EXPERIMENTAL

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The investigation of the phase diagrams of the binary systems was carried out by the following methods: (1) the optical method (2) the thermal method and (3) the microscopic method.

A two-component system can be investigated and the equilibrium diagrams can be constructed by the usual methods of melting point determination and thermal analysis (cooling curve method).

It is a general concept that a substance melts to an isotropic liquid and its melting point can be easily determined by the common method of melting point determination. A mesomorphic substance, however, first melts to an anisotropic liquid which later transforms to a true isotropic liquid on further heating. The temperature at which it melts to an anisotropic liquid is known as its melting point and the higher temperature at which the anisotropic liquid changes to clear isotropic liquid is called the transition point or the transition temperature. An accurate determination of the melting point and the transition point of a mesomorphic substance by the usual melting point method is rather difficult. But, by virtue of the birefringence of the anisotropic liquid, its melting point and the transition point can be very conveniently determined by the use of polaroids. This is known as the optical method.

The binary systems studied in this investigation are of two types :

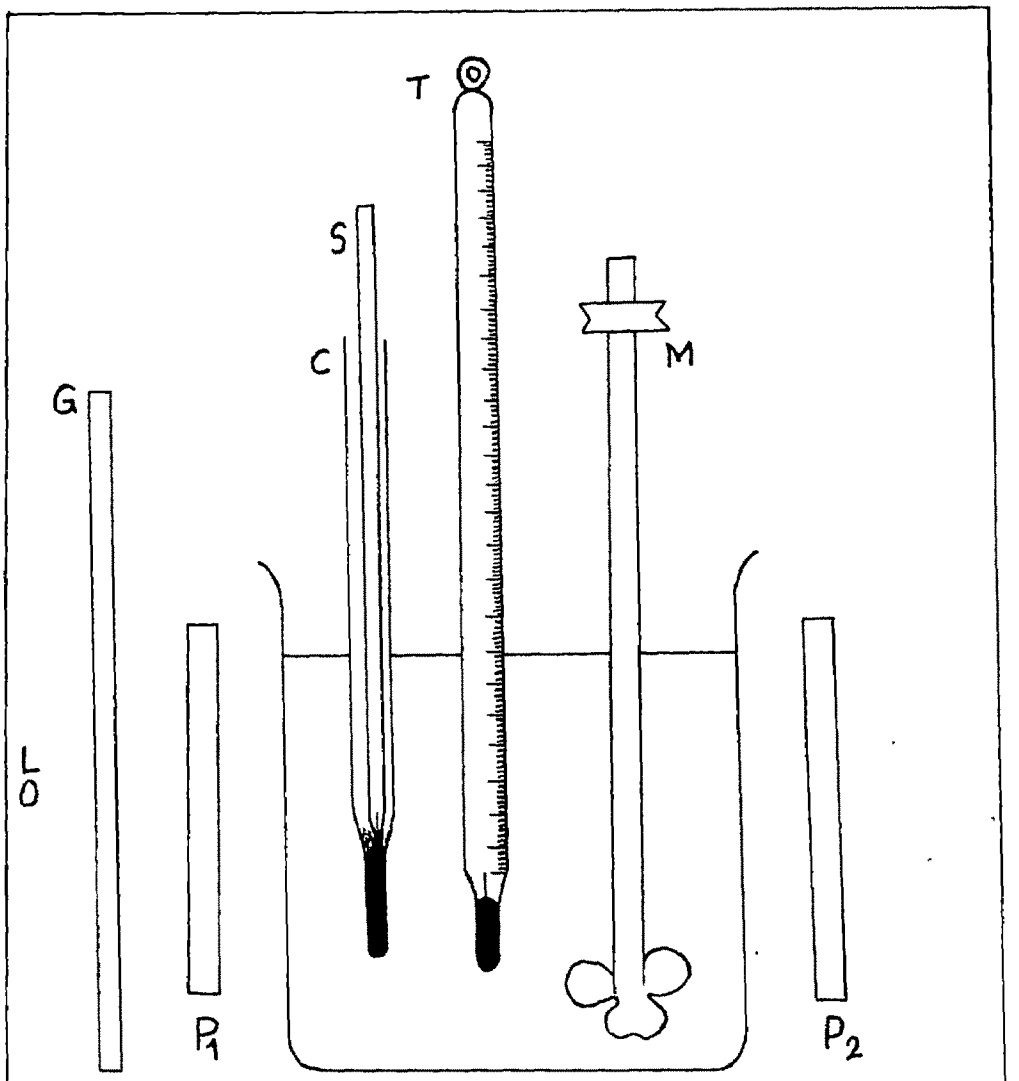
1. Where one component is a liquid crystal and the other a non-liquid crystal ; and
2. Where both the components are non-liquid crystalline substances.

The investigation of the phase diagrams of these binary systems was carried out by the optical method. The critical regions were, however, investigated by the thermal analysis method.

Investigation of the Phase Diagrams by the Optical Method :

The Apparatus :

The experimental set up used for this method is diagrammatically shown in the figure 4. The capillary tube C in which the mixture was heated was made by drawing out an ordinary glass tubing to form a capillary about 2 mm. in diameter. It was provided with a thin glass stirrer S, made by drawing out a glass rod so that it worked easily within the capillary to stir the mixture throughout. The powdered substance was introduced into the capillary and pressed down with the stirrer S, so that the material occupied 10-15 mm. at the bottom of the capillary tube. This capillary tube was immersed in a liquid bath consisting of one litre beaker containing dibutyl phthalate. The liquid in the bath was continuously and vigorously stirred by means of an electrically run mechanical stirrer M. The beaker was lagged by wrapping asbestos paper round it in order to minimise loss of heat through radiation. The asbestos covering was provided with two windows 1-1/2" square opposite one another. A previously calibrated



L - LAMP
C - CAPILLARY TUBE
S - STIRRER
G - GROUND GLASS SCREEN
T - THERMOMETER
M - MECHANICAL STIRRER
P_1 - } POLAROID SQUARES
P_2 -

FIG. 4

standard thermometer T, graduated in 1/10th of a degree was suspended in the bath and was used to record the temperature. The capillary tube C containing the mixture under investigation was held in the bath by the side of the thermometer in such a way that it could be seen through the square windows in the asbestos lagging. A source of light L, provided by an electric lamp, passed through a ground glass screen G and illuminated the substance in the capillary, which was observed by means of a magnifying glass. The two polaroid squares P_1 and P_2 were placed on either side of the beaker facing the windows in the asbestos lagging so that P_1 stood in between the glass screen and the beaker, while P_2 stood in front of the beaker. The capillary tube C containing the mixture was thus held between the two polaroid squares. The polaroid squares were held crossed to each other so that the light only passed through them when the medium between them was anisotropic but was cut off when the medium changed over to isotropic liquid.

Preparation of a Sample Mixture :

The two substances comprising the binary mixture were carefully and accurately weighed in known proportions, in a small test tube of 2" x 1/4" size. The total weight of the mixture was about 0.2 g. (exactly weighed). The test tube along with its contents was then heated in an oil bath to a temperature slightly higher than that at which the two components melted in presence of one another.

After melting, the mixture in the test tube was thoroughly stirred by means of a glass rod to ensure a thorough and complete mixing of the components. The homogeneous liquid melt was then quickly cooled by quenching the test tube in a beaker of cold water. The solid mixture was later removed from the test tube and reduced to a fine powder by intimately grinding in an agate mortar. In this way different mixtures of different proportions were prepared and their melting points and transition points determined by heating them in a capillary tube in the liquid bath as illustrated in the diagram (fig 4). The small test tubes in which the mixture was prepared were previously cleaned with dilute nitric acid, washed with hot distilled water and dried with alcohol and ether.

Observations :

The capillary tube containing a small portion of the finely powdered mixture was heated in the liquid bath of dibutyl phthalate. The capillary tubes and the glass rods were thoroughly cleaned and dried previously. The rate of heating was adjusted to about 1 ^{o}C per 5-10 minutes by means of microburner possessing a fine control arrangement so that the temperature of the bath could be slowly raised and maintained within 1/10th of a degree as desired. By raising the temperature of the bath slowly and by proper manipulation of heating and stirring, and by a vigilant observation of the outline of the substance against the side of the capillary, it was not difficult to ascertain the point at which the mixture began to melt.

At this point the mixture became soft enough so as to be easily stirred by the glass stirrer. Small droplets of the liquid adhering to the side of the capillary could be easily observed with the help of a magnifying glass. This temperature was the thaw-point or the sintering point corresponding to the eutectic point in the thermal analysis method and was observed without polaroids.

On further heating the mixture while continously stirring, the temperature at which the fused mass in the capillary melted to a homogeneous liquid was taken as the melting point of the mixture. The melting point of the mixed solids could be determined very accurately when the liquid phase formed was isotropic, from the disappearance of the birefringence of solid particles on melting (C-L point). However, it was not easy to determine the melting point accurately when the liquid phase first formed was anisotropic. But with care and experience this could be measured fairly accurately within 0.2 ^{o}C. For this, the bath temperature was allowed to change exceedingly slowly and the solid particles were allowed to settle down periodically. On slowly raising the temperature, with continuous stirring, the solid particles melted to a homogeneous liquid which was birefringent when looked through crossed polaroids. When the homogeneous birefringent liquid was allowed to stand at this temperature, no solid particles separated. This was the melting point or C - M point (solid crystal-mesomorphic point) of the mixture when it gave rise first to an

anisotropic liquid phase.

On slowly increasing the temperature further, the homogeneous birefringent anisotropic liquid changed at a definite temperature to isotropic liquid which appeared non-birefringent through crossed polaroids. This was the transition point or the transition temperature or the M - L point (mesomorphic - liquid point). In contrast to the difficulty observed in ascertaining the melting point (C - M point), this point is easily marked due to sharp disappearance of birefringence. This transition from anisotropic to isotropic and vice versa was very sharp and could be reproduced very accurately within 0.1 ^{o}C, when the bath temperature was slowly raised or lowered. It should be borne in mind that this birefringence was altogether different from the birefringence of the solid particles in the former case (C - L point). In this latter case (M - L point) the whole melt was birefringent and the birefringence was reproducible on cooling, whereas in the former, the birefringence was due to the unmelted floating particles (the liquid being non-birefringent) and was not reproducible on lowering the temperature of the bath.

Thus the sintering points, melting points and the transition points of various compositions of different components were determined and the phase diagrams were constructed therefrom.

Investigation of the Phase Diagrams by the Thermal Method:

The Apparatus :

It has been mentioned before that the melting point

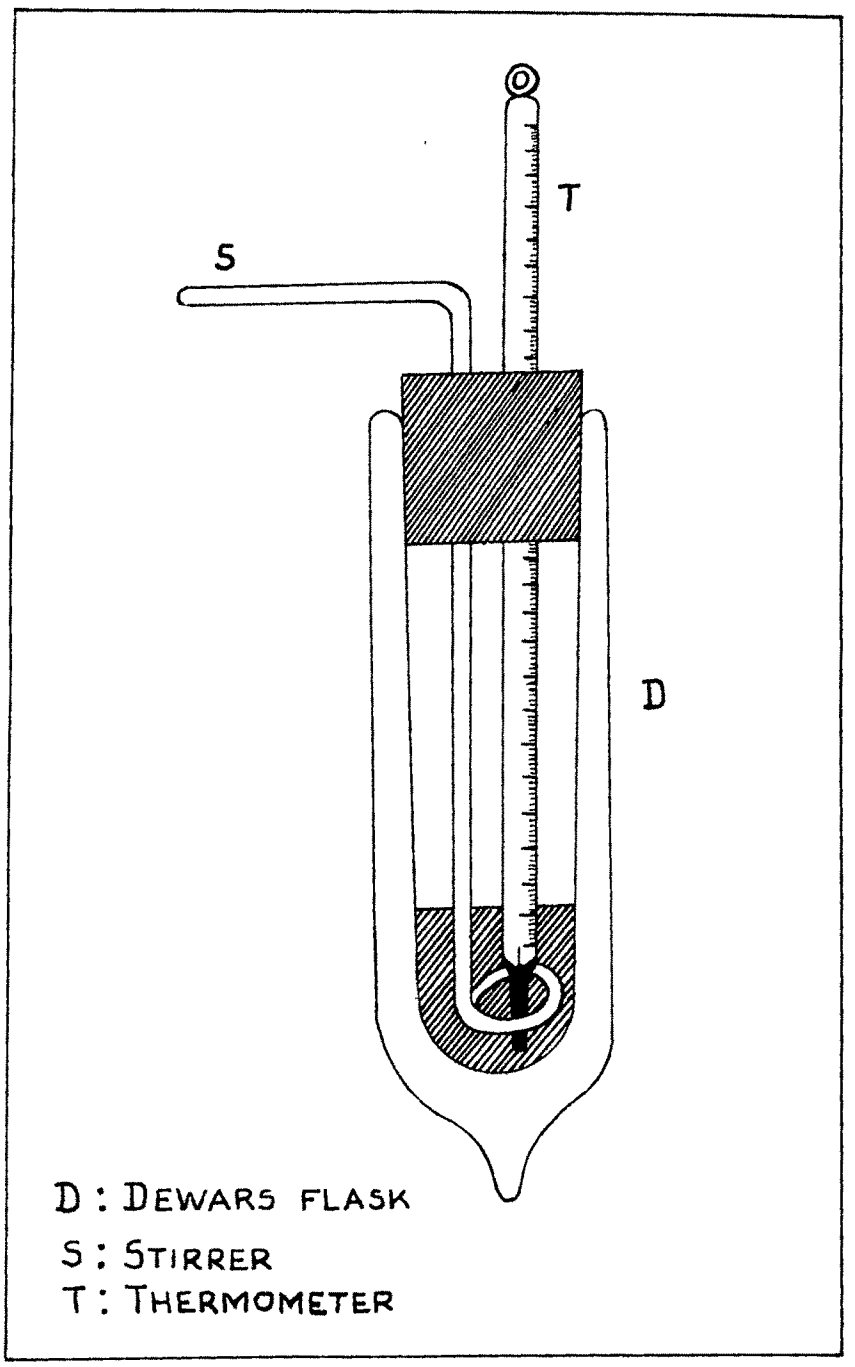


FIG. 5

determination of the mixtures which form an anisotropic liquid phase was not quite easy. Hence, the critical regions of the anisotropic liquid phase were investigated by the standard thermal analysis (cooling curve) method.

Very low rates of cooling were employed for the investigation of the phase diagrams of the mixtures forming mesomorphic melts as the heats of transition from mesomorphic to isotropic liquid are very small. The measurements were, therefore, carried out in a small Dewar flask (6" x 1") immersed in an oil thermostat bath maintained at a constant temperature. The Dewar flask D was fitted with a cork provided with two holes. A calibrated thermometer T graduated in 1/10 th of a degree was inserted through one of the holes just reaching the bottom of the flask. Through another hole passed a stirrer S also just reaching the bottom of the flask, so constructed that it surrounds the bulb of the thermometer without hitting it. The stirring was done by raising and lowering the stirrer. Fig 5 represents an illustration of the apparatus used.

Observations :

The two substances in definite proportions were accurately weighed so that the total weight of the mixture was about 10 g. (exactly weighed). The weighed mixture was carefully transferred to the flask and the flask was closed with the cork carrying the thermometer and the stirrer. The mixture was melted by heating the flask in an oil

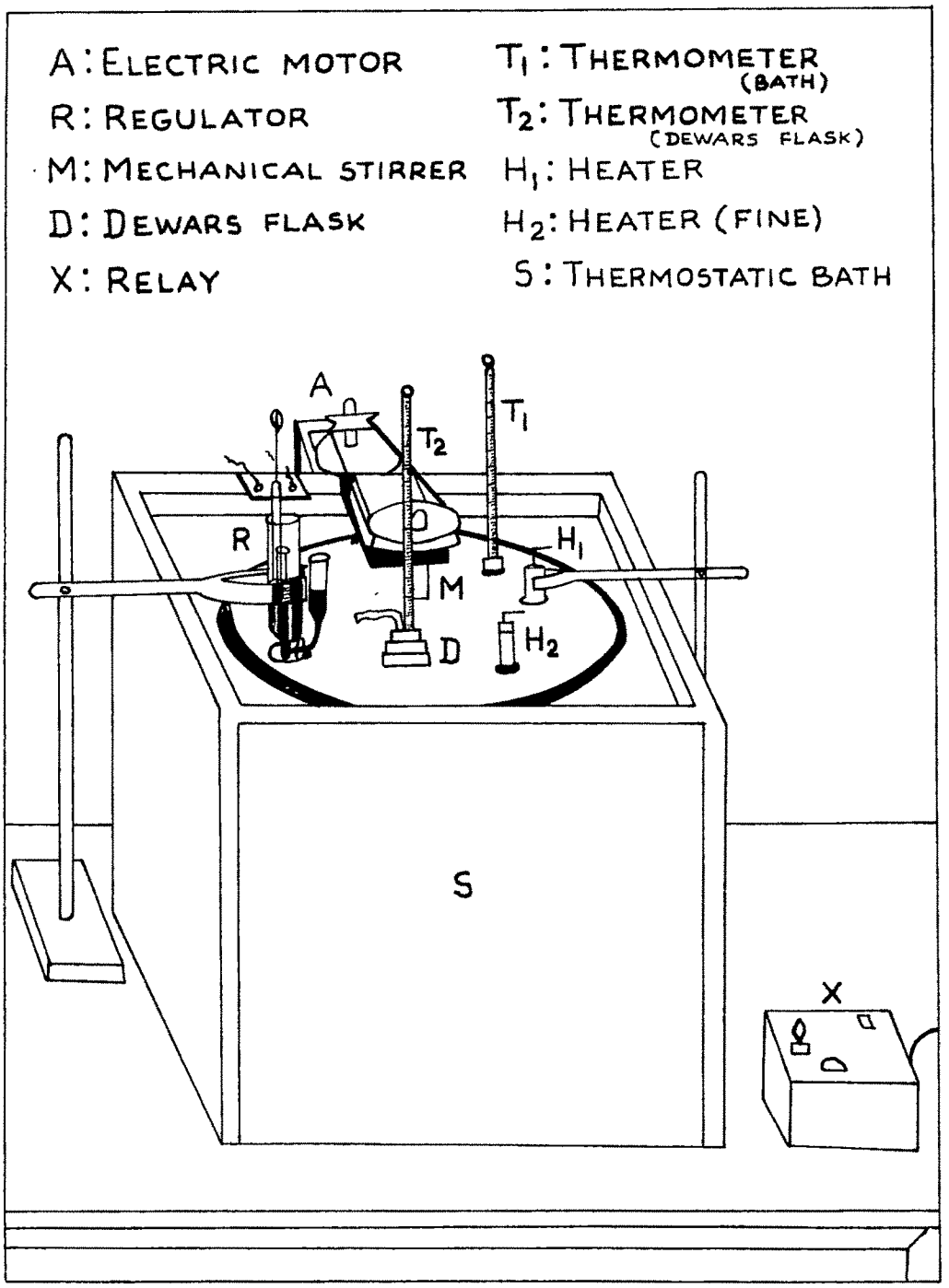

A : ELECTRIC MOTOR
R : REGULATOR
M : MECHANICAL STIRRER
D : DEWARS FLASK
X : RELAY
T1 : THERMOMETER (BATH)
T2 : THERMOMETER (DEWARS FLASK)
H1 : HEATER
H2 : HEATER (FINE)
S : THERMOSTATIC BATH
A
T2
T1
R
H1
M
D
H2
S
X

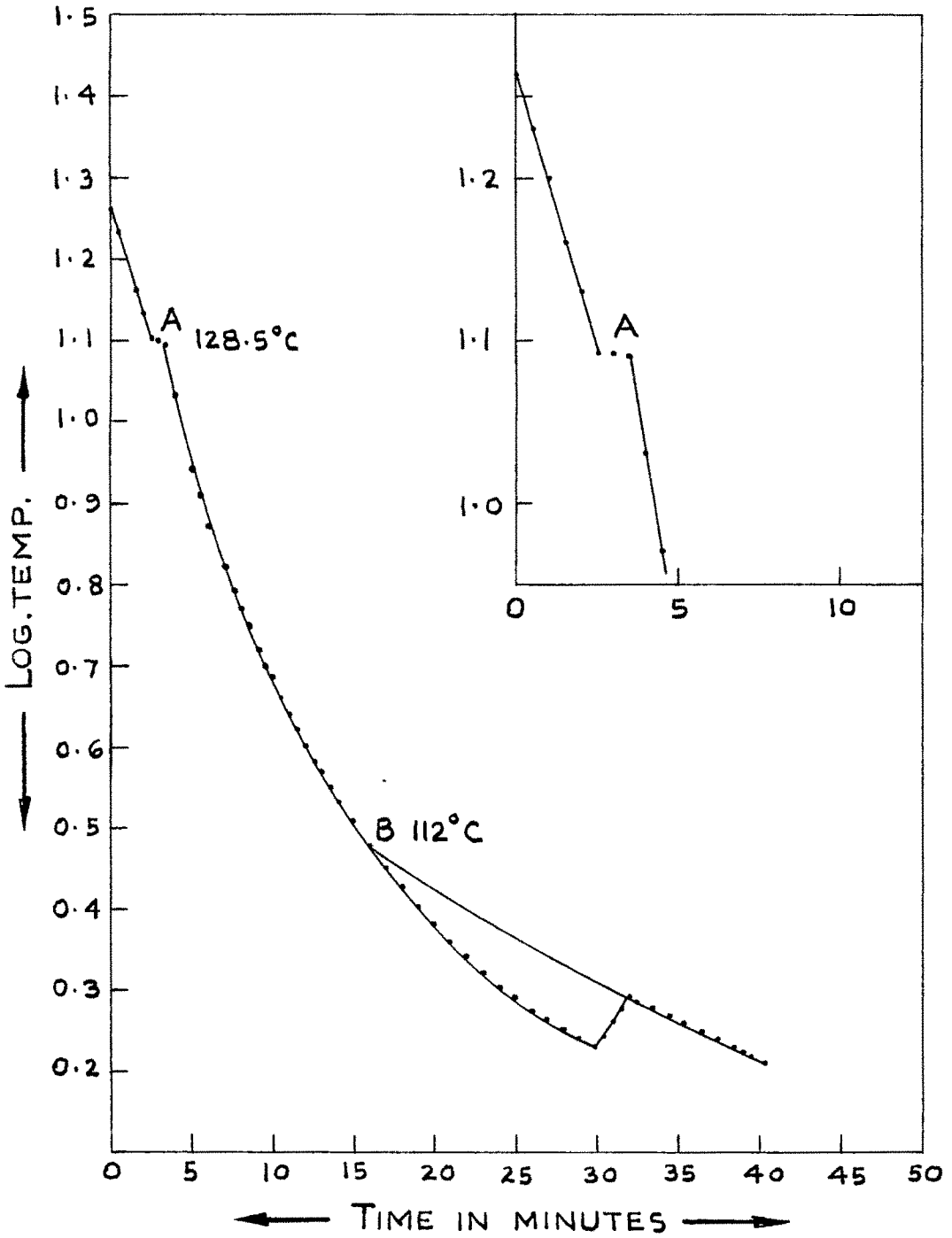
FIG. 6

bath and the temperature of the molten mixture was raised to about 10 degrees above the transition temperature to be noted. The flask was then removed from the oil bath and immediately immersed in a large oil thermostat bath maintained at a temperature within 10 degrees below the transition temperature to be observed. The temperature of the thermostat bath was maintained within $\pm 0.05^{\circ}C$ by means of an electrically controlled thermoregulator. Fig.6 illustrates the arrangement of the thermostat bath equipment.

The mixture in the Dewar flask was continuously stirred by raising and lowering the stirrer S. The fall of temperature was noted at every half a minute interval by a chronometer ; the readings were plotted as logarithms of the temperature against time. This should give a continuous smooth curve except when there is a transition change when the curve would show a discontinuity. The heat of transition from isotropic to anisotropic being very small the observation of the transition break was confronted with a difficulty ; however, by using a Dewar flask and maintaining the temperature of the bath sufficiently within the temperature to be observed, the rate of fall of temperature was sufficiently minimised so as to make the transition break appreciable. Fig. 7 shows a typical cooling curve of the system : p-acetoxybenzal-p-phenetidine : p-chlorobenzal-p-anisidine containing 89.13 mole percent p-acetoxybenzal-p-phenetidine in the mixture. The temperature of the thermostat bath was maintained at $104.3^{\circ}C$. The break at A illustrates the isotropic liquid-anisotropic liquid transition which is

A-REPRESENTS THE LIQUID-LIQUID CRYSTAL TRANSITION.

B-THE NORMAL MELTING POINT.



A TYPICAL COOLING CURVE OF THE SYSTEM

p-ACETOXYBENZAL-p-PHENETIDINE(L.C.):p-CHLOROBENZAL-p-ANISIDINE(N.L.C.)

89·13 MOLE % L.C. ; BATH TEMP. = 104·3°C.

FIG. 7

shown on a magnified scale in the small diagram inset in the top right hand corner in the figure 7. B is the anisotropic liquid - solid transition break and this represents the freezing point of the mixture corresponding to the normal melting point. This transition is usually associated with supercooling and therefore, the melting point is obtained by extrapolation of the cooling curve.

The critical liquid crystalline regions of different mixtures of different components were examined in this way. Different transitions for the same mixture were observed separately in different experiments. In some cases, for accurate determination, the same transition was observed by separate individual experiments with different bath temperatures.

All temperatures are corrected.

O in the phase diagrams represents melting curve points.

X in the phase diagrams represents cooling curve points.

Microscopic Method for the Determination of Mesomorphic and Transition Temperatures :

The polymesomorphic transitions i.e., smectic-smectic and smectic-nematic etc., changes could not be detected accurately by the usual optical method. Hence, the use of a microscope became essential for the detection of such changes with great accuracy. The microscope used for the determination of mesomorphic and polymesomorphic transition temperatures was a Leitz Ortholux polarizing

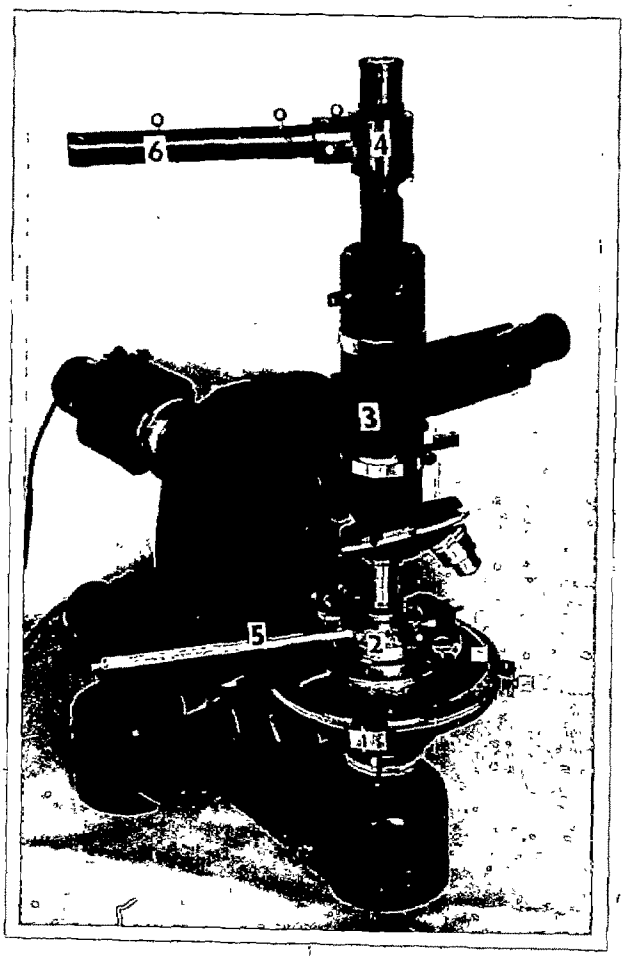


FIG. 8

Microscope :

1. Revolving stage.
2. Heating stage.
3. Binocular.
4. Monocular.
5. Thermometer.
6. Travelling prism for following the thermometer range.

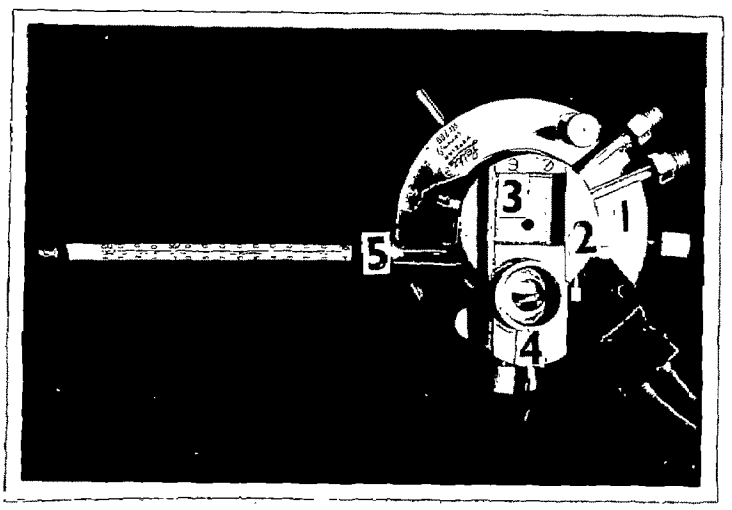


FIG. 9

Heating stage :

1. Circular base.
2. Heating stage.
3. Specimen chamber.
4. Cover for the specimen chamber.
5. Thermometer.

microscope having a binocular and monocular attachments (fig.8) for observing the specimen on the slide. It was provided with an electrical heating stage fitted to the round, revolving object stage with vertical rock and pinion focusing motion (fig.9). The specimen chamber in the heating stage accomodated the object slide and the thermometer was simply inserted in a lateral aperture of the specimen chamber. The temperature of the specimen chamber can be electrically controlled by a regulator between room temperature and 360° C and could be easily read on specially made thermometers dependable for use in the horizontal position and graduated in 0.5° C. The light source from an electric lamp was allowed to pass through a filter polarizer to illuminate the specimen. The special eye piece in the monocular tube enabled to read the thermometer scale inside the field of view of the microscope by the side of the image of the specimen so that the transition processes could be studied uninterruptedly and the temperature could be read simultaneously at any time its recording may be found necessary.

The specimen was heated and melted on a clean glass slide inserted in the specimen chamber of the heating stage and a clean glass coverslip was pressed over it to remove air bubbles and get a possible thin section of the material. The slide and the heating stage were then cooled to necessary desired temperature.

The accuracy of the heating device was checked by taking melting points and / or transition points of purified known compounds such as benzoic acid, α-naphthol,

anthracene, p-azoxyanisole, p-methoxycinnamic acid, p-acetoxybenzal-p-phenetidine etc. The temperatures determined in these cases agreed with the values given in the literature within $\pm$ 0.2 ^{o}C.

To determine the various transitions the prepared slide with a thin section of the material was inserted in the specimen chamber of the heating stage and the temperature was raised fairly fast (5 ^{o}C / min) to find the approximate transition temperatures. The heating stage was then cooled till the stable solid reappeared on the slide. The measurements were then repeated with a rate of heating of 1 ^{o}C / min. from 5 ^{o}C below the transition points. The transitions and various phases were clearly observed and recorded by the appearance of the focal-conic and the threaded structures of the smectic and nematic phases respectively in the polarized light. The transition to the isotropic liquid was clearly marked when the field of vision became extinct in polarized light.

In the compounds exhibiting smectic mesomorphism, the focal-conic pattern was frequently maintained in the solid when the thin section on the glass slide was prepared by cooling the slide slowly. This pseudomesomorphic condition often created a difficulty in detecting the solid-smectic transition. However, the disappearance of cleavage lines in the solid was taken as the solid - smectic transition point. In the enantiotropic mesomorphism, all the transitions could be sharply detected while cooling the isotropic liquid, the reverse transitions taking place at

the same temperature or within ± 0.2 °C . The isotropic liquid - nematic transition could be observed by virtue of the appearance of small bubbles from the isotropic liquid. These bubbles then coalesced and a threaded region characteristic of the nematic phase was formed. The isotropic-smectic transition was indicated by the separation of batonnets which coalesced to form fine mosaic of focal-conic pattern, a distinguishing character of a smectic phase. Smectic-nematic and smectic-smectic changes were also clearly detected with great accuracy with the help of the polarizing microscope. The monotropic transition points were determined by carefully observing the isotropic liquid as it cooled slowly until the batonnets of the smectic phase or bubbles of nematic phase appeared. In the case of monotropic mesomorphism, it was possible to raise the temperature before crystallisation took place, and the mesophase disappeared at the same temperature at which it had appeared, thus confirming the monotropic transition temperature. All the mixtures were observed continuously under the microscope from their solid state to the isotropic liquid state while heating and from isotropic to solid state while cooling so that no transition could escape unnoticed.

Preparation of Materials :

I Alkoxybenzoic acids :

These acids were prepared by boiling under reflux for nearly 2-3 hours 1 mole of p-hydroxybenzoic acid, dissolved in 2 moles of aqueous potassium hydroxide with

1.1 mole of alkyl iodide. Under these conditions little or no esterification took place ; the free acid liberated by the addition of concentrated hydrochloric acid was crystallised thrice from small volumes of glacial acetic acid to obtain fine crystals. The yield was practically quantitative.

1. p-Ethoxybenzoic acid : obtained as white prism-like crystals, m.p. 197°C (100).
2. p-n-Butoxybenzoic acid :obtained as white shining prism-like crystals, m.p. 147°C and t.p. 160°C (109).

II Aldehydes :

1. p-Acetoxybenzaldehyde :

p-Acetoxybenzaldehyde was prepared from p-hydroxybenzaldehyde by condensing it with acetic anhydride for three to four hours and distilling the product under vacuum. B.P. 265°C. Richter gives B.P. 266°C (144).

2. p-n-Alkoxybenzaldehydes :

These were prepared by the following method described by Gray and Jones (113).

p-Hydroxybenzaldehyde (0.1 mole), anhydrous potassium carbonate (0.4 mole), cyclohexanone (80 ml.) and n-alkyl iodide or bromide (0.15 mole) were mixed and refluxed in an oil bath at the boiling temperature of the solvent with vigorous shaking from time to time for 2 to 3 hours. The supernatant solution was decanted from potassium carbonate. The potassium carbonate left was throughly washed with ether and the washings were added to the

decanted portion of the liquid. In practice, complete removal of adherent liquid from potassium carbonate was not successful even after several washings with ether. However, after washing throughly with ether, potassium carbonate was dissolved in water and the liquid layer so obtained was separated and collected with the decanted cyclohexanone and ether solution. The solvents were distilled off on a water-bath under reduced pressure. The residual p-n-alkoxy-benzaldehydes were then obtained as colourless or yellow liquids or waxy solids in their pure form, by distilling under reduced pressure. The yields were in the range of 55 to 70 %.

The boiling points of the p-n-alkoxybenzaldehydes are given below :

n-Alkyl group	B.P. °C (found)	B.P. °C (reported)
a. Ethyl	146°/20 mm. or 249°	106°/3 mm. (113)
b. Propyl	130°/10 mm. or 268°	144°/14 mm.(113)
c. Dodecyl	195°/8 mm.	194°/8 mm. (113)

p-n-Dodecyloxybenzaldehyde is a waxy solid melting at 24° C. The purity of these aldehydes was further tested by condensing them with either benzidine (145) or p-phenetidine (146).

III p-n-Butoxyaniline :

p-n-Butoxyaniline was prepared by the reduction of p-n-butoxynitrobenzene (147).

Spiegel and Sabbath (148), Reiss (149),

Gutekunst and Gray (147) and Weygand and Gabler (150) have described the preparation of several p-alkoxynitrobenzenes ; here, the following procedure (147) was successfully used .

Recrystallised dry p-nitrophenol (0.1 mole), anhydrous potassium carbonate (0.4 mole), ethyl methyl ketone (80 ml.) and n-butyl iodide (1.5 mole) were mixed and refluxed on a sand-bath for about 3 to 4 hours with vigorous shaking from time to time. The solution was then decanted, the residue washed with ether and the ethereal washings were added to the decanted solution. To ensure complete separation of the solution from potassium carbonate, it was dissolved in water and the liquid layer thus formed was collected and added to the decanted solution. The solvents were distilled off and the residual p-n-butoxynitrobenzene was obtained in its pure form as an orange coloured liquid by distillation under reduced pressure. The yield was 50-60 % . p-n-Butoxynitrobenzene boils at 165 ^{o}C/7 mm., the reported value in the literature being 160-3 ^{o}C / 7 mm. (150).

The prepared p-n-butoxynitrobenzene (0.05 mole) was slowly added to a hot solution (80 ^{o}C) of stannous chloride (40 g.) in concentrated hydrochloric acid (60 ml.) During the addition of p-n-butoxynitrobenzene the temperature rose to 107-109 ^{o}C. The mixture was boiled for a few minutes and then cooled. It was then made alkaline by adding cold solution of sodium hydroxide. The red coloured oil floating on the surface of the solution

was extracted with ether, dried over anhydrous calcium chloride and distilled under reduced pressure. The product was an yellow liquid which on standing became dark red. The yield was 50-60 %. The B.P. of the product was found to be 143°C./ 13 mm., the value reported in the literature being 143-4°C / 12 mm. (147).

IV Schiff's bases :

The Schiff's bases were prepared by heating under reflux on a water-bath an alcoholic solution of the purified appropriate aldehydes and anilines in equimolecular proportions, until condensation was complete. The products were isolated by distilling the solvent and were crystallised from a suitable solvent like alcohol, benzene etc., into fine crystals which gave sharp, constant melting points. The following Schiff's bases were prepared.

1. p-Anisal-p-anisidine : White needles from alcohol, m.p. 148°C. Senior and Foster (151) give m.p. 146-147°C.
2. p-Anisal-p-bromoaniline : White plates from alcohol, m.p. 120°C. Senior and Foster (151) give m.p. 120°C.
3. p-Anisal-p-chloroaniline : White plates from alcohol, m.p. 92°C. Senior and Foster (151) give m.p. 93-94°C.
4. p-Anisal-p-toluidine : White needles from alcohol, m.p. 93°C. Senior and Foster (151) give m.p. 92-93°C.
5. p-Anisal-p-phenetidine : Colourless plates from alcohol, m.p. 128.5°C and on cooling gives isotropic-nematic transition at 121.5°C. Vorlander (13) gives the same melting and transition points.

6. p-Dimethylaminobenzal-p-phenetidine : Yellow needles from alcohol, m.p. 148°C. Sachs and Lewin (152) give m.p. 145-146°C.

7. p-Nitrobenzal-p-chloroaniline : Yellow needles from alcohol, m.p. 132°C. Hantzsch and Schwab (153) give m.p. 128°C.

8. p-Chlorobenzal-p-toluidine : White shining plates from alcohol, m.p. 128°C. Law (154) gives m.p. 128°C.

9. p-Nitrobenzal-p-bromoaniline : Greenish-yellow needles from alcohol, m.p. 163°C. Lowy and King (155) give m.p. 160.5°C while Ingold and Piggott (156) give m.p. 160-161°C.

10. p-Chlorobenzal-p-dimethylaminoaniline : Light yellow crystals from alcohol, m.p. 165.5°C. Fritz Krohnke (157) gives m.p. 165.5°C.

11. p-Tolual-p-toluidine : White prisms from petroleum ether, m.p. 93°C. Law (154) gives m.p. 92-93°C.

12. p-Chlorobenzal-p-chloroaniline : Yellow leaflets from alcohol, m.p. 112°C. Walther and Raetze (158) give m.p. 112°C.

13. p-Chlorobenzal-p-anisidine : White shining plates from alcohol, m.p. 123.5°C. Dave (159) gives m.p. 124°C.

14. p-Anisal-p-iodoaniline : White plates from alcohol, m.p. 152°C. Lohar (160) gives m.p. 152.5°C.

15. p-Chlorobenzal-p-phenetidine : Fine white leaflets from alcohol, m.p. 123°C. Lohar (160) gives m.p. 121°C.

16. p-Dimethylaminobenzal-p-bromoaniline : Yellow needles from alcohol, m.p. 158°C. Lohar (160) gives m.p. 158.5°C.

17. p-Dimethylaminobenzal-p-iodoaniline : Brownish yellow needles from alcohol, m.p. 159°C. Lohar (160) gives m.p. 159°C.

18. p-Nitrobenzal-p-phenetidine : Bright yellow needles from alcohol, m.p. 123.5°C. Dave and Lohar (143) give m.p. 123.5°C.

19. p-Ethoxybenzal-p-phenetidine : Colourless plates from alcohol, m.p. 148°C and on cooling gives isotropic-nematic transition at 143°C. Weygand and Gabler (146) give the same melting and transition points.

20. p-Nitrobenzal-p-nitroaniline : Yellow prisms from alcohol m.p. 200°C. Ingold and Piggott (156) give m.p. 199-200°C.

21. p-Nitrobenzal-p-anisidine : Yellow plates from alcohol, m.p. 135°C. Dave (159) gives m.p. 136°C. Pope and Fleming (161) give m.p. 139°C.

22. p-Acetoxybenzal-p-phenetidine : Pale yellow needles from alcohol, m.p. 118.5°C and T.P. 137.5°C. Dave and Lohar (142) report the same temperatures.

23. p-Dimethylaminobenzal-p-fluoroaniline : Shining yellow plates from alcohol, m.p. 136°C.

Found : C = 74.29 % ; H = 6.03 % ; N = 11.59 %.

$C_{15}H_{15}N_2F$ requires : C = 74.39 % ; H = 6.19 % ; N = 11.57 %.

24. p-Dimethylaminobenzal-p-chloroaniline : Shining yellow needles from alcohol and benzene, m.p. 152°C.

Found : C = 69.63 % ; H = 5.74 % ; N = 11.26 %.

$C_{15}H_{15}N_2Cl$ requires : C = 69.63 % ; H = 5.80 % ; N = 10.83 %.

25. p-Ethoxybenzal-p-chloroaniline : White prisms from alcohol, m.p. 100°C.

Found : C = 69.19 % ; H = 5.16 % ; N = 5.39 %.

$C_{15}H_{14}NOCl$ requires : C = 69.36 % ; H = 5.39 % ; N = 5.39 %.

26. p-Nitrobenzal-p-fluoroaniline : Yellow needles from alcohol, m.p. 113°C.

Found : C = 63.89 % ; H = 3.22 % ; N = 11.14 %.

$C_{13}H_9N_2O_2F$ requires : C = 63.93 % ; H = 3.68 % ; N = 11.48 %.

27. p-Nitrobenzal-p-iodoaniline : Yellow needles from alcohol and benzene, m.p. 198°C.

Found : C = 44.62 % ; H = 2.78 % ; N = 7.72 %.

$C_{13}H_9N_2O_2I$ requires : C = 44.32 % ; H = 2.55 % ; N = 7.95 %.

28. p-Tolual-p-bromoaniline : White plates from alcohol m.p. 125°C.

Found : C = 61.29 % ; H = 4.22 % ; N = 5.02 %.

$C_{14}H_{12}NBr$ requires : C = 61.31 % ; H = 4.37 % ; N = 5.10 %.

29. p-Chlorobenzal-p-bromoaniline : Colourless needles from alcohol, m.p. 125°C.

Found : C = 52.78 % ; H = 3.02 % ; N = 4.72 %.

$C_{13}H_9NClBr$ requires : C = 52.98 % ; H = 3.05 % ; N = 4.75 %.

30. p-Tolual-p-iodoaniline : Colourless plates from alcohol, m.p. 142°C.

Found : C = 52.22 % ; H = 3.55 % ; N = 4.23 %.

$C_{14}H_{12}NI$ requires : C = 52.34 % ; H = 3.73 % ; N = 4.36 %.

31. p-Chlorobenzal-p-iodoaniline : Colourless plates from alcohol, m.p. 140°C.

Found : C = 45.22 % ; H = 2.19 % ; N = 3.97 %.

$C_{13}H_9NClI$ requires : C = 45.67 % ; H = 2.63 % ; N = 4.10 %.

32. p-Diethylaminobenzal-p-diethylaminoaniline : Yellowish brown needles from alcohol, m.p. 122°C.

Found : C = 78.06 % ; H = 8.62 % ; N = 12.85 %.

$C_{21}H_{29}N_3$ requires : C = 78.02 % ; H = 8.97 % ; N = 13.00 %.

33. p-Chlorobenzal-p-diethylaminoaniline : Shining yellow plates from alcohol, m.p. 99°C.

Found : C = 71.7 % ; H = 6.73 % ; N = 9.83 %.

$C_{17}H_{19}N_2Cl$ requires : C = 71.2 % ; H = 6.60 % ; N = 9.80 %.

34. p-Anisal-p-diethylaminoaniline : Yellow plates from alcohol, m.p. 92°C.

Found : C = 76.20 % ; H = 7.33 % ; N = 10.22 %.

$C_{18}H_{22}N_2O$ requires : C = 76.61 % ; H = 7.80 % ; N = 9.93 %.

35. p-Dimethylaminobenzal-p-diethylaminoaniline : Glistening yellow needles from alcohol, m.p. 139°C.

Found : C = 77.04 % ; H = 8.16 % ; N = 14.43 %.

$C_{19}H_{25}N_3$ requires : C = 77.29 % ; H = 8.47 % ; N = 14.23 %.

36. p-n-Propoxybenzal-p-anisidine : White plates from alcohol, m.p. 119°C.

Found : C = 75.65 % ; H = 6.91 % ; N = 5.27 %.

$C_{17}H_{19}NO_2$ requires : C = 75.82 % ; H = 7.06 % ; N = 5.20 %.

37. p-n-Propoxybenzal-p-bromoaniline : Colourless plates from alcohol, m.p. 98°C.

Found : C = 60.20 % ; H = 4.88 % ; N = 4.21 %.
$C_{16}H_{16}NOBr$ requires : C = 60.39 % ; H = 5.03 % ; N = 4.40 %.

38. p-n-Propoxybenzal-p-dimethylaminoaniline : Yellow needles from alcohol, m.p. 116.5°C.

Found : C = 76.26 % ; H = 7.54 % ; N = 9.47 %.
$C_{18}H_{22}N_2O$ requires : C = 76.61 % ; H = 7.80 % ; N = 9.94 %.

39. p-n-Propoxybenzal-p-chloroaniline : Colourless crystals from alcohol, m.p. 84°C.

Found : C = 70.52 % ; H = 5.75 % ; N = 5.32 %.
$C_{16}H_{16}NOCl$ requires : C = 70.20 % ; H = 5.84 % ; N = 5.11 %.

40. p-Chlorobenzal-p-nitroaniline : Pale yellow fibres from alcohol, m.p. 167°C.

Found : C = 59.82 % ; H = 3.31 % ; N = 10.59 %.
$C_{13}H_9N_2O_2Cl$ requires : C = 59.88 % ; H = 3.45 % ; N = 10.80 %.

41. p-Anisal-p-n-butoxyaniline : Colourless plates from alcohol, m.p. 115°C and monotropic transition point 108.5°C.

Found : N = 4.945 %.
$C_{18}H_{21}NO_2$ requires : N = 4.947 %.

42. p-Anisal-p-n-propoxyaniline : Colourless plates from alcohol, m.p. 119.5° C.

Found : N = 5.349 %.

$C_{17}H_{19}NO_2$ requires : N = 5.204 %.

43. p-n-Dodecyloxybenzal-p-n-butoxyaniline : Colourless plates from benzene. Solid melts at 101°C giving a smectic phase ; smectic phase changes to nematic at 111.0°C and finally gives isotropic liquid at 111.5°C. While cooling the changes are reversible and before crystallization an additional smectic monotropic phase is observed at 95°C.

Found : N = 3.267 %.

$C_{29}H_{43}NO_2$ requires : N = 3.204 %.

44. p-Anisal-p-fluoroaniline : Yellow plates from alcohol, m.p. 67°C.

Found : C = 73.01 % ; H = 5.10 % ; N = 5.94 %.

$C_{14}H_{12}NOF$ requires : C = 73.36 % ; H = 5.24 % ; N = 6.11 %.

V. Preparation of other substances :

1. Triphenylmethane :

Triphenylmethane was prepared (162) by adding to a mixture of 3.7 mole of dry benzene and 0.75 mole of dry carbon tetrachloride in a flask fitted with a reflux condenser and a calcium chloride tube, 0.75 mole of anhydrous aluminium chloride, in an ice bath and allowing to stand for 24 hours, the temperature of the bath rising to that of the room. 110 g. of anhydrous ether is then added in small portions with occassional shaking and the mixture allowed

to stand for twentyfour hours. The mixture was later poured into ice (650 g.) containing 25 ml. of conc. HCl. A litre of benzene was then added and the whole mixture was gently boiled for 5 to 10 minutes on a steam bath. After cooling, the benzene layer was separated and washed with warm water containing little quantity of HCl. Benzene was distilled off and the residue was distilled under reduced pressure and the fraction boiling over the range 190-215°C /10 mm. was collected. The product solidified on cooling and gave colourless needles from ethanol, m.p. 92°C.

2. 6,6''',-Dihydroxy-3,3''',-bichalconyl :

To 4,4'-dihydroxy-3,3'-diacetyl-biphenyl (2.7 g. ; 0.01 mole) and potassium hydroxide, benzaldehyde (6.3 g. ; 0.06 mole) and alcohol (60 ml.) were added followed by more potassium hydroxide (10 g. ; 10 ml. of water) . The mixture was kept overnight at room temperature. The dark red solution was diluted with water and extracted with ether. The ether layer was rejected. The aqueous layer was acidified and the precipitated material was crystallised from toluene in red needles, m.p. 203°C. (163). Yield 66%.

3. 6,6'''-Dihydroxy-4,4''-dimethoxy-3,3'''-bichalconyl :

4,4'-Dihydroxy-3,3'-diacetyl-biphenyl (2.7 g. ; 0.01 mole) was dissolved in sodium hydroxide and anisaldehyde (8 g. ; 0.06 mole) was added. Alcohol was added to the above mixture till the anisaldehyde completely dissolved. Potassium hydroxide (10 g.; 10 ml.water)

was then added and the mixture kept overnight. The red reaction mixture was diluted with water and extracted with ether. The ether layer was discarded. The aqueous layer was acidified and the precipitated bichalconyl derivative was crystallised from nitrobenzene in red needles melting at 226°C. (164). Yield 50-60 %.

4. 4,4'-Dimethoxy-3,3'-diacetylbiphenyl :

4,4'-Dihydroxy-3,3'-diacetylbiphenyl, m.p. 219°C (165) was methylated with dimethylsulphate and anhydrous potassium carbonate in acetone to obtain 4,4'-dimethoxy-3,3'-diacetylbiphenyl. The solvent was distilled off and the product obtained after treating with water was crystallised from acetic acid., m.p. 148°C.

	Found	: C = 72.22 % ; H = 6.20 %.
$C_{18}H_{18}O_4$	requires	: C = 72.49 % ; H = 6.04 %.

5. 2,2',6,6'-Tetramethoxybiphenyl :

5 g. of dimethyl ether of 2-iodoresorcinol, m.p. 103°C (166) was mixed with 7 g. of copper powder and heated over an oil bath at 200-220°C for two hours. The product was cooled, extracted with chloroform, the solvent evaporated and recrystallised from benzene, m.p. 175°C.

6. Chalkones :

An alcoholic solution of aromatic ketone and p-substituted benzaldehyde were condensed in equimolecular proportions in presence of caustic potash solution.

The reaction mixture was kept over-night at room temperature. The product obtained was washed with large quantities of water to remove the alkali and finally crystallised from alcohol.

(a) 4,4'-Dimethoxychalkone : Yellow prisms from alcohol, m.p. 102°C. Straus (167) gives m.p. 101-102°C.

(b) 4,4'-Dichlorochalkone : Yellow needles from ethanol-benzene mixture, m.p. 156°C. Straus and Ackermann (168) give m.p. 156-157°C.

7. Azines :

Azines were prepared by condensing an alcoholic solution of two moles of aromatic aldehydes with one mole of hydrazine hydrate. The product obtained was crystallised from a suitable solvent like benzene, alcohol and acetone.

(a) 4,4'-Dichlorobenzalazine : Golden yellow plates from a mixture of benzene and acetone, m.p. 210°C. Pascal and Normand (169) give m.p. 211°C.

(b) 4,4'-Di(dimethylamino)benzalazine : Yellow prisms from a mixture of benzene and acetone, m.p. 260°C. Vorlander (170) gives m.p. 250-253°C.

8. 7-Benzoyloxy-3-benzoyl flavone : Prepared by the method given by Baker (171) and was crystallised from alcohol-benzene mixture to get pale yellow prismatic needles, m.p. 167°C. Baker gives m.p. 167°C.

Purification of Materials :

The following substances of pure or commercial quality were purchased from B.D.H. and were purified by repeated crystallisation from suitable solvents till sharp melting points agreeing with those given in the literature were obtained.

1. p-Azoxyanisole : was purified by repeated crystallisation from alcohol to give fine yellow needles, m.p. 118°C and T.P. 136°C.
2. p-Methoxybenzoic acid : (anisic acid) was purified by repeated crystallisation from water to give fine white needles, m.p. 184°C.
3. p-Nitrobenzoic acid : was recrystallised from dilute alcohol to give fine colourless prisms, m.p. 241°C.
4. p-Chlorobenzoic acid : was recrystallised from dilute alcohol to give fine leaflets, m.p. 236°C.
5. p-Bromobenzoic acid : was recrystallised from alcohol to give fine white prisms, m.p. 251°C.
6. p-Toluic acid : was recrystallised from hot water to give fine long needles, m.p. 177°C.
7. p-Iodobenzoic acid : was recrystallised from alcohol to give colourless plates, m.p. 269°C.
8. p-Hydroxybenzoic acid : was recrystallised from water to give fine white needles, m.p. 213°C.