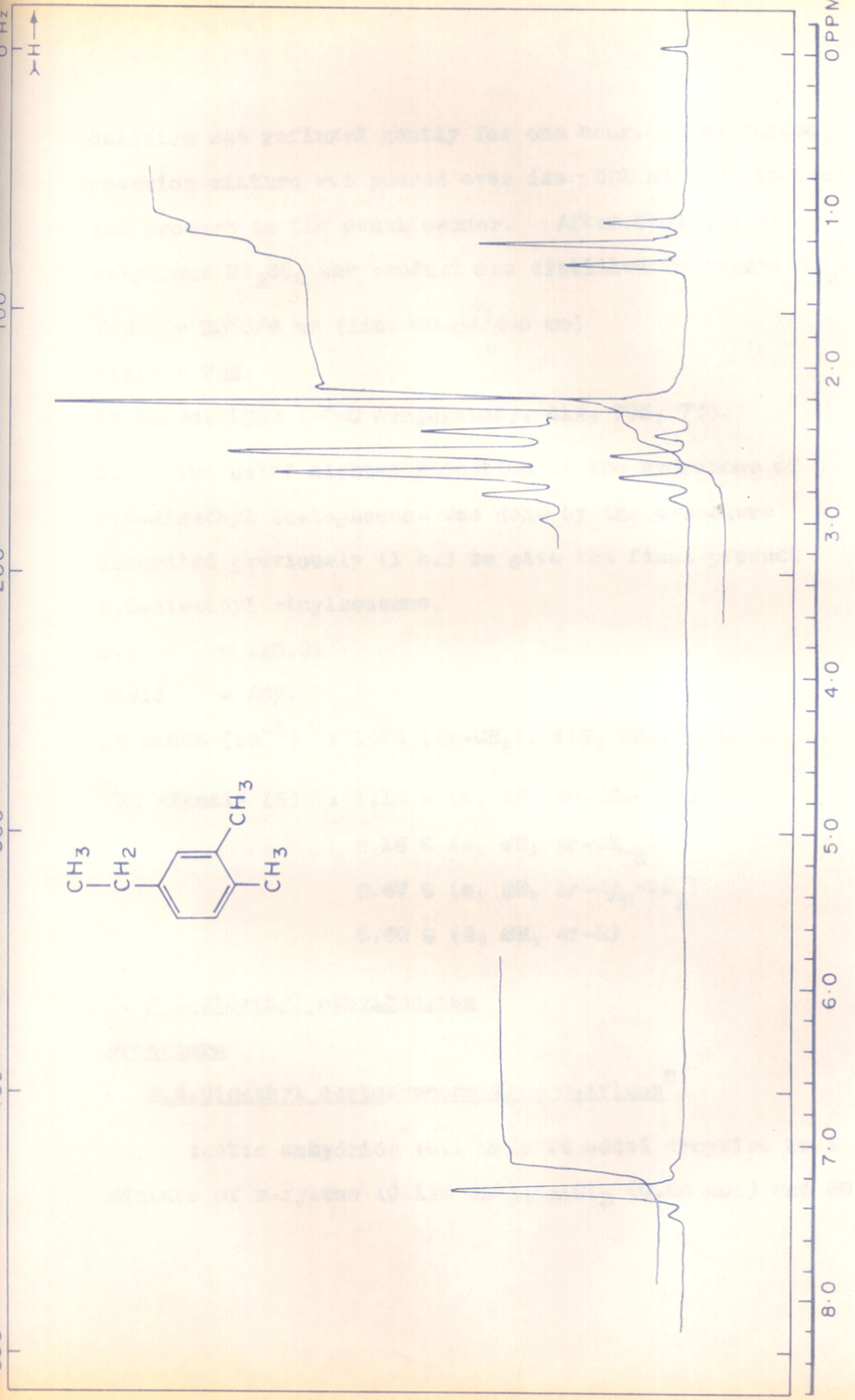


FIG. 10. PMR SPECTRUM OF 3, 4-DIMETHYL ETHYL BENZENE

solution was refluxed gently for one hour. The cooled reaction mixture was poured over ice - HCl mixture to isolate the product in the usual manner. After drying over anhydrous Na_2SO_4 the product was distilled to remove CS_2.

B.p. = 80°C/4 mm (lit. 80-85/4-5 mm)

Yield = 72%.

IR bands: 1680 (-C=O conjugated), 812, 795, 725.

b. The Wolff Kishner reduction of the hydrazone of 2,5-dimethyl acetophenone was done by the procedure described previously (1 b.) to give the final product 2,5-dimethyl ethylbenzene.

B.p. = 186.91°C

Yield = 60%.

IR bands (cm^{-1}) : 1450 ($Ar-CH_2$), 812, 795, 725.

PMR signals (δ) : 1.16 δ (t, 3H, $Ar-CH_2-C\underline{H}_3$)

2.16 δ (s, 6H, $Ar-C\underline{H}_3$)

2.47 δ (q, 2H, $Ar-C\underline{H}_2-CH_3$)

6.60 δ (d, 3H, Ar-H)

7. 2,4-Dimethyl ethylbenzene

Procedure

a. 2,4-Dimethyl acetophenone from m-xylene[9]

Acetic anhydride (0.1 mol) is added dropwise to a mixture of m-xylene (0.125 mol), $AlCl_3$ (0.28 mol) and 50 ml carbondilsulphide (CS_2) kept for stirring in a three neck R.B. flask equipped with a stirrer, a reflux condenser (with a $CaCl_2$ guard tube) and an addition funnel. A gentle refluxing of CS_2 was affected by the slow addition of acetic anhydride. The gentle refluxing was continued for one hour after the addition. Then the reaction mixture was cooled and poured over iced HCl. The product was isolated in the usual manner, dried over Na_2SO_4 and was distilled to remove CS_2.

B.p. = 92°C 5.5 mm (lit. 92-94/5 mm)

Yield = 79%.

IR bands (cm^{-1}): 1680 (-C=O conjugated), 812.

b. The Wolff Kishner reduction of the hydrazone of 2,4-dimethyl acetophenone was carried out using the same procedure described earlier (1 b.), to obtain the final compound 2,4-dimethyl ethylbenzene.

B.p. = 188.41°C.

Yield = 64%.

IR bands (cm^{-1}) : 1440 ($Ar\text{-}CH_2$), 812.

PMR signals (δ) : 1.16 δ (t, 3H, $Ar\text{-}CH_2\text{-}C\underline{H}_3$)

2.23 δ (s, 6H, $Ar\text{-}C\underline{H}_3$)

2.50 δ (q, 2H, $Ar\text{-}C\underline{H}_2\text{-}CH_3$)

6.85 δ (s, 3H, $Ar\text{-}\underline{H}$)

8. 1,3,5-Triethylbenzene[10]

Procedure

($AlCl_3$ catalysed alkylation of ethylbenzene using an organic ester, ethyl formate)

Ethyl benzene (0.2 mol) and ethyl formate (0.08 mol) was placed in a 3 neck R.B. flask equipped with a reflux condenser, a thermometer and stirring arrangement. $AlCl_3$ (0.3 mol) was added through the reflux condenser within a short time, when stirring was vigorous. The reaction flask was kept cool using a ice water bath during the addition of $AlCl_3$ to maintain the temperature below 40°C. Then the cooling bath was removed, the outlet of the reflux condenser was protected by a $CaCl_2$ guard-tube and the reaction mixture was kept stirring at room temperature for 10 hours, at the end of which the reaction mixture was quenched over ice water. The organic layer was extracted in CCl_4, washed with water and dried over anhydrous Na_2SO_4. The CCl_4 extract analysed by GLC showed 79.2% of 1,3,5-triethyl benzene. The remaining low boiling components, ethylbenzene, m- and p-diethylbenzene were removed by fractional distillation. The purity of 1,3,5-triethylbenzene was checked by GLC and PMR data.

IR bands (cm^{-1}): 3000 (C-H), 882, 865, 710 (Ar-CH, 1,3,5-substituted) (Fig. No.11)

PMR signals (δ) : 1.27 δ (t, 9H, Ar-CH_2-$\underline{CH_3}$)
2.56 δ (q, 6H, Ar-$C\underline{H}_2$-CH_3)
6.80 δ (s, 3H, Ar-$\underline{H}$) (Fig. No.12)

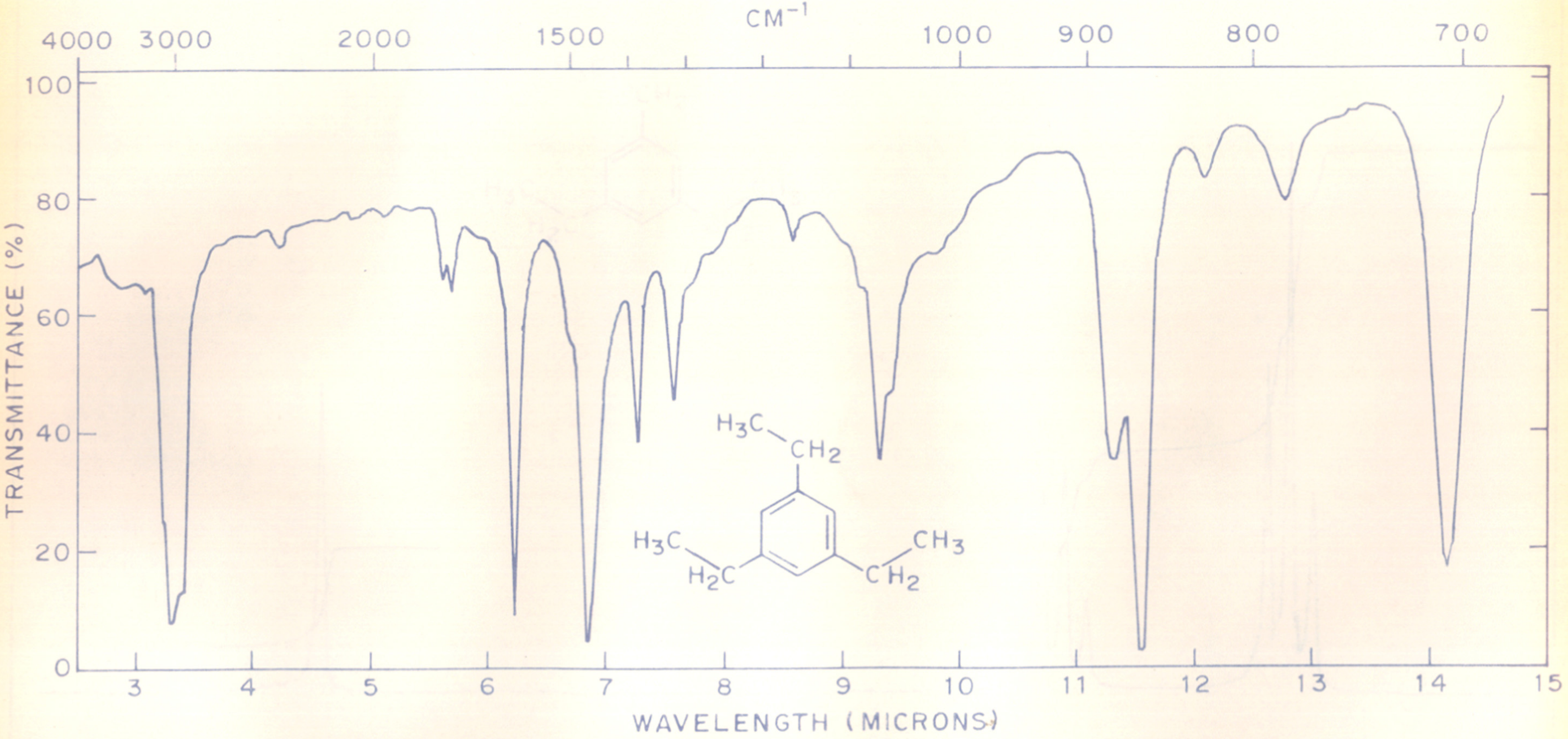


FIG. 11. IR SPECTRUM OF 1,3,5-TRI ETHYL BENZENE

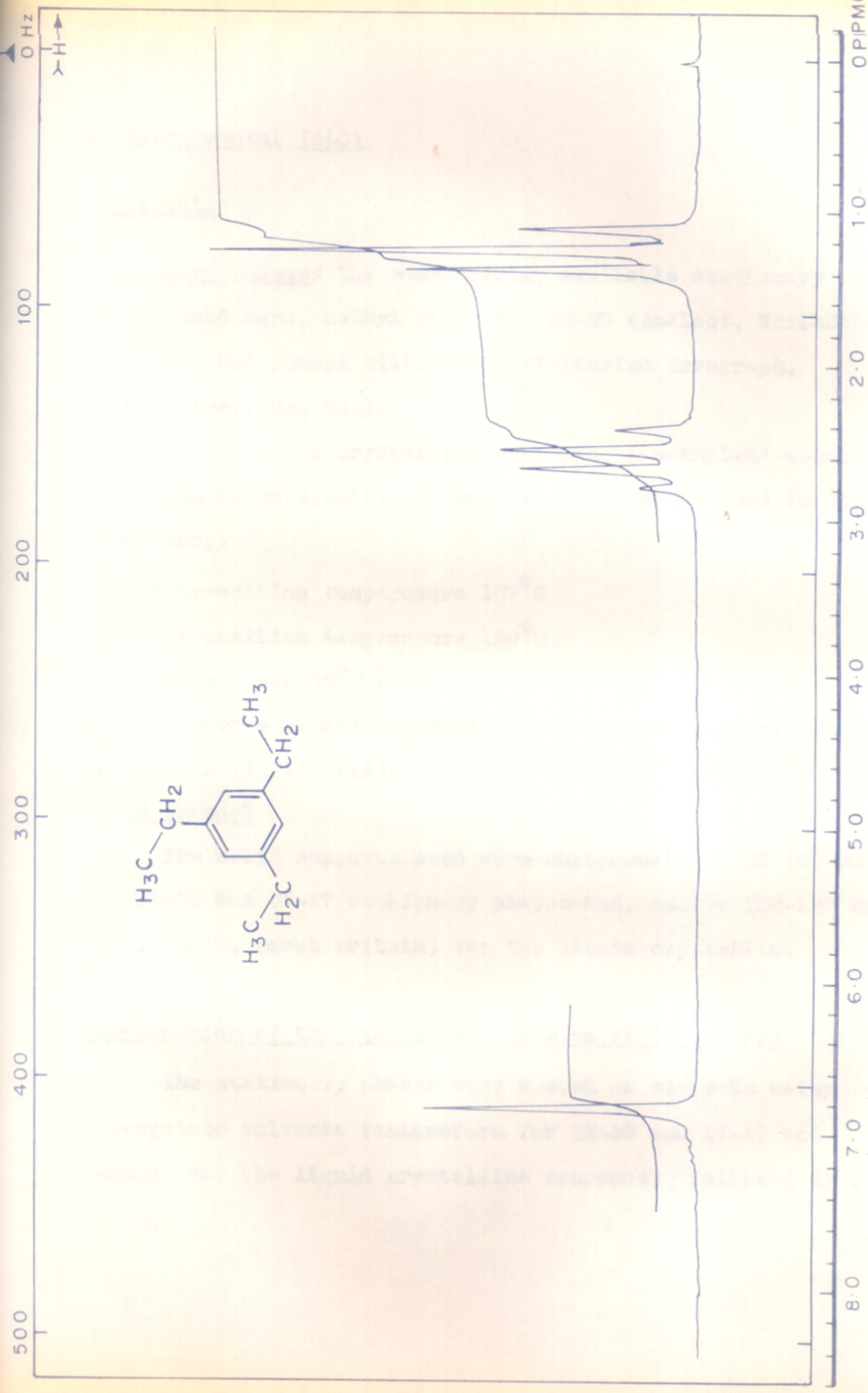


FIG. 12. PMR SPECTRUM OF 1, 3, 5-TRIETHYL BENZENE

(C.) Experimental (GLC)

Materials

Stationary phases: The commercially available stationary phases used were, methyl silicone, SE-30 (Analabs, NorthHaven, CT, USA), and phenyl silicone OV-17 (Varian Aerograph, Walnut Creek, CA, USA).

The nematic liquid crystalline compound, 2-methyl-4'-n-butyl-4-(4"-ethoxybenzoyloxy) azobenzene*, was synthesized in our laboratory.

*[C-N transition temperature 107°C
N-I transition temperature 199°C
nematic range 92°C]

The structures of the three stationary phases used are shown in Fig. 13 (I, II, III).

Solid support

The solid supports used were chromosorb W DMCS (60-80 mesh) for SE-30 and OV-17 stationary phases and, celite (80-120 mesh) (BDH, Poole, Great Britain) for the liquid crystalline compound.

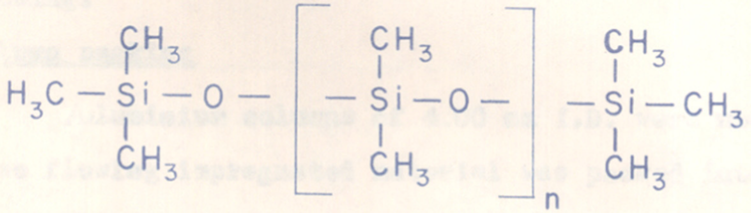
Impregnation of the stationary phase on solid support

The stationary phases were coated on supports using appropriate solvents (chloroform for SE-30 and OV-17 and benzene for the liquid crystalline compound), followed by the

FIGURE 13

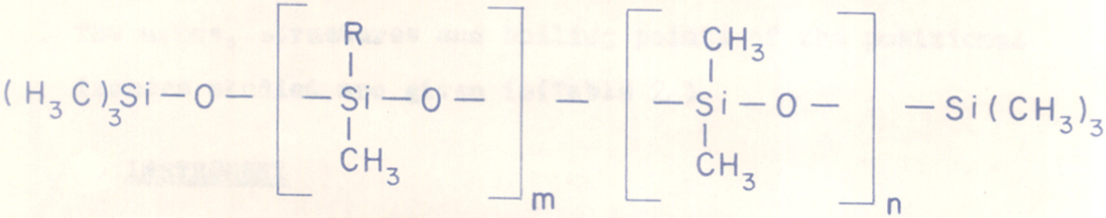
STRUCTURES OF THE STATIONARY PHASES USED

I METHYL SILICONE (SE-30)



$$H_3C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

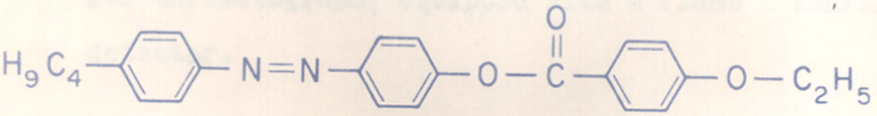
II PHENYL SILICONE (OV-17)



$$(H_3C)_3Si-O-\left[-\underset{CH_3}{\overset{R}{Si}}-O-\right]_m-\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_n-Si(CH_3)_3$$

Where, R = 35 % phenyl

III LIQUID CRYSTALLINE COMPOUND



2-METHYL-4'-n-BUTYL-4-(-4''-ETHOXYBENZOYLOXY) AZOBENZENE gradual elimination of the solvent by evaporation on a hot water bath. The coated phases were dried in an oven at 100°C for two hours. The impregnated material was free flowing.

Column packing

Aluminium columns of 4.00 mm I.D. were used. The free flowing impregnated material was packed into the previously washed and dried aluminium columns. The column parameters are given in(Table 1).

Solutes: The alkylbenzene positional isomer samples were GLC pure, most of them from BDH. A few samples were synthesised in our laboratory.
The names, structures and boiling points of the positional isomers studied are given in(Table 2.).

INSTRUMENT

An AIMIL (Associated Instrument Manufacturers (India) Prviate Limited) dual column chromatograph equipped with a thermal conductivity detector (TCD), with hydrogen as a carrier gas was used to measure the retention times of the alkyl benzenes. Some of the chromatograms shown in the figures in Chapter III were obtained on a Hewlett-Packard 5730A gas chromatograph, equipped with a flame ionisation detector.

Table 1

Column parameters

Column No.	Stationary phase used	Length of the column (m)	Total Weight of packing (g)	Amount of stationary phased used (%, w/w)
I	SE-30	2.28	11.5103	5
II	OV-17	2.26	9.6122	5
III	Liquid crystalline compound	1.84	9.7990	8

TABLE 2

POSITIONAL ISOMERS STUDIED

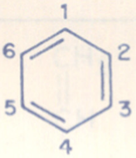
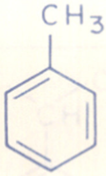
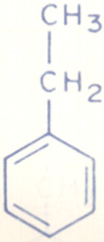
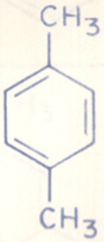
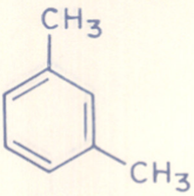
No.	NAME	STRUCTURE	BOILING POINT (°C)
1	BENZENE		80·10
2	TOLUENE		110·60
3	ETHYLBENZNE		136·25
4	p-XYLENE		137 – 138
5	m-XYLENE		139·00

TABLE 2 (contd)

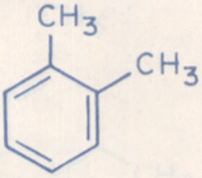
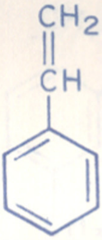
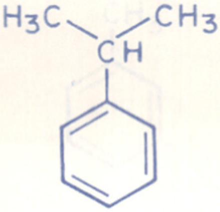
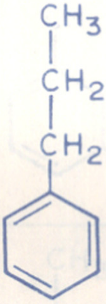
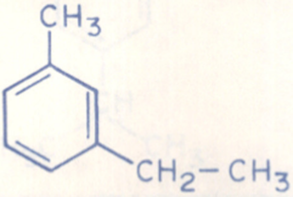
No.	NAME	STRUCTURE	BOILING POINT (°C)
6	o-XYLENE		144·00
7	STYRENE		145 – 146
8	ISOPROPYLBENZENE		152 – 153
9	n-PROPYLBENZENE		159·20
10	m-ETHYLTOLUENE		161·30
11	p-ETHYLTOLUENE		161·98

TABLE 2 (contd)

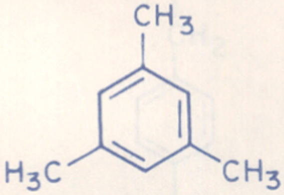
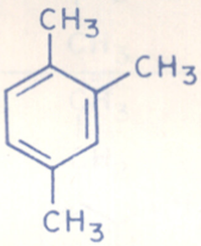
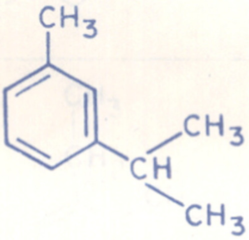
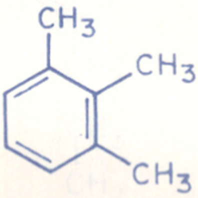
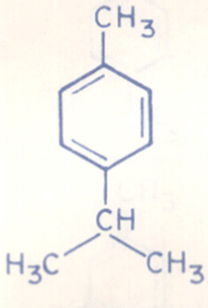
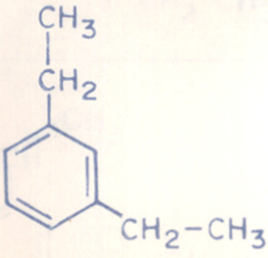
No.	NAME	STRUCTURE	BOILING POINT (°C)
12	1,3,5-TRIMETHYLBENZENE		164·71
13	1,2,4-TRIMETHYLBENZENE		169·40
14	m-CYMENE		175·00
15	1,2,3-TRIMETHYLBENZENE		176·08
16	p-CYMENE		177·00
17	m-DIETHYLBENZENE		181·25

TABLE 2 (contd.)

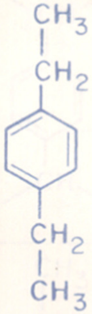
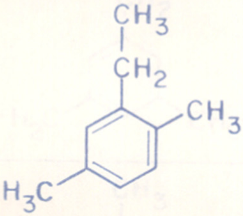
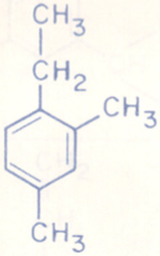
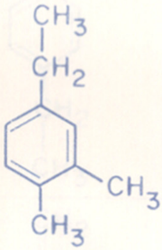
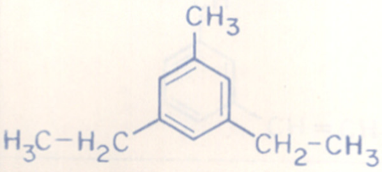
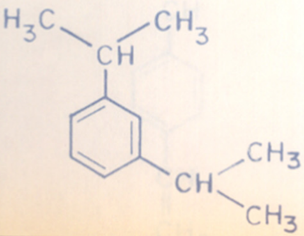
No.	NAME	STRUCTURE	BOILING POINT (°C)
18	P-DIETHYLBENZENE		183·75
19	2,5-DIMETHYL-ETHYLBENZENE		186·91
20	2,4-DIMETHYL-ETHYLBENZENE		188·41
21	3,4-DIMETHYL-ETHYLBENZENE		189·75
22	3,5-DIETHYL-TOLUENE		200·71
23	m-DIISOPROPYL-BENZENE		203·18

TABLE 2 (contd.)

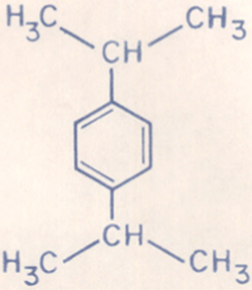
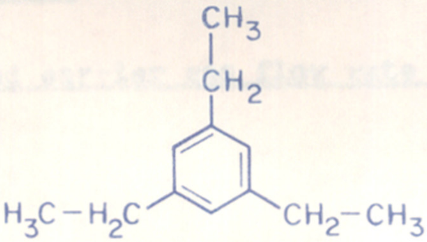
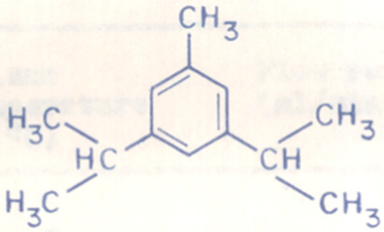
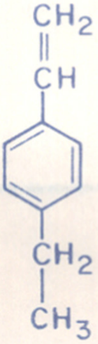
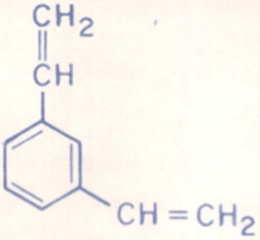
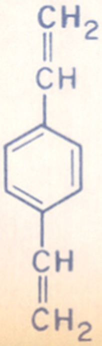
No.	NAME	STRUCTURE	BOILING POINT (°C)
24	P-DIISOPROPYLBENZENE		210·36
25	1,3,5-TRIETHYLBENZENE		215·92
26	3,5-DIISOPROPYLTOLUENE		218
27	P-ETHYLVINYLBENZENE		73/10 mm Hg
28	m-DIVINYLBENZENE		52/3 mm Hg
29	P-DIVINYLBENZENE		52/4 mm Hg

Table 3

Column temperatures and carrier gas flow rate (ml/min)

Column No.	Column Temperature (°C)	Flow rate (ml/min)
I	107°C	37.91
II	107°C	37.91
III	107°C	25.20

Procedure

SE-30 and OV-17 columns were conditioned at 200°C for twelve hours, and the liquid crystal column was conditioned at 180°C for four hours.
The injection and detector temperatures were 150°C and 225°C respectively.
Individual samples were injected with a 10 µl syringe using the smallest detectable volume. Retention time t'R was measured from sample injection to sample peak maxima.
Retention times for all three columns were measured at 107°C.
The flow rate of the carrier gas was measured using a soap-film flowmeter (Table 13.). For obtaining the chromatograms on the Hewlett-Packard 5730A gas chromatograph the alkyl benzene sample mixtures were diluted with carbondisulphide (CS_2) (GLC pure).

REFERENCES

1. K.P. Naikwadi, B.V. Bapat and B.B. Ghatge, Indian J.Chem.Sec. B 20, 165 (1981).

2. B.M. Bolotin, L.K. Tarygina, R.V. Popnava, D.E. Ostromogoiskii, Zh.Org.Khim., 11, 782 (1975) CA. 83: 9353p.

3. J. Brynmar, J.Chem.Soc., 1874 (1935).

4. H. Venderhaeghe, P. Kolosy and M. Claisen, J.Pharm.and Pharmacol 6, 119 (1954).

5. J.P. Schroeder in 'Liquid Crystals and Plastic Crystals', Vol. I, G.W. Gray and P.A. Winsor (Eds.), Elis Horwood, Chichester, England, 356 (1974).

6. P.H. Groggins and R.H. Nagel, Indust. and Eng.Chem., 26, 1313 (1934).

7. J.F. Norris, J.N. Ingraham, J.A.C.S., 60, 1421 (1938).

8. I.P. Tsukervanik and G. Kh. Khakimov, J.Gen.Chem., 32, 1272 (1962).

9. L. Friedman and R. Koca, J.Org.Chem., 33(3), 1255 (1968).

10. K.P. Naikwadi, P.P. Powar, B.V. Bapat and B.B. Ghatge, Ind.J. Tech. (Communicated)

CHAPTER III

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The conventional stationary phases employed in GLC discriminate between samples on the basis of their boiling points (non-polar phases) or on the degree of solute-stationary phase interactions (polar phases). It is therefore very difficult to separate positional isomers having similar boiling points and only very small differences in polarity.

Generally the aliphatic and aromatic hydrocarbons are the compounds which cannot interact through their functional groups with the liquid stationary phase. They can be classified as regular dilute solutions[1], in which it is supposed that specific orienting and chemical effects are not present, and that the distribution and orientation of the solutes in the solvent are random.

Rohrschneider[2] proposed the following rules for gas chromatographic behaviour in regular solutions:-

(1) Substances with identical boiling points can be separated only if they differ in their molar volume, i.e. if they differ in their polarities. The smaller molecule will appear to be more polar. The smaller molecule will be retained more strongly with increasing polarity of the stationary phase.

(2) Molar volumes being same, two substances differ in polarity if they have different boiling points or heats of evaporation. The molecule having higher boiling point will appear more polar.

(3) If two substances are not separated on a stationary liquid phase, the substance with smaller molar volume will emerge first, after that, the one with the greater molar volume will emerge on anotherphase with greater polarity.

(4) The polarity of a stationary phase is significantly dependant on the internal pressure. In regular solutions, the internal pressure and boiling point of the stationary phase and the molar volume of the dissolved substances have a decisive influence on retention.

Mechanism of elution in the nematic state

The elution of positional isomers having similar boiling points, in the nematic state of the liquid crystalline phase is dependant on the shape of the solute molecules. The nematic state being an ordered solution state causes a strong interaction with a solute having a favourable geometry. Linear solute molecules have smaller disruptive effect on the nematic state rather than bulky non-linear solute molecules, since they fit more readily into the nematic lattice, being oriented with their long axes parallel to those of the solvent molecules. Hence the nematic state acts selectively towards solutes on the basis of molecular shape, i.e. everything else being equal, a solute consisting of linear molecules should adapt sterically to the parallel alignment in the mesophase more readily than one with relatively bulky molecules. Thus it was observed from the study of a number of pairs of meta- and para-substituted alkyl benzenes with similar boiling points, the more linear para-isomer was invariably found to have the longer retention time in GLC on the nematic stationary phase.

In the present work the application of a laterally substituted nematic liquid crystalline stationary phase for the separation of 26 alkyl benzenes is compared with two conventional stationary phases SE-30 and OV-17respectively.

A non-polar stationary phase is taken in column I, which is the most commonly used, methyl silicone or SE-30. OV-17 can be described as a medium polar stationary phase with some percentage of phenyl grouping in the structure. The efficiency of column II is observed to have increased for the separation of alkyl benzenes due to the introduction of phenyl group in its structure.

The nematic liquid crystalline stationary phase in column III is usually classified as a specific stationary phase. This phase proves to be highly selective, as the mechanism of separation on this phase is different from that of the conventional phases. With the conventional phases the disubstituted alkyl benzenes e.g.: xylene isomers are eluted in the order, para-, meta-, ortho-, their boiling points being 137-138°C, 139°C and 144°C respectively. The ordering of the liquid crystal stationary phase is decisive for the separation ability of column III. The order of elution of xylene isomers is meta-, para-, ortho, i.e. the retention is selective depending upon the shape of the respective xylene isomer. In addition to the major role of the liquid crystal structure and shape of the molecules to be separated, the separations obtained are influenced by many other factors, which are often decisive in chromatographic processes involving conventional stationary phases. The properties of separating substances, that deserve particular attention are their boiling points and size, polarity, polarizability and elasticity of the molecules. For the liquid crystalline phase, the chemical structure and the related polarity affects the results obtained.

The conventional columns I and II are containing 5% of the respective stationary phases, the same as generally used in routine analytical columns. Column III contains 8% of the liquid crystal phase so as to obtain comparable retention times with columns I and II.

It is known that the surface of the support affects the orientation of the liquid crystalline stationary phase molecules and this effect is greater, than with non-liquid crystalline phases. The solid support chromosorb W DMCS was observed to be unsuitable and therefore the earlier used[3] support, celite, was used as solid support for the liquid crystalline stationary phase (Table I).

All the retention data given in (Table II) is at a constant temperature 107°C. The selective affinity of a GLC column towards the separation of the components can be shown by the relative retention (α) of one component with respect to the other component. It is observed that the maximum value of relative retention (α) on the liquid crystal stationary phase (column III) is achieved at a lower temperature in the nematic state. It decreases as the temperature increases for most of the samples. The anisotropic forces are strong in the beginning of the nematic state ie. at a lower temperature. As the temperature is increased these anisotropic forces become weaker and less prominent and the selectivity for para isomer decreases resulting in a decrease in (α) value. For column III the crystal to nematic transition takes place at 107°C, therefore the retention data for all the three columns is recorded at this temperature,at which maximum

Table I

Effect of solid support on the behaviour of the stationary phase

Relative retentions (α) for p-xylene isomer.

Temp. (°C)	70	75	80	85	90	95	100	107*	110	130
(α)A	1.018	1.136	1.120	1.109	1.101	1.093	1.074	1.087	1.077	1.038
(α)B	1.027	1.029	1.036	1.042	1.046	1.053	1.059	1.104	1.086	1.035

A - Liquid Crystal phase on chromosorb W. DMCS

B - Liquid crystal phase on celite

*C-N transition temperature for the L.C. Phase selectivity of the liquid crystalline phase for positional isomer separations is observed.

The previous work on laterally substituted and unsubstituted liquid crystalline stationary phases indicated that due to lateral substitution a gap is formed between adjacent molecules of the liquid crystal compound and in this gap the para substituted probe molecules fit more tightly. Hence their retention time increases as compared to the meta isomers. Also, (α) values were found to be higher on laterally substituted liquid crystalline stationary phases. Thus, a laterally substituted nematic liquid crystalline phase has been used in column III.

Differences in retention times (t'R) are a measure of the separating power of a stationary phase. The retention times of the alkyl benzenes studied are given in (Table II).

At a particular temperature, the retention times of the alkyl benzenes increase with increase in their boiling points on columns I and II, but column III shows abnormal behaviour in this respect. For instance, of the C_6-C_8 mono- and di-alkyl benzenes, para-xylene with a lower boiling point than meta-xylene elutes more slowly with a longer retention time. This behaviour of alkyl benzenes on liquid crystalline stationary phases can be explained on the basis of the size and shape of the eluting molecules.

Table II

Retention times for alkylbenzenes on columns
I, II and III at 107°C

Compound	Boiling point (°C)	t'R (min)		
		Column I	Column II	Column III
Benzene	80.10	1.21	1.30	1.68
Toluene	110.60	1.61	1.81	2.47
Ethylbenzene	136.25	2.26	2.71	3.56
p-Xylene	137-138	2.34	2.77	4.31
m-Xylene	139	2.32	2.78	3.97
o-Xylene	144	2.55	3.28	4.73
Styrene	145-146	2.48	3.44	5.56
Isopropylbenzene	152-153	2.90	3.57	4.40
n-propylbenzene	159.20	3.33	4.23	5.73
m-Ethyltoluene	161.30	3.39	4.48	5.98
p-Ethyltoluene	161.98	3.43	4.57	6.73
1,3,5-Trimethylbenzene	164.71	3.56	4.65	6.78
1,2,4-Trimethylbenzene	169.4	-	-	-
m-Cymene	175	4.67	6.10	6.76
1,2,3-Trimethylbenzene	176.08	-	-	-
p-Cymene	177	4.67	6.10	8.21

Continued ...

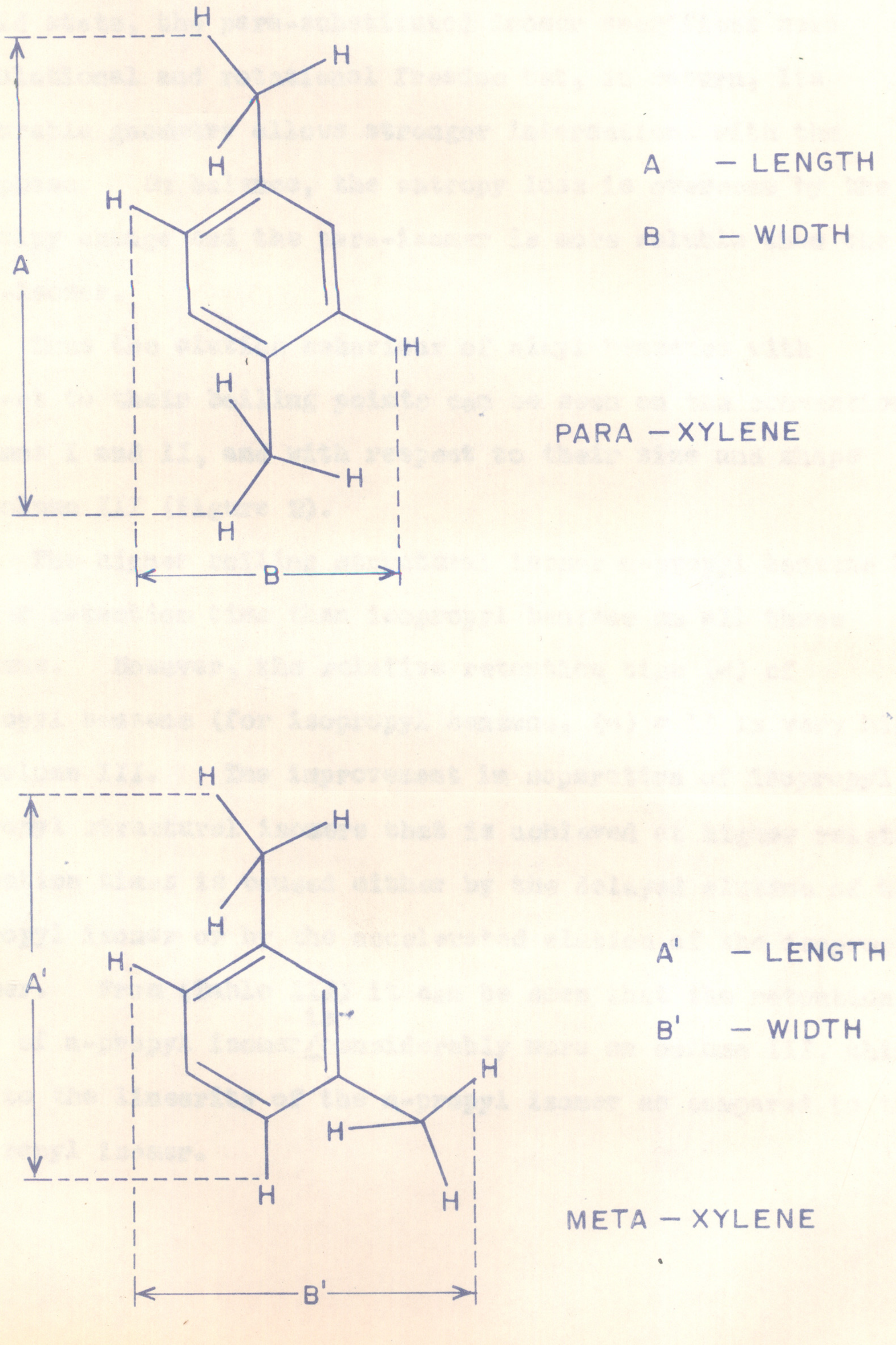
Table II (continued)

Compound	Boiling point °C	t'R (min.)		
		Column I	Column II	Collumn III
m-Diethylbenzene	181.25	5.23	7.06	8.57
p-Diethylbenzene	183.75	5.40	7.34	10.83
2,5-Dimethylethylbenzene	186.91	6.35	8.64	12.62
2,4-Dimethylethylbenzene	188.41	6.13	8.87	13.12
3,4-Dimethylethylbenzene	189.75	6.35	9.21	13.13
3,5-Diethyltoluene	200.71	8.62	12.51	13.92
m-Diisopropyl benzene	203.18	9.40	12.25	11.96
p-Diisopropyl benzene	210.36	10.66	14.40	17.30
1,3,5-Triethyl benzene	215.92	13.65	20.56	21.94
3,5-Diisopropyltoluene	218	14.71	20.16	15.54
p-Ethylvinylbenzene	73/10 mm Hg	5.45	9.76	14.85
m-Divinylbenzene	52/3 mm Hg	7.92	13.60	19.97
p-Divinylbenzene	52/4 mm Hg	7.52	12.68	24.50

Considering the meta- and para- xylene isomers, the molecular length to width ratio is higher for para-xylene than meta-xylene (Figure 1). In the nematic state of the liquid crystalline phase the molecules are highly oriented and possess a rod-like molecular structure[4]. When an alkyl benzene passes through this oriented state in the GLC column, the more linear molecules (example para-xylene of para- and meta-xylene isomers) fit readily into the nematic 'lattice' and thus have a longer retention time, than less linear molecules (meta-xylene in this instance). Ortho-xylene isomer has a higher boiling point than the close boiling meta- and para-xylenes, is eluted after para-xylene. The unusual solvent properties of the nematic stationary phase, due to the ordered arrangement of their molecules has one obvious consequence that the different positional isomers show different solubilities owing to the differences in shape between their molecules. The linear isomers dissolve more easily, their molecules resembling more closely the rod-shaped molecules of the solvent. The observed selectivity of the nematic solvent, between close boiling meta- and para-disubstituted benzenes can also be rationalised in thermodynamic terms[5]. The enthalpy and entropy of solution, of the para-isomers in the mesophase are lower indicating, respectively, stronger solvent-solute interactions

FIGURE 1.

LENGTH TO WIDTH RATIO OF META– AND PARA–XYLENES SCHEMATIC REPRESENTATION



$$\frac{A}{B} > \frac{A'}{B'}$$

and a better ordered solution state. In going from the disordered vapour (similar for both isomers) to the ordered liquid state, the para-substituted isomer sacrifices more translational and rotational freedom but, in return, its favourable geometry allows stronger interactions with the mesophase. On balance, the entropy loss is overcome by the enthalpy change and the para-isomer is more soluble than the meta-isomer.

Thus the elution behaviour of alkyl benzenes with respect to their boiling points can be seen on the conventional columns I and II, and with respect to their size and shape on column III (Figure 2).

The higher boiling structural isomer n-propyl benzene has a longer retention time than isopropyl benzene on all three columns. However, the relative retention time (α) of n-propyl benzene (for isopropyl benzene, (α) = 1) is very high on column III. The improvement in separation of isopropyl and n-propyl structural isomers that is achieved at higher relative retention times is caused either by the delayed elution of the n-propyl isomer or by the accelerated elution of the isopropyl isomer. From (Table III) it can be seen that the retention time of n-propyl isomer is considerably more on column III, this is due to the linearity of the n-propyl isomer as compared to the isopropyl isomer.

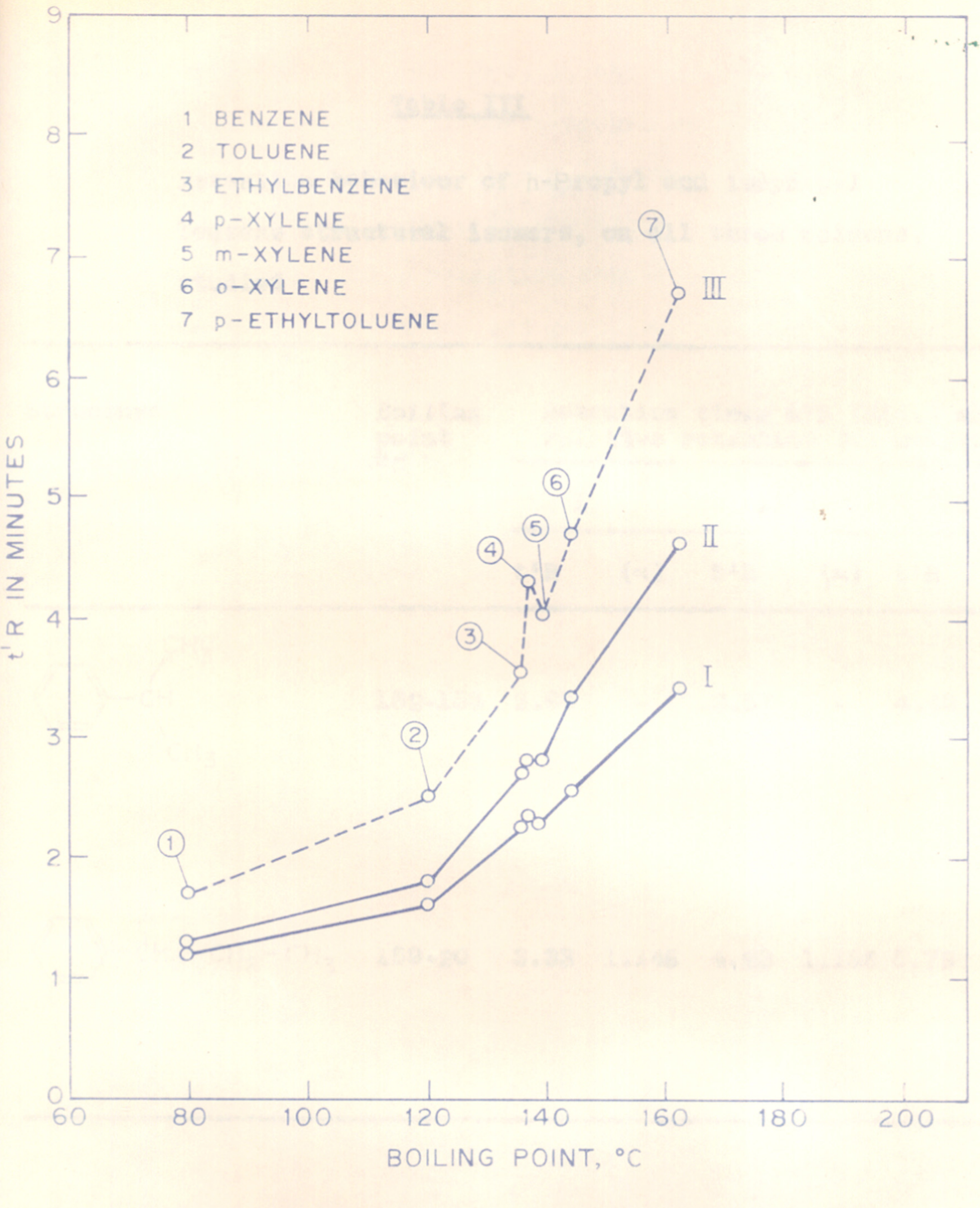
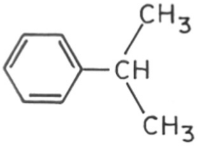
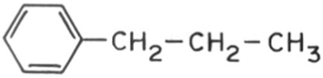


FIG. 2. t'R vs. BOILING POINT FOR COLUMN Nos. I, II, III

Table III

Retention behaviour of n-Propyl and isopropyl benzene structural isomers, on all three columns, studied

Structure	Boiling point °C	Retention times t'R (Mins) and relative retention (α) values					
		I		II		III	
		t'R	(α)	t'R	(α)	t'R	(α)
	152-153	2.90	-	3.57	-	4.40	-
	159·20	3.33	1.148	4.23	1.185	5.73	1.302

Hence it can be concluded, that, at the higher relative retention times the more linear n-propyl benzene isomer is eluted slowly as compared with the isopropyl benzene.

The alkyl chain length in the alkyl benzenes has a profound effect on their retention behaviour. When the retention behaviour of meta- and para-isomers of ethyl toluenes, cymenes, diethyl benzenes and diisopropyl benzenes is considered on all three columns studied, it is observed that the retention of these meta- and para-isomers depends solely on their boiling points for columns I and II, giving nearly identical retention times (Table IV). However as the alkyl chain length increases, the difference in retention time ($t'R_{para}$ - $t'R_{meta}$) increases on column III.

It is already obvious from the above results discussed that the separations obtained on the liquid crystal nematic phase are determined by the linearity of the molecule. But, the planarity of a molecule can also play an important role in the retention behaviour of a particular solute on the liquid crystalline phase. As shown in (Table V) a large difference in retention time is observed between close boiling 1,3,5-triethyl benzene and 3,5-diisopropyl toluene on column III. On column I the elution takes place on the basis of boiling point. The retention time for both the solutes has increased on

TABLE - IV

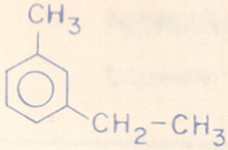
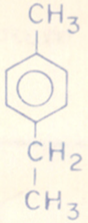
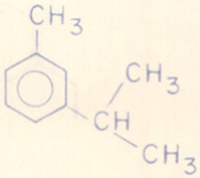
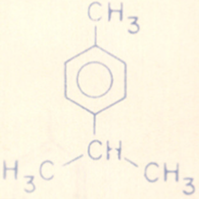
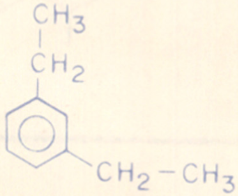
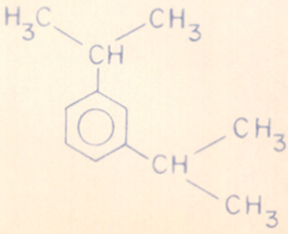
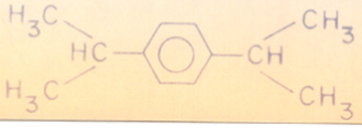
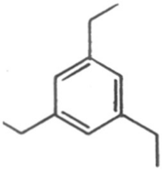
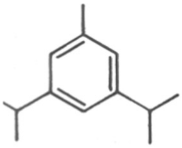
STRUCTURE OF THE ISOMER	BOILING POINT(°C.)	t′R (MINS)		
		COLUMN I	COLUMN II	COLUMN III
	161·30	3·39	4·48	5·98
	161·98	3·43	4·57	6·73
	175	4·67	6·10	6·76
	179	4·67	6·10	8·21
	181·25	5·23	7·06	8·57
	183·75	5·40	7·34	10·83
	203·18	9·40	12·25	11·96
	210·36	10·66	14·40	17·30

Table V

Retention behaviour of symmetrical triethylbenzene and 2,5-diisopropyl toluene

Structure	Boiling point (oC)	Molecular weight	Retention time t'R (Min)		
			Column I	Column II	Column III
	215.92	162	13.65	20.56	21.94
	218.0	176	14.71	20.16	15.54

column II, this may be due to the polar phenyl groups in the OV-17 stationary phase. In the case of column III, the interesting point is that inspite of the fact that 3,5-diisopropyl toluene has both a higher boiling point and molecular weight than 1,3,5-triethyl benzene, the former elutes faster than the latter. This is due to the planarity of the molecules of 1,3,5-triethyl benzene, which fit tightly in the oriented molecules of the liquid crystalline compound and hence elute slowly. A similar example of separation on basis of planarity on a liquid crystal column has been reported by Witkiewicz et al.[6] (benzene when compared with cyclohexane and cyclohexene).

<u>Relative retention times (α)values.</u>

Selectivity of a particular column for the separation of two components is determined by the relative retention of one component with respect to other and is denoted by(α). The relative retention times (for para-isomers relative to the corresponding meta isomer = 1), calculated from (Table II) are presented in (Table VI). The (α) values have been obtained on all three columns at the crystal to nematic transition temperature of the liquid crystal phase ie. at 107°C. The high (α) values obtained on column III for the positional and structural isomers point out to the superiority and selectivity of the liquid crystal nematic

Table VI

Relative retentions (α) of para-substituted alkyl benzenes

(m-isomer = 1.00)

Compound	(α)		
	I	II	III
p-Xylene	1.009	1.00	1.104
n-Propylbenzene*	1.148	1.185	1.302
p-Ethyl toluene	1.012	1.022	1.126
p-Cymene	1.00	1.00	1.213
p-Diethylbenzene	1.032	1.040	1.261
2,4-Dimethyl ethylbenzene**	1.01	1.020	1.01
p-Diisopropyl benzene	1.140	1.64	1.44

*Isopropyl benzene = 1

**3,4-dimethyl ethylbenzene = 1

stationary phase as compared to the conventional phases.

The three dimethyl ethylbenzene isomers considered cannot be separated on any of the three columns (Table VII)a,b) Being very close boiling they cannot be separated on columns I and II. When the linearity of the isomers is considered for obtaining separations on column III, the two isomers 2,4-dimethyl ethyl benzene and 3,4-dimethyl ethylbenzene are slightly linear than the 2,5-dimethyl ethylbenzene isomers, due to which 2,5-dimethyl ethylbenzene elutes with a slightly shorter retention time. But on the whole the length to breadth ratios of the three isomers do not differ significantly so as to obtain separation. The actual length to width ratios calculated (approx) for all the pairs of isomers studied are given in (Table VIII). The length and width of the molecule is calculated using the literature* values for the C-C, C-H (aliphatic); C-C, C-H, C=C, (aromatic) bond lengths in Angstrom units.

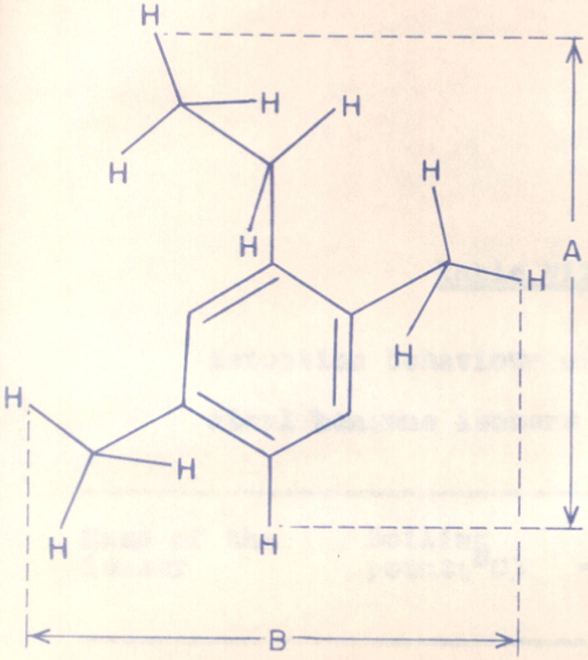
---

*Interatomic distances and bond angles compiled by Yonezo Morino in, Handbook of organic structural analysis- Yasuhide Yukawa, Edt. W.A. Benjamin, Inc., N.Y. (1963).

TABLE VII a

LENGTH TO WIDTH RATIOS OF DIMETHYLETHYLBENZENE ISOMERS

$$\frac{A}{B} < \frac{A'}{B'} \backsim \frac{A''}{B''}$$



2,5-DIMETHYLETHYLBENZENE

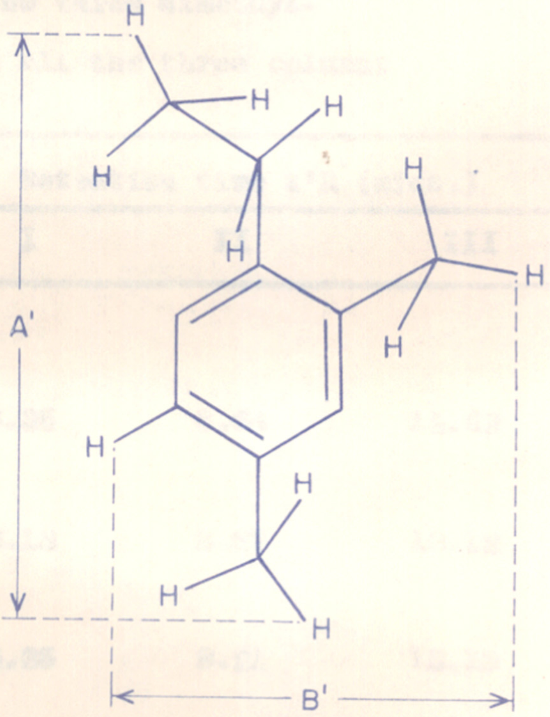
A – LENGTH

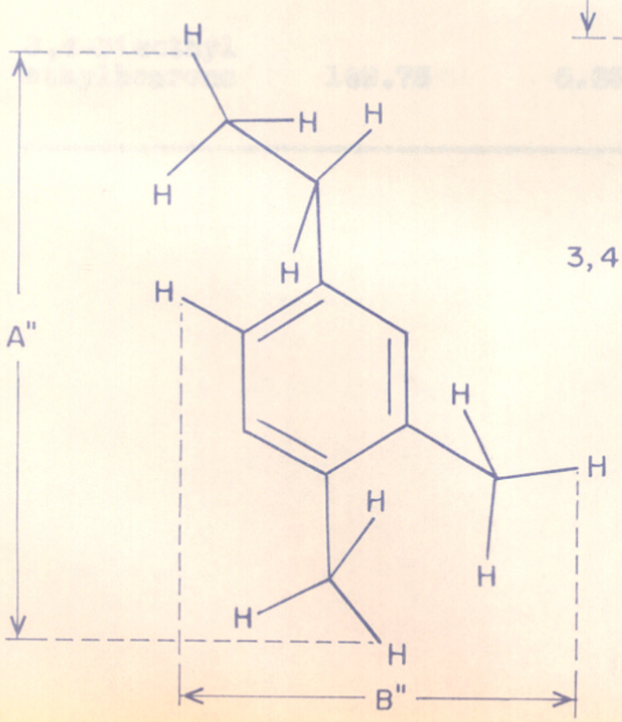
B – WIDTH

2,4-DIMETHYLETHYLBENZENE

A' – LENGTH

B' – WIDTH





3,4-DIMETHYLETHYLBENZENE

A" – LENGTH

B" – WIDTH

Table VIIb

Retention behaviour of the three dimethylethyl benzene isomers on all the three columns

Name of the isomer	Boiling point(°C)	Retention time t'R (mins.)		
		I	II	III
2,5-Dimethyl ethylbenzene	186.91	6.35	8.64	12.62
2,4-Dimethyl ethylbenzene	188.41	6.13	8.87	13.12
3,4-Dimethyl ethylbenzene	189.75	6.35	9.21	13.13

Table VIII

Length to width ratios of m-, p-isomers

B.P. (°C)	Isomer	Length A°	Width A°	Length/width Ratio	para/meta	Relative retention (α) Col. III
139	m-Xylene	6.49	6.09	1.065	1.312	1.104
137-138	p-Xylene	8.02	4.56	1.397		
152-153	Isopropyl benzene	7.99	4.56	1.752	1.161	1.302
159.2	n-Propyl benzene	9.49	4.56	2.081		
161.30	m-Ethyltoluene	6.49	7.59	0.8539	2.444	1.126
161.98	p-Ethyltoluene	9.52	4.56	2.087		
164.71	1,3,5-Trimethyl benzene	6.49	7.62	0.8515		
169.4	1,2,4-Trimethyl benzene	8.02	6.09	1.317	1.346	1.288
176.08	1,2,3-Trimethyl-benzene	6.49	6.09	1.068	1.254	1.621
175	m-Cymene	6.49	7.59	0.8539	2.444	1.213
177	p-Cymene	9.52	4.56	2.087		
181.25	m-Diethyl-benzene	7.99	7.59	1.053	2.295	1.261
181.75	p-Diethyl-benzene	11.02	4.56	2.416		
186.91	2,5-Dimethylethyl benzene	7.99	7.62	1.048		
188.41	2,4-Dimethylethyl benzene	9.52	6.09	1.563	1.491	1.04
189.75	3,4-Dimethyl-ethylbenzene	9.52	6.09	1.563	1.491	1.04

continued..

Table VIII (continued)

B.P. (°C)	Isomer	Length A°	Width A°	Length/Width Ratio	para/meta	Relative retention (α) Col. III
203.18	m-Diisopropyl benzene	7.99	7.59	1.053	2.295	1.44
210.36	p-Diisopropyl benzene	11.02	4.56	2.416		
52/3 mm	m-Divinylbenzene	7.86	7.46	1.054	2.239	1.227
52/4 mm	p-Divinylbenzene	10.76	4.56	2.359		

Applications of column III as an analytical column

The separation of the three xylene isomers from low boiling ethylbenzene and higher boiling styrene is very difficult on conventional columns I and II. These separations have been tried by many workers using different stationary phases and varying column lengths[7], wherein Bentone-34 seems to give good resolution when mixed with silicone stationary phases[8]. A rapid separation of these is obtained on column III (Figures 3 and 10).

The separation of benzene, toluene, ethylbenzene and o-, m-, and p-xylenes using a polar solid stationary phase was carried out by Belyakova et al.[9] Carbopack C modified with 2,4,5,7-tetranitrofluorenone (TeNF) as a stationary phase was used by Dicorcia et al.[10], to separate alkyl benzenes. Bentone-34 in a modified form was also used by several workers[7,8,11,12] giving improved resolution and separation, but here too, the columns are of considerable length and the analysis time is long. Separation was achieved by using 7,6 or 5 meter columns with liquid crystals as stationary phases. Separation of benzene, toluene and xyleneisomers is achieved on a 1.84 m. column III in a very short time (Figure 3).

The separation and identification of structural and positional isomers of mono-, di-, and tri-substituted alkyl

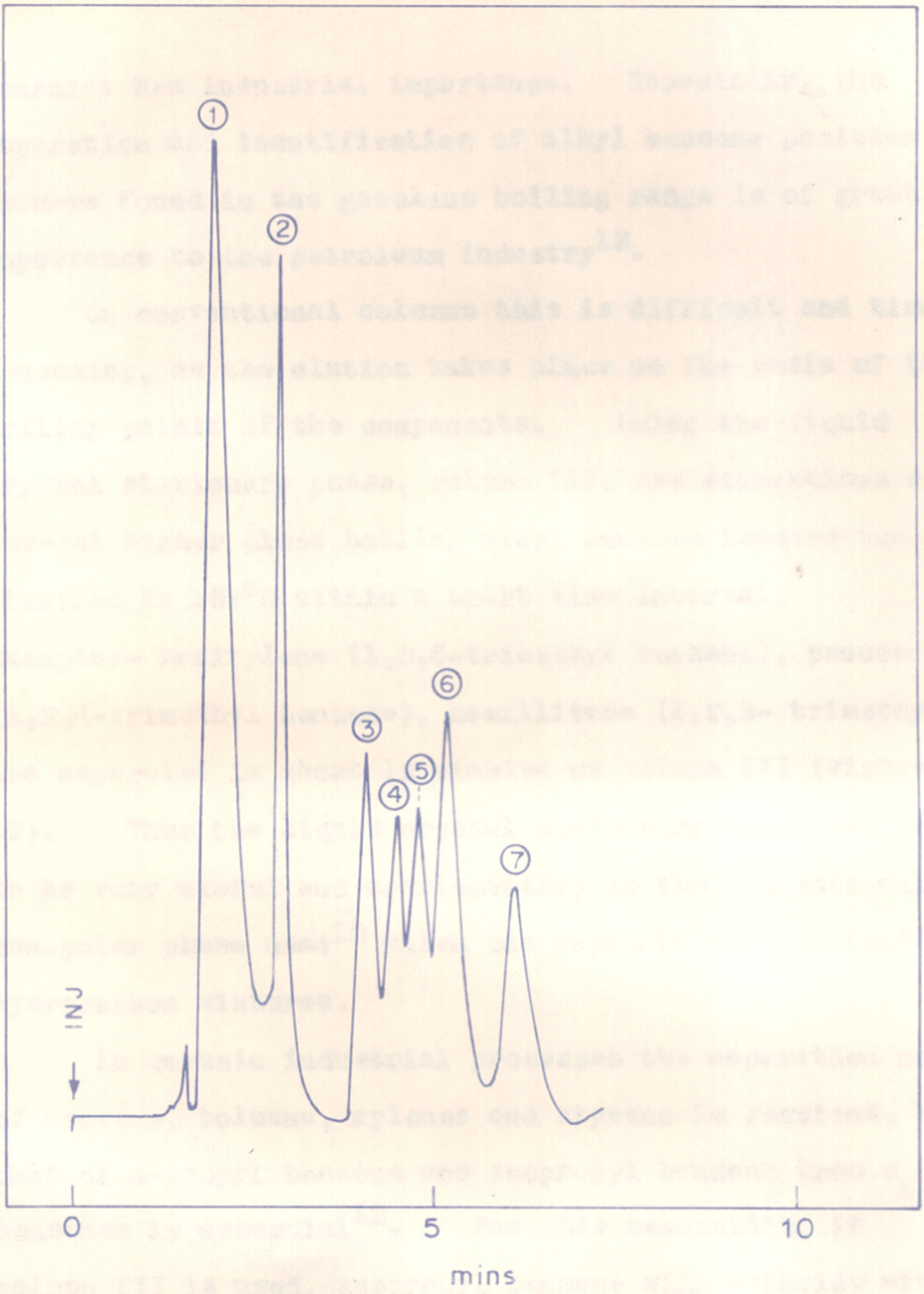


FIG. 3. GAS CHROMATOGRAM OF A MIXTURE OF ALKYL BENZENES ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 200 °C; DETECTOR TEMPERATURE 300 °C; FLAME IONISATION DETECTOR; NITROGEN FLOW-RATE, 40 ml / min.

PEAKS: 1. BENZENE; 2. TOLUENE; 3. ETHYLBENZENE; 4. m-XYLENE; 5. p-XYLENE; 6. o-XYLENE; 7. STYRENE.

benzenes has industrial importance. Especially, the separation and identification of alkyl benzene positional isomers found in the gasoline boiling range is of great importance to the petroleum industry[13].

On conventional columns this is difficult and time consuming, as the elution takes place on the basis of the boiling points of the components. Using the liquid crystal stationary phase, column III, the separations of several higher close boiling alkyl benzene isomers are obtained at 107°C within a short time interval. Example:- Mesitylene (1,3,5-trimethyl benzene), pseudocumene (1,2,4-trimethyl benzene), hemillitene (1,2,3- trimethyl benzene) are separated in about 12 minutes on column III (Figures 4 and 10). Thus the liquid crystal stationary phase can prove to be very useful and complementary to the conventional non-polar phase used[13] which can separate the low boiling hydrocarbon mixtures.

In certain industrial processes the separation not only of benzene, toluene, xylenes and styrene is required, but also that of n-propyl benzene and isopropyl benzene from C_8 alkyl benzenes is essential[12]. For this separation, if column III is used, isopropyl benzene will coincide with para-xylene and n-propyl benzene with styrene, but all four compounds can be separated on column II (Table IX).

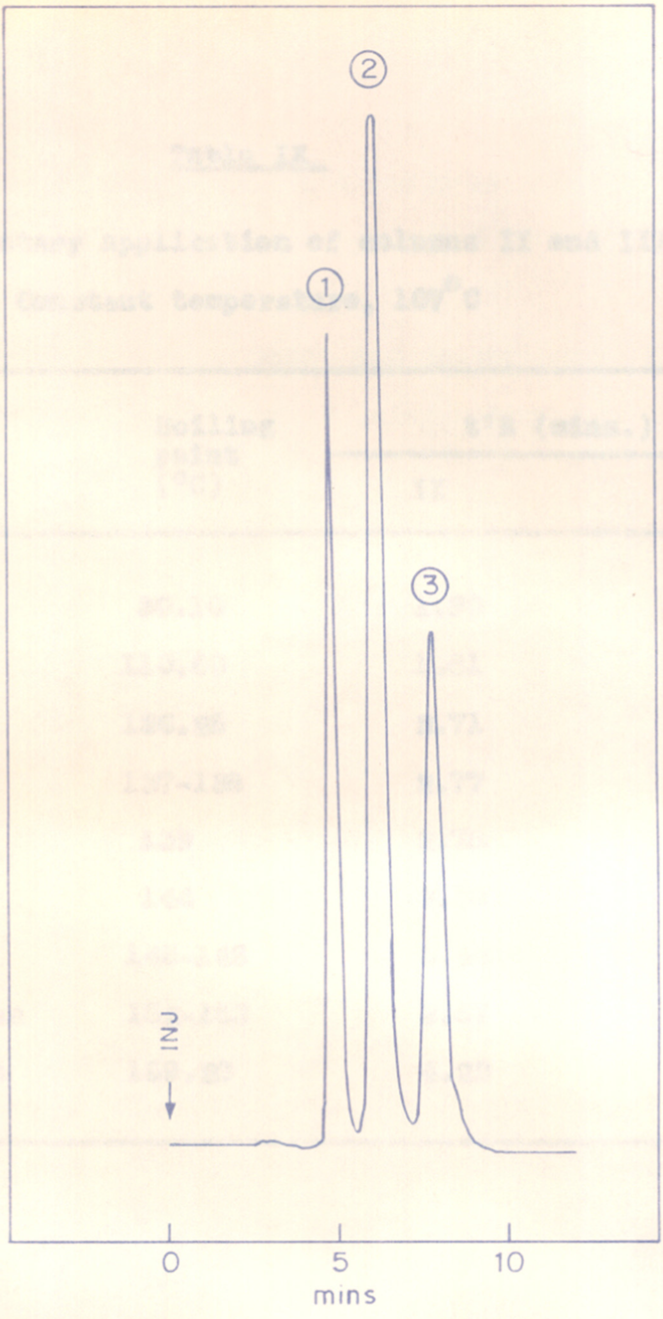


FIG. 4. GAS CHROMATOGRAM OF A MIXTURE OF THE THREE TRIMETHYL BENZENE ISOMERS ON COLUMN III

OVEN TEMPERATURE 110 °C; INJECTOR TEMPERATURE 200 °C; DETECTOR TEMPERATURE 300 °C; FLAME IONISATION DETECTOR; NITROGEN FLOW-RATE, 40 ml / min

PEAKS: 1. 1, 3, 5-TRIMETHYLBENZENE; 2. 1, 2, 4-TRIMETHYLBENZENE; 3. 1, 2, 3-TRIMETHYLBENZENE

Table IX

Complementary application of columns II and III

Constant temperature, 107°C

Compound	Boiling point (°C)	t'R (mins.)	
		II	III
Benzene	80.10	1.30	1.68
Toluene	110.60	1.81	2.47
Ethyl benzene	136.25	2.71	3.56
para-Xylene	137-138	2.77	4.31
meta-Xylene	139	2.78	3.97
ortho-Xylene	144	3.28	4.73
Styrene	145-146	3.44	5.56
Isopropylbenzene	152-153	3.57	4.40
n-Propylbenzene	159.20	4.23	5.73

Thus using two columns in the same instrument at a particular temperature (in this instance 107°C) one can rapidly achieve an effective separation of all components within 5 to 6 minutes.

Recently, Brian L. Booth and co-workers[14] have reported the methylation of para-cymene using methyl triflate in the presence of aluminium chloride which gives rise to number of products, due to alkylation, isomerisation and dialkylation. The determination of these products is very difficult, unless they can be resolved by GLC. Of the nine products (benzene, toluene, o-, m-, p-xylenes, isopropyl benzene, m- and p-cymene and 3,5-diisopropyl toluene) only six can be resolved using columns I and II, the conventional columns, whereas eight components are resolved using column III at a constant temperature (Figure 10). Several other isomeric alkyl benzene products obtained which are not studied here could be resolved using only column III.

There are several references cited in the literature where the alkyl benzene product analyses has presented several difficulties in identification and determination.

Interactions of xylenes with ethylbenzene

In the studies of interactions of xylenes with ethylbenzene by M.C. Hoff[15], the products were analysed by fractional and infra-red absorption of cuts and blends.

R.H. Allen et al. have carried out a study of kinetics of three compound equilibrium, presented in a series of papers:

I Isomerisation of cymene[16] in which analysis was done by IR spectroscopy.

II Isomerisation of xylenes[17], here the analysis was carried out by GLC and IR. A 10 feet column was used, packed with a conventional phase. Meta- + para-xylene and ortho-xylene areas were obtained, and differential IR was used for ortho-xylene calculation.

III. Isomerisation of ethyl toluenes[18], analysis was done by IR spectroscopy.

Friedel-Crafts reactions (product analysis)

The Friedel-Crafts reaction is one of the important reactions by which alkylation, acylation and isomerisation of organic compounds can be carried out. This reaction is associated with isomerisation, rearrangement, unusual orientation or degradation of the alkyl group. The products are usually liquids, difficult to separate and identify. Several methods[19-25] of chemical analysis employed previously are laborious and time consuming. Even IR and UV spectroscopy prove to be a cumbersome technique for the analyses of alkylated benzenes and isomeric alkyl benzenes[26]

GLC is the most reliable analytical method for the separation and identification of alkylated aromatic hydrocarbons. The simplicity and accuracy of this analytical technique has made it popular in industry as well as research laboratories.

The use of conventional analytical columns brings a limitation to this technique. Alkylated aromatic hydrocarbons can be identified qualitatively and quantitatively by this method within a short time interval, provided they differ in their boiling points. The identification of the positional isomers of di- and tri-alkyl benzenes proves to be very difficult.

G.A. Olah and co-workers while carrying out Friedel-Crafts isomerisation of t-butyl toluenes[27], diisopropyl benzenes[28], and the $AlCl_3$-catalysed, Friedel-Crafts alkylation of benzene and toluene with esters and haloesters[29], analysed the alkyl benzene products by GLC using 150 feet Golay-type capillary columns coated with modified conventional stationary phases.

Column III, with the liquid crystal phase is promising for the analysis of the products of reactions similar to these.

Recently we have carried out the Friedel-Crafts alkylation of benzene, toluene and ethylbenzene with organic esters using $AlCl_3$ as a catalyst. The products formed were completely analysed, quantitatively with identification, by

GLC, using a liquid crystalline analytical column[30], of normal length.

Also, the liquid crystal column was successfully used to analyse the products of the reactions of cyclo alkylation of aromatic hydrocarbons, isomerisations of p-cymene and 3-carene carried out in our laboratory[31].

The clear separation of meta- and para-cymenes [$(\alpha) = 1.213$] (Figure 5); meta- and para-diisopropylbenzenes [$(\alpha) = 1.264$] (Figure 6); meta- and para-diethyl benzenes [$(\alpha) = 1.261$] (Figure 7) and of meta- and para-ethyl toluenes [$(\alpha) = 1.126$] (Figure 8) is obtained within a very short time on column III.

[Witkiewicz et al.[32] have recently reported the separation of meta- and para- ethyl toluenes with very long retention times on 5 meter column using a liquid crystalline phase].

Separation of m- p-divinyl benzenes and p-ethyl vinyl benzene

Divinyl benzene (DVB) has extensive commercial use as a cross linking monomer in the preparation of poly (styrene/DVB) copolymer. Such copolymers serve as important precursors in the production of anionic and cationic exchange resins. GLC separations of meta- and para-DVB have been reported in the past on Carbowax 6000 and di-2-ethyl hexyl sebacate[33], on Bentone-34[34,35] and on a liquid crystal column of 10 feet

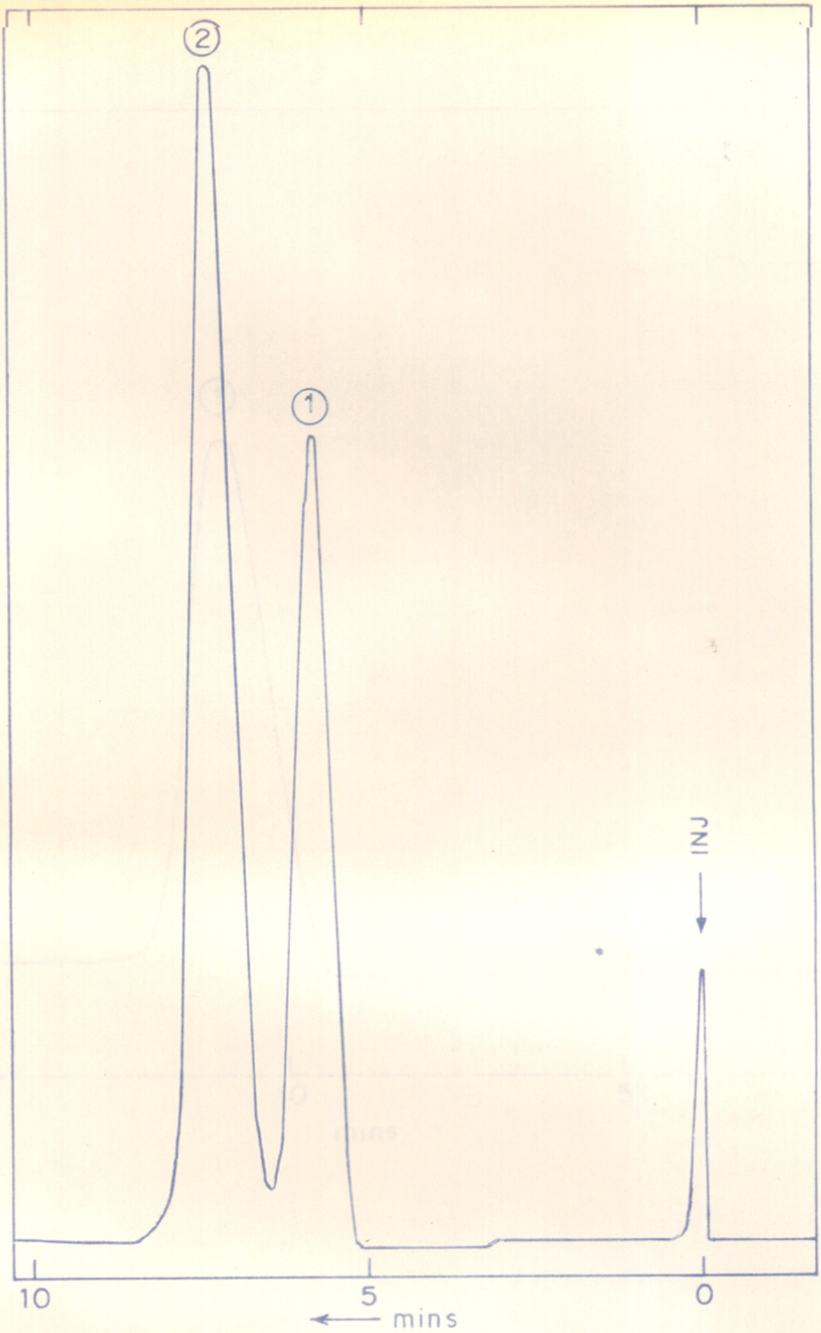


FIG. 5. GAS CHROMATOGRAM OF A MIXTURE OF META- AND PARA-CYMENES ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 150 °C; DETECTOR TEMPERATURE 225 °C; THERMAL CONDUCTIVITY DETECTOR; HYDROGEN FLOW-RATE 25·20 ml/min

PEAKS: 1. m-CYMENE; 2. p-CYMENE

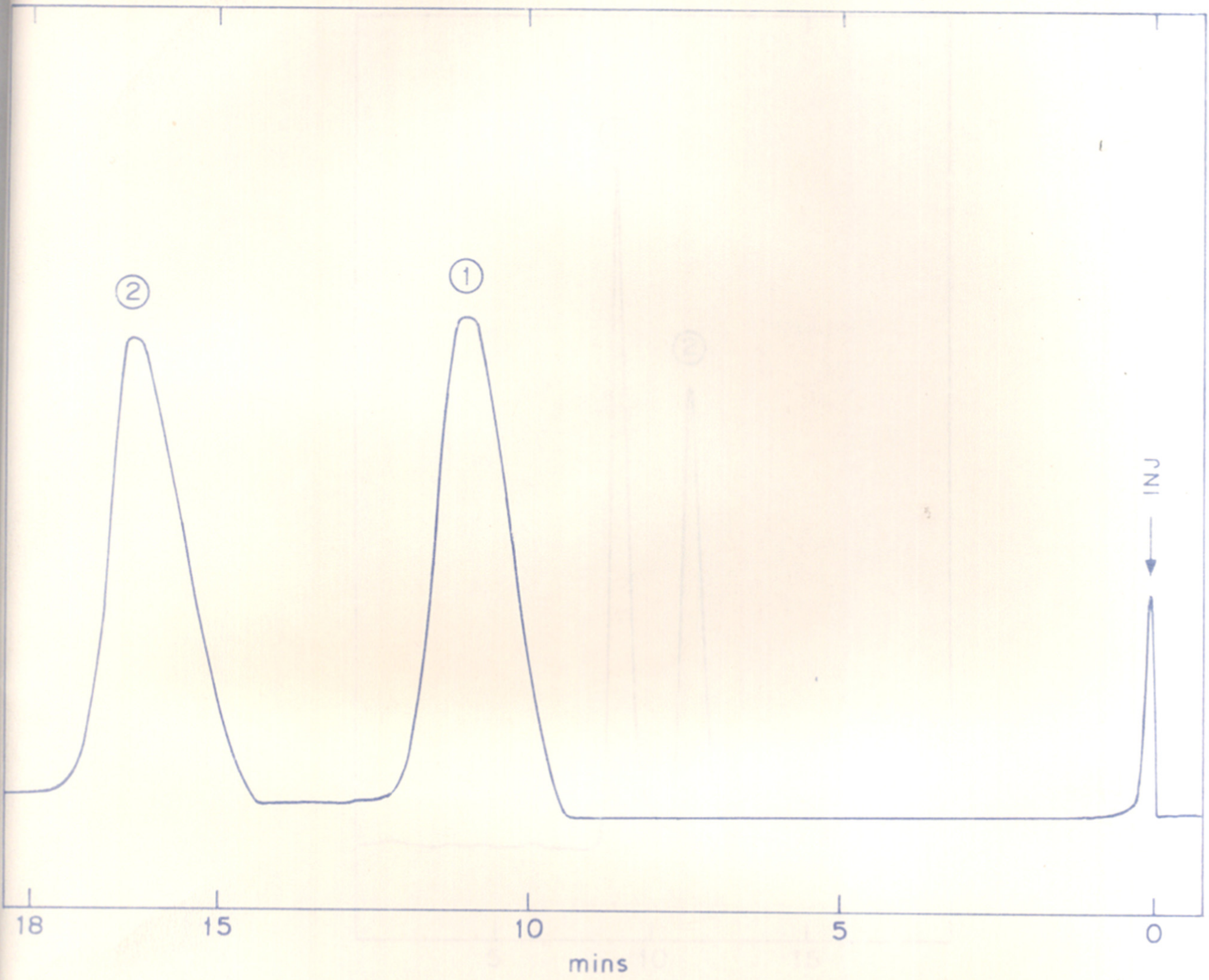


FIG. 6. GAS CHROMATOGRAM OF A MIXTURE OF META AND PARA-DIISOPROPYL BENZENES ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 150 °C; DETECTOR TEMPERATURE 225 °C; THERMAL CONDUCTIVITY DETECTOR; HYDROGEN FLOW-RATE 25·20 ml/min

PEAKS: 1. m-DIISOPROPYL BENZENE; 2. p-DIISOPROPYL BENZENE.

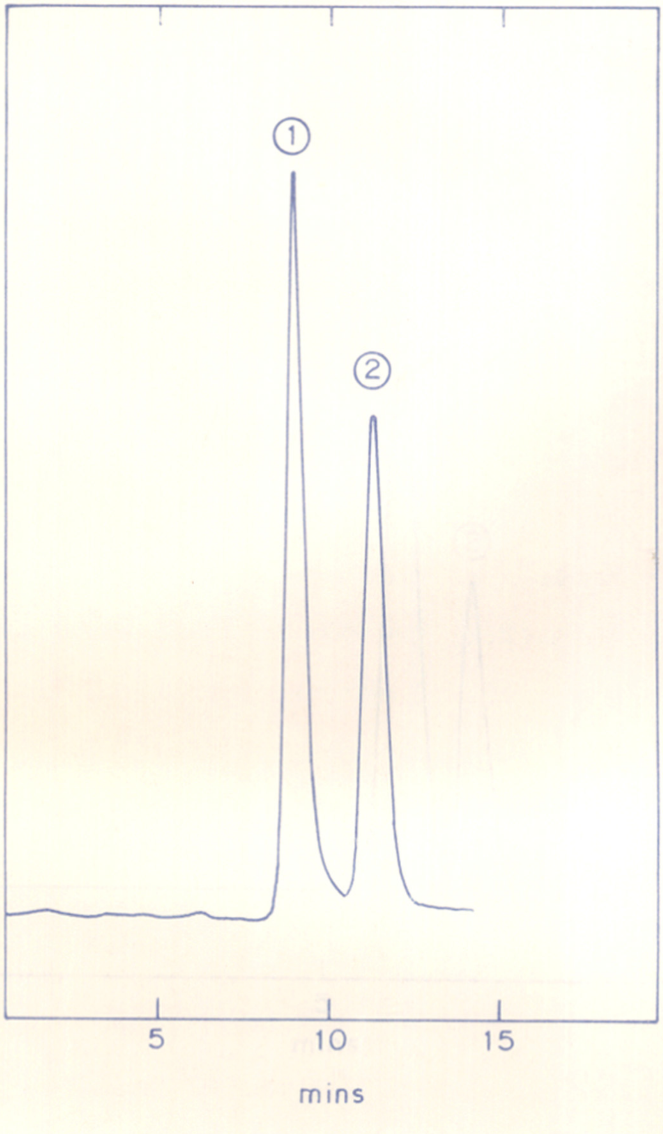


FIG. 7. GAS CHROMATOGRAM OF A MIXTURE OF META-AND PARA-DIETHYL BENZENES ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 200 °C; DETECTOR TEMPERATURE 300 °C; FLAME IONISATION DETECTOR; NITROGEN FLOW-RATE, 40 ml / min

PEAKS: 1. m-DIETHYLBENZENE; 2. p-DIETHYLBENZENE.

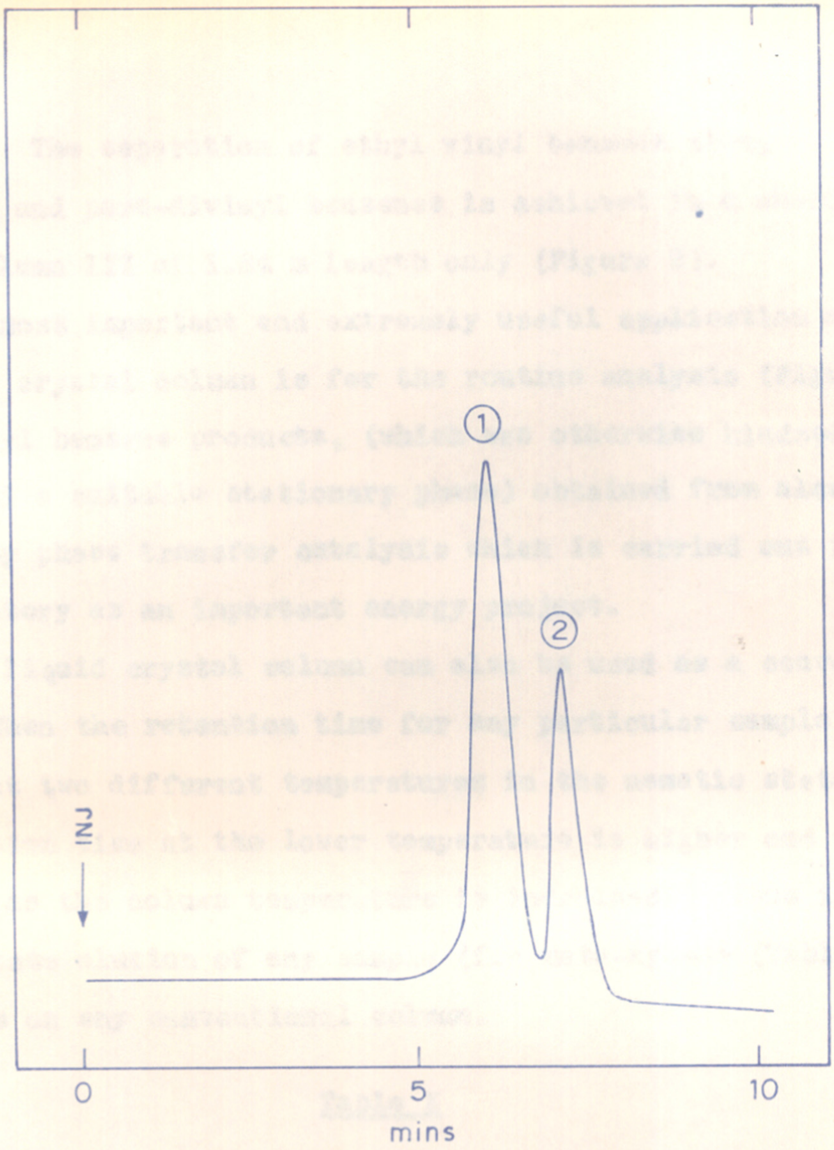


FIG. 8. GAS CHROMATOGRAM OF A MIXTURE OF META-AND PARA-ETHYL TOLUENES ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 200 °C; DETECTOR TEMPERATURE 300 °C; FLAME IONISATION DETECTOR; NITROGEN FLOW-RATE, 40 ml / min

PEAKS: 1. m-ETHYL TOLUENE; 2. p-ETHYL TOLUENE.

Length[36]. The separation of ethyl vinyl benzene along with meta- and para-divinyl benzenes is achieved in a short time on column III of 1.84 m length only (Figure 9).

The most important and extremely useful application of the liquid crystal column is for the routine analysis (Figure 10) of the alkyl benzene products, (which was otherwise hindered for the want of a suitable stationary phase) obtained from alcohol cracking by phase transfer catalysis which is carried out in our laboratory as an important energy project.

The liquid crystal column can also be used as a conventional column. When the retention time for any particular sample is observed at two different temperatures in the nematic state the retention time at the lower temperature is higher and it decreases as the column temperature is increased. Thus in the nematic state elution of any sample (for meta-xylene (Table X)) behaves as on any conventional column.

Table X

Column III as a conventional column

Test Substance	Temp. °C	90	95	100	107	110	120	130
Meta-Xylene	t'_R (mins.)	1.3	1.68	2.24	3.97	3.46	2.908	2.808

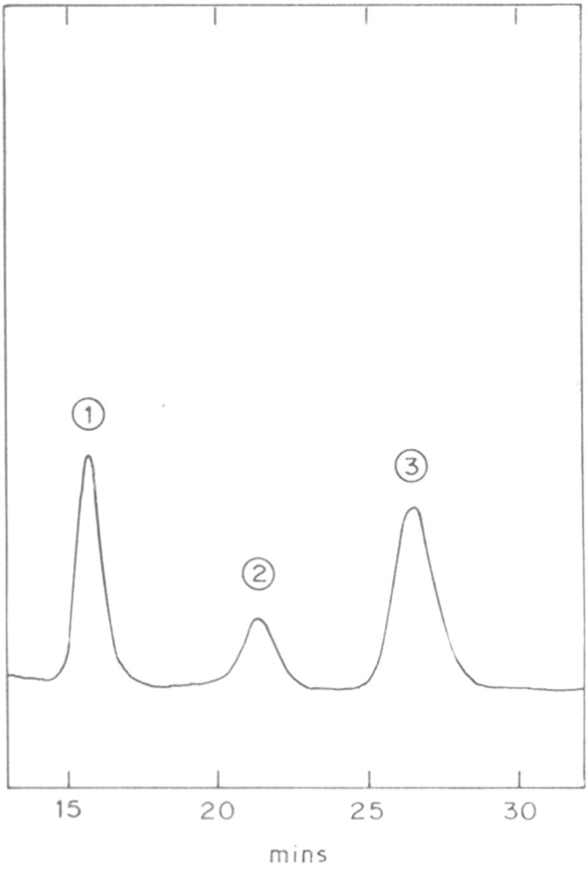


FIG. 9. GAS CHROMATOGRAM OF A MIXTURE OF p-ETHYL VINYL BENZENE, m-DIVINYL BENZENE AND p-DIVINYL BENZENE ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 200 °C; DETECTOR TEMPERATURE 300 °C; FLAME IONISATION DETECTOR; NITROGEN FLOW-RATE, 40 ml / min.

PEAKS: 1. p-ETHYL VINYLBENZENE; 2. m-DIVINYL BENZENE; 3. p-DIVINYL BENZENE.

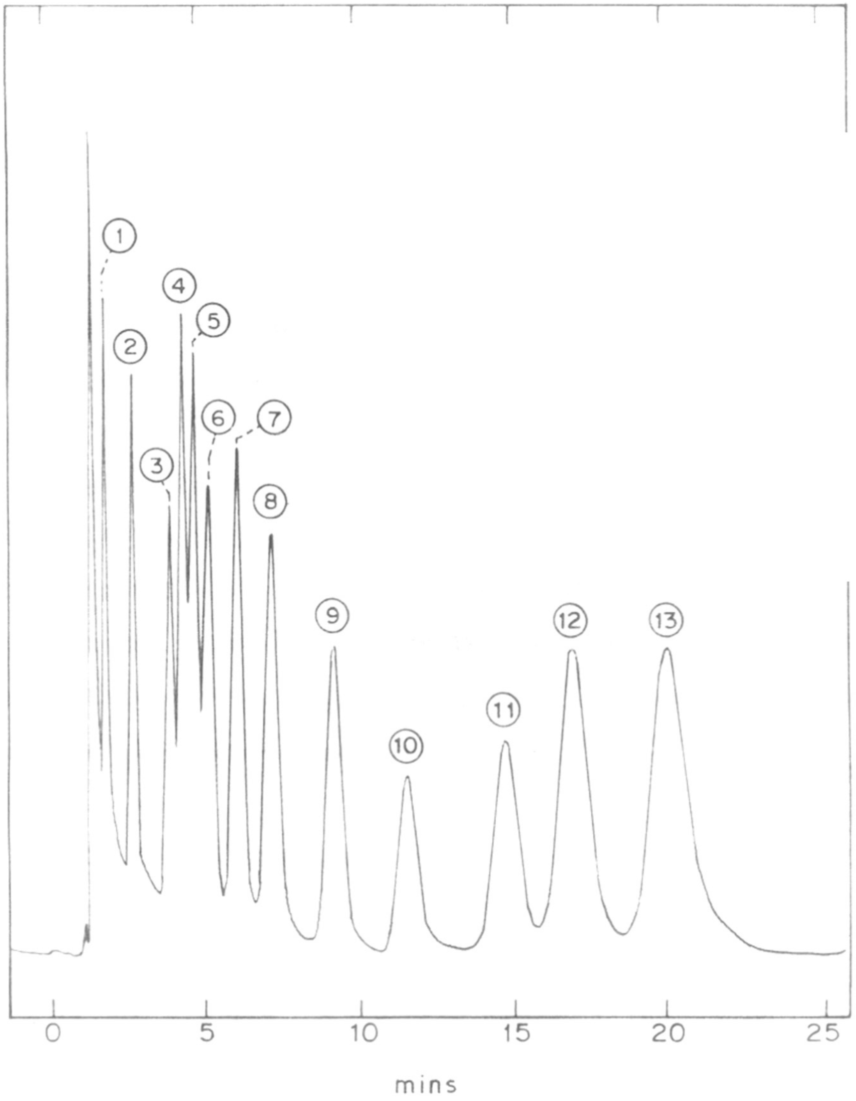


FIG. 10. GAS CHROMATOGRAM OF A MIXTURE OF ALKYL BENZENES ON COLUMN III

OVEN TEMPERATURE 107 °C; INJECTOR TEMPERATURE 200 °C; DETECTOR TEMPERATURE 300 °C; FLAME IONISATION DETECTOR; NITROGEN FLOW-RATE, 40 ml/min

PEAKS: 1. BENZENE; 2. TOLUENE; 3. ETHYLBENZENE; 4. m-XYLENE; 5. p-XYLENE; 6. o-XYLENE; 7. STYRENE; 8. 1,3,5-TRIMETHYLBENZENE; 9. 1,2,4-TRIMETHYLBENZENE; 10. 1,2,3-TRIMETHYBENZENE; 11. 3,5-DIETHYLTOLUENE; 12. p-DIISOPROPYLBENZENE; 13. 1,3,5-TRIETHYLBENZENE.

Therefore this column can also be used for the separation of components on the basis of boiling point, if compounds are not positional isomers.

The liquid crystal stationary phases are promising as universal sorbents with a controlable selectivity. They can be considered in view of their usefulness in all their regions of existance[37]- solid, liquid-crystal and isotropic liquid.

The efficiency of the liquid crystalline column is lower than that of the conventional columns[38], this is due to the high mass transfer resistance in the liquid crystalline phase. This resistance is caused by the high viscocity of the liquid crystal and it can vary depending on the kind of support and thus on the different arrangement of the liquid crystal molecules.

It can be inferred from the results that the liquid crystalline stationary phase can replace the conventional stationary phases. It resembles the conventional phases, because it can operate over a wide range of temperature to discriminate solutes on the basis of their boiling points. It has a high selectivity towards the separation of positional and structural isomers on the basis of linearity and planarity of t solutes. In addition, the analyses times are short.

REFERENCES

1. G.E. Baiulescu and V.A. Ilie in, 'Stationary phases in gas chromatography', Pergamon Press, Oxford (1975).
2. L. Rohrscheider, Gas Chromatogr., 6, 5 (1968).
3. K.P. Naikwadi, D.G. Panse, B.V. Bapat and B.B. Ghatge, J.Chromatogr., 195, 309 (1980).
4. T.S. Dewar and J.P. Schroeder, J.A.C.S., 86, 5236 (1964).
5. J.P. Schroeder, in 'Liquid Crystals and plastic crystals' Vol. I, G.W. Gray and P.A. Winsor (Eds.), Ellis Horwood, Chichester, England, 356 (1974).
6. Z. Witkiewicz and S. Popiel, J.Chromatogr., 154, 60 (1978).
7. H.W. Durbeck, Z. Anal.Chem., 251, 108 (1970).
8. J.V. Mortimer and P.L. Gent, Nature (London), 197, 789 (1963).
9. L.D. Belyakova, A.V. Kiselev, G.A. Soloyan, Chromatographia, 3, 254 (1970).
10. A. Dicorcia, A. Liberti and R. Samperi, J.Chromatogr, 122, 459 (1976).
11. F. Matausek, Z. Anal.Chem., 236, 201 (1968).
12. D.M. Ottenstein, D.A. Bartley and W.R. Supina, Anal.Chem., 46, 2225 (1974).
13. E.R. Adland, A.W. Bowen, D.G. Salmon, J.Chromatogr., 186, 207 (1979).

14. B.L. Booth, R.N. Hazeldiine, L. Khosrowhaali, J.Chem.Soc., Perkin Trans. I, 12, 2287 (1980).

15. M.C. Hoff, J.A.C.S., 80, 6046 (1958).

16. R.H. Allen, A. Turner Jr., L.D. Yats, J.A.C.S. 81, 42, (1959).

17. R.H. Allen and L.D. Yats, J.A.C.S., 81, 5289 (1959).

18. R.H. Allen, L.D. Yats and D.S. Erley, J.A.C.S., 82, 4853 (1960).

19. J.F. Norris, J.N. Ingraham, J.A.C.S., 60, 1421 (1938).

20. Bodroux, Ann.Chim., 11, 511 (1929).

21. Hennion, J.A.C.S., 66, 1801 (1944).

22. Shriner and Fusion, 'Identification of organic compounds', John Wiley and Sons, New York, 2nd Edn., 1940 (1941). .

23. Huntress and Autenrieth, J.A.C.S., 63, 3446 (1941).

24. Ipatieff and Schmerting, J.A.C.S., 59, 1056 (1937).

25. Price and Ciskowaski, J.A.C.S., 60, 2499 (1938).

26. D.A.Mc-Caulay, A.P. Lien, J.A.C.S., 74, 6246 (1952).

27. G.A. Olah, M.W. Meyer, N.A. Overchuk, J.Org.Chem., 29, 2310 (1964).

28. G.A. Olah, M.W. Meyer, N.A. overchuk, J.Org.Chem., 29, 2315 (1964).

29. G.A. Olah and J. Nishimura, J.A.C.S., 96, 2214 (1974).

30. K.P. Naikwadi, P.P. Powar, B.V. Bapat and B.B. Ghatge, Ind.J. of Tech., (Communicated).

31. D.G. Panse, B.V. Bapat, B.B. Ghatge, Ind.J. of Techn., 19, 518 (1981).

32. Z. Witkiewicz, J. Szulc, R. Dabrowski, J. Sudowski, J.Chromatogr., 200, 65 (1980).

33. R.E. Hannah, M.L. Cook, J.A. Blanchette, Anal.Chem., 39, 358 (1967).

34. R.H. Wiley, G. DeVenuto and T.K. Venkatachalam, J.Gas.Chromatogr., 5, 590 (1967).

35. Natl.Bur.Stds., Tech.Note, 459, 19 (1968).

36. W.L. Zielinski Jr., D.H. Freeman, D.E. Martire, L.C. Chow, Anal.Chem., 42, 176 (1970).

37. M.S. Vigdergauz, R.N. Vigalok, G.V. Dmitrieva, Russ.Chem.Rev., 50 (5), 498 (1981).

38. Z. Witkiewicz, J.Chromatogr., 251 (3), 311 (1982).