# E X P E R I M E N T A L

# EXPERIMENTAL

## 1. Preparation of Compounds :

### 1.1. n-Alkyl halides :

Higher alkyl halides from amyl to octadecyl were of B.D.H. or Riedel quality. Lower alkyl halides, ethyl, n-propyl and n-butyl were prepared by the following method (276).

8.27 g. purified red phosphorous and 55.0 g. (70 ml.) absolute ~~alcohol~~ ethanol are taken in a 250 ml. round bottom flask fitted with a reflux condenser and 127.0 g. of well powdered iodine is added to the contents of the flask in small portions of about two to three g. at a time, at an interval of two to three minutes between consecutive additions. The iodine is added by removing the condenser and replacing it immediately after adding iodine. A little heat is evolved during the addition of iodine. After adding all the iodine, the contents are refluxed on sand-bath for about ninety minutes. The contents are then distilled and the fraction in the range of 72°- 75°C is collected. The distillate is washed with equal volumes of ten percent aqueous sodium carbonate solution followed by water to remove traces of sodium carbonate. The ethyl iodide so obtained is dried over calcium chloride granules. It is then filtered and redistilled. The distillate in the temperature range of 72° - 75°C is collected. The yield is 60 %. B.P. 72°C (lit. 72°C).

n-Propyl and n-butyl iodides are prepared by the above method. The boiling point of n-propyl iodide is 102°C (lit. 102°C) and that of n-butyl iodide is 130°C (lit. 130°C).

1.2. p-n-Alkoxybenzoic acids :

Anisic acid was of B.D.H. quality. Lower members of the series, ethoxy, n-propoxy and n-butoxy derivatives are prepared by the method of Jones (98).

One mole of p-hydroxybenzoic acid is dissolved in concentrated aqueous solution of potassium hydroxide (2 mole). To this 1.1 mole of alkyl iodide or bromide is added and the mixture is refluxed for two to three hours for the completion of the reaction. The mass is then transferred to a beaker and acidified with concentrated hydrochloric acid. Solid is filtered, dried and crystallized from acetic acid.

In the case of higher homologues, n-amyloxy to n-octadecyloxy derivatives, the above method gives less yield and requires more heating period. So, the following modified method which gives better yield in one to three hours reflux period is adopted. The aqueous potassium hydroxide is replaced by a solution of potassium hydroxide (2 mole) in 250 ml. methanol. The potassium salt of the alkoxy acid is obtained which is filtered, dissolved in water and treated with hydrochloric acid. The alkoxy acid separates out, which is filtered and crystallized from glacial acetic acid till it gives constant transition temperatures. The yield is 60 to 70 %. The melting points and transition temperatures compare well with those given in the literature (101) and are listed in table 4.

1.3. p-n-Alkoxybenzaldehydes :

Hildesheimer (277), Steermer and Wodarg (278), Weygand

Table 4

p-n-Alkoxybenzoic acids.

| | Transition temperatures (°C) (Found) | | | (Reported) (101) | | |
|---|---|---|---|---|---|---|
| n-Alkyl group | Smectic | Nematic | Isotropic | Smectic | Nematic | Isotropic |
| Methyl | - | - | 184.0 | - | - | 184.0 |
| Ethyl | - | - | 196.0 | - | - | 196.0 |
| Propyl | - | 145.0 | 154.0 | - | 145.0 | 154.0 |
| Butyl | - | 147.0 | 160.0 | - | 147.0 | 160.0 |
| Pentyl | - | 124.0 | 150.5 | - | 124.0 | 151.0 |
| Hexyl | - | 105.0 | 153.0 | - | 105.0 | 153.0 |
| Heptyl | 94.0 | 99.5 | 147.5 | 92.0 | 98.0 | 146.0 |
| Octyl | 101.0 | 108.0 | 148.0 | 101.0 | 108.0 | 147.0 |
| Nonyl | 94.5 | 117.5 | 143.5 | 94.0 | 117.0 | 143.0 |
| Decyl | 95.0 | 122.0 | 140.0 | 97.0 | 122.0 | 142.0 |
| Dodecyl | 95.0 | 130.5 | 138.5 | 95.0 | 129.0 | 137.0 |
| *Tetradecyl | 93.0 | 134.5 | 136.0 | - | - | - |
| Hexadecyl | 86.0 | - | 133.0 | 85.0 | - | 132.5 |
| Octadecyl | 103.0 | - | 131.5 | 102.0 | - | 131.0 |

* Analytical data of p-n-tetradecyloxybenzoic acid is given below :

C, required 75.46 %, found 75.80 %; H, required 10.48 %, found 10.26 %.

and Gabler (279,280) and Gray and Jones (281) have described the preparation of p-n-alkoxybenzaldehydes. Here, the following method (282) is used.

0.1 mole of p-hydroxybenzaldehyde, 0.15 mole of anhydrous potassium carbonate and 0.15 mole of n-alkyl iodide or bromide are added to dry acetone (60 ml.). The mixture is refluxed using water-bath for three to four hours. In the case of higher homologues the reflux period is extended upto six to eight hours. The whole mass is then added to water and the aldehydes thus separated are extracted with ether. Ether extract is washed with dilute sodium hydroxide solution to remove unreacted p-hydroxybenzaldehyde, followed by water and dried. Ether is evaporated and the p-n-alkoxybenzaldehydes thus obtained are purified by distilling under reduced pressure. Boiling points almost agree with the reported one.

Analytical data of p-n-tetradecyloxybenzaldehyde is given below :

B.P. 253 - 257°C/10 mm. (decomp.)

C, found 79.11 %, required, 79.24 %; H, found 10.88 %, required, 10.69 %.

p-methoxybenzaldehyde (anisaldehyde) used was of B.D.H. quality.

1.4. Trans-p-n-alkoxycinnamic acids :

Trans-p-n-alkoxycinnamic acids are prepared by the method of Gray and Jones (281).

The p-n-alkoxybenzaldehyde (0.02 mole), malonic acid (3.2 g., 0.04 mole), pyridine (8 ml.) and piperidine (three drops) are heated at 100°C for three hours on a

steam-bath. The mixture is poured in ice (25 g.) and concentrated hydrochloric acid (25 ml.). The precipitates are filtered and washed with dilute hydrochloric acid followed by water. Compounds are crystallized from 98 % acetic acid. Yield of the colourless products is 85-90 %. Higher homologues are crystallized twice from benzene and then from acetic acid till constant transition temperatures are obtained. The melting points and transition temperatures compare well with the literature and are listed in table 5.

1.5. 4-n-Alkoxy-1-naphthoic acids :

Gray and Jones (101) prepared 4-n-alkoxy-1-naphthoic acids by two different routes. Both the methods involve more than one step after the alkylation of the compound. To get the alkoxy acid in good yield, it is desirable to have minimum number of steps after alkylation of the compound. Here, a different route involving one step after alkylation is used; the 4-n-alkoxy-1-naphthoic acids are prepared by the following method.

(i) 4-Hydroxy-1-acetylnaphthalene :

This is prepared by the modified method of Akram and Desai (283). α-Naphthol (40 g.), anhydrous $ZnCl_2$ (40 g.) and 20 ml. dry nitrobenzene are taken into a flat bottom flask. To this, 24 g. acetyl chloride is slowly added while stirring. The mixture is stirred for three hours and allowed to stand for forty eight hours. Nitrobenzene is then steam distilled. A mixture of isomers, 4-hydroxy-1-acetyl-naphthalene and 1-hydroxy-2-acetylnaphthalene is obtained

Table 5

Trans-p-n-alkoxycinnamic acids..

Transition temperatures (°C)

| | (Found) | | | (Reported) (281) | | |
|---|---|---|---|---|---|---|
| n-Alkyl group | Smectic | Nematic | Isotropic | Smectic | Nematic | Isotropic |
| Methyl | - | 174.0 | 190.5 | - | 173.5 | 190.0 |
| Ethyl | - | 194.0 | 200.0 | - | 194.0 | 198.5 |
| Propyl | - | 169.5 | 184.5 | - | 167.0 | 184.5 |
| Butyl | - | 156.0 | 189.5 | - | 156.0 | 189.5 |
| Pentyl | - | 144.0 | 180.5 | - | 139.5 | 179.5 |
| Hexyl | - | 152.0 | 180.5 | - | 153.0 | 181.5 |
| Heptyl | - | 148.0 | 175.0 | - | 148.0 | 175.0 |
| Octyl | - | 145.0 | 172.0 | - | 146.0 | 174.5 |
| Nonyl | 139.0 | 143.0 | 170.0 | 138.5 | 144.0 | 171.0 |
| Decyl | 136.0 | 150.5 | 169.0 | 136.0 | 150.5 | 169.0 |
| Dodecyl | 132.0 | 157.0 | 164.5 | 132.0 | 157.0 | 165.0 |
| *Tetradecyl | 127.0 | - | 160.0 | - | - | - |
| Hexadecyl | 118.0 | - | 159.0 | 118.0 | - | 159.0 |
| Octadecyl | 120.5 | - | 157.5 | 120.5 | - | 157.5 |

* Analytical data of trans-p-n-tetradecyloxycinnamic acid is given below :

C, found 77.09 %, required, 76.67 %; H, found 10.00 %, required, 10.00 %.

from which 1-hydroxy-2-acetylnaphthalene is removed by the treatment with benzene; the 4-hydroxy-1-acetylnaphthalene is practically insoluble in benzene. The 4-hydroxy-1-acetylnaphthalene is then crystallized from alcohol. M.P. 199-200°C (lit. 199-200°C). Yield 40-60 %.

(ii) 4-n-Alkoxy-1-acetylnaphthalenes :

4-n-Alkoxy-1-acetylnaphthalenes are prepared by the same method as for p-n-alkoxybenzaldehydes (282). 4-hydroxy-1-acetylnaphthalene (0.1 mole), anhydrous potassium carbonate (0.15 mole) and alkyl iodide or bromide (0.15 mole) are added to dry acetone (60 ml.). The mixture is refluxed on water-bath for three to four hours. In the case of higher homologues the reflux period is increased upto six to eight hours. The whole mass is then added to water. Acetone is evaporated. Solid separates out which is filtered, washed with water, dried and crystallized from alcohol. Melting points and analytical data are reported in table 6. Yield 60-70 %.

(iii) 4-n-Alkoxy-1-naphthoic acids :

To a stirred solution of 5 g. 4-n-alkoxy-1-acetylnaphthalene in 50 ml. dioxane is slowly added within fifteen minutes a solution of sodium hypobromite obtained by adding 5 ml. liquid bromine with constant stirring at 0-5°C to 70 ml. ice cold water containing 14 g. sodium hydroxide. During the addition of sodium hypobromite the temperature is allowed to rise to 35-45°C. Stirring is continued for two hours maintaining the temperature to

Table 6

4-n-Alkoxy-1-acetylnaphthalenes.

| n-Alkyl group | M.P.(°C) | Crystallized from | Shape and colour | Molecular formula | % Found C | % Found H | % Required C | % Required H |
|---|---|---|---|---|---|---|---|---|
| 1. Methyl | 73.0* | Alcohol | Yellow needles | - | - | - | - | - |
| 2. Ethyl | 81.0** | Alcohol | Yellow needles | - | - | - | - | - |
| 3. Propyl | 68.0 | Alcohol | Yellow needles | $C_{15}H_{16}O_2$ | 78.92 | 7.32 | 78.95 | 7.00 |
| 4. Butyl | 52.0 | Alcohol | Yellow needles | $C_{16}H_{18}O_2$ | 79.39 | 7.40 | 79.34 | 7.44 |
| 5. Pentyl | 61.0 | Alcohol | Yellow plates | $C_{17}H_{20}O_2$ | 79.89 | 7.42 | 79.69 | 7.81 |
| 6. Hexyl | 79.0 | Alcohol | Yellow needles | $C_{18}H_{22}O_2$ | 79.93 | 8.00 | 80.00 | 8.15 |
| 7. Heptyl | 60.5 | Alcohol | Yellow needles | $C_{19}H_{24}O_2$ | 80.61 | 8.60 | 80.28 | 8.45 |
| 8. Octyl | 73.0 | Alcohol | Yellow needles | $C_{20}H_{26}O_2$ | 80.21 | 8.60 | 80.54 | 8.73 |
| 9. Nonyl | 57.0 | Alcohol | Yellow needles | $C_{21}H_{28}O_2$ | 80.69 | 8.93 | 80.76 | 8.97 |
| 10. Decyl | 63.0 | Alcohol | Yellow needles | $C_{22}H_{30}O_2$ | 80.93 | 8.96 | 80.98 | 9.20 |
| 11. Dodecyl | 66.0 | Alcohol | Yellow needles | $C_{24}H_{34}O_2$ | 81.08 | 9.51 | 81.36 | 9.61 |
| 12. Tetradecyl | 69.0 | Alcohol | Yellow needles | $C_{26}H_{38}O_2$ | 81.53 | 9.97 | 81.68 | 9.95 |
| 13. Hexadecyl | 73.0 | Alcohol | Yellow needles | $C_{28}H_{42}O_2$ | 82.37 | 10.31 | 81.94 | 10.24 |
| 14. Octadecyl | 73.5 | Alcohol | Yellow needles | $C_{30}H_{46}O_2$ | 81.77 | 10.35 | 82.19 | 10.51 |

* Reported (284) 72-3°C.

** Reported (285) 77.0°C.

Alcohol = ethanol

60-70°C. The solution is then treated with sodium bisulphite to remove excess of hypobromite. 300 ml. water is added to the solution and boiled till about 200 ml. of the liquid is boiled off to remove bromoform formed and some of the dioxane. Acidification of the hot solution on cooling gives 4-n-alkoxy-1-naphthoic acid. It is filtered, dried and crystallized from acetic acid. Yield 80-90 %. The melting points of all the acids agree well with the literature and are recorded in table 7.

1.6. Trans-p-n-alkoxy-α-methylcinnamic acids :

The acids are prepared by the Perkin's method (286). A mixture of 0.2 mole of freshly distilled p-n-alkoxy-benzaldehyde, 0.25 mole of propionic anhydride and 0.2 mole of fused sodium propionate is heated with occasional shaking for thirty hours in an oil-bath at 130-135°C. The warm mixture is poured into about 500 ml. of water, stirred thoroughly and neutralized by the addition of solid sodium carbonate. The unreacted alkoxybenzaldehyde is removed by ether extraction and the solution is warmed with 3-4 g. animal charcoal and filtered hot. The warm filtrate is poured slowly with stirring into an excess of concentrated hydrochloric acid mixed with chopped ice. Crude product is crystallized from dilute ethanol ~~alcohol~~. In the case of higher homologues the sodium salts are less or sparingly soluble in water. For these compounds, the solid separated after the treatment with sodium carbonate is filtered and washed with ether to remove unreacted p-n-alkoxybenzaldehydes.

Table 7

4-n-Alkoxy-1-naphthoic acids.

| n-Alkyl group | Melting points (°C) (Found) | (Reported) (101) |
|---|---|---|
| Methyl | 248.0 | 248.0 |
| Ethyl | 220.5 | 220.0 |
| Propyl | 202.5 | 203.0 |
| Butyl | 212.5 | 213.5 |
| Pentyl | 206.0 | 207.0 |
| Hexyl | 210.0 | 212.0 |
| Heptyl | 188.0 | 189.0 |
| Octyl | 183.0 | 183.5 |
| Nonyl | 160.0 | 161.0 |
| Decyl | 174.5 | 174.5 |
| Dodecyl | 148.5 | 147.5 |
| *Tetradecyl | 143.5 | - |
| Hexadecyl | 138.5 | 136.0 |
| Octadecyl | 136.0 | 137.5 |

* Analytical data of 4-n-tetradecyloxy-1-naphthoic acid is given below :

C, found 78.27 %, required, 78.08 %; H, found 9.33 %, required, 9.44 %.

Sodium salt of trans-p-n-alkoxy-α-methylcinnamic acid is then acidified with hydrochloric acid. The solid obtained is filtered and dried. Acids are crystallized from acetic acid or alcohol. The transition temperatures and analytical data are given in table 8 and 9.

Yield for the lower members is 80-90 %. In the case of higher members, the reactivity decreases with the increase in the chain length; the yield is poor. For the last few members the yield is 10-20 %. Some members which could not be crystallized satisfactorily were purified by column chromatography.

1.7. Preparation of Cholesteryl Esters :

(a) Preparation of acid chlorides :

1 to 2 g. of the acids are treated with 4.0 ml. of thionyl chloride on a water-bath. heating is continued till the evolution of the hydrochloric acid gas ceases. The excess of thionyl chloride is distilled off.

(b) Esterification :

Equimolecular proportions (0.01 mole) of cholesterol and appropriate acid chloride are taken in a round bottom flask and N,N'-dimethylaniline (20 ml.) is added as a solvent. The whole mixture is heated at 120°C in an oil-bath for two hours. In the preparation of cholesteryl 4-n-alkoxy-1-naphthoates the mixture is heated at 175-200°C for ten minutes. After heating, the whole mass is added to cold water when the oily mass separates out as solid. The blue mass is filtered and washed with acetone to remove

Table 8

Trans-p-n-alkoxy-∝-methylcinnamic acids.

| | Transition temperatures (°C) | |
|---|---|---|
| n-Alkyl group | Nematic | Isotropic |
| - | - | 81.0* |
| Methyl | - | 156.5** |
| Ethyl | (155.5)+ | 167.0*** |
| Propyl | 130.0 | 139.5 |
| Butyl | 104.0 | 144.5 |
| Pentyl | 97.0 | 131.0 |
| Hexyl | 102.5 | 128.0 |
| Heptyl | 91.0 | 124.5 |
| Octyl | 84.0 | 124.0 |
| Nonyl | 82.5 | 116.2 |
| Decyl | 78.0 | 115.0 |
| Dodecyl | 87.0 | 111.5 |
| Tetradecyl | 91.0 | 106.0 |
| Hexadecyl | 93.0 | 100.5 |
| Octadecyl | ( 91.5) | 93.0 |

* Reported (286) 81.0°C.

** Reported (20 ) as non-mesomorphic.

*** Reported (20 ) as monotropic nematic, M.P. 168.0°C.

+ Values in the parenthesis indicate monotropy.

N,N'-dimethylaniline. The white solid is crystallized from chloroform + acetone mixture (1:2) or chloroform + alcohol mixture (1:2) till constant transition temperatures are obtained. Average yields of the esters are 50-60 %.

Last members of the series cholesteryl trans-p-n-alkoxy-∝-methylcinnamate, which did not crystallize satisfactorily, were purified by column chromatography.

The analytical data for the five series are summarized in tables 10 to 14 and their transition temperatures are summarized in tables 17 to 21.

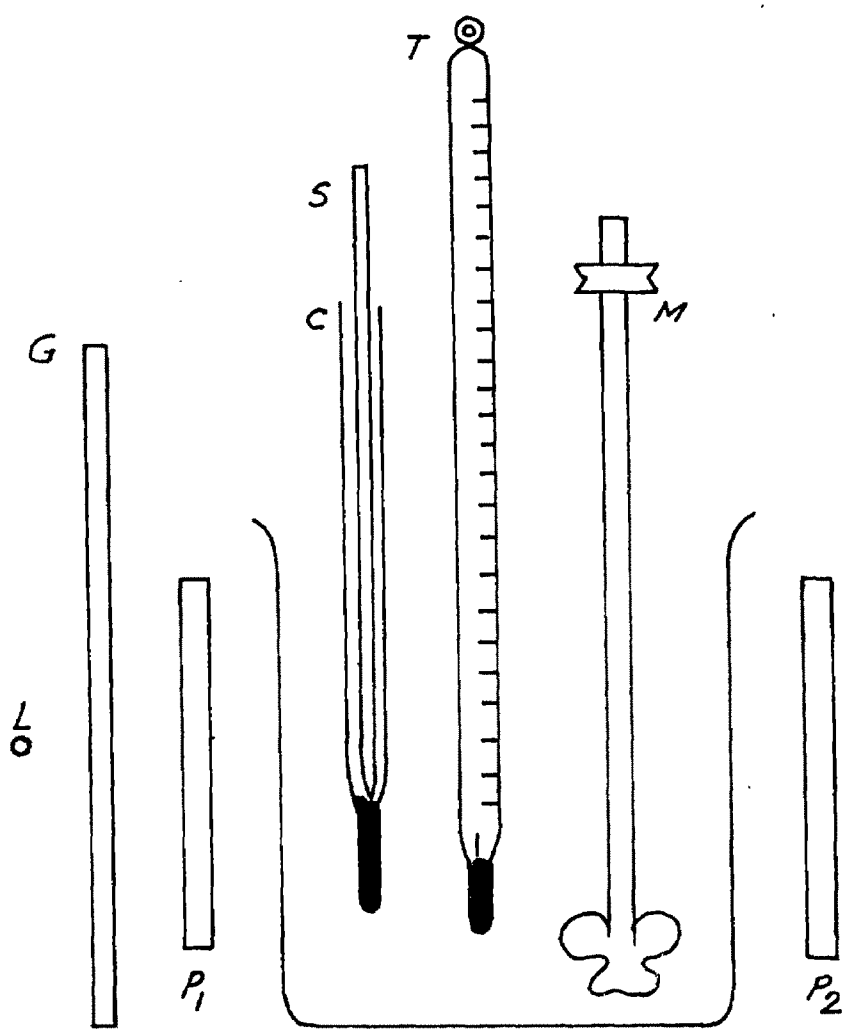
1.8. Preparation of biphenyl-4-p-n-alkoxybenzoates :

Equimolecular amounts of p-n-alkoxybenzoyl chlorides and 4-hydroxybiphenyl (p-phenylphenol) are taken in 10 ml. pyridine, heated to just boiling and allowed to stand for two hours. Solid separates which is filtered and washed with alcohol to remove pyridine. The solid ester is then treated with dilute sodium hydroxide solution to remove unreacted 4-hydroxybiphenyl and filtered, washed with water and dried. It is crystallized first from chloroform + alcohol mixture (1:1) and then from acetic acid till constant transition temperatures are obtained. The analytical data and transition temperatures are given in tables 15 and 22 respectively.

1.9. Preparation of biphenyl-4-trans-p-n-alkoxycinnamates:

These are prepared by the same method used for the preparation of biphenyl-4-p-n-alkoxybenzoates. The analytical

FIG. 5




L - LAMP
C - CAPILLARY TUBE
S - STIRRER
G. - GROUND GLASS SCREEN

T - THERMOMETER
M - MECHANICAL STIRRER
$P_1$, $P_2$ } POLAROID SQUARES

data and transition temperatures are summarized in tables 16 and 23 respectively.

2. Study of Transition Temperatures :

Preliminary measurements (i.e., solid-mesomorphic-isotropic transitions) of pure compounds are made by the optical method which is described below :

2.1. Optical method :

The apparatus used in this method is diagrammatically shown in the figure 5. The capillary tube is prepared by drawing out an ordinary glass tubing to form a capillary of about 2 mm. diameter. It is provided with a thin glass stirrer S, made by drawing out a glass rod so that it works easily within the capillary and the compound can be easily stirred throughout. The small amount of powdered substance is introduced into the capillary and pressed down with the stirrer S so that the material occupied 1.0-1.5 cm. at the bottom of the capillary tube. The capillary tube C, filled with the substance is immersed in an oil-bath and observed between crossed square polaroid sheets $P_1$ and $P_2$.

The bath consists of one litre beaker containing dibutylphthalate. This is continuously stirred uniformly by means of an electrically-run mechanical stirrer M. To minimize the loss of heat through radiation, the beaker is lagged by wrapping asbestos paper round it. The asbestos covering is provided with two windows 1½" square opposite one another. A calibrated standard

thermometer T, graduated in 1/10th of a degree is suspended in the bath and measures the temperature. The capillary is placed in such a way that it can be seen clearly through the windows in the asbestos lagging. A source of light L, provided by an electric lamp, passing through a ground glass screen G illuminates the substance in the capillary. The two polaroid sheets are placed on either side of the beaker facing the windows in the asbestos lagging so that $P_1$ stands in between the glass screen and the beaker and $P_2$ stands in front of the beaker. The polaroid sheets are placed crossed to each other so that the light only passes through them when the medium between them is anisotropic but is cut off when the medium becomes isotropic. The bath temperature is raised at the rate of 1°C per two minutes by using a micro-burner.

The melting points, solid-mesomorphic points and mesomorphic-isotropic points of pure compounds are determined preliminarily by this method.

2.2. Determination of Transition temperatures with the help of Microscope :

It is rather difficult to detect polymesomorphic i.e., smectic-smectic and smectic-nematic or smectic-cholesteric transitions and different textures of cholesteric mesophase accurately by the usual optical method. Hence, the use of microscope becomes essential for the detection of such changes with great accuracy. The microscope used in this investigation for the

mesomorphic and polymesomorphic transition temperatures was a Leitz Ortholux II 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 insert 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 0.5°C. The specimen is illuminated by polarized light, the light source being an electric lamp. By means of the special eye piece in the monocular tube, the specimen and the temperature can be seen side by side simultaneously.

The slides are prepared by three different methods. In the first case the substance is heated on the slide upto its isotropic temperature; a coverslip is placed over it and cooled. In the second method the substance is dissolved in a suitable solvent. A few drops of the solution of the compound are placed on the slide and the solvent allowed to evaporate. A coverslip is then placed over it. In the third case the slides are prepared by heating the substance on the slide upto its mesomorphic temperature and putting the coverslip over it and cooling.

The accuracy of the heating device is checked by taking melting points and/or transition points of the known compounds such as benzoic acid, $\alpha$-naphthol,

succinic acid, anthracene, p-azoxyanisole, p-methoxy-cinnamic acid, p-acetoxybenzylidene-p-phenitidine, ethyl p-azoxybenzoate etc.

To determine the various transitions, the prepared slide with a thin section of the material, is inserted in the specimen chamber and the temperature is raised fairly fast (5°C/minute) to find the approximate transition temperatures. The heating stage is then allowed to cool until the stable solid reappears. The measurements are then repeated with a rate of heating of 1°C per minute from 5°C below the transition points to be observed. The transitions and the various phases are clearly observed and recorded by the appearance of the focal-conic, plane, homeotropic and the threaded structures of the cholesteric, smectic and nematic phases in the polarized light. The transition to the isotropic liquid is clearly marked when the field of vision becomes extinct in polarized light.

In the compounds exhibiting cholesteric and smectic mesomorphism, the focal-conic pattern is frequently maintained in the solid when the thin section on the glass slide is prepared by cooling the slide slowly. This pseudomesomorphic condition often created a difficulty to find solid-cholesteric and solid-smectic transition; however, the disappearance of cleavage lines in the solid is taken as the solid-cholesteric or solid-smectic transition. To confirm the change the slide was disturbed with the help of a spatula; in the case of cholesteric phase highly birefringent plane texture is generally observed

exhibiting vivid colours and in the case of smectic phase the disturbed texture can be seen indicating that it is not solid and the transition has taken place. In the enantiotropic mesomorphism, all the transitions are clearly detected while cooling the isotropic liquid, the reverse transitions taking place at the same temperature or within ± 0.2°C to 1.5°C. Isotropic-cholesteric changes are observed by the separation of small bâtonnets which coalesce to form focal-conic cholesteric texture or to the plane texture. In some cases isotropic-cholesteric changes are observed by plane texture. Plane texture is highly birefringent and exhibits vivid colours. Isotropic-nematic changes are observed by the separation of small ~~bubbles~~ droplets from the isotropic liquid. These ~~bubbles~~ droplets then coalesce and a threaded region which is a characteristic of the nematic phase is formed. The isotropic-smectic transition is indicated by the separation of bâtonnets which coalesce to form fine mosaic of focal-conic pattern. Smectic-cholesteric, cholesteric-isotropic, smectic-nematic and smectic-smectic changes are also clearly detected with great accuracy under the microscope. At the juncture of cholesteric-smectic transition generally on cooling, the plane texture gives different colours for the short temperature interval. The monotropic transition points are determined by carefully observing the isotropic liquid as it cools slowly until the bâtonnets of the cholesteric or smectic phase or ~~bubbles~~ droplets of the nematic phase appear. 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.

In the first type of the slides, on heating, the solid changes to a focal-conic cholesteric texture which in some cases transforms to homeotropic cholesteric texture; this sometimes makes the transition to isotropic form rather difficult to judge because both the homeotropic and isotropic forms are non-birefringent. In the other two types of the slides, on heating, generally the focal-conic texture gives the plane texture. The change from plane cholesteric texture to isotropic transition can be clearly observed due to the high birefringence and colourful plane texture of the cholesteric phase.

Table 9

Trans-p-n-alkoxy-α-methylcinnamic acids.

| | n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % Found C | % Found H | % Required C | % Required H |
|---|---|---|---|---|---|---|---|---|
| 1. | Propyl | Aqueous alcohol | White plates | $C_{13}H_{16}O_3$ | 71.03 | 6.96 | 70.89 | 7.32 |
| 2. | Butyl | Aq.alcohol | White plates | $C_{14}H_{18}O_3$ | 71.55 | 7.52 | 71.77 | 7.74 |
| 3. | Pentyl | Aq.alcohol | White needles | $C_{15}H_{20}O_3$ | 72.56 | 7.64 | 72.56 | 8.12 |
| 4. | Hexyl | Aq.alcohol | White needles | $C_{16}H_{22}O_3$ | 73.24 | 8.18 | 73.25 | 8.45 |
| 5. | Heptyl | Aq.alcohol | White plates | $C_{17}H_{24}O_3$ | 73.38 | 8.31 | 73.88 | 8.75 |
| 6. | Octyl | Aq.alcohol | White plates | $C_{18}H_{26}O_3$ | 74.27 | 8.87 | 74.44 | 9.03 |
| 7. | Nonyl | Aq.alcohol | White plates | $C_{19}H_{28}O_3$ | 75.21 | 9.51 | 74.96 | 9.27 |
| 8. | Decyl | Alcohol | White plates | $C_{20}H_{30}O_3$ | 75.32 | 9.23 | 75.43 | 9.50 |
| 9. | Dodecyl | Alcohol | White plates | $C_{22}H_{34}O_3$ | 75.73 | 9.44 | 76.26 | 9.89 |
| 10. | Tetradecyl | Alcohol | White plates | $C_{24}H_{38}O_3$ | 76.88 | 9.81 | 76.96 | 10.23 |
| 11. | Hexadecyl | Alcohol | White plates | $C_{26}H_{42}O_3$ | 77.56 | 10.02 | 77.56 | 10.52 |
| 12. | Octadecyl | Alcohol | White plates | $C_{28}H_{46}O_3$ | 78.09 | 10.64 | 78.09 | 10.77 |

Alcohol = ethanol

Table 10

Cholesteryl p-n-alkoxybenzoates.

| n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % Found C | % Found H | % Required C | % Required H |
|---|---|---|---|---|---|---|---|
| 1. Methyl | Chloroform + acetone (1:1) | White plates | $C_{35}H_{52}O_3$ | 80.48 | 10.30 | 80.77 | 10.00 |
| 2. Ethyl | -do- | White plates | $C_{36}H_{54}O_3$ | 80.87 | 9.96 | 80.90 | 10.11 |
| 3. Propyl | -do- | White plates | $C_{37}H_{56}O_3$ | 81.25 | 10.27 | 81.02 | 10.22 |
| 4. Butyl | -do- | White needles | $C_{38}H_{58}O_3$ | 81.23 | 10.55 | 81.14 | 10.32 |
| 5. Pentyl | -do- | White plates | $C_{39}H_{60}O_3$ | 80.79 | 10.21 | 81.25 | 10.42 |
| 6. Hexyl | -do- | White needles | $C_{40}H_{62}O_3$ | 81.27 | 10.75 | 81.36 | 10.51 |
| 7. Heptyl | -do- | White plates | $C_{41}H_{64}O_3$ | 81.28 | 10.48 | 81.46 | 10.60 |
| 8. Octyl | -do- | White needles | $C_{42}H_{66}O_3$ | 81.51 | 10.76 | 81.55 | 10.68 |
| 9. Nonyl | -do- | White plates | $C_{43}H_{68}O_3$ | 81.60 | 10.83 | 81.65 | 10.76 |
| 10. Decyl | -do- | White plates | $C_{44}H_{70}O_3$ | 81.39 | 10.96 | 81.77 | 10.87 |
| 11. Dodecyl | -do- | White plates | $C_{46}H_{74}O_3$ | 81.94 | 10.93 | 81.90 | 10.98 |
| 12. Tetradecyl | -do- | White plates | $C_{48}H_{78}O_3$ | 82.54 | 10.89 | 82.06 | 11.11 |
| 13. Hexadecyl | -do- | White plates | $C_{50}H_{82}O_3$ | 82.39 | 11.45 | 82.19 | 11.23 |
| 14. Octadecyl | -do- | White plates | $C_{52}H_{86}O_3$ | 81.91 | 11.14 | 82.32 | 11.35 |

Table 11

Cholesteryl trans-p-n-alkoxycinnamates.

| | n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % Found C | % Found H | % Required C | % Required H |
|---|---|---|---|---|---|---|---|---|
| 1. | - | Chloroform + acetone (1:1) | White needles | $C_{36}H_{52}O_2$ | 83.60 | 9.92 | 83.75 | 10.08 |
| 2. | Methyl | -do- | White needles | $C_{37}H_{54}O_3$ | 81.12 | 9.88 | 81.32 | 9.87 |
| 3. | Ethyl | -do- | White needles | $C_{38}H_{56}O_3$ | 81.64 | 9.98 | 81.43 | 10.00 |
| 4. | Propyl | -do- | White needles | $C_{39}H_{58}O_3$ | 81.55 | 9.83 | 81.52 | 10.10 |
| 5. | Butyl | -do- | White needles | $C_{40}H_{60}O_3$ | 81.83 | 10.16 | 81.62 | 10.21 |
| 6. | Pentyl | -do- | White needles | $C_{41}H_{62}O_3$ | 81.66 | 10.48 | 81.74 | 10.30 |
| 7. | Hexyl | -do- | White needles | $C_{42}H_{64}O_3$ | 81.85 | 9.92 | 81.81 | 10.39 |
| 8. | Heptyl | -do- | White needles | $C_{43}H_{66}O_3$ | 82.02 | 10.51 | 81.91 | 10.47 |
| 9. | Octyl | -do- | White needles | $C_{44}H_{68}O_3$ | 82.10 | 10.65 | 81.98 | 10.45 |
| 10. | Nonyl | -do- | White needles | $C_{45}H_{70}O_3$ | 82.08 | 10.51 | 82.08 | 10.64 |
| 11. | Decyl | -do- | White needles | $C_{46}H_{72}O_3$ | 81.78 | 10.35 | 82.13 | 10.71 |
| 12. | Dodécyl | -do- | White needles | $C_{48}H_{76}O_3$ | 82.02 | 10.43 | 82.28 | 10.86 |
| 13. | Tetradecyl | -do- | White needles | $C_{50}H_{80}O_3$ | 82.88 | 10.79 | 82.43 | 10.96 |
| 14. | Hexadecyl | -do- | White needles | $C_{52}H_{84}O_3$ | 82.31 | 11.18 | 82.54 | 11.11 |
| 15. | Octadecyl | -do- | White needles | $C_{54}H_{88}O_3$ | 82.41 | 11.22 | 82.66 | 11.23 |

Table 12

Cholesteryl trans-p-n-alkoxy-∝-methylcinnamates.

| n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % Found C | % Found H | % Required C | % Required H |
|---|---|---|---|---|---|---|---|
| 1. - | Chloroform + alcohol(1:1) | White needles | $C_{37}H_{54}O_2$ | 83.87 | 10.23 | 83.77 | 10.19 |
| 2. Methyl | -do- | White needles | $C_{38}H_{56}O_3$ | 81.16 | 9.91 | 81.42 | 10.07 |
| 3. Ethyl | -do- | White needles | $C_{39}H_{58}O_3$ | 81.06 | 9.81 | 81.52 | 10.17 |
| 4. Propyl | -do- | White needles | $C_{40}H_{60}O_3$ | 81.75 | 10.02 | 81.62 | 10.27 |
| 5. Butyl | -do- | White needles | $C_{41}H_{62}O_3$ | 81.57 | 10.15 | 81.72 | 10.37 |
| 6. Pentyl | -do- | White needles | $C_{42}H_{64}O_3$ | 81.39 | 10.37 | 81.76 | 10.46 |
| 7. Hexyl | -do- | White needles | $C_{43}H_{66}O_3$ | 81.96 | 10.87 | 81.85 | 10.54 |
| 8. Heptyl | -do- | White needles | $C_{44}H_{68}O_3$ | 81.94 | 10.31 | 81.93 | 10.63 |
| 9. Octyl | -do- | White needles | $C_{45}H_{70}O_3$ | 82.15 | 10.60 | 82.01 | 10.71 |
| 10. Nonyl | -do- | White needles | $C_{46}H_{72}O_3$ | 82.49 | 10.41 | 82.08 | 10.78 |
| 11. Decyl | -do- | White needles | $C_{47}H_{74}O_3$ | 82.08 | 10.43 | 82.16 | 10.86 |
| 12. Dodecyl | -do- | White needles | $C_{49}H_{78}O_3$ | 82.21 | 10.87 | 82.30 | 10.99 |
| 13. Tetradecyl | -do- | White needles | $C_{51}H_{82}O_3$ | 82.33 | 10.70 | 82.42 | 11.12 |
| 14. Hexadecyl | -do- | White needles | $C_{53}H_{86}O_3$ | 82.44 | 11.55 | 82.60 | 11.17 |
| 15. Octadecyl | -do- | White needles | $C_{55}H_{90}O_3$ | 82.60 | 11.00 | 82.69 | 11.28 |

Alcohol = Ethanol

Table 13

Cholesteryl 4-n-alkoxy-1-naphthoates.

| n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % Found C | % Found H | % Required C | % Required H |
|---|---|---|---|---|---|---|---|
| 1. Methyl | Chloroform + acetone(2:1) | White needles | $C_{39}H_{54}O_3$ | 82.04 | 9.25 | 82.06 | 9.54 |
| 2. Ethyl | -do- | White needles | $C_{40}H_{56}O_3$ | 82.21 | 9.80 | 82.14 | 9.65 |
| 3. Propyl | -do- | White needles | $C_{41}H_{58}O_3$ | 81.94 | 9.69 | 82.22 | 9.76 |
| 4. Butyl | -do- | White needles | $C_{42}H_{60}O_3$ | 82.33 | 9.64 | 82.30 | 9.87 |
| 5. Pentyl | -do- | White needles | $C_{43}H_{62}O_3$ | 82.06 | 9.95 | 82.37 | 9.97 |
| 6. Hexyl | -do- | White needles | $C_{44}H_{64}O_3$ | 82.69 | 9.78 | 82.45 | 10.07 |
| 7. Heptyl | -do- | White needles | $C_{45}H_{66}O_3$ | 82.33 | 10.08 | 82.51 | 10.16 |
| 8. Octyl | -do- | White plates | $C_{46}H_{68}O_3$ | 82.24 | 10.00 | 82.58 | 10.25 |
| 9. Nonyl | -do- | White plates | $C_{47}H_{70}O_3$ | 82.47 | 10.18 | 82.64 | 10.33 |
| 10. Decyl | -do- | White plates | $C_{48}H_{72}O_3$ | 82.58 | 10.22 | 82.72 | 10.41 |
| 11. Dodecyl | -do- | White plates | $C_{50}H_{76}O_3$ | 82.45 | 10.27 | 82.82 | 10.57 |
| 12. Tetradecyl | -do- | White plates | $C_{52}H_{80}O_3$ | 82.74 | 10.86 | 82.92 | 10.71 |
| 13. Hexadecyl | -do- | White plates | $C_{54}H_{84}O_3$ | 82.94 | 10.99 | 83.08 | 10.76 |
| 14. Octadecyl | -do- | White plates | $C_{56}H_{88}O_3$ | 82.96 | 10.65 | 83.18 | 10.89 |

Table 14

Substitutedbenzoates of cholesterol.

| Substituent and Position | Crystallized from | Shape and colour | Molecular formula | % Found | | | % Required | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | Halogen | C | H | Halogen |
| Ortho : | | | | | | | | | |
| Cl | Chloroform + acetone(1:1) | White plates | $C_{34}H_{49}O_2Cl$ | 77.71 | 9.22 | 7.02 | 77.82 | 9.35 | 6.76 |
| Br | -do- | White plates | $C_{34}H_{49}O_2Br$ | 71.74 | 8.22 | 14.05 | 17.73 | 8.61 | 14.05 |
| I | -do- | White plates | $C_{34}H_{49}O_2I$ | 66.15 | 7.73 | 20.71 | 66.25 | 7.96 | 20.62 |
| $NO_2$ | -do- | White plates | $C_{34}H_{49}O_4N$ | 76.58 | 9.56 | 2.95N | 76.22 | 9.22 | 2.61N |
| Meta : | | | | | | | | | |
| Cl | -do- | White plates | $C_{34}H_{49}O_2Cl$ | 77.41 | 9.20 | 6.49 | 77.82 | 9.35 | 6.76 |
| Br | -do- | White plates | $C_{34}H_{49}O_2Br$ | 71.63 | 8.54 | 13.60 | 71.73 | 8.61 | 14.05 |
| I | -do- | White plates | $C_{34}H_{49}O_2I$ | 66.01 | 7.65 | 20.72 | 66.25 | 7.96 | 20.62 |
| $CH_3$ | -do- | White plates | $C_{35}H_{52}O_2$ | 83.30 | 10.41 | - | 83.33 | 10.31 | - |
| Para : | | | | | | | | | |
| Cl | -do- | White plates | $C_{34}H_{49}O_2Cl$ | 77.52 | 9.21 | 7.00 | 77.82 | 9.35 | 6.76 |
| Br | -do- | White plates | $C_{34}H_{49}O_2Br$ | 71.69 | 8.44 | 14.35 | 71.73 | 8.61 | 14.05 |
| I | -do- | White plates | $C_{34}H_{49}O_2I$ | 66.15 | 7.79 | 20.53 | 66.25 | 7.96 | 20.62 |

Table 15

Biphenyl-4-p-n-alkoxybenzoates.

| n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % C | Found H | % C | Required H |
|---|---|---|---|---|---|---|---|
| 1. - | Acetic acid | White needles | $C_{19}H_{14}O_2$ | 83.01 | 4.88 | 83.21 | 5.1 |
| 2. Methyl | Acetic acid | White needles | $C_{20}H_{16}O_3$ | 78.63 | 5.11 | 78.94 | 5.26 |
| 3. Ethyl | Acetic acid | White needles | $C_{21}H_{18}O_3$ | 79.43 | 5.74 | 79.25 | 5.66 |
| 4. Propyl | Acetic acid | White needles | $C_{22}H_{20}O_3$ | 79.23 | 5.88 | 79.49 | 6.06 |
| 5. Butyl | Acetic acid | White needles | $C_{23}H_{22}O_3$ | 79.52 | 6.22 | 79.74 | 6.40 |
| 6. Pentyl | Acetic acid | White needles | $C_{24}H_{24}O_3$ | 80.39 | 6.64 | 79.97 | 6.71 |
| 7. Hexyl | Acetic acid | White needles | $C_{25}H_{26}O_3$ | 80.63 | 6.95 | 80.18 | 7.00 |
| 8. Heptyl | Acetic acid | White needles | $C_{26}H_{28}O_3$ | 80.24 | 7.10 | 80.38 | 7.27 |
| 9. Octyl | Acetic acid | White needles | $C_{27}H_{30}O_3$ | 80.97 | 7.34 | 80.56 | 7.51 |
| 10. Nonyl | Acetic acid | White needles | $C_{28}H_{32}O_3$ | 80.56 | 7.92 | 80.73 | 7.74 |
| 11. Decyl | Acetic acid | White needles | $C_{29}H_{34}O_3$ | 80.63 | 7.77 | 80.89 | 7.96 |
| 12. Dodecyl | Acetic acid | White needles | $C_{31}H_{38}O_3$ | 80.98 | 8.39 | 81.18 | 8.35 |
| 13. Tetradecyl | Acetic acid | White needles | $C_{33}H_{42}O_3$ | 81.77 | 8.53 | 81.44 | 8.70 |
| 14. Hexadecyl | Acetic acid | White needles | $C_{35}H_{46}O_3$ | 81.56 | 8.98 | 81.67 | 9.01 |
| 15. Octadecyl | Acetic acid | White needles | $C_{37}H_{50}O_3$ | 81.61 | 9.10 | 81.87 | 9.29 |

Table 16

Biphenyl 4-trans-p-n-alkoxycinnamates.

| n-Alkyl group | Crystallized from | Shape and colour | Molecular formula | % C | Found H | % C | Required H |
|---|---|---|---|---|---|---|---|
| 1. - | Acetic acid | White needles | $C_{21}H_{16}O_2$ | 84.28 | 5.44 | 84.01 | 5.00 |
| 2. Methyl | Acetic acid | White needles | $C_{22}H_{18}O_3$ | 79.65 | 5.18 | 80.00 | 5.50 |
| 3. Ethyl | Acetic acid | White needles | $C_{23}H_{20}O_3$ | 80.23 | 5.55 | 80.24 | 5.81 |
| 4. Propyl | Acetic acid | White needles | $C_{24}H_{22}O_3$ | 80.26 | 5.90 | 80.44 | 6.15 |
| 5. Butyl | Acetic acid | White needles | $C_{25}H_{24}O_3$ | 80.48 | 6.55 | 80.65 | 6.45 |
| 6. Pentyl | Acetic acid | White needles | $C_{26}H_{26}O_3$ | 80.98 | 6.97 | 80.83 | 6.76 |
| 7. Hexyl | Acetic acid | White needles | $C_{27}H_{28}O_3$ | 80.93 | 7.26 | 80.96 | 7.05 |
| 8. Heptyl | Acetic acid | White needles | $C_{28}H_{30}O_3$ | 81.06 | 7.38 | 81.12 | 7.30 |
| 9. Octyl | Acetic acid | White needles | $C_{29}H_{32}O_3$ | 81.56 | 7.45 | 81.27 | 7.53 |
| 10. Nonyl | Acetic acid | White needles | $C_{30}H_{34}O_3$ | 81.56 | 7.72 | 81.41 | 7.74 |
| 11. Decyl | Acetic acid | White needles | $C_{31}H_{36}O_3$ | 81.49 | 8.04 | 81.54 | 7.95 |
| 12. Dodecyl | Acetic acid | White needles | $C_{33}H_{40}O_3$ | 81.91 | 8.43 | 81.78 | 8.32 |
| 13. Tetradecyl | Acetic acid | White needles | $C_{35}H_{44}O_3$ | 82.05 | 8.44 | 82.03 | 8.59 |
| 14. Hexadecyl | Acetic acid | White needles | $C_{37}H_{48}O_3$ | 82.28 | 8.96 | 82.18 | 8.95 |
| 15. Octadecyl | Acetic acid | White needles | $C_{39}H_{52}O_3$ | 82.04 | 9.18 | 82.35 | 9.22 |

Table 17

Cholesteryl p-n-alkoxybenzoates.

| n-Alkyl group | Transition temperatures (°C) | | |
|---|---|---|---|
| | Smectic | Cholesteric | Isotropic |
| 1. Methyl | - | 180.0 | 268.0 |
| 2. Ethyl | - | 149.5 | 265.0 |
| 3. Propyl | - | 141.0 | 253.0 |
| 4. Butyl | - | 134.0 | 248.0 |
| 5. Pentyl | - | 148.5 | 236.5 |
| 6. Hexyl | - | 150.0 | 234.5 |
| 7. Heptyl | 138.5 | 160.5 | 222.0 |
| 8. Octyl | 138.0 | 171.5 | 220.5 |
| 9. Nonyl | 128.0 | 176.0 | 213.0 |
| 10. Decyl | 110.0 | 177.5 | 209.0 |
| 11. Dodecyl | 128.5 | 179.5 | 200.5 |
| 12. Tetradecyl | 116.0 | 177.5 | 191.5 |
| 13. Hexadecyl | 92.0 | 170.5 | 179.5 |
| 14. Octadecyl | 106.0 | 165.5 | 173.0 |

Table 18

Cholesteryl trans-p-n-alkoxycinnamates.

| | n-Alkyl group | Transition temperatures (°C) | | | |
|---|---|---|---|---|---|
| | | $Smectic_{II}$ | $Smectic_{I}$ | Cholesteric | Isotropic |
| 1. | - | - | - | 160.5 | 215.0 |
| 2. | Methyl | - | - | 173.0 | 292.5 |
| 3. | Ethyl | - | - | 152.0 | 293.5 |
| 4. | Propyl | - | - | 146.0 | 280.0 |
| 5. | Butyl | - | - | 134.0 | 281.0 |
| 6. | Pentyl | - | - | 128.0 | 268.0 |
| 7. | Hexyl | - | - | 128.5 | 262.5 |
| 8. | Heptyl | - | - | 142.5 | 254.0 |
| 9. | Octyl | - | - | 144.0 | 249.0 |
| 10. | Nonyl | - | - | 142.5 | 244.0 |
| 11. | Decyl | 133.0 | 158.5 | 167.0 | 238.5 |
| 12. | Dodecyl | 133.0 | 178.5 | 181.5 | 226.5 |
| 13. | Tetradecyl | 121.0 | 181.0 | 183.5 | 213.0 |
| 14. | Hexadecyl | - | 107.0 | 181.5 | 200.0 |
| 15. | Octadecyl | - | 108.0 | 167.0 | 186.0 |

Table 19

Cholesteryl trans-p-n-alkoxy-α-methyl cinnamates.

| | n-Alkyl group | Transition temperatures (°C) | | | |
|---|---|---|---|---|---|
| | | Smectic$_{II}$ | Smectic$_{I}$ | Cholesteric | Isotropic |
| 1. | - | - | - | 108.0 | 183.0 |
| 2. | Methyl | - | - | 122.0<br>87.0* | 259.0 |
| 3. | Ethyl | - | - | 122.0 | 261.0 |
| 4. | Propyl | - | - | 125.0 | 257.0 |
| 5. | Butyl | - | - | 138.0 | 252.0 |
| 6. | Pentyl | - | - | 135.0 | 243.0 |
| 7. | Hexyl | - | - | 100.0 | 239.0 |
| 8. | Heptyl | - | - | 100.0 | 234.5 |
| 9. | Octyl | 92.0 | 141.0 | 150.0 | 221.5 |
| 10. | Nonyl | - | 87.0 | 158.0 | 215.0 |
| 11. | Decyl | - | 79.0 | 162.0 | 209.0 |
| 12. | Dodecyl | - | 89.0 | 166.5 | 199.0 |
| 13. | Tetradecyl | - | 74.0 | 169.0 | 190.5 |
| 14. | Hexadecyl | - | 70.0 | 166.0 | 181.5 |
| 15. | Octadecyl | - | 83.0 | 160.5 | 172.5 |

* Transition temperature for the solid ($C_{II}$)- cholesteric change.

Table 20

Cholesteryl-4-n-alkoxy-1-naphthoates.

| n-Alkyl group | Transition temperatures (°C) | | |
|---|---|---|---|
| | Smectic | Cholesteric | Isotropic |
| 1. Methyl | - | 183.0 | 186.0 |
| 2. Ethyl | - | (190.0)* | 221.0 |
| 3. Propyl | - | (173.0) | 210.0 |
| 4. Butyl | - | (178.0) | 186.0 |
| 5. Pentyl | - | (170.0) | 177.0 |
| 6. Hexyl | - | (169.0) | 177.0 |
| 7. Heptyl | - | (160.0) | 167.0 |
| 8. Octyl | - | 144.0 | 157.5 |
| 9. Nonyl | - | 124.0 | 151.5 |
| 10. Decyl | - | 134.0 | 148.5 |
| 11. Dodecyl | ( 94.0) | 127.0 | 141.5 |
| 12. Tetradecyl | (100.0) | 134.0 | 134.5 |
| 13. Hexadecyl | (102.0) | 125.0 | 129.0 |
| 14. Octadecyl | ( 99.5) | 112.0 | 122.0 |

* Values in the parenthesis indicate monotropy.

Table 21

Substitutedbenzoates of Cholesterol.



| Substituent and Position | Transition temperatures (°C) Smectic | Cholesteric | Isotropic |
|---|---|---|---|
| Ortho : | | | |
| Cl | - | 106.0 | 146.0 |
| Br | - | 105.0 | 134.0 |
| I | - | 109.0 | 112.0 |
| $CH_3$ | - | 110.0 | 134.0[a] |
| $NO_2$ | (98.5)* | 147.0 | 155.0[b] |
| Meta : | | | |
| Cl | - | (146.5) | 147.0 |
| Br | - | (135.0) | 142.0 |
| I | - | (113.0) | 130.0 |
| $CH_3$ | - | (130.0) | 143.5 |
| $NO_2$ | - | 140.0 | 174.0[c] |
| Para : | | | |
| Cl | - | 170.0 | 257.0[d] |
| Br | - | 179.0 | 257.5 |
| I | - | 187.0 | 252.0 |
| $CH_3$ | - | 179.0 | 246.0[e] |
| $NO_2$ | - | 191.5 | 260.0(decomp.)[f] |
| MeO | - | 180.0 | 268.0 |
| Cholesterylbenzoate : | - | 150.0 | 178.0 |

* Values in the parenthesis indicate monotropy.

a. Wiegand (287) reports 120-121°, 133°C.

b. Sandquist and Gorton (288) report m. (149.6-) 150.4-0.9°, clears 156.2-6.9°C. Vorländer (289) mentions that it also gives smectic mesophase.

c. Sandquist and Gorton (288) report m. (140.3-) 140.8-1.0°, clears 174.6-5.3°C.

d. Gray (67) reports Ch-I temperature as 245-6°C.

e. Wiegand (287) reports 179.5-180.5, 241.0°C.

f. Sandquist and Gorton (288) report m. (188.2-) 189.9-92.8°, clears 261°C (d); Gray reports (67) Ch-I temperature as 258-9°C (d).

Table 22

Biphenyl 4-p-n-alkoxybenzoates.

| n-Alkyl group | Transition temperatures (°C) | | |
|---|---|---|---|
| | Smectic | Nematic | Isotropic |
| 1. - | - | - | 151.5 |
| 2. Methyl | - | (145.0)* | 157.0 |
| 3. Ethyl | - | (157.0) | 160.0 |
| 4. Propyl | - | (137.0) | 146.5 |
| 5. Butyl | - | (143.0) | 157.0 |
| 6. Pentyl | - | (133.0) | 154.5 |
| 7. Hexyl | - | 134.0 | 136.0 |
| 8. Heptyl | - | 126.5 | 131.0 |
| 9. Octyl | - | 120.0 | 131.0 |
| 10. Nonyl | (102.0) | 116.5 | 128.0 |
| 11. Decyl | 108.0 | 110.0 | 128.5 |
| 12. Dodecyl | 110.5 | 114.5 | 125.0 |
| 13. Tetradecyl | 111.0 | 116.5 | 122.0 |
| 14. Hexadecyl | 100.0 | - | 118.5 |
| 15. Octadecyl | 100.0 | - | 117.0 |

* Values in the parenthesis indicate monotropy.

Table 23

Biphenyl-4-trans-p-n-alkoxycinnamates.

| n-Alkyl group | | Transition temperatures (°C) | | |
|---|---|---|---|---|
| | | Smectic | Nematic | Isotropic |
| 1. | - | - | - | 166.0 |
| 2. | Methyl | - | 188.0 | 211.5 |
| 3. | Ethyl | - | 169.0 | 215.5 |
| 4. | Propyl | - | 163.0 | 199.5 |
| 5. | Butyl | - | 154.0 | 197.5 |
| 6. | Pentyl | - | 146.0 | 187.5 |
| 7. | Hexyl | - | 141.5 | 186.5 |
| 8. | Heptyl | (127.5)* | 137.5 | 179.0 |
| 9. | Octyl | 134.0 | 141.0 | 178.0 |
| 10. | Nonyl | 130.0 | 147.0 | 173.0 |
| 11. | Decyl | 126.0 | 151.0 | 170.0 |
| 12. | Dodecyl | 125.0 | 156.0 | 165.5 |
| 13. | Tetradecyl | 122.0 | 156.0 | 159.0 |
| 14. | Hexadecyl | 118.5 | - | 157.0 |
| 15. | Octadecyl | 114.0 | - | 153.5 |

* Value in the parenthesis indicates monotropy.

FIG. 6

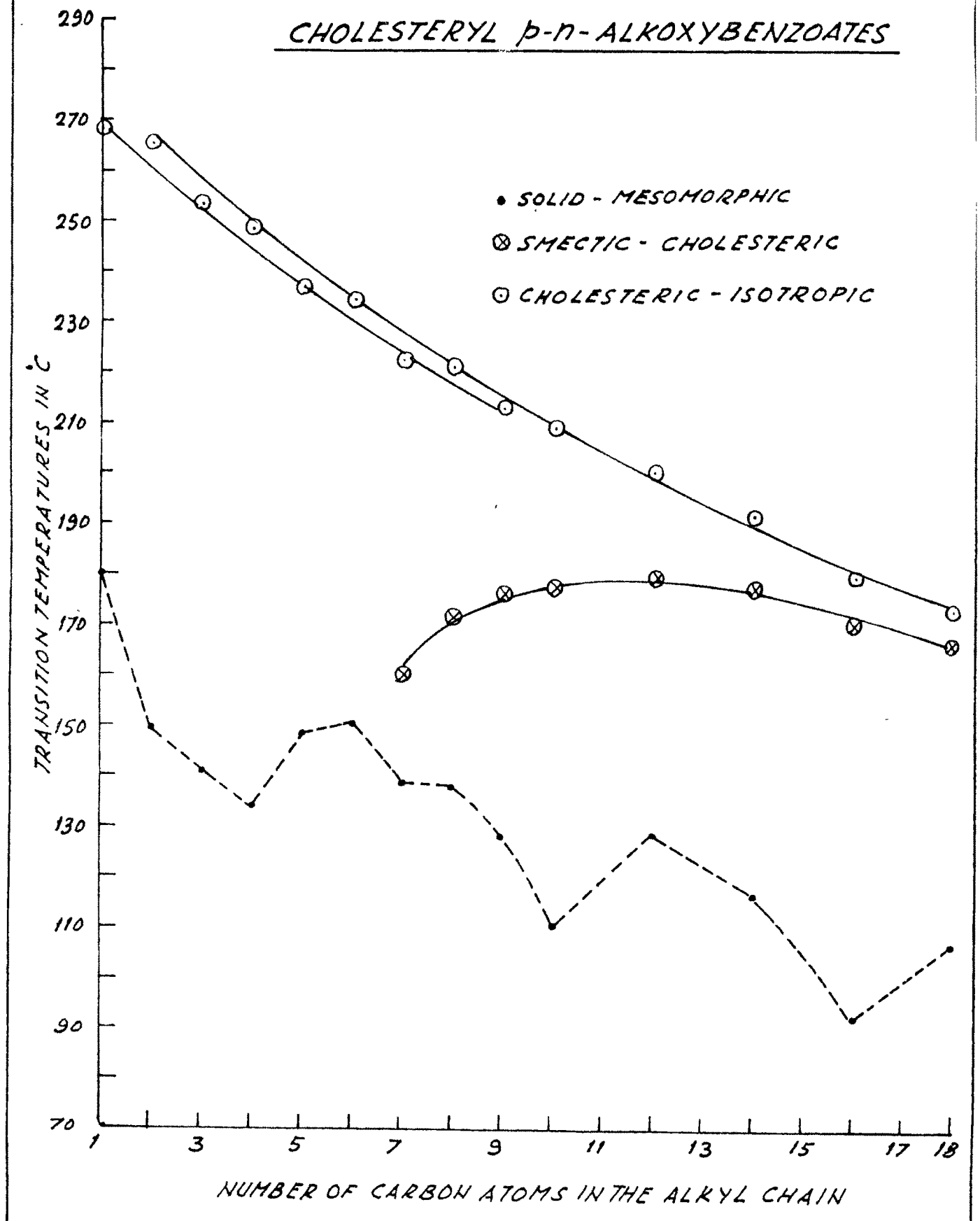

CHOLESTERYL p-n-ALKOXYBENZOATES
• SOLID - MESOMORPHIC
⊗ SMECTIC - CHOLESTERIC
⊙ CHOLESTERIC - ISOTROPIC
TRANSITION TEMPERATURES IN °C
290
270
250
230
210
190
170
150
130
110
90
70
1
3
5
7
9
11
13
15
17
18
NUMBER OF CARBON ATOMS IN THE ALKYL CHAIN

FIG. 7

# CHOLESTERYL TRANS p-n-ALKOXYCINNAMATES

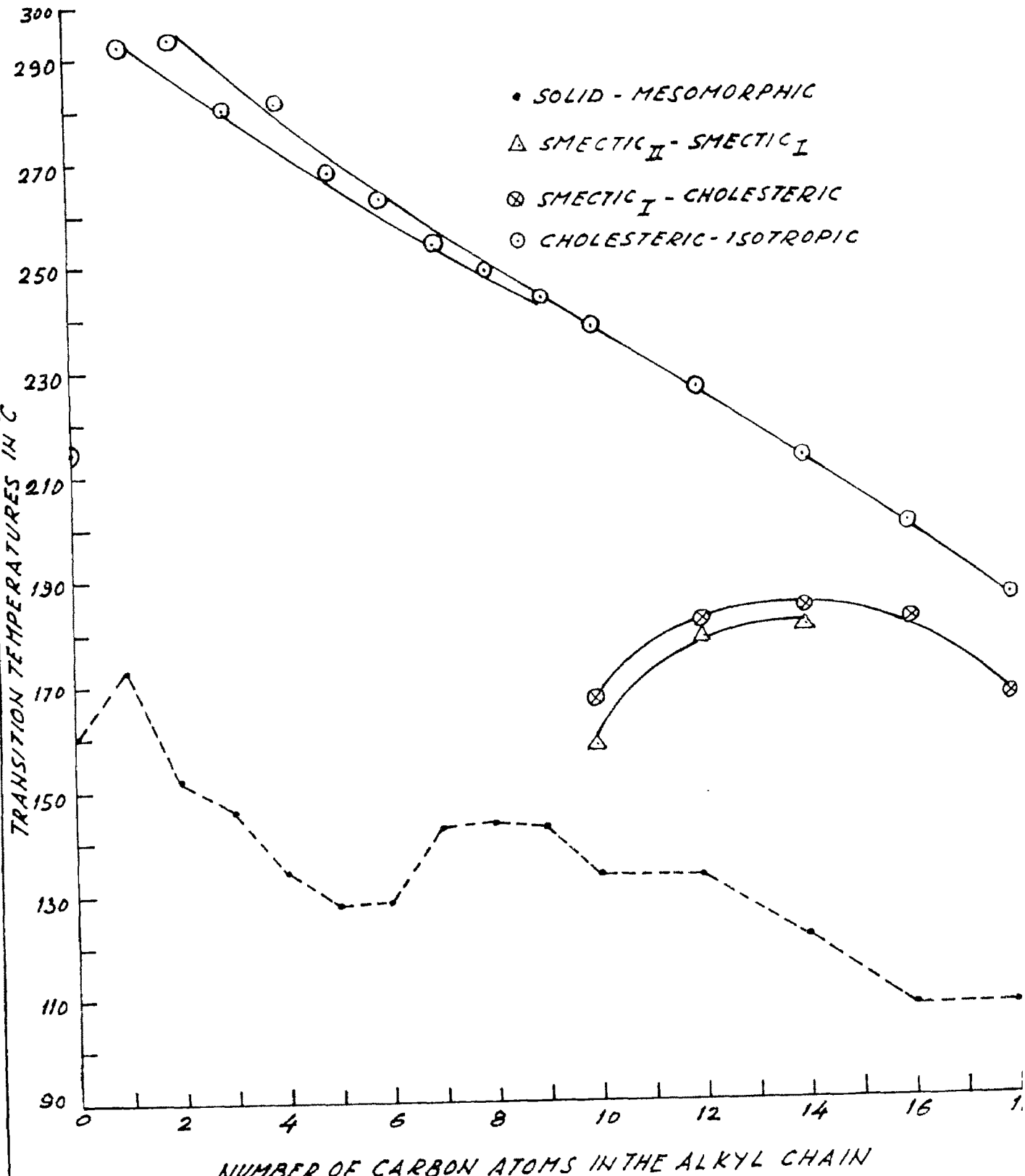


FIG. 8

# CHOLESTERYL TRANS-p-n-ALKOXY-α-METHYL CINNAMATES

× M. P. OF SOLID $C_{II}$ MODIFICATION

• SOLID - MESOMORPHIC

△ SMECTIC$_{II}$ - SMECTIC$_{I}$

⊗ SMECTIC$_{I}$ - CHOLESTERIC

⊙ CHOLESTERIC - ISOTROPIC

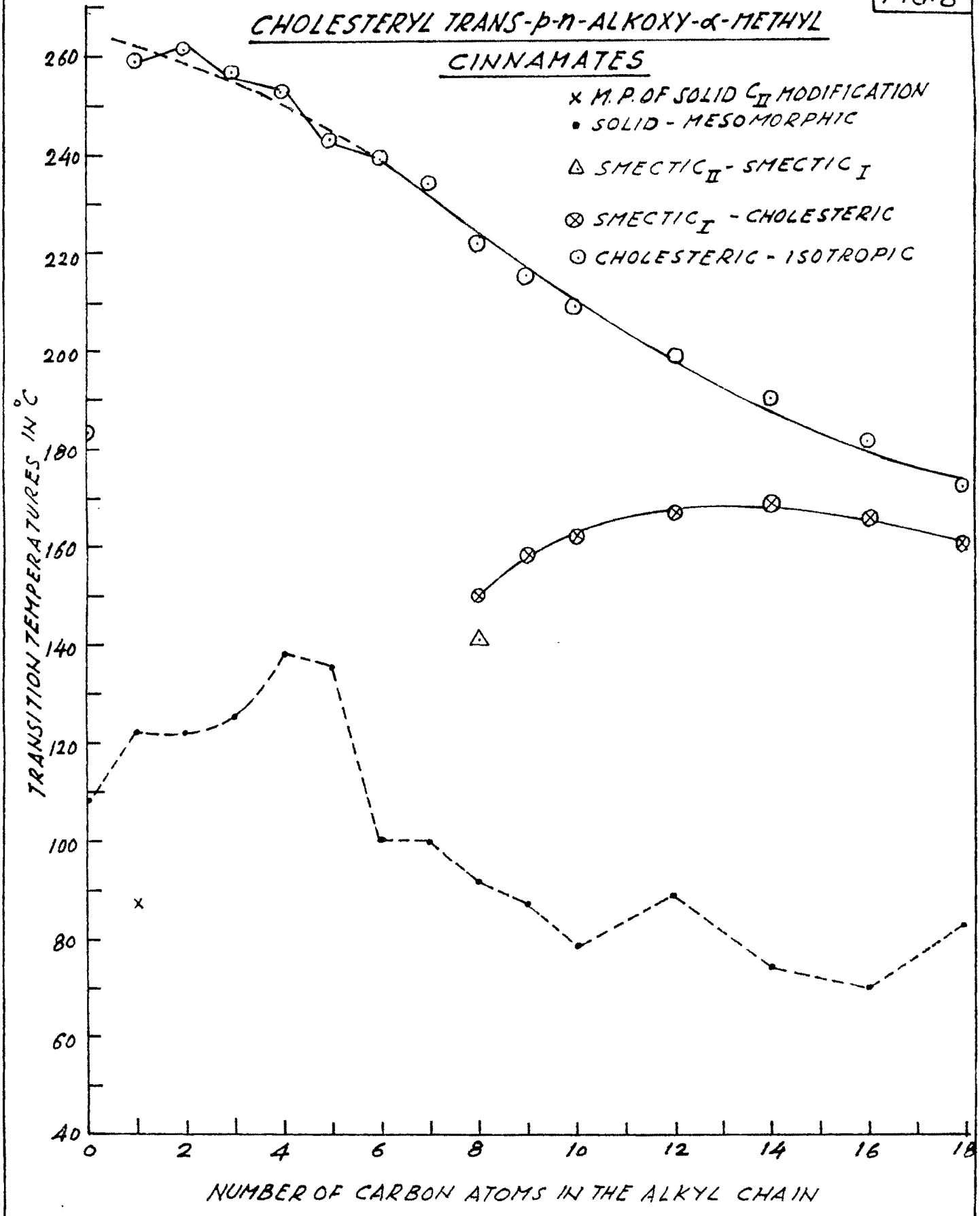


FIG. 9

# CHOLESTERYL 4-n-ALKOXY-1-NAPHTHOATES

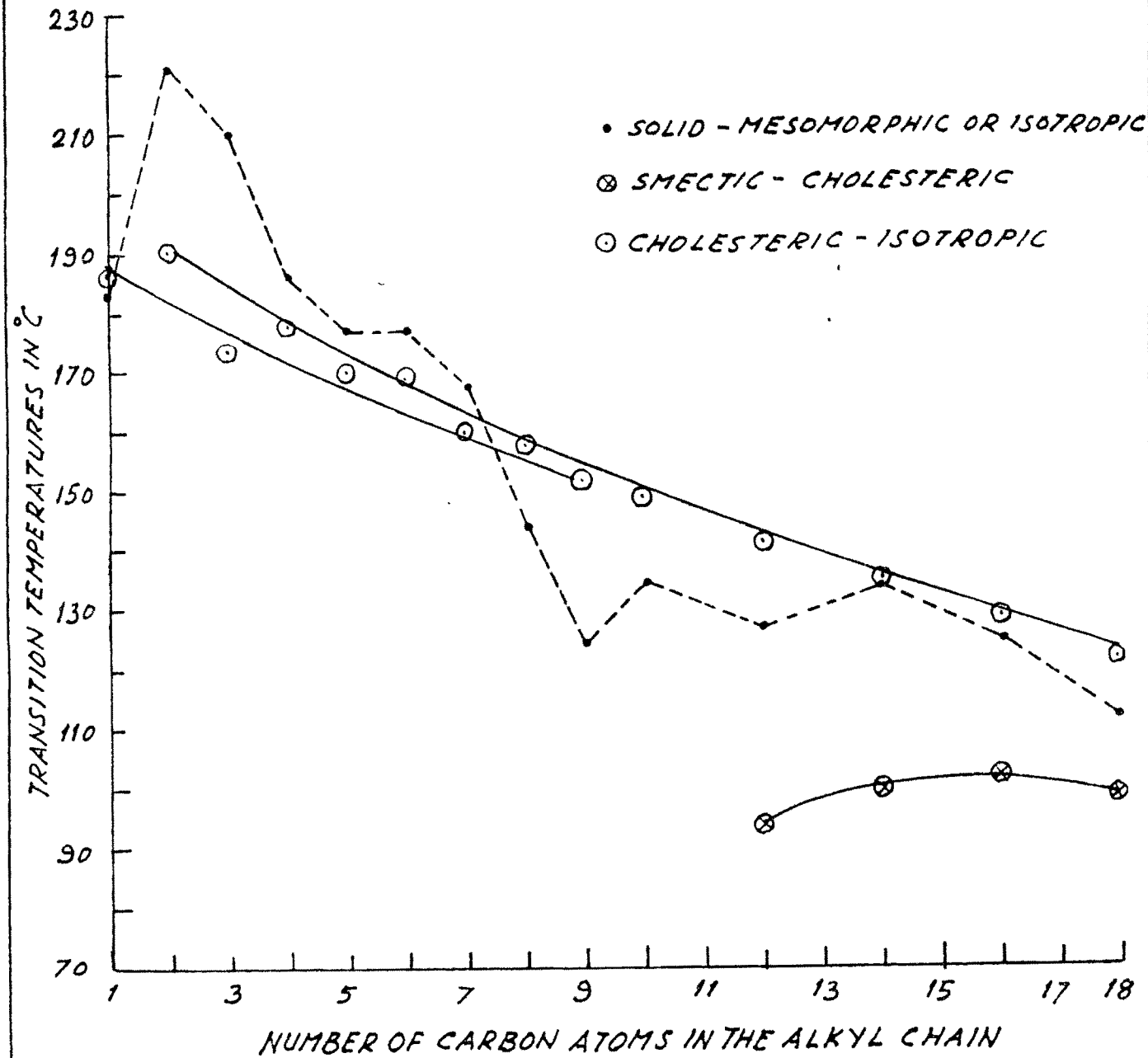


FIG. 10

# BIPHENYL 4-p-n-ALKOXY BENZOATES

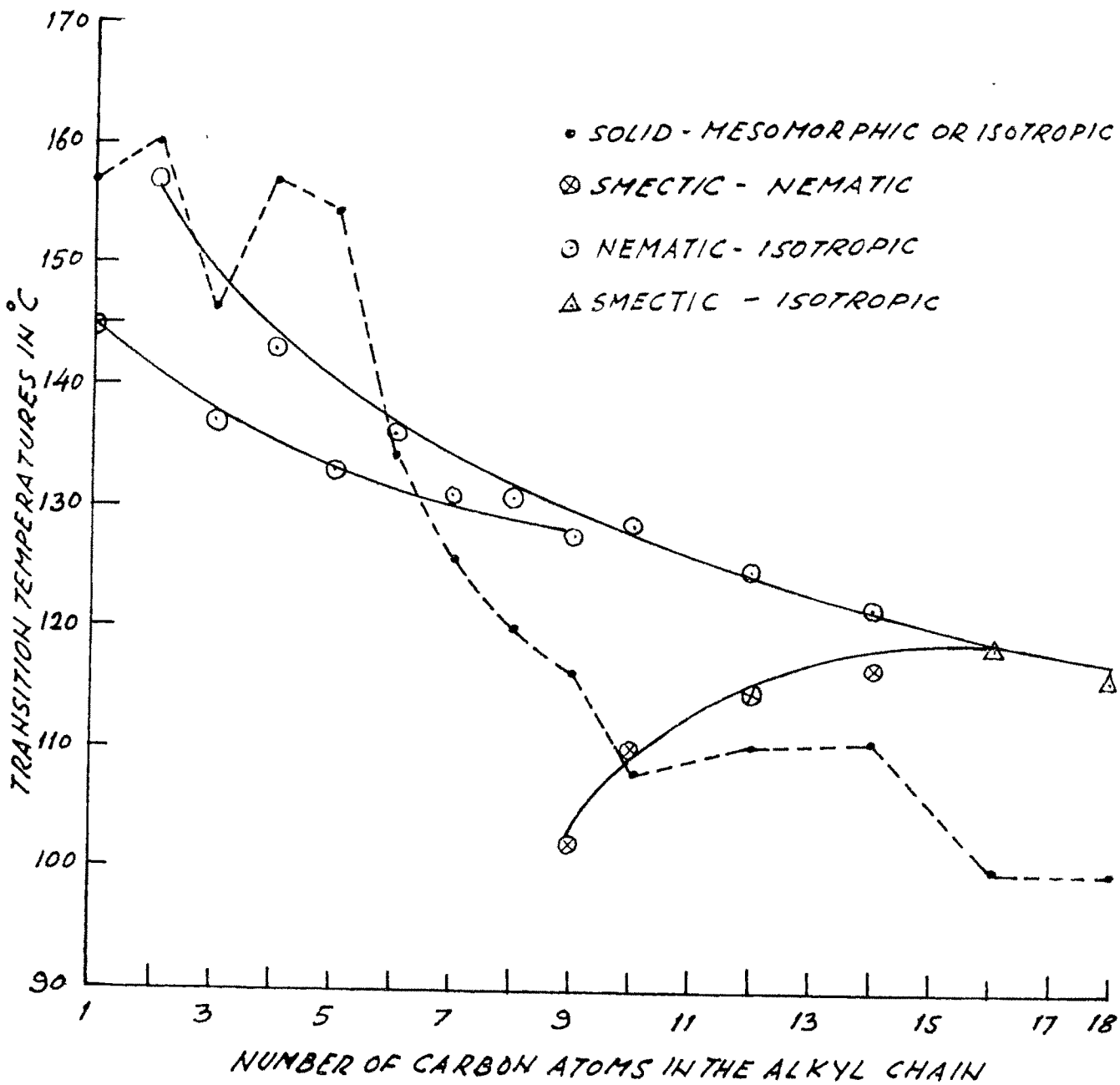


FIG. 11

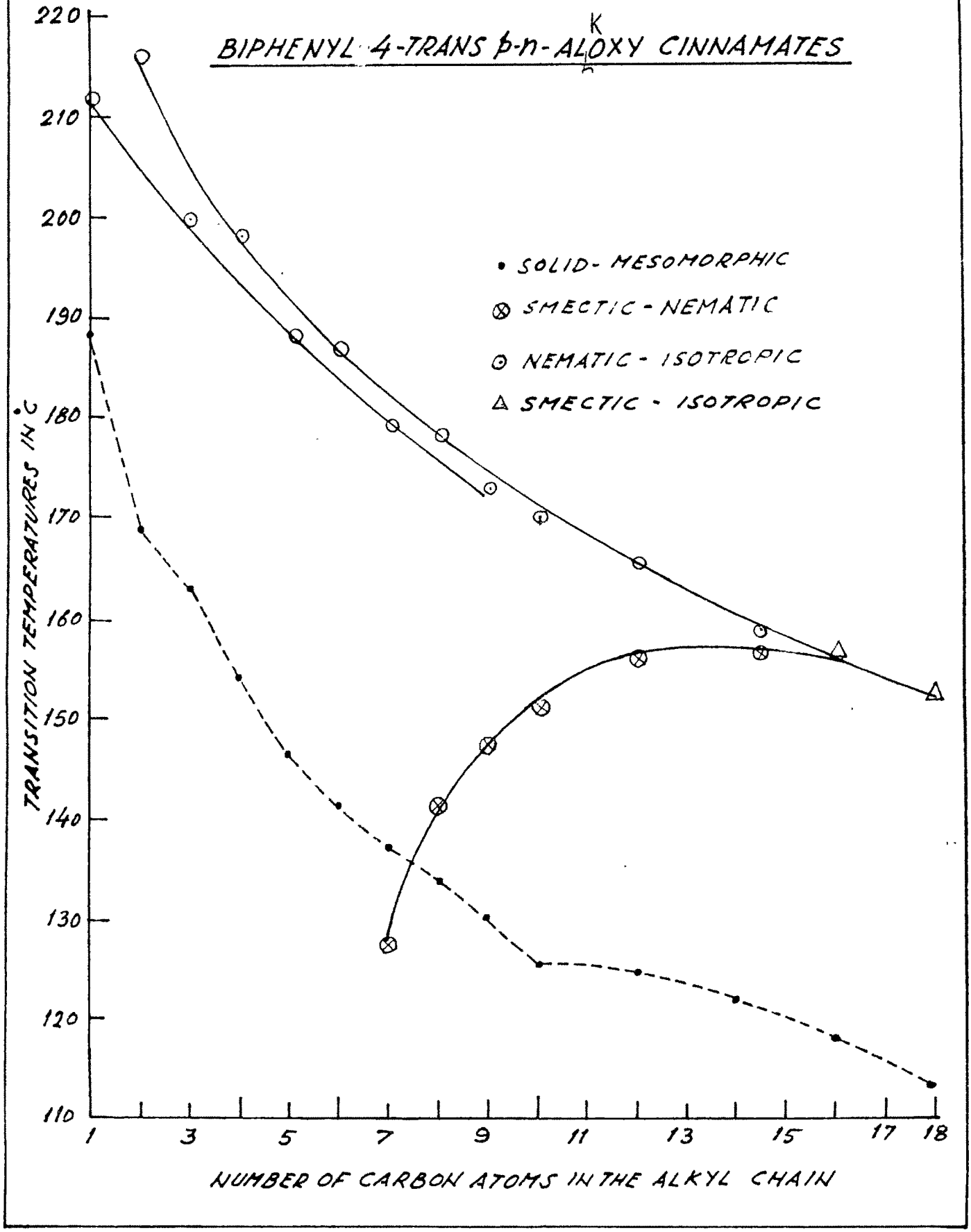

BIPHENYL 4-TRANS p-n-ALOXY CINNAMATES
K
n
• SOLID - MESOMORPHIC
⊗ SMECTIC - NEMATIC
⊙ NEMATIC - ISOTROPIC
△ SMECTIC - ISOTROPIC
TRANSITION TEMPERATURES IN °C
220
210
200
190
180
170
160
150
140
130
120
110
1
3
5
7
9
11
13
15
17
18
NUMBER OF CARBON ATOMS IN THE ALKYL CHAIN

FIG. 12

# TRANS-p-n ALKOXY-α-METHYL-CINNAMIC ACIDS