

## EXPERIMENTAL

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### 1. PREPARATION OF COMPOUNDS

#### 1.1 n-Alkyl halides

Most of the alkyl halides (bromides or iodides) used were of B.D.H., E.Merk or equivalent quality. Ethyl, n-propyl, n-butyl, n-amyl and iso amyl iodides were prepared by the following general method (146) described for preparation of n-amyl iodide.

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°-157°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°-156°C was collected. The yield was 60 %.

## 1.2 4-n-Alkoxy-1-naphthaldehydes

4-n-Alkoxy-1-naphthaldehydes were prepared by the alkylation of 4-hydroxy-1-naphthaldehyde. 4-hydroxy-1-naphthaldehyde was prepared by the Gattermann aldehyde synthesis method (147) described by Adams and Levine (148).

### 1.2 (a) 4-Hydroxy-1-naphthaldehyde

In a 250 ml round bottom flask a solution of 1-naphthol (0.1 mol) dissolved in 100 ml dry ether was taken and after addition of zinc cyanide (0.2 mol), the flask with contents was kept in an ice-bath. Dry hydrogen chloride gas was then passed through the mixture for about three hours when the solid product, imidehydrochloride was obtained. The liquid was decanted and the solid was washed with ether to remove the soluble impurities and then it was dried. The product was then hydrolyzed with warm distilled water containing a few mililitres of ethanol. The crude naphthaldehyde obtained was filtered and crystallized from dilute ethanol (30 percent) to pale yellow needles which melted at 180°C (reported value 180°C). The yield was about 60-65 %.

### 1.2 (b) 4-n-Alkoxy-1-naphthaldehydes (82)

4-Hydroxy-1-naphthaldehyde (0.05 mol) was dissolved in dry acetone (50 ml) and anhydrous potassium carbonate (0.2 mol) and alkyl halide (0.075 mol) were added. The reaction mixture was refluxed for about eight hours on a water-bath. In the case of alkyl bromide the heating period was extended to about twelve hours. The solvent was decanted from potassium carbonate which was then dissolved in water. The solution was extracted with ether and the ether extract was added to the decanted portion. The ether was evaporated and the crude product was washed with a dilute solution of sodium hydroxide to remove unreacted hydroxy compound. The product was then crystallized several times from ethanol till it gave sharp melting point. The melting points agree well with the reported ones. The yield was about 50 %.

### 1.3 p-Alkoxyanilines

#### 1.3 (a) p-Alkoxynitrobenzenes i.e. (p-Nitrophenol alkyl ethers).

Spiegel and Sabbath (149), Reiss (150), Gutekunst and Gray (151) and Weygand and Gabler (152) have described the preparations of several p-alkoxynitrobenzenes ; here, the following procedure (151) was used :

Recrystallized dry *p*-nitrophenol (0.1 mol), anhydrous  $K_2CO_3$  (0.4 mol), ethyl methyl ketone (80 ml) and *n*-alkyl iodide (1.5 mol) 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*-alkoxynitrobenzenes were obtained in the pure form (orange coloured) by distillation under reduced pressure (Yield 50-60 %). The boiling points of *p*-alkoxynitrobenzenes are given in Table 2 and they are compared with the values reported in the literature.

Table 2

*p*-Alkoxynitrobenzenes

<u><i>p</i>-Alkoxy group</u>	<u>B.P.°C(found)</u>	<u>B.P.°C(reported)</u>
1. <i>n</i> -Propoxy	286°/760 mm.	285-7°/760 mm (151)
2. <i>n</i> -Butoxy	165°/7 mm.	160-3°/7/mm. (152)
3. <i>n</i> -Amyloxy	161°/5 mm.	162-3°/5 mm. (152)
		309-10° (149)
4. iso-Amyloxy	206-9°/45 mm	--

### 1.3 (b) p-Alkoxyanilines from p-alkoxynitrobenzenes

The reduction of the above nitro-compounds was carried out by the following method (151).

Stannous chloride (40.0 g) was dissolved in concentrated HCl (60.0 ml) and the solution was heated upto 80°C. p-Alkoxynitrobenzene (0.05 mol) was then slowly added. During the addition of p-alkoxynitrobenzene, the temperature rose to 107-109°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-alkoxy anilines are given in Table 3.

Table 3

<u>p-Alkoxy group</u>	<u>p-Alkoxyanilines</u>	
	<u>B.P.°C(found)</u>	<u>B.P.°C(reported)</u>
1. n-Propoxy	285.0°	285-0° (152)
2. n-Butoxy	143-0°/13 mm.	143-4°/12 mm.(151)
3. n-Amyloxy	152.0°/10 mm.	307.0° (152)
4. iso-Amyloxy	183-6°/45 mm.	--

### 1.3 (c) Preparation of naphthalene Schiff bases

The Schiff base compounds were prepared by refluxing equimolecular quantities (0.01 mol) of 4-n-alkoxy-1-naphthaldehydes with different p-alkoxyanilines (0.01 mol) for an hour in 20 ml ethanol. All the Schiff base compounds were crystallized from ethanol till they gave constant transition temperatures.

The following homologous series of naphthalene Schiff bases were synthesised.

- (1) 4-n-Alkoxy-1-naphthylidene-p-n-propoxyanilines
- (2) 4-n-Alkoxy-1-naphthylidene-p-n-butoxyanilines
- (3) 4-n-Alkoxy-1-naphthylidene-p-n-amyloxyanilines
- (4) 4-n-Alkoxy-1-naphthylidene-p-i-amyloxyanilines

The transition temperatures are summarized in Tables 4 to 7. The analytical data are recorded in Tables 14 to 17.

### 1.4 p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-alkyl or p"-alkoxyanilines(p-phenylene derivatives)

#### 1.4 (a) p-n-Alkoxybenzoic acids

p-Methoxybenzoic acid used was B.D.H. quality while other members were prepared. Jones (153), Gray and Jones (82) and Dave and Vora (154) have described the

preparation of these acids. Here the following method was used :

p-Hydroxybenzoic acid (0.1 mol), alkyl halides (0.12 mol), and potassium hydroxide (0.25 mol) were dissolved in methanol (100 ml) and refluxed for 3 to 4 hours. Ten percent aqueous potassium hydroxide solution (20 ml) was added and refluxing continued for 2 hours to hydrolyse any ester formed. The solution was cooled and acidified with hydrochloric acid to precipitate the acids. The alkoxy acids were crystallized from ethanol or acetic acid till they gave constant melting and transition temperatures. The transition temperatures compare well with those found in the literature.

#### 1.4 (b) p-n-Alkoxybenzoyl chlorides (154)

p-n-Alkoxybenzoyl chlorides were prepared by treating the corresponding p-n-alkoxybenzoic acids with excess of thionyl chloride and heating on a water bath till evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using a water pump. The acid chlorides which are left behind as the residue were used for further reaction without purification.

#### 1.4 (c) p(p'-n-Alkoxybenzoyloxy)benzaldehydes (155)

p(p'-n-Alkoxybenzoyloxy)benzaldehydes were prepared



by reacting p-n-alkoxybenzoyl chlorides with p-hydroxybenzaldehyde.

p-Hydroxybenzaldehyde (B.D.H.) (0.01 mol) was dissolved in dry pyridine (A.R., 10 ml) and p-n-alkoxybenzoyl chloride (0.015 mol) was added slowly with stirring. The mixture was warmed with stirring for an hour and was allowed to stand overnight. It was acidified with cold dilute hydrochloric acid and the precipitates were collected by filtration and washed with cold dilute sodium hydroxide solution followed by water. The solid esters were crystallized from methanol. The transition temperatures compare well with the literature. The yield was about 60 %.

#### 1.4 (d) Preparation of Schiff bases

##### p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-alkyl or p"-alkoxyanilines

The equimolecular quantities (0.01 mol) of p(p'-n-alkoxybenzoyloxy)benzaldehydes and pure p-substituted anilines (0.01 mol) were condensed by refluxing for an hour in 20 ml ethanol. In the case of cyano and nitro substituted anilines a drop of acetic acid was added in the solution as condensing agent. The Schiff bases were crystallized from ethanol.

The following Schiff base series were synthesized.

- (5) p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethylanilines
- (6) p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-phenetidines
- (7) p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butylanilines
- (8) p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butoxyanilines
- (9) p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-cyanoanilines
- (10) p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-nitroanilines

The transition temperatures are summarized in Tables 8 to 13. The analytical data are given in Tables 18 to 23.

#### 1.5 Schiff bases studied in mixed mesomorphism

- (a) 4-n-butoxy-1-naphthylidene-p-i-amyloxyaniline  
(From series 4)
- (b) 4-n-hexyloxy-1-naphthylidene-p-i-amyloxyaniline  
(From series 4)
- (c) 4-n-dodecyloxy-1-naphthylidene-p-n-propoxyaniline  
(From series 1)
- (d) 4-n-dodecyloxy-1-naphthylidene-p-n-butoxyaniline  
(From series 2)
- (e) 4-n-nonyloxy-1-naphthylidene-p-n-amyloxyaniline  
(From series 3)

#### 1.6 Preparation of Mixture

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

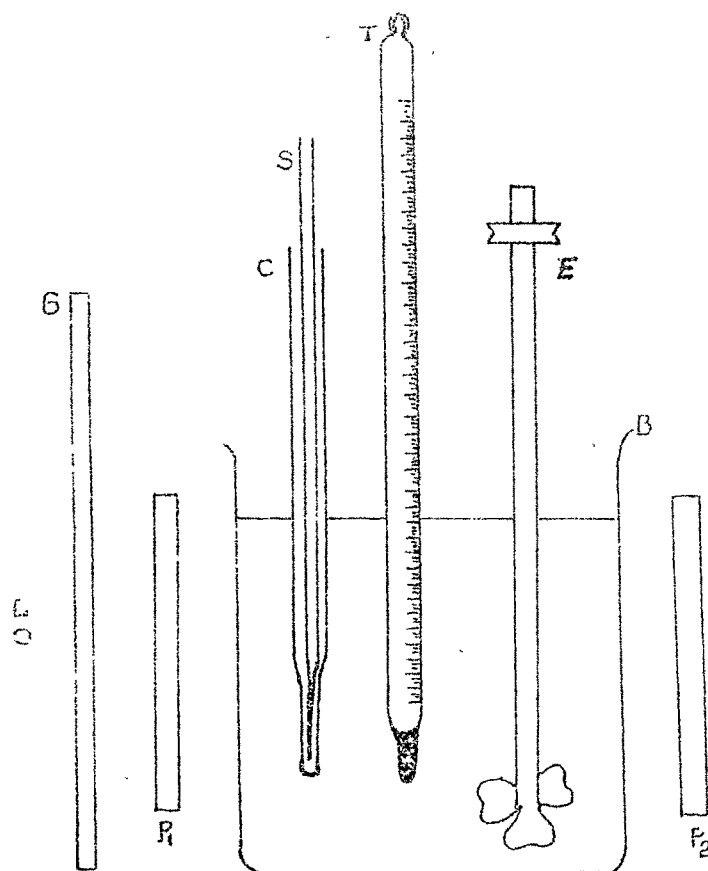
was then heated in a paraffin or dibutyl phthalate bath so as to melt the contents at the possible lowest temperature. When the mixture melted, it was thoroughly stirred by means of a glass rod to ensure complete mixing of the components. The homogeneous liquid was then quickly cooled by quenching the tube in an ice-bath. 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. Determination of Transition Temperatures

Preliminary measurements, i.e., solid-mesomorphic-isotropic transitions of pure compounds were made by the optical method of Dave and Dewar which is described below :

### 2.1 Optical Method (90)

The experimental set up used for this method is shown diagrammatically in figure 4. The capillary tube C in which the substance was heated was made by drawing out an ordinary glass tubing to form a capillary of 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 could be easily stirred throughout. The powdered substance was introduced



L - LAMP  
 C - CAPILLARY TUBE  
 S - STIRRER (GLASS ROD)  
 G - GROUND GLASS SCREEN

T - THERMOMETER  
 E - ELECTRIC STIRRER  
 P<sub>1</sub> } POLAROID SQUARES  
 P<sub>2</sub> }  
 B - BEAKER

FIG. 4.

in the capillary and pressed down with the narrow glass rod so that the material occupied 10-15 mm at the bottom of the capillary tube. The 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 stirrer E. The beaker was lagged by wrapping asbestos paper around it in order to minimise the loss of heat through radiation. The asbestos covering was provided with two windows 4 cm square opposite one another. A calibrated 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 containing the substance under investigation was held in the bath by the side of the thermometer in such a way that it could be seen clearly 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. Two polaroid squares P<sub>1</sub> and P<sub>2</sub> were placed on either side of the beaker facing the windows in the asbestos lagging so that P<sub>1</sub> stood in front of the beaker. The polaroid squares were held crossed to each other so that the light 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°C per two minutes by using a

micro burner. When the compound 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. The temperature at which this transformation takes place is known as mesomorphic-isotropic transition temperature.

## 2.2 Determination of transition temperatures with the help of a polarizing microscope

It was rather difficult to detect polymesomorphism i.e. smectic-smectic, smectic-nematic or smectic-cholesteric transitions and different textures of the mesophase by the optical method. Hence the use of microscope became essential for the detection of such changes with greater accuracy. The microscope used in this investigation was a Leitz Ortholux II polarizing microscope equipped with a Leitz heating stage.

To determine the various transitions a glass slide carrying a thin section of the material with a cover slip on it was observed under the microscope. The slide was inserted into the specimen chamber of the heating stage and the temperature was raised fairly fast ( $5^{\circ}\text{C}/\text{min}$ ) to find the approximate transition temperatures. The measurements were then repeated and near the transition to be observed the rate of heating was regulated to about  $1^{\circ}\text{C}$  per minute.

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

Many compounds of these series except p(p'-alkoxybenzoyloxy)benzylidene-p"-n-butoxyanilines) on heating, gives mesomorphic state (smectic or nematic) which adopt a homeotropic texture. On further heating and before changing to the isotropic liquid a bright spec like wave front appears which makes the determination of the transition easy. The isotropic liquid on cooling gives a smectic or nematic mesophase as the case may be, which immediately changes to homeotropic texture. In the case of poly mesomorphic compound the isotropic liquid on cooling changes to a homeotropic nematic phase which on further cooling gives the bâtonnets of the smectic phase which then gradually change to a homeotropic texture. Because of this behaviour it was possible to determine transition temperatures accurately even though the textures may be homeotropic.

Table 44-n-Alkoxy-1-naphthylidene-p-n-propoxyanilines

Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C	
		Nematic	Isotropic
1	Methyl	(35.0)*	83.0
2	Ethyl	(48.0)*	98.0
3	Propyl	(42.5)*	84.0
4	Butyl	(55.0)*	90.0
5	Pentyl	(50.0)	87.0
6	Hexyl	(59.5)	85.5
7	Heptyl	-	74.5
8	Octyl	-	81.5
9	Nonyl	(58.0)	59.0
10	Decyl	(61.0)	70.0
11	Dodecyl	(57.0)	71.0
12	Tetradecyl	(53.0)	76.5
13	Hexadecyl	(47.0)*	74.0
14	Octadecyl	(40.0)*	78.0

\* Extrapolated values

Figures in parentheses indicate monotropy



Table 5

4-n-Alkoxy-1-naphthylidene-p-n-butoxyanilines

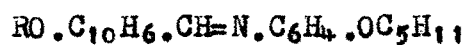
Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C	
		Nematic	Isotropic
1	Methyl	(50.0)*	91.0
2	Ethyl	(70.5)	88.0, 84.0 (C <sub>I</sub> ) (C <sub>II</sub> )
3	Propyl	(56.5)	80.0
4	Butyl	(70.5)	87.5
5	Pentyl	(61.5)	80.0, 74.0 (C <sub>I</sub> ) (C <sub>II</sub> )
6	Hexyl	(70.0)	75.5
7	Heptyl	59.5	66.0
8	Octyl	(69.5)	73.0
9	Nonyl	(67.0), 55.0 (C <sub>II</sub> )	72.5 (C <sub>I</sub> )
10	Decyl	(70.0), 66.5 (C <sub>II</sub> )	82.5 (C <sub>I</sub> )
11	Dodecyl	59.0	67.0
12	Tetradecyl	(57.0)	70.0
13	Hexadecyl	(42.0)*	70.5
14	Octadecyl	(10.0)*	76.5

\* Extrapolated values

Figures in parentheses indicate monotropy

C<sub>I</sub> Stable solidmodificationC<sub>II</sub> Metastable solidmodification

Table 6

4-n-Alkoxy-1-naphthylidene-p-n-amyloxyanilines

Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C	
		Nematic	Isotropic
1	Methyl	(22.5)*	86.5
2	Ethyl	(61.5)	81.5, 74.5 (CI) (CII)
3	Propyl	(35.0)*	78.0, 68.0 (CI) (CII)
4	Butyl	62.5	64.5
5	Pentyl	(46.5)*	64.5
6	Hexyl	(65.5)	68.5
7	Heptyl	(55.5)	73.5
8	Octyl	(66.0)	80.0
9	Nonyl	55.5	84.0
10	Decyl	(66.0)	73.5
11	Dodecyl	62.5	64.5
12	Tetradecyl	58.0	61.5
13	Hexadecyl	(55.5)*	71.5
14	Octadecyl	(45.0)*	58.5

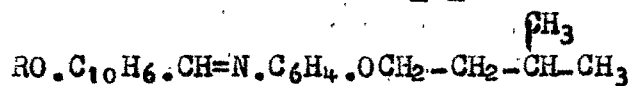
\* Extrapolated values

Figures in parentheses indicate monotropy

CI Stable solidmodification

CII Metastable solidmodification

Table 7

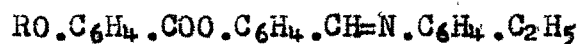
4-n-Alkoxy-1-naphthylidene-p-i-amyloxyanilines

Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C	
		Nematic	Isotropic
1	Methyl	(28.5)*	104.5
2	Ethyl	(48.0)*	102.5
3	Propyl	(35.0)*	78.0
4	Butyl	(50.0)	68.5
5	Pentyl	(40.5)	56.0
6	Hexyl	(51.5)	58.0
7	Heptyl	(43.0)	67.0
8	Octyl	(48.5)	56.5
9	Nonyl	(44.5)	56.5
10	Decyl	(47.5)	53.5
11	Dodecyl	(36.0)	52.0
12	Tetradecyl	(15.0)*	52.5
13	Hexadecyl	-	72.0
14	Octadecyl	-	80.0

\* Extrapolated values

Figures in parentheses indicate monotropy

Table 8

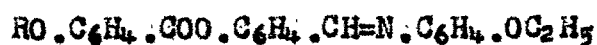
p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethylanilines

Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	125.0	255.0
2	Ethyl	-	126.0	256.5
3	Propyl	-	136.0	241.5
4	Butyl	-	128.0	240.0
5	Pentyl	-	115.0	228.0
6	Hexyl	(86.0)	98.5	222.0
7	Heptyl	95.0	103.5	211.5
8	Octyl	101.0	115.5	207.5
9	Nonyl	101.0	126.5	200.0
10	Decyl	84.0	136.5	197.0
11	Dodecyl	90.0	150.0	186.5
12	Tetradecyl	94.0	155.0	180.0
13	Hexadecyl	94.0	157.0	172.0
14	Octadecyl	95.0	157.5	166.5

Figure: in parenthesis indicates monotropy

Table 9

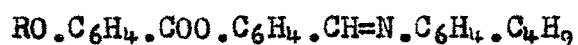
$p(p' - n\text{-Alkoxybenzoyloxy})\text{benzylidene-}p''\text{-phenetidines}$



Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	144.0	300.0
2	Ethyl	-	165.0	293.0
3	Propyl	-	131.0	282.0
4	Butyl	-	140.0	277.0
5	Pentyl	-	135.0	267.0
6	Hexyl	-	124.0	259.5
7	Heptyl	-	105.0	250.5
8	Octyl	-	110.0	246.5
9	Nonyl	-	107.0	233.5
10	Decyl	110.5	113.5	233.0
11	Dodecyl	104.5	133.0	219.0
12	Tetradecyl	102.5	148.0	210.5
13	Hexadecyl	103.0	157.0	203.0
14	Octadecyl	102.0	160.0	192.5

Table 10

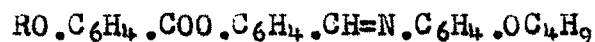
p(p'-n-Alkoxybenzoyloxy)benzylidene-p''-n-butylanilines



Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	110.0	247.0
2	Ethyl	-	129.0	246.0
3	Propyl	-	125.0	230.5
4	Butyl	-	117.0	227.5
5	Pentyl	-	111.0	214.5
6	Hexyl	95.0	115.0	213.0
7	Heptyl	88.0	127.5	204.0
8	Octyl	77.0	137.0	200.0
9	Nonyl	85.0	144.0	194.0
10	Decyl	80.0	151.5	191.5
11	Dodecyl	91.5	158.0	184.5
12	Tetradecyl	92.5	164.0	173.5
13	Hexadecyl	95.0	165.0	171.0
14	Octadecyl	95.0	157.5	161.0

Table 11

p(p'-n-Alkoxybenzoyloxy)benzylidene-p''-n-butoxyanilines



Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	129.0	272.0
2	Ethyl	-	144.0	280.0
3	Propyl	-	140.0	261.0
4	Butyl	-	133.0	260.0
5	Pentyl	-	126.0	246.0
6	Hexyl	-	112.0	244.0
7	Heptyl	97.0	126.0	229.0
8	Octyl	95.0	137.0	228.0
9	Nonyl	97.0	147.0	221.0
10	Decyl	104.0	156.0	218.5
11	Dodecyl	98.0	165.0	209.5
12	Tetradecyl	102.0	170.5	201.0
13	Hexadecyl	104.5	173.0	195.0
14	Octadecyl	105.5	173.0	188.0

Table 12

$p(p'-n\text{-Alkoxybenzoyloxy})\text{benzylidene-}p''\text{-cyanoanilines}$



Compound No.	<u>n</u> -Alkyl Group (R)	Transition Temperatures in °C	
		Smectic	Isotropic
1	Methyl	170.0	301.0
2	Ethyl	165.0	298.0
3	Propyl	134.0	284.0
4	Butyl	130.0	280.0
5	Pentyl	120.0	268.0
6	Hexyl	106.0	261.0
7	Heptyl	106.0	254.0
8	Octyl	108.0	247.5
9	Nonyl	95.0	240.0
10	Decyl	95.0	236.0
11	Dodecyl	96.0	228.5
12	Tetradecyl	105.0	224.0
13	Hexadecyl	86.0	221.5
14	Octadecyl	104.0	215.0



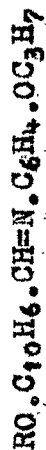
Table 13

$p(p'-n\text{-Alkoxybenzoyloxy})\text{benzylidene-}p''\text{-nitroanilines}$



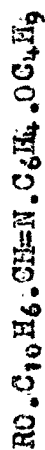
Compound No.	$n$ -Alkyl Group (R)	Transition Temperatures in °C	
		Smectic	Isotropic
1	Methyl	216.0	289.0
2	Ethyl	204.0	300.0
3	Propyl	172.0	279.0
4	Butyl	158.0	278.0
5	Pentyl	141.0	266.0
6	Hexyl	138.0	260.0
7	Heptyl	130.0	249.0
8	Octyl	130.0	245.0
9	Nonyl	125.0	235.0
10	Decyl	121.0	236.5
11	Dodecyl	126.0	236.0
12	Tetradecyl	120.0	230.0
13	Hexadecyl	125.0	224.0
14	Octadecyl	125.0	224.0

Table 14

4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-propoxyanilines

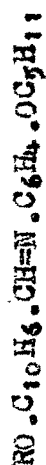
Compound No.	<i>n</i> -Alkyl Group (R)	Molecular Formula	Percent Required			Percent Found		
			C	H	N	C	H	N
1	Methyl	C <sub>21</sub> H <sub>21</sub> O <sub>2</sub> N	78.97	6.63	4.39	78.84	6.16	4.11
2	Ethyl	C <sub>23</sub> H <sub>23</sub> O <sub>2</sub> N	79.25	6.95	4.20	78.81	6.68	4.22
3	Propyl	C <sub>25</sub> H <sub>25</sub> O <sub>2</sub> N	79.50	7.25	4.03	79.86	7.16	4.33
4	Butyl	C <sub>27</sub> H <sub>27</sub> O <sub>2</sub> N	79.74	7.53	3.88	79.87	7.08	4.07
5	Pentyl	C <sub>29</sub> H <sub>29</sub> O <sub>2</sub> N	79.96	7.79	3.73	80.13	7.41	4.13
6	Hexyl	C <sub>31</sub> H <sub>31</sub> O <sub>2</sub> N	80.17	8.02	3.60	79.73	7.77	4.03
7	Heptyl	C <sub>33</sub> H <sub>33</sub> O <sub>2</sub> N	80.36	8.24	3.47	79.87	7.83	3.05
8	Octyl	C <sub>35</sub> H <sub>35</sub> O <sub>2</sub> N	80.53	8.46	3.35	80.35	8.14	3.26
9	Nonyl	C <sub>37</sub> H <sub>37</sub> O <sub>2</sub> N	80.70	8.64	3.25	80.22	8.26	3.16
10	Decyl	C <sub>39</sub> H <sub>39</sub> O <sub>2</sub> N	80.85	8.82	3.14	80.40	8.51	3.41
11	Dodecyl	C <sub>41</sub> H <sub>41</sub> O <sub>2</sub> N	81.14	9.15	2.96	81.16	8.69	3.04
12	Tetradecyl	C <sub>43</sub> H <sub>43</sub> O <sub>2</sub> N	81.39	9.44	2.79	81.08	8.97	2.61
13	Hexadecyl	C <sub>45</sub> H <sub>45</sub> O <sub>2</sub> N	81.61	9.70	2.64	81.34	9.46	2.69
14	Octadecyl	C <sub>47</sub> H <sub>47</sub> O <sub>2</sub> N	81.81	9.94	2.51	81.39	9.59	2.39

Table 15

4- $\bar{n}$ -Alkoxy-1-naphthylidene-2- $\bar{n}$ -butoxyanilines

Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required C	Percent Required H	Percent Required N	Percent Found C	Percent Found H	Percent Found N
1	Methyl	C <sub>22</sub> H <sub>23</sub> O <sub>2</sub> N	79.29	6.91	4.20	79.49	6.56	4.70
2	Ethyl	C <sub>23</sub> H <sub>25</sub> O <sub>2</sub> N	79.54	7.20	4.03	79.21	6.82	4.31
3	Propyl	C <sub>24</sub> H <sub>27</sub> O <sub>2</sub> N	79.81	7.48	3.88	79.82	7.01	4.38
4	Butyl	C <sub>25</sub> H <sub>29</sub> O <sub>2</sub> N	80.00	7.73	3.73	79.57	7.26	4.20
5	Pentyl	C <sub>26</sub> H <sub>31</sub> O <sub>2</sub> N	80.23	7.97	3.60	79.91	7.51	4.05
6	Hexyl	C <sub>27</sub> H <sub>33</sub> O <sub>2</sub> N	80.39	8.19	3.47	79.90	7.71	3.15
7	Heptyl	C <sub>28</sub> H <sub>35</sub> O <sub>2</sub> N	80.58	8.39	3.36	80.23	7.98	3.22
8	Octyl	C <sub>29</sub> H <sub>37</sub> O <sub>2</sub> N	80.74	8.58	3.25	80.60	8.11	3.52
9	Nonyl	C <sub>30</sub> H <sub>39</sub> O <sub>2</sub> N	80.89	8.76	3.15	80.93	8.49	3.18
10	Decyl	C <sub>31</sub> H <sub>41</sub> O <sub>2</sub> N	81.04	8.93	3.05	81.19	9.25	3.24
11	Dodecyl	C <sub>33</sub> H <sub>45</sub> O <sub>2</sub> N	81.32	9.24	2.88	80.84	9.42	3.30
12	Tetradecyl	C <sub>35</sub> H <sub>49</sub> O <sub>2</sub> N	81.55	9.51	2.72	81.14	9.03	2.26
13	Hexadecyl	C <sub>37</sub> H <sub>53</sub> O <sub>2</sub> N	81.77	9.76	2.58	81.43	9.44	2.42
14	Octadecyl	C <sub>39</sub> H <sub>57</sub> O <sub>2</sub> N	81.96	9.98	2.45	81.60	9.91	2.05

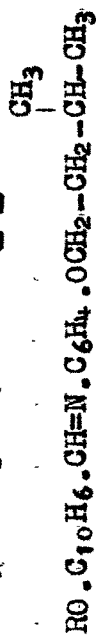
Table 16

4- $\bar{n}$ -Alkoxy-1-naphthylidene-p- $\bar{n}$ -amloxyanilines

Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required		Percent Found	
			C	H	C	H
1	Methyl	C <sub>23</sub> H <sub>25</sub> O <sub>2</sub> N	79.54	7.20	79.98	7.01
2	Ethyl	C <sub>24</sub> H <sub>27</sub> O <sub>2</sub> N	79.79	7.48	79.69	7.51
3	Propyl	C <sub>25</sub> H <sub>29</sub> O <sub>2</sub> N	80.00	7.73	80.05	7.96
4	Butyl	C <sub>26</sub> H <sub>31</sub> O <sub>2</sub> N	80.23	7.97	79.76	7.94
5	Pentyl	C <sub>27</sub> H <sub>33</sub> O <sub>2</sub> N	80.39	8.19	80.13	8.53
6	Hexyl	C <sub>28</sub> H <sub>35</sub> O <sub>2</sub> N	80.58	8.40	80.65	8.42
7	Heptyl	C <sub>29</sub> H <sub>37</sub> O <sub>2</sub> N	80.74	8.58	80.44	8.37
8	Octyl	C <sub>30</sub> H <sub>39</sub> O <sub>2</sub> N	80.89	8.76	81.30	8.56
9	Nonyl	C <sub>31</sub> H <sub>41</sub> O <sub>2</sub> N	81.04	8.93	81.45	8.97
10	Decyl	C <sub>32</sub> H <sub>43</sub> O <sub>2</sub> N	81.17	9.09	81.32	8.65
11	Dodecyl	C <sub>34</sub> H <sub>47</sub> O <sub>2</sub> N	81.45	9.38	81.51	9.36
12	Tetradecyl	C <sub>36</sub> H <sub>51</sub> O <sub>2</sub> N	81.66	9.64	81.75	9.54
13	Hexadecyl	C <sub>38</sub> H <sub>55</sub> O <sub>2</sub> N	81.87	9.87	81.89	10.10
14	Octadecyl	C <sub>40</sub> H <sub>59</sub> O <sub>2</sub> N	82.04	10.09	82.24	10.33

Table 17

## 4-n-Alkoxy-1-naphthylidene-p-i-amyloxyanilines



Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required			Percent Found		
			C	H	N	C	H	N
1	Methyl	C <sub>23</sub> H <sub>25</sub> O <sub>2</sub> N	79.54	7.20	4.03	79.39	6.98	4.53
2	Ethyl	C <sub>25</sub> H <sub>27</sub> O <sub>2</sub> N	79.79	7.48	3.88	80.09	7.33	4.09
3	Propyl	C <sub>27</sub> H <sub>29</sub> O <sub>2</sub> N	80.00	7.73	3.73	79.68	7.35	4.07
4	Butyl	C <sub>29</sub> H <sub>31</sub> O <sub>2</sub> N	80.23	7.97	3.60	80.34	7.51	4.04
5	Pentyl	C <sub>31</sub> H <sub>33</sub> O <sub>2</sub> N	80.39	8.19	3.47	80.89	7.78	3.97
6	Hexyl	C <sub>33</sub> H <sub>35</sub> O <sub>2</sub> N	80.58	8.40	3.36	80.70	8.07	3.85
7	Heptyl	C <sub>35</sub> H <sub>37</sub> O <sub>2</sub> N	80.74	8.58	3.25	80.65	8.27	3.32
8	Octyl	C <sub>37</sub> H <sub>39</sub> O <sub>2</sub> N	80.89	8.76	3.15	80.40	8.43	2.95
9	Nonyl	C <sub>39</sub> H <sub>41</sub> O <sub>2</sub> N	81.04	8.93	3.05	80.69	8.45	3.04
10	Decyl	C <sub>41</sub> H <sub>43</sub> O <sub>2</sub> N	81.17	9.09	2.96	81.28	8.65	2.49
11	Dodecyl	C <sub>43</sub> H <sub>47</sub> O <sub>2</sub> N	81.45	9.38	2.79	80.97	8.97	2.47
12	Tetradecyl	C <sub>45</sub> H <sub>51</sub> O <sub>2</sub> N	81.66	9.64	2.65	81.47	9.18	2.24
13	Hexadecyl	C <sub>47</sub> H <sub>55</sub> O <sub>2</sub> N	81.87	9.87	2.51	81.40	10.14	3.00
14	Octadecyl	C <sub>49</sub> H <sub>59</sub> O <sub>2</sub> N	82.04	10.09	2.39	81.54	10.04	2.55

Table 18

p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethylanilines  
 $\text{RO} \cdot \text{C}_6\text{H}_4 \cdot \text{COO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_2\text{H}_5$

Compound No	n-Alkyl Group (R)	Molecular Formula	Percent Required C	Percent Required H	Percent Required N	Percent Found C	Percent Found H	Percent Found N
1	Methyl	$\text{C}_2\text{H}_5\text{O}_3\text{N}$	76.88	5.85	3.90	77.32	6.06	3.95
2	Ethyl	$\text{C}_4\text{H}_9\text{O}_3\text{N}$	77.21	6.16	3.75	76.74	6.06	3.64
3	Propyl	$\text{C}_6\text{H}_{11}\text{O}_3\text{N}$	77.52	6.46	3.62	77.09	6.57	3.66
4	Butyl	$\text{C}_8\text{H}_{13}\text{O}_3\text{N}$	77.82	6.73	3.49	77.85	7.10	3.65
5	Pentyl	$\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$	78.07	6.99	3.37	78.05	7.18	3.24
6	Hexyl	$\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$	78.30	7.23	3.26	78.77	7.49	2.80
7	Heptyl	$\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}$	78.56	7.45	3.16	79.00	7.72	2.90
8	Octyl	$\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$	78.77	7.66	3.06	78.68	7.96	3.48
9	Nonyl	$\text{C}_{18}\text{H}_{23}\text{O}_3\text{N}$	78.96	7.86	2.97	78.74	7.83	2.65
10	Decyl	$\text{C}_{20}\text{H}_{25}\text{O}_3\text{N}$	79.18	8.04	2.88	79.11	8.06	2.95
11	Dodecyl	$\text{C}_{24}\text{H}_{29}\text{O}_3\text{N}$	79.54	8.38	2.73	79.38	8.15	2.65
12	Tetradecyl	$\text{C}_{28}\text{H}_{33}\text{O}_3\text{N}$	79.86	8.69	2.59	80.11	9.08	2.66
13	Hexadecyl	$\text{C}_{32}\text{H}_{37}\text{O}_3\text{N}$	80.15	8.96	2.46	79.75	8.51	2.92
14	Octadecyl	$\text{C}_{36}\text{H}_{41}\text{O}_3\text{N}$	80.39	9.21	2.34	80.17	9.12	2.45

Table 19

$p(p'-n\text{-Alkoxybenzoyloxy})\text{benzylidene-}p''\text{-phenetidines}$



Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required			Percent Found		
			C	H	N	C	H	N
1	Methyl	$C_2H_5O_4N$	73.60	5.60	3.73	74.03	5.86	4.01
2	Ethyl	$C_2H_5O_4N$	74.04	5.91	3.60	74.09	6.08	3.72
3	Propyl	$C_2H_5O_4N$	74.44	6.20	3.47	74.52	6.63	3.96
4	Butyl	$C_2H_5O_4N$	74.84	6.48	3.36	75.08	6.57	3.57
5	Pentyl	$C_2H_5O_4N$	75.14	6.73	3.25	75.60	7.19	3.45
6	Hexyl	$C_2H_5O_4N$	75.50	6.97	3.15	75.61	7.17	2.92
7	Heptyl	$C_2H_5O_4N$	75.82	7.19	3.05	75.35	7.64	3.13
8	Octyl	$C_3H_7O_4N$	76.10	7.40	2.96	75.66	7.84	3.42
9	Nonyl	$C_3H_7O_4N$	76.38	7.60	2.87	76.85	7.80	3.14
10	Decyl	$C_3H_7O_4N$	76.65	7.78	2.79	76.86	8.06	3.04
11	Dodecyl	$C_3H_7O_4N$	77.13	8.13	2.65	77.03	8.14	3.14
12	Tetradecyl	$C_3H_7O_4N$	77.56	8.44	2.55	77.10	8.53	3.07
13	Hexadecyl	$C_3H_7O_4N$	77.94	8.72	2.39	77.91	8.70	2.21
14	Octadecyl	$C_4H_9O_4N$	78.29	8.97	2.28	77.89	8.88	1.95

Table 20

p(p'-n-Alkoxybenzoyloxy)benzylidene-p-n-butylanilines

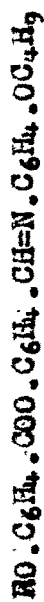


Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required		Percent Found	
			C	H	C	H
1	Methyl	C <sub>25</sub> H <sub>25</sub> O <sub>3</sub> N	77.49	6.50	77.87	6.92
2	Ethyl	C <sub>26</sub> H <sub>27</sub> O <sub>3</sub> N	77.78	6.78	77.59	6.45
3	Propyl	C <sub>27</sub> H <sub>29</sub> O <sub>3</sub> N	78.04	7.04	77.94	6.81
4	Butyl	C <sub>28</sub> H <sub>31</sub> O <sub>3</sub> N	78.29	7.27	78.54	6.84
5	Pentyl	C <sub>29</sub> H <sub>33</sub> O <sub>3</sub> N	78.52	7.50	78.05	7.14
6	Hexyl	C <sub>30</sub> H <sub>35</sub> O <sub>3</sub> N	78.74	7.71	79.14	7.59
7	Heptyl	C <sub>31</sub> H <sub>37</sub> O <sub>3</sub> N	78.94	7.91	79.30	7.48
8	Octyl	C <sub>32</sub> H <sub>39</sub> O <sub>3</sub> N	79.14	8.09	79.62	7.66
9	Nonyl	C <sub>33</sub> H <sub>41</sub> O <sub>3</sub> N	79.32	8.27	79.30	8.05
10	Decyl	C <sub>34</sub> H <sub>43</sub> O <sub>3</sub> N	79.49	8.44	79.39	8.30
11	Dodecyl	C <sub>36</sub> H <sub>47</sub> O <sub>3</sub> N	79.81	8.75	79.79	8.32
12	Tetradecyl	C <sub>38</sub> H <sub>51</sub> O <sub>3</sub> N	80.09	9.02	80.53	9.04
13	Hexadecyl	C <sub>40</sub> H <sub>55</sub> O <sub>3</sub> N	80.35	9.27	80.85	8.82
14	Octadecyl	C <sub>42</sub> H <sub>59</sub> O <sub>3</sub> N	80.60	9.50	80.34	9.13



Table 21

$p(p'-n\text{-Alkoxybenzoyloxy})$  benzylidene- $p''-n\text{-butoxyanilines}$



Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required			Percent Found		
			C	H	N	C	H	N
1	Methyl	$C_2H_5O_4N$	74.42	6.25	3.47	74.90	6.44	3.65
2	Ethyl	$C_2H_7O_4N$	74.80	6.52	3.36	74.56	6.56	3.35
3	Propyl	$C_2H_9O_4N$	75.15	6.77	3.25	75.23	6.95	3.35
4	Butyl	$C_2H_{11}O_4N$	75.48	7.01	3.14	75.07	6.83	3.43
5	Pentyl	$C_2H_{13}O_4N$	75.79	7.24	3.05	75.35	6.85	3.16
6	Hexyl	$C_{30}H_{15}O_4N$	76.08	7.45	2.96	75.67	7.31	3.05
7	Heptyl	$C_{31}H_{17}O_4N$	76.35	7.65	2.87	76.05	7.18	3.23
8	Octyl	$C_{32}H_{19}O_4N$	76.61	7.84	2.79	76.83	7.90	2.85
9	Nonyl	$C_{33}H_{21}O_4N$	76.86	8.01	2.72	76.43	7.90	2.89
10	Decyl	$C_{34}H_{23}O_4N$	77.04	8.18	2.64	76.81	8.08	2.82
11	Dodecyl	$C_{36}H_{27}O_4N$	77.52	8.49	2.51	77.32	8.62	2.57
12	Tetradecyl	$C_{38}H_{31}O_4N$	77.91	8.78	2.39	78.14	8.75	2.76
13	Hexadecyl	$C_{40}H_{35}O_4N$	78.26	9.03	2.28	77.87	8.85	2.78
14	Octadecyl	$C_{42}H_{39}O_4N$	78.58	9.26	2.18	78.25	9.45	2.19

Table 22

$\bar{p}(\bar{p}'-\bar{n}$ -Alkoxybenzoyloxy)benzylidene- $\bar{p}''$ -cyanoanilines

RO.C<sub>6</sub>H<sub>4</sub>.OOO.C<sub>6</sub>H<sub>4</sub>.CH=N.C<sub>6</sub>H<sub>4</sub>.CN

Compound No.	$\bar{n}$ -Alkyl Group (R)	Molecular Formula	Percent C	Percent H	Percent Required N	Percent Found C	Percent Found H	Percent Found N
1	Methyl	C <sub>22</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub>	74.14	4.53	7.86	74.50	4.77	7.73
2	Ethyl	C <sub>23</sub> H <sub>18</sub> O <sub>3</sub> N <sub>2</sub>	74.58	4.90	7.56	74.44	5.09	7.22
3	Propyl	C <sub>24</sub> H <sub>20</sub> O <sub>3</sub> N <sub>2</sub>	75.01	5.21	7.29	74.55	5.56	7.24
4	Butyl	C <sub>25</sub> H <sub>22</sub> O <sub>3</sub> N <sub>2</sub>	75.36	5.57	7.03	75.73	5.75	7.09
5	Pentyl	C <sub>26</sub> H <sub>24</sub> O <sub>3</sub> N <sub>2</sub>	75.70	5.87	6.79	75.70	6.07	6.64
6	Hexyl	C <sub>27</sub> H <sub>26</sub> O <sub>3</sub> N <sub>2</sub>	76.03	6.15	6.57	75.91	5.89	6.55
7	Heptyl	C <sub>28</sub> H <sub>28</sub> O <sub>3</sub> N <sub>2</sub>	76.34	6.41	6.36	76.80	6.42	6.39
8	Octyl	C <sub>29</sub> H <sub>30</sub> O <sub>3</sub> N <sub>2</sub>	76.62	6.65	6.16	77.04	6.52	6.42
9	Nonyl	C <sub>30</sub> H <sub>32</sub> O <sub>3</sub> N <sub>2</sub>	76.89	6.88	5.98	76.61	6.97	5.92
10	Decyl	C <sub>31</sub> H <sub>34</sub> O <sub>3</sub> N <sub>2</sub>	77.15	7.10	5.81	77.60	6.93	5.39
11	Dodecyl	C <sub>33</sub> H <sub>38</sub> O <sub>3</sub> N <sub>2</sub>	77.61	7.50	5.49	78.04	7.48	5.47
12	Tetradecyl	C <sub>35</sub> H <sub>42</sub> O <sub>3</sub> N <sub>2</sub>	78.03	7.86	5.20	77.64	7.54	5.43
13	Hexadecyl	C <sub>37</sub> H <sub>46</sub> O <sub>3</sub> N <sub>2</sub>	78.41	8.18	4.94	78.39	8.17	5.20
14	Octadecyl	C <sub>39</sub> H <sub>50</sub> O <sub>3</sub> N <sub>2</sub>	78.75	8.47	4.71	78.30	8.05	4.88

Table 23

p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-nitroanilines



Compound No.	n-Alkyl Group (R)	Molecular Formula	Percent Required		Percent Found	
			C	H	C	H
1	Methyl	C <sub>24</sub> H <sub>16</sub> O <sub>5</sub> N <sub>2</sub>	67.02	4.25	7.45	4.63
2	Ethyl	C <sub>22</sub> H <sub>18</sub> O <sub>5</sub> N <sub>2</sub>	67.69	4.61	7.18	4.85
3	Propyl	C <sub>23</sub> H <sub>20</sub> O <sub>5</sub> N <sub>2</sub>	68.31	4.95	6.93	5.23
4	Butyl	C <sub>24</sub> H <sub>22</sub> O <sub>5</sub> N <sub>2</sub>	68.89	5.30	6.70	5.31
5	Pentyl	C <sub>25</sub> H <sub>24</sub> O <sub>5</sub> N <sub>2</sub>	69.43	5.59	6.48	5.50
6	Hexyl	C <sub>26</sub> H <sub>26</sub> O <sub>5</sub> N <sub>2</sub>	69.94	5.87	6.27	5.74
7	Heptyl	C <sub>27</sub> H <sub>28</sub> O <sub>5</sub> N <sub>2</sub>	70.72	6.13	6.08	6.15
8	Octyl	C <sub>28</sub> H <sub>30</sub> O <sub>5</sub> N <sub>2</sub>	70.86	6.37	5.90	6.41
9	Nonyl	C <sub>29</sub> H <sub>32</sub> O <sub>5</sub> N <sub>2</sub>	71.29	6.60	5.73	6.66
10	Decyl	C <sub>30</sub> H <sub>34</sub> O <sub>5</sub> N <sub>2</sub>	71.69	6.82	5.57	6.49
11	Dodecyl	C <sub>32</sub> H <sub>38</sub> O <sub>5</sub> N <sub>2</sub>	72.43	7.22	5.28	7.23
12	Tetradecyl	C <sub>34</sub> H <sub>42</sub> O <sub>5</sub> N <sub>2</sub>	73.09	7.58	5.01	7.22
13	Hexadecyl	C <sub>36</sub> H <sub>46</sub> O <sub>5</sub> N <sub>2</sub>	73.69	7.90	4.77	7.55
14	Octadecyl	C <sub>38</sub> H <sub>50</sub> O <sub>5</sub> N <sub>2</sub>	74.23	8.20	4.56	8.40
						4.41