

## SUMMARY

S U M M A R YP A R T - 1

Anthracene and its derivatives are very reactive and they undergo a large number of reactions to give products of industrial, agricultural, medicinal and other importance. In the first chapter of general introduction different reactions viz. oxidation, hydrogenation, halogenation, nitration, sulphonation, alkylation, acetylation etc. on anthracene studied by different workers have been reviewed. Further more reactions carried on 1- and 2-hydroxyanthracene are also summarized,

The studies on biphenols and dihydroxy anthracenes are comparatively meagre. Investigations on the electrophilic substitutions in phenols and the synthesis of oxygen heterocycles from such compounds, are of interest. Chapter 2 deals with the synthesis of diketones by means of Friedel-Crafts, Fries and Nencki reactions,  $\alpha$ -dipyrones by Pechmann reaction and difurans from 1,5- and 1,8-dihydroxyanthracenes.

1,5-Dihydroxyanthracene on Friedel-Crafts acetylation yielded a ketone which has been assigned the 2,6-diacetyl-1,5-dihydroxyanthracene on the basis of elemental analysis, u.v. and i.r. spectra. The Nencki acetylation of 1,5-dihydroxy

anthracene also provided the same ketone in good yield, but the Fries rearrangement of 1,5-diacetoxanthracene at 140° gave the ketone in poor yield. 1,8-Dihydroxyanthracene when subjected to the similar type of reactions, give 2,7-diacetyl-1,8-dihydroxyanthracene. The i.r.spectra of these derivatives showed the characteristic peak for the carbonyl group around  $1720\text{ cm}^{-1}$ . In the course of syntheses of oxygen heterocycles such as bicoumarinyls and biflavenyls, 1,5-dihydroxyanthracene was condensed with ethyl acetoacetate in the presence of 80% sulphuric acid to obtain 4',4"-dimethyl-1,2,5,6-anthra- $\alpha$ -dipyrone. The product thus obtained by Pechmann Reaction was treated with aqueous sodium hydroxide and dimethyl sulphate produces unsaturated acid- a diagnostic test for coumarin derivative. following a similar condensation reaction, 4',4"-dimethyl-1,2,7,8,-anthra- $\alpha$ -dipyrone has been synthesized from 1,8-dihydroxyanthracene. Both the pyrone derivatives show the characteristic peak for  $\alpha$ -pyrone at  $1730\text{ cm}^{-1}$  and the u.v. spectra of bicoumarinyl gave the characteristic  $\lambda_{\text{max}}$ .

For the synthesis of difuran derivative, 2,6-diacetyl 1,5-dihydroxyanthracene was condensed with ethyl bromoacetate and the resulting diester was hydrolysed to the corresponding dicarboxylic acid. This was cyclised to give 3',3"-dimethyl-anthra-(1,2b, 5.6-b') difuran. Similarly 3',3"-dimethyl anthra (1,2b, 5,6d') difuran was prepared. All the intermediate

derivatives and final product have been characterized by elemental analysis, m.p., i.r. and u.v. spectra.

Chapter 3 deals with the utilization of hydroxyanthracene derivatives in azoic dyeing on cotton. The fundamental truth is that in azoic dyeing, increase in molecular weight by increasing the complexity of the fused ring system in phenols and naphthols leads to greater substantivity and also has a bathochromic effect. Keeping this view in mind, naphthalene ring of naphthol has been replaced by its analogous anthracene. The following seven anthracene derivatives have been evaluated as azoic coupling components.

(1) 1-Hydroxyanthracene, (2) 2-Hydroxyanthracene (3) 1-Hydroxyanthracene-2-carboxylic acid (4). 4-Acetyl-1-hydroxyanthracene, (5). 1-Acetyl-2-hydroxyanthracene (6). 1,5-Dihydroxyanthracene and (7). 1,8-Dihydroxyanthracene.

The cotton hanks were impregnated in the alkaline solution of anthracene derivative by usual method and were developed with 3% neutral diazonium chloride of various substituted amines in ice bath.

The following effect of different groups of anthracene on colour obtained is observed. Dihydroxy groups in anthracene gives reddish brown to reddish violet shade, monohydroxy derivative produces brown shades, ortho carboxyhydroxy group gives brownish orange shade and monoacetyl monohydroxy derivative produces light pink shades. This behaviour was

further studied by absorption spectra of chloroform extract of the dyed material. The maxima obtained are in the following decreasing order :

1,5-dihydroxy	>	1,8-dihydroxy	>	1-hydroxy	>	2-hydroxy	>
540 nm		530 nm		515 nm		500 nm	
1-hydroxy-2-carboxylic	>	4-acetyl-1-hydroxy	>	1-acetyl-2-hydroxy			
495 nm		470 nm		460 nm			

The dyed fibres have been evaluated for their washing light and crocking fastness. The fastness properties varies with the groups present in the coupling component, position occupied by them and the diazo salt used for coupling. The washing fastness for (1) is in the range of 2 to 5, while that for (2) is in the range of 3 to 5. The acetyl derivatives (3) and (4) have less washing fastness than the corresponding hydroxyl derivatives (1) and (2). The introduction of carboxylic group in (1) compounds<sup>5</sup> results in increasing the washing fastness, however introduction of hydroxyl group (6 and 7) results in lowering the fastness.

The light fastness properties of compounds 1,2 and 5 are in the range of 2 to 3, while that of 3,4,6, and 7 are varied from 2 to 6. The rubbing fastness of compounds 1 to 5 are in the range of 2 to 3 and for compounds 6 and 7 is 1 to 2.

In chapter.4, eight new azo derivatives of 1-hydroxy-anthracene have been prepared and studied for their visible, i.r. and fluorescence spectral properties. o-Nitro, o-chloro,

m-chloro, p-chloro, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro and p-methoxy aniline are diazotized in the usual manner by sodium nitrite solution and coupled with alcoholic solution of 1-hydroxyanthracene. Dyes are isolated and purified by repeated crystallization. Purified dyes are characterized by melting point, elemental analysis, visible spectra, i.r. spectra and fluorescence spectra.

The absorption spectra of dyes in the visible region is studied in alcohol and in acetone. In ethanol the bands obtained are very broad, but well defined. Similarly in acetone, the bands are little sharper than ethanol. All dyes absorb around 500 nm region indicating the hydrazone form of these derivatives. From the infrared spectral study the similar information reveals. In their spectrum of dyes stretching vibration due to -OH group around  $3500\text{ cm}^{-1}$  is absent, except in the dye, 4-(p-chlorophenylazo)-1-hydroxyanthracene, it is observed around  $3405\text{ cm}^{-1}$ . This confirms that the compounds are in azo-hydrazone (or keto-enol) tautomeric and only compound 4 exist in the enol form. In all the compounds the carbonyl stretching vibrations are assigned around  $1620 \pm 20\text{ cm}^{-1}$ . Similarly the NH bending vibrations are assigned around  $1590\text{ cm}^{-1}$ .

The emission and excitation spectra of dyes are recorded in ethanol as a solvent. Except two dyes, 4-(2,4-dichloro-

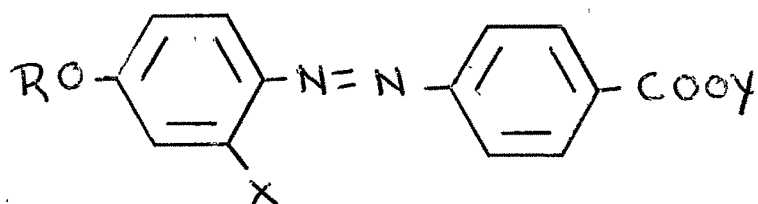
phenylazo)-1-hydroxyanthracene and 4-(2,6-dichlorophenylazo)-1-hydroxyanthracene all are exhibiting fluorescence.

#### PART - 2

Dyes are being used in the coloured liquid crystal optical display devices. The utility value of a dye in an optical display is decided by studying the guest-host interaction in a liquid crystal solvent and under electric field and polarized light. Recent work on the guest-host interaction suggests that azo dyes would be better in such displays. The liquid crystals are also finding uses in fields like optical storing devices, in non-destructive testing of materials, chromatography etc. In quest of new mesogenic materials due to their above mentioned applications, recently some mesogenic homologous series are also reported comprising an azo group.

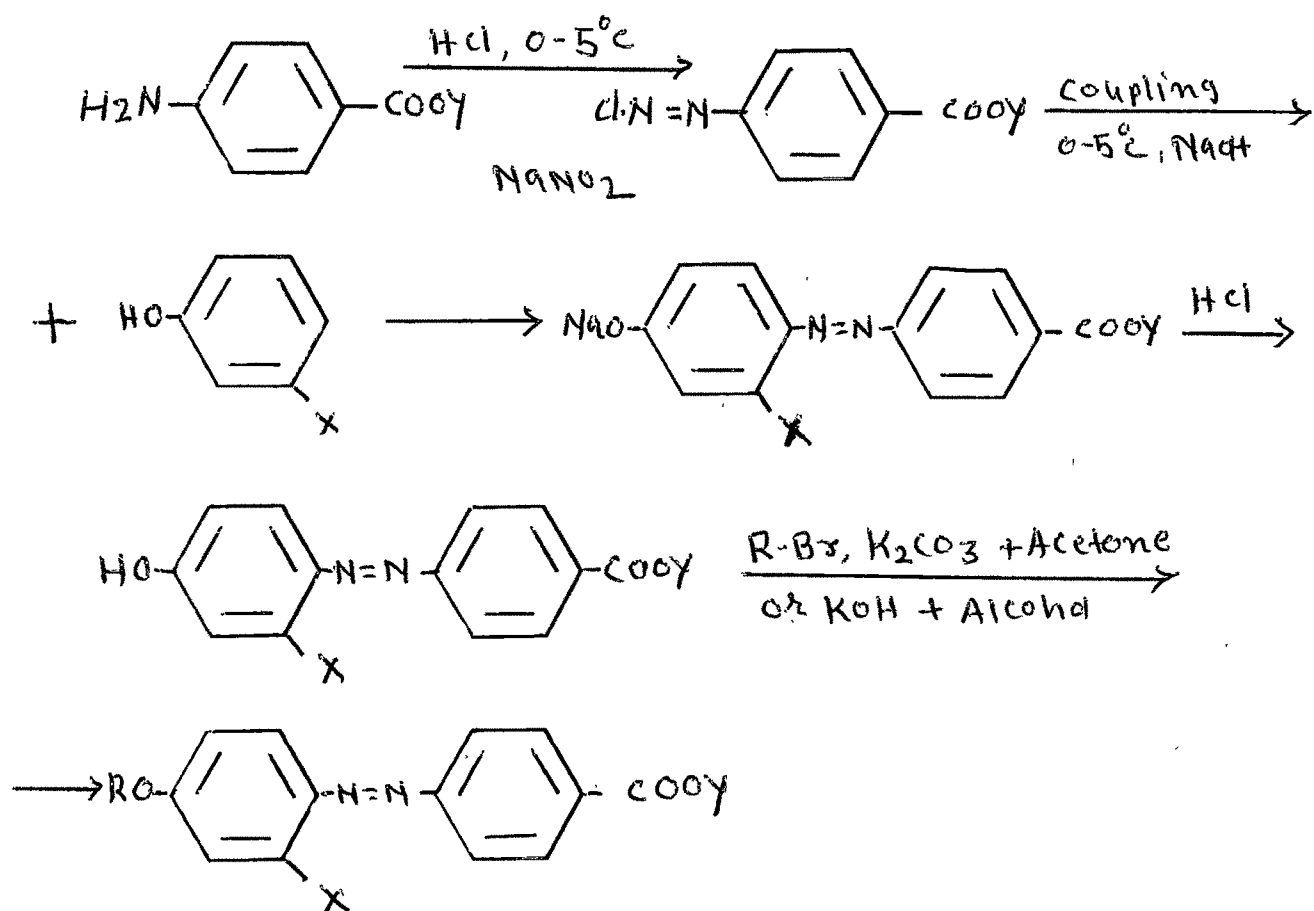
In continuation of our work on azo dyes (Part 1), the work was extended towards synthesis of new liquid crystal azo dyes (azomesogens) and the effect of chemical constitution on the mesomorphic behaviour of these compounds is studied.

Following four mesogenic homologous series are synthesized and their liquid crystalline behaviour is studied.



Series I	: X = CH <sub>3</sub>	Y = H
II	: X = H	Y = CH <sub>3</sub>
III	: X = H	Y = C <sub>2</sub> H <sub>5</sub>
IV	: X = H	Y = C <sub>3</sub> H <sub>7</sub>

The above series are synthesized by the following route :





Series I : 4-(4'-n-alkoxy-2'-methylphenylazo) benzoic acids:

All the members are nematogenic in nature. Even though lateral methyl group is present, the thermal stabilities are quite high. The smectic mesophase does not commence even in the last member of the series which is quite an interesting observation. Looking to the length of the dimer unit of the acid molecule trans methyl groups would not increase breadth to a greater extent, but it seems that methyl group ortho to the azo linkage might be causing steric hindrance in the molecules. Because of this, molecules of series I would be less linear and it would be more deterrent to smectic mesophases. The thermal stabilities of this series are compared with those of other related homologous series and are discussed on the basis of relative geometry and other factors operating in the molecules of these series.

The transition temperatures are plotted against the number of carbon atoms in the alkyl chain which exhibits usual odd-even effects. The behaviour of nematic-isotropic transition temperature curve is discussed.

Series II : Methyl 4-(4'-n-alkoxyphenylazo) benzoates:

First six members are non-mesogenic. Smectic mesophases commence at heptyl derivative. Heptyl to dodecyl derivatives exhibit <sup>nematotropic</sup> smectic mesophases. Tetradecyl to octadecyl derivatives are non-mesogenic.

Series III : Ethyl 4-(4'-n-alkoxyphenylazo) benzoates :

Smectic mesophase commences at the pentyl member as a monotropic phase. Hexyl to octadecyl members are enantiotropic smectic.

Series IV : Propyl 4-(4'-n-alkoxyphenylazo) benzoates :

Smectic mesophase commences at the butyl derivative. Butyl to octadecyl derivatives are enantiotropic smectic.

§ Smectic mesophases as inferred from their fan-shaped textures are of smectic A type.

General Characteristics of Series II, III, and IV :

All the three series are smectogenic in nature. Series III and IV are more mesogenic compared to series II. However, the thermal stabilities of series II are higher than those of series III and IV. The smectic-isotropic transition temperature curve in the case of series II and III does not exhibit usual odd-even effect, whereas, in the case of series IV the smectic-isotropic transition temperature curve exhibits odd-even effect.

The smectic thermal stabilities of these three series are compared with those of other related homologous series. The comparison exhibits certain interesting relations in the decrease of smectic thermal stability between different series.

The increase in alkyl chain of the ester by a  $-CH_2$  unit decreases the smectic thermal stability in all the series.

However, decrease is greater when methyl ester is changed to ethyl. Ethyl to propyl addition does not decrease the smectic stability to such a great extent as is in the previous case. This type of phenomenon is observed in other esters also compared with the present series. Not only this, irrespective of the geometry of other series having minor variations, the decrease in smectic thermal stabilities from methyl to ethyl and ethyl to propyl is same. These observation throw some light on the smectic-isotropic transition of a system where alkyl chain is systematically increased. The esters exhibiting smectogenic tendencies, so far studied are quite less in number. Compared to the study of nematogenic compounds. The result of the present study has helped to understand the effect of chemical constitution on such mesogenic compounds.