EXPERIMENTAL

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1. Preparation of compounds (all temperatures are corrected):

1.1. n-Alkyl halides :

All alkyl halides (bromides or iodides) used except n-amyl iodide were of B.D.H. quality. n-Amyl iodide was prepared by the following method (162a) :

5.44 g. of purified red phosphorus and 34.7 g. of n-amyl alcohol were taken in a 250 ml. round bottom flask fitted with a reflux condenser and 50.0 g. of well powdered iodine was added to the contents of the flask in small portions of about 3 to 4 g. at a time, at an interval of 2 to 3 minutes between consecutive additions. The addition of iodine was done by removing the condenser and replacing it immediately after adding iodine. A moderate evolution of heat took place during the addition of iodine. After adding all the iodine, the contents were refluxed on the sand-bath for about 90 minutes. The contents were then distilled and the fraction in the range of 150^{0} - 157^{0}C was collected. The distillate was washed with equal volume of 10 % aqueous sodium carbonate solution and subsequently with water to remove traces of sodium carbonate. n-Amyl iodide so obtained was dried on calcium chloride granules. It was then filtered and redistilled; the distillate in the temperature range of 153^{0} - 156^{0}C was collected. The yield was 60 %.

1.2. p-n-Alkoxybenzaldehydes :

p-Methoxybenzaldehyde used was of B.D.H. quality while other p-n-alkoxybenzaldehydes were prepared.

Hildesheimer (163), Steermer and Wodarg (164), Weygand and Gabler (165,166) and Gray and Jones (132) have described the preparation of p-n-alkoxybenzaldehydes. Here, the following method (132) was used :

p-Hydroxybenzaldehyde (0.1 mole), anhydrous K_2CO_3 (o.4 mole), cyclohexanone (80.0 ml.) and n-alkyl iodide or bromide (0.15 mole) were 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 solution was then decanted from K_2CO_3 which was washed thoroughly with ether and the washings added to the decanted portion. In practice, complete removal of adherent liquid from K_2CO_3 was not successful even after several washings with ~~w~~ ether. In such cases, after washing thoroughly with ether, K_2CO_3 was dissolved in water and the liquid layer so obtained was separated and added to the decanted cyclohexanone and ether solution. The solvents were distilled off on the water-bath under reduced pressure. The residual p-n-alkoxybenzaldehydes were then obtained as colourless or yellow liquids or waxy solids in pure form by distilling under reduced pressure. Yields were in the range of 55 to 70 %. In Table 3 are listed p-n-alkoxybenzaldehydes and their boiling points alongwith the values found in the literature.

TABLE - 3

p-n-Alkoxybenzaldehydes

n-Alkyl group	B.P. °C (found)	B.P. °C (reported)
1. Ethyl	146°/20 mm. or 249°	106°/3 mm. (132)
2. Propyl	130°/10 mm. or 268°	144°/14 mm. (132); 268° (164)
3. Butyl	158°/10 mm. or 285°	148-9°/10 mm.(165); 285° (174)
4. Amyl	157°/10 mm.	145-6°/5 mm. (165)
5. Hexyl	186°/13 mm.	154-5°/6 mm. (165)
6. Heptyl	170°/10 mm.	162-4°/7 mm. (165)
7. Octyl	182°/7 mm.	162-3°/4 mm. (165)
8. Nonyl	185°/5 mm.	181°/4 mm. (166)
9. Decyl	190°/5 mm.	185°/4 mm. (132)
10. Dodecyl	195°/8 mm.	194°/8 mm. (132)
11. Hexadecyl	248°/5 mm.	230°/3 mm. (132)
12. Octadecyl	252°/5 mm.	240°/2 mm. (132)

p-n-Dodecyloxybenzaldehyde, p-n-hexadecyloxybenzaldehyde and p-n-octadecyloxybenzaldehyde are waxy solids which melt at 24.0°C, 34.0°C and 49.0°C respectively. The purity of these aldehydes was tested by condensing them with either benzidine (136) or p-phenetidine (166).

1.3. p-n-Alkoxyanilines :

1.3a. p-n-Alkoxynitrobenzenes (p-nitrophenol-n-alkyl ethers) :

Spiegel and Sabbath (167), Reiss (168), Gutekunst and Gray (169) and Weygand and Gabler (165) have described the preparations of several p-n-alkoxynitrobenzenes; here, the following procedure (169) was used :

Recrystallised dry p-nitrophenol (0.1 mole), anhydrous K_2CO_3 (0.4 mole), ethyl methyl ketone (80 ml.) and n-alkyl 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 was washed thoroughly with ether and the ethereal washings were added to the decanted solution. To ensure complete removal of solution from K_2CO_3, it was dissolved in water and the liquid layer thus formed was collected and added to the decanted solution. The solvents were removed by distillation and the residual p-n-alkoxynitrobenzenes were obtained in the pure form (orange coloured) by distillation under reduced pressure (yield 50-60 %). In Table 4 are given the boiling points of p-n-alkoxynitrobenzenes together with the values found in the literature.

TABLE - 4

p-n-Alkoxynitrobenzenes

n-Alkyl group	B.P. $^{\circ}$C (found)	B.P. $^{\circ}$C (reported)
1. Propyl	286°/760 mm.	285-7° (169)
2. Butyl	165°/ 7 mm.	160-3°/7 mm. (165)
3. Amyl	161°/ 5 mm.	162-3°/5 mm. (165); 309-10° (167).

1. 3b. p-n-Alkoxyanilines from p-n-alkoxynitrobenzenes :

The reduction of the above nitro-compounds was carried out by the following method (169) :

Stannous chloride (40.0 g.) was dissolved in concentrated HCl (60.0 ml.) and the solution was heated upto 80 $^{\circ}$C. p-n-Alkoxynitrobenzene (0.05 mole) was then slowly added. During the addition of p-n-alkoxynitrobenzene, the temperature rose to 107-109 $^{\circ}$C. The mixture was boiled for a few minutes and then cooled. It was then made alkaline by adding cold solution of NaOH. The oil (red or dark red) floating on the surface of the solution was extracted with ether, dried over anhydrous calcium chloride and distilled under reduced pressure. The product was yellow liquid which on standing became dark red. The yield was about 55 %. The boiling points of p-n-alkoxyanilines are given in Table 5.

TABLE - 5

p-n-Alkoxyanilines

n-Alkyl group	B.P. $^{\circ}$C (found)	B.P. $^{\circ}$C (reported)
1. Propyl	285.0°	285.0° (165)
2. Butyl	143.0°/13 mm.	143-4°/12 mm. (169)
3. Amyl	152.0°/10 mm.	> 307.0° (165)

1.4. p-Aminobenzoic acid :

p-Aminobenzoic acid used was of laboratory reagent quality. It was recrystallised from alcohol in white needles melting at 192.0 $^{\circ}$C.

1.5. Methyl p-aminobenzoate :

Methyl p-aminobenzoate was prepared by the following method (162b) :

Dry methanol (180 ml.) was taken in a 500 ml.

conical flask fitted with a two-holed cork and wash bottle tubes. Dry hydrogen chloride gas was passed through methanol till it became saturated; the weight increased by about 40.0 g. The solution was then transferred to a 500 ml. round bottom flask, p-aminobenzoic acid (35.0 g.) was added to it and the mixture was refluxed on a sand-bath for two hours using a water condenser. The hot solution was then poured into excess of water and was neutrallized with sodium carbonate. The precipitated ester was filtered and dried in air. The product was crystallised from aqueous methanol in leaflets which melted at 112 ^{o}C. The yield was 70 %.

1.6. <u>Ethyl p-aminobenzoate</u> :

Ethyl p-aminobenzoate was similarly prepared (162b) by using absolute ethyl alcohol (200 ml.) and p-aminobenzoic acid (30.0 g.). The crude product was recrystallised from alcohol into fine needles melting at 91.5 ^{o}C. The yield was 65 %.

1.7. <u>p-Acetoxybenzaldehyde</u> :

p-Acetoxybenzaldehyde was prepared by the following method (170) :

A mixture of p-hydroxybenzaldehyde (0.1 mole), acetic anhydride (0.11 mole) and pyridine (2 ml.) was kept in a flask for eight hours with occasional shaking. It was then poured into 100 ml. of water and kept for about six hours. The oily layer so obtained was separated and distilled to get pure p-acetoxybenzaldehyde which distilled out at 264-265 ^{o}C.

1.8. <u>Preparation of Schiff's base compounds</u> :

The Schiff's base compounds were prepared by refluxing equimolecular quantities of the corresponding aromatic aldehyde and aniline in alcohol for about 10 minutes. The product was recrystallised several times from suitable solvents (e.g. alcohol, benzene etc.) into fine crystals which gave sharp melting and/or transition points.

The analytical data for the five series are summarised in Table 6 to 10 and the melting points and various transition points are given in Tables 11 to 15.

TABLE - 6

Series I : p-n-Alkoxybenzylidene-p-aminobenzoic acids.

Alkyl group	Crystallised from	Shape and colour	Molecular formula	Found % N	Required % N
1. Methyl	Benzene	Yellow needles	$C_{15}H_{13}O_3N$	5.557	5.490
2. Ethyl	Benzene	Yellowish small cubes.	$C_{16}H_{15}O_3N$	5.101	5.204
3. Propyl	Alcohol	Yellow blades	$C_{17}H_{17}O_3N$	4.916	4.946
4. Butyl	Alcohol	Pale yellow needles.	$C_{18}H_{19}O_3N$	4.683	4.713
5. Amyl	Alcohol	Pale yellow plates.	$C_{19}H_{21}O_3N$	4.683	4.501
6. Hexyl	Benzene	Yellowish crystalline powder	$C_{20}H_{23}O_3N$	4.341	4.307
7. Heptyl	Benzene	Crystalline yellow powder	$C_{21}H_{25}O_3N$	4.194	4.129
8. Octyl	Alcohol	Small yellow prisms	$C_{22}H_{27}O_3N$	3.910	3.966
9. Nonyl	Alcohol	Colourless flakes	$C_{23}H_{29}O_3N$	4.054	3.814
10. Decyl	Alcohol	Colourless flakes	$C_{24}H_{31}O_3N$	3.589	3.674
11. Dodecyl	Benzene	Colourless flakes	$C_{26}H_{35}O_3N$	3.219	3.422
12. Hexadecyl	Benzene	White powder	$C_{30}H_{43}O_3N$	2.828	3.010
13. Octadecyl	Benzene	White powder	$C_{32}H_{47}O_3N$	2.653	2.839

TABLE - 7

Series II : Methyl p-n-alkoxybenzylidene-p-aminobenzoates.

Alkyl group	Crystallised from	Shape and colour	Molecular formula	Found % N	Required % N
1. Methyl	Alcohol	Shining white small prisms	$C_{16}H_{15}O_3N$	5.299	5.204
2. Ethyl	Alcohol	White needles	$C_{17}H_{17}O_3N$	4.712	4.946
3. Propyl	Alcohol	Colourless flakes	$C_{18}H_{19}O_3N$	4.711	4.713
4. Butyl	Alcohol	Colourless plates	$C_{19}H_{21}O_3N$	4.618	4.501
5. Amyl	Alcohol	White needles	$C_{20}H_{23}O_3N$	4.404	4.307
6. Hexyl	Alcohol	Colourless flakes	$C_{21}H_{25}O_3N$	4.189	4.129
7. Heptyl	Alcohol	Colourless tufts of prisms	$C_{22}H_{27}O_3N$	3.944	3.966
8. Octyl	Alcohol	Pale yellow plates	$C_{23}H_{29}O_3N$	3.773	3.814
9. Nonyl	Alcohol	Pale yellow plates	$C_{24}H_{31}O_3N$	3.696	3.674
10. Decyl	Alcohol	White small flakes	$C_{25}H_{33}O_3N$	3.456	3.544
11. Dodecyl	Alcohol	Colourless flakes	$C_{27}H_{37}O_3N$	3.210	3.335
12. Octadecyl	Alcohol	Colourless flakes	$C_{33}H_{49}O_3N$	2.701	2.761

TABLE - 8

Series IIIa : p-n-Alkoxybenzylidene-p-n-propoxyanilines

Alkyl group	Crystallised from	Shape and colour	Molecular formula	Found % N	Required % N
1. Methyl	Alcohol	Colourless plates	$C_{17}H_{19}O_2N$	5.349	5.204
2. Ethyl	Benzene	White small needles	$C_{18}H_{21}O_2N$	4.966	4.947
3. Propyl	Alcohol	Yellow plates	$C_{19}H_{23}O_2N$	4.953	4.713
4. Butyl	Alcohol	Pale yellow flakes	$C_{20}H_{25}O_2N$	4.686	4.501
5. Amyl	Benzene	White flakes	$C_{21}H_{27}O_2N$	4.366	4.307
6. Hexyl	Alcohol	White plates	$C_{22}H_{29}O_2N$	4.277	4.129
7. Heptyl	Alcohol	White small prisms	$C_{23}H_{31}O_2N$	4.086	3.966
8. Octyl	Alcohol	White flakes	$C_{24}H_{33}O_2N$	3.915	3.814
9. Nonyl	Benzene	Colourless plates	$C_{25}H_{35}O_2N$	3.655	3.674
10. Decyl	Benzene	White small prisms	$C_{26}H_{37}O_2N$	3.664	3.544
11. Dodecyl	Benzene	White flakes	$C_{28}H_{41}O_2N$	3.321	3.301
12. Hexadecyl	Benzene	Colourless flakes	$C_{32}H_{49}O_2N$	2.843	2.923
13. Octadecyl	Benzene	Colourless flakes	$C_{34}H_{53}O_2N$	2.671	2.761

TABLE - 9

Series IIIb : p-n-Alkoxybenzylidene-p-n-butoxyanilines

Alkyl group	Crystallised from	Shape and colour	Molecular formula	Found % N	Required % N
1. Methyl	Alcohol	Colourless plates	$C_{18}H_{21}O_2N$	4.945	4.947
2. Ethyl	Alcohol	White crystals	$C_{19}H_{23}O_2N$	4.506	4.713
3. Propyl	Alcohol	White fibers	$C_{20}H_{25}O_2N$	4.418	4.501
4. Butyl	Alcohol	White fibrous needles	$C_{21}H_{27}O_2N$	4.065	4.307
5. Amyl	Alcohol	Pale yellow flakes	$C_{22}H_{29}O_2N$	3.930	4.129
6. Hexyl	Benzene	Tan coloured small prisms	$C_{23}H_{31}O_2N$	3.759	3.966
7. Heptyl	Benzene	White small prisms	$C_{24}H_{33}O_2N$	3.574	3.814
8. Octyl	Alcohol	White crystals	$C_{25}H_{35}O_2N$	3.516	3.674
9. Nonyl	Benzene	White powder	$C_{26}H_{37}O_2N$	3.376	3.544
10. Decyl	Benzene	Brown powder	$C_{27}H_{39}O_2N$	3.415	3.423
11. Dodecyl	Benzene	Colourless flakes	$C_{29}H_{43}O_2N$	3.267	3.204
12. Hexadecyl	Benzene	Colourless flakes	$C_{33}H_{51}O_2N$	2.647	2.840
13. Octadecyl	Benzene	Colourless flakes	$C_{35}H_{55}O_2N$	2.654	2.688

TABLE - 10

Series IIIc : p-n-Alkoxybenzylidene-p-n-amyloxyanilines

Alkyl group	Crystallised from	Shape and colour	Molecular formula	Found % N	Required % N
1. Methyl	Alcohol	Colourless plates	$C_{19}H_{23}O_2N$	4.974	4.713
2. Ethyl	Alcohol	Pinkish powder	$C_{20}H_{25}O_2N$	4.333	4.501
3. Propyl	Alcohol	Colourless crystals	$C_{21}H_{27}O_2N$	4.262	4.307
4. Butyl	Alcohol	Yellow plates	$C_{22}H_{29}O_2N$	3.973	4.129
5. Amyl	Alcohol	Colourless flakes	$C_{23}H_{31}O_2N$	3.883	3.966
6. Hexyl	Benzene	Colourless needles	$C_{24}H_{33}O_2N$	3.634	3.814
7. Heptyl	Benzene	Colourless flakes	$C_{25}H_{35}O_2N$	3.793	3.674
8. Octyl	Alcohol	Brown crystalline powder	$C_{26}H_{37}O_2N$	3.358	3.544
9. Nonyl	Alcohol	Colourless plates	$C_{27}H_{39}O_2N$	3.234	3.423
10. Decyl	Alcohol	White small crystals	$C_{28}H_{41}O_2N$	3.601	3.301
11. Dodecyl	Benzene	Colourless small prisms	$C_{30}H_{45}O_2N$	3.277	3.104
12. Hexadecyl	Benzene	White powder	$C_{34}H_{53}O_2N$	2.653	2.761
13. Octadecyl	Benzene	White powder	$C_{36}H_{57}O_2N$	2.487	2.617

1.9. Schiff's bases studied in mixed-mesomorphism :

(1) Methyl p-chlorobenzylidene-p-aminobenzoate :

Colourless needles from alcohol + benzene, m.p. 161.5 °C.

Found % N = 4.954

$C_{15}H_{12}O_2NCl$ requires % N = 5.118

(2) Methyl p-nitrobenzylidene-p-aminobenzoate :

Yellow fibrous needles from benzene, m.p. 213.0 °C.

Found % N = 10.29

$C_{15}H_{12}O_4N_2$ requires % N = 9.86

(3) Ethyl p-nitrobenzylidene-p-aminobenzoate :

Pale yellow fibrous needles from benzene, m.p. 180 °C.

Found % N = 9.210

$C_{16}H_{14}O_4N_2$ requires % N = 9.399

(4) Methyl p-dimethylaminobenzylidene-p-aminobenzoate :

Yellow plates from alcohol, m.p. 163.5 °C.

Found % N = 9.921

$C_{17}H_{18}O_2N_2$ requires % N = 9.931

(5) p-Acetoxybenzylidene-p-bromoaniline :

Colourless needles from alcohol, m.p. 108.5 °C.

Found % N = 4.360

$C_{15}H_{12}O_2NBr$ requires % N = 4.402

(6) p-Dimethylaminobenzylidene-p-chloroaniline :

Pale yellow needles from alcohol, m.p. 152.0 °C.

Found % N = 11.26

$C_{15}H_{15}N_2Cl$ requires % N = 10.83

(7) Ethyl p-chlorobenzylidene-p-aminobenzoate :

White needles from alcohol, m.p. 120.0° C.

Found % N = 4.620

$C_{16}H_{14}O_2NCl$ requires % N = 4.868

(8) Ethyl p-methoxybenzylidene-p-aminobenzoate :

White needles from alcohol, m.p. 80.0° C.

Found % N = 4.816

$C_{17}H_{17}O_3N$ requires % N = 4.946

(9) p-Nitrobenzylidene-p-toluidine :

Yellow leaflets from alcohol, m.p. 124.0° C.

Ullmann (171) gives m.p. 124.5° C.

(10) p-Nitrobenzylidene-p-bromoaniline :

Greenish-yellow needles from alcohol, m.p. 163.0° C.

Lowy and King (172) give m.p. 160.5° C while Ingold and Piggott (173) give m.p. 160-161° C.

(11) p-Nitrobenzylidene-p-phenetidine :

Yellow needles from alcohol, m.p. 123.5° C.

Dave and Lohar (157) give m.p. 123.5° C.

(12) p-Anisylidene-p-toluidine :

White needles from alcohol, m.p. 93.0° C.

Senior and Foster (174) give m.p. 92-93° C.

(13) p-Chlorobenzylidene-p-phenetidine :

Colourless plates from alcohol, m.p. 123.0° C.

Lohar (175) give m.p. 121.0° C.

(14) p-Methylbenzylidene-p-toluidine :

White leaflets from alcohol, m.p. 94.0° C.

Law (176) gives m.p. 92-93° C.

(15) p-Chlorobenzylidene-p-dimethylaminoaniline :

Light yellow crystals from alcohol, m.p. 164.0 °C.
Krohnke (177) gives m.p. 165.5 °C.

(16) p-Chlorobenzylidene-p-toluidine :

White shining plates from alcohol, m.p. 128.0 °C.
Law (176) gives m.p. 128.0 °C.

(17) p-Anisylidene-p-bromoaniline :

White plates from alcohol, m.p. 120.0 °C.
Senior and Foster (174) give m.p. 120.0 °C.

(18) p-Anisylidene-p-anisidine :

White needles from carbon tetrachloride, m.p. 148.0 °C.
Senior and Foster (174) give m.p. 146.0-147.0 °C.

(19) p-Anisylidene-p-chloroaniline :

White plates from alcohol, m.p. 92.0 °C.
Senior and Foster (174) give m.p. 93.0-94.0 °C.

(20) p-Anisylidene-p-phenetidine :

Colourless plates from alcohol, m.p. 128.5 °C. On cooling gives isotropic-nematic transition at 122.0 °C. Weygand and Gabler (166) give the same melting and transition points.

1.10. Ethyl p-azoxybenzoate :

Elliott (178) has described the preparation of p-azoxybenzoic acid. However, the following method of Vorlander (179) for the preparation of p-azoxycinnamic acid and ethyl p-azoxycinnamate was employed :

A mixture of 25.0 g. p-nitrobenzoic acid, 30.0 g. arsenious acid (anhydride) and 42.5 g. NaOH in 250 ml. water was warmed at 70 °C when it became solid due to the separation of the sparingly soluble nature of the sodium salt of azoxybenzoic acid in NaOH. On further warming and addition of more water, the salt was brought into solution and the free acid was precipitated out with dilute HCl. The acid in the form of fine yellowish powder was purified by repeatedly decanting with water. p-Azoxybenzoic acid is insoluble in most of the solvents and does not melt but becomes darker in colour when heated to a high temperature (240.0 °C). The yield was 80 %.

The acid was then dissolved in liquor ammonia. From this solution, the silver salt of the acid was precipitated by treatment with silver nitrate solution. The silver salt was then dried (30.0 g.), and reacted with ethyl iodide (30.0 g.) in 300 ml. benzene on the water-bath under reflux condenser for two hours. The benzene solution was filtered out from solid silver iodide which was washed thoroughly with benzene. The washings and the filtrate were mixed and the solvent was evaparated. The red mass so obtained was recrystallised several times from ethyl alcohol into fine light orange plates. The yield was 75 %.

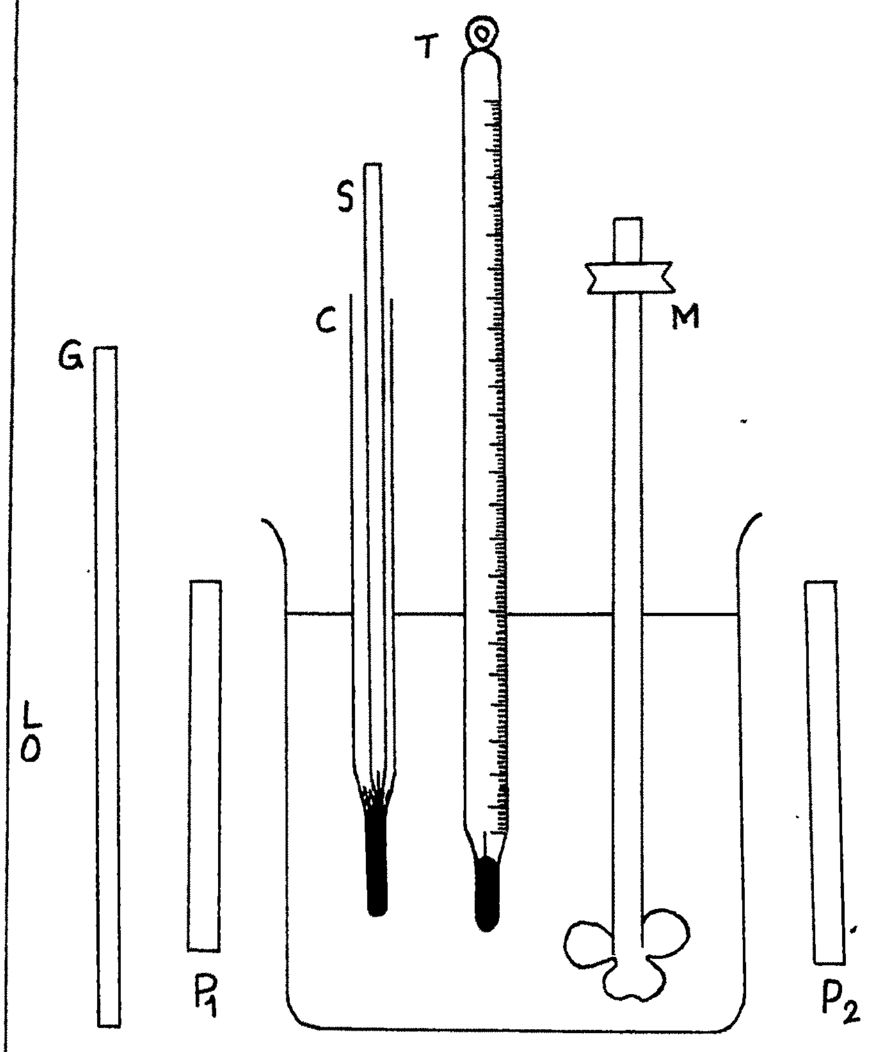
$$\text{Solid} \xrightarrow{114.0\,^{\circ}C} \text{Smectic} \xrightarrow{122.5\,^{\circ}C} \text{Isotropic.}$$

2. <u>Study of transition temperatures</u> :

Preliminary measurements (i.e. solid-mesomorphic-isotropic transitions) of pure compounds as well as of binary mixtures were taken by the optical method (159) which is described below :

2.1. <u>Optical Method</u> :

A small portion of finely powdered compound or mixture was heated in a wide capillary tube C in an oil-bath



L - Lamp
C - Capillary tube
S - Stirrer
G - Ground glass screen
T - Thermometer
M - Mechanical stirrer
P_1 - } Polaroid squares
P_2 - }

Fig. 3

and observed between crossed square polaroid sheets p_1 and P_2 (Fig. 3). The capillary tube was prepared 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 and the compound or mixture could be easily stirred throughout. The powdered substance was introduced into the capillary and pressed down with narrow glass rod so that the material occupied 1.0 - 1.5 cm. at the bottom of the capillary tube.

The bath consisted of 1 litre beaker containing dibutyl phthalate. This was continuously stirred uniformly by means of an electrically run mechanical stirrer M. The beaker was wrapped with asbestos paper to minimise loss of heat through radiation. The asbestos wrapper was provided with two windows 1.1/2" square opposite one another. A calibrated standard thermometer T, graduated in 1/10th of a degree was suspended in the bath and measured the temperature. The capillary was placed in such a way that it could be seen clearly through the windows in the asbestos lagging. A source of light L, provided by an electric lamp and passed through a ground glass screen G illuminated the substance in the capillary. The two polaroid sheets 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 and P_2 stood in front of the beaker. The polaroid sheets were placed 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 became isotropic. The bath temperature was raised at the rate of $1^{o}C$ per two minutes by using a micro-burner.

When the compound or mixture melted to give a mesomorphic state, due to the birefringent nature of the mesophase, bright light was seen through the molten mass. This bright light disappeared when the mesophase disappeared and the isotropic liquid was formed. On cooling the isotropic liquid, again bright light through molten mass appeared. The temperature at which this transformation takes place is known as mesomorphic-isotropic transition temperature.

In the case of mixtures of certain compositions which were not giving mesomorphism, the contents in the capillary melted over a range of temperature and the solid particles in such state were giving an illusion of birefringence but when the solid completely melted to homogenous isotropic liquid, this liquid on cooling did not give the birefringence within the limit of $0.5^{o}C$ of temperature at which it had become clear. The temperature at which the mixture just started to melt was taken as the sintering point.

The melting points, solid-mesomorphic points and mesomorphic-isotropic points of pure compounds as well as of mixtures were determined preliminarily by this method.

2.2. <u>Preparation of mixture</u> :

The two substances in known proportions were carefully and accurately weighed in a small fusion tube (2" x 1/4"), so that the total weight of the mixture was about 0.2 g. (exactly weighed). The tube with its contents was then heated in a paraffin or dibutyl phthalate bath so as to melt the contents at the possible lowest temperature. When the mixture melted, it was throughly stirred by means of a glass rod to ensure complete mixing of the components. The homogeneous liquid was then quickly cooled by quenching the tube in a beaker of cold water. The solid mixture was then removed from the tube and was converted to fine powder by intimately grinding it in an agate mortar. Various mixtures of different proportions were prepared in this way and their various transition points were studied first by the optical method and then more accurately by the microscopic method described below :

2.3. Determination of Transition Temperatures by Microscope :

It is rather difficult to detect smectic-smectic and smectic-nematic changes sharply by the optical method. Hence, the uses of microscope has become essential for the detection of such changes with great accuracy. Gray (180) has described the polarizing microscope fitted with a heating stage used by him. The microscope used in this investigation for the mesomorphic and polymesomorphic transition temperatures was a Leitz Ortholux Polarizing microscope having a binocular and monocular attachments for observing the specimen on the slide. It is fitted with an electrical heating-block. This block is provided with a slide slot to insert the slide and a hole to keep the thermometer. The temperature of the heating block can be electrically controlled by a regulator from room temperature to 360°C and can be conveniently read by the suitable thermometers graduated in o.5°C. The specimen is illuminated by polarized light, the light source being an electric lamp. By means of the monocular tube, the specimen and the temperature can be seen side by side simultaneously. The specimen was heated and melted on the clean glass slide inserted in the heating slot and a clean glass cover slip was pressed ovėr it to remove air bubbles and get a possible thin section of the material. The slide and the heating block were then cooled to necessary desired temperature.

The accuracy of the heating-device was checked by taking melting points and/or transition points of the known compounds such as benzoic acid, α-naphthol, succinic acid, anthracene, p-azoxyanisole, p-methoxycinnamic acid, p-acetoxybenzylidene-p-phenetidine, ethyl p-azoxybenzoate etc.

To determine the various transitions, the prepared slide with a thin section of the material, was inserted in the heating cavity and the temperature was raised fairly fast (5°C/min.) to find approximate transition temperatures. The heating block was then allowed to cool until the stable solid reappeared. The measurements were then repeated with a rate of heating of 1°C/min. from 5° 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 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 to find solid-smectic transition; however, the disappearance of cleavage lines in the solid was taken as the solid-smectic transition. In the enantiotropic mesomorphism, all the transitions are clearly detected while cooling the isotropic liquid - the reversal taking place at the same temperature or within $\pm$ 0.2 °C. Isotropic-nematic changes were observed by the separation of small bubbles from the isotropic liquid. These bubbles then coalesce and a threaded region which is a characteristic of the nematic phase is formed. The isotropic-smectic transition was indicated by the separation of batonnets which coalesce to form fine mosaic of focal-conic pattern which is a distinguishing character of the smectic phase. Smectic-nematic and smectic-smectic changes were also clearly detected with great accuracy under the 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 the nematic phase appeared. In the case of monotropic mesomorphism, it was possible to raise the temperature before crystallization took place and the mesophase disappeared at the same temperature at which it had appeared, thus confirming the isotropic-mesomorphic transition temperature. All the compounds were observed continuously under the microscope from their solid state to the isotropic state while heating and from isotropic state to the solid state while cooling so that no transition could escape unnoticed.