EXPERIMENTAL

EXPERIMENTAL

3.a. Synthesis of New Homologous Series:

Inspired by the existing literature on liquid crystals, the following new homologous series of mesogens have been synthesized. These series can be classified into three distinct categories:

A. Esters of p-n-alkoxycinnamic acids and p-n-alkoxy phenols.

1. p-Ethoxyphenyl-p'-n-alkoxycinnamates
2. p-n-Propoxyphenyl-p'-n-alkoxycinnamates
3. p-n-Butoxyphenyl-p'-n-alkoxycinnamates
4. p-n-Amyloxyphenyl-p'-n-alkoxycinnamates

B. Esters of p-n-alkoxycinnamic acids and p-iso-alkoxyphenols

5. p-iso-Propoxyphenyl-p'-n-alkoxycinnamates
6. p-iso-Butoxyphenyl-p'-n-alkoxycinnamates
7. p-iso-Amyloxyphenyl-p'-n-alkoxycinnamates

C. Esters of p-n-alkoxycinnamic acids and chlorophenols

8. m-Chlorophenyl-p'-n-alkoxycinnamates
9. o-Chlorophenyl-p'-n-alkoxycinnamates

Following are the different steps for the synthesis of the above homologous series of mesogens.

1. p-n-Alkoxybenzaldehydes

Synthesis of p-n-alkoxybenzaldehyde, where alkoxy group varies from $-OCH_3$ to $-OC_{16}H_{33}$ has been described by Hildesheimer (454), Stoermer and Wodarg (455), Weygard and Gabler (456) and Gray and Jones (232). In this study, however, the following procedure has been adopted with better results. The first member viz. p-methoxybenzaldehyde also known as p-anisaldehyde has been used of BDH grade and was purified before use.

0.15 mole of anhydrous potassium carbonate and 0.15 mole of the corresponding n-alkyl bromide or iodide were added to 0.1 mole of p-hydroxybenzaldehyde in dry acetone (60 ml). The mixture was refluxed in water-bath for three to four hours. In the case of higher members the reaction time was extended upto six to eight hours. The whole mass was then added to water, extracted with ether and the ether extract was washed with dilute sodium hydroxide to remove any unreacted p-hydroxybenzaldehyde followed by water and dried. Ether was evaporated and the p-n-alkoxybenzaldehydes thus obtained were purified by distillation under reduced pressure. Boiling points almost agreed with those reported in literature (457).

2. Trans-p-n-alkoxycinnamic acids

Trans-p-n-alkoxycinnamic acids were prepared by the method of Gray and Jones (232).

The appropriate p-n-alkoxybenzaldehyde (0.02 mole), malonic acid (0.04 mole), pyridine (8 ml) and piperidine (three drops) were mixed and heated at 100°C on a steam bath for three to four hours. In the case of higher members the refluxing period was extended to five to six hours. The mass was poured into mixture of ice (25 g) and concentrated hydrochloric acid (25 ml). Stirred it for sometime, allowed to settle, filtered and washed with dilute hydrochloric acid followed by water. Crystallized the compounds from 98% acetic acid. Yield of the colorless products was 85 to 90%. Higher homologues were crystallized twice from benzene and then from acetic acid till constant transition temperatures (232) were obtained, these are listed in Table 3.

3. Trans-p-n-alkoxycinnamoyl chlorides

Trans-p-n-alkoxycinnamoyl chlorides were prepared (458) by treating the corresponding trans-p-n-alkoxycinnamic 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 left behind as residue, were used for further reaction.

4. p-Alkoxyphenols

Number of methods are available in literature for the preparation of monoalkoxyphenols (459-463). The following p-alkoxyphenols were prepared.

(i) p-Hydroxyphenetole

Hydroquinone (0.45 M) in 20% sodium hydroxide was stirred with diethylsulfate (0.27 M) for 30 minutes. A solution of 5 gm

Table 3

Trans-p-n-alkoxycinnamic acids (232)

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	174.0	190.0
Ethyl	-	194.0	200.0
Propyl	-	169.0	184.0
Butyl	-	156.0	189.0
Pentyl	-	144.0	180.0
Hexyl	-	152.0	180.0
Heptyl	-	148.0	175.0
Octyl	-	145.0	172.0
Decyl	136.0	150.0	169.0
Dodecyl	132.0	157.0	164.0
Tetradecyl	127.0	-	160.0
Hexadecyl	118.0	-	159.0
Octadecyl	120.0	-	157.5

sodiumhydroxide was added and refluxed for 30 minutes. After cooling, 50 ml 10 % sodiumhydroxide was added and extracted with ether to remove diethoxybenzene. The alkaline solution was acidified and extracted with benzene. Benzene extract was dried and distilled off. Yield is approximately 55-60% (459) M.P. 65°C.

(ii) p-n-Propoxyphenol

To the solution of hydroquinone (0.4 M) in 160 ml ethanol was added n-propylbromide (0.4M). The mixture was heated till it just starts to reflux and added solution of potassium hydroxide (1.43 M) in 240 ml water drop by drop. After the addition was over, it was refluxed for four hours and allowed to cool, followed by filtration to remove solid p-di-n-propoxybenzene. The filterate was extracted with ether to ensure complete removal of p-di-n-propoxybenzene. The alkaline solution was acidified and extracted with benzene. Benzene extract was dried and distilled off. Yield was approximately 40-45 %. M.P. 56-7°C.

(iii) p-n-Butoxyphenol

The method of preparation is as per 4 (ii) of this section. Yield was approximately 40-45 % M.P. 64°C.

(iv) p-n-Amyloxyphenol

A solution of potassiumhydroxide (0.36 M) in 40 ml water was added drop by drop to the boiling mixture of hydroquinone

(0.34 M), 40 ml alcohol and n-amylbromide (0.33 M). After the addition was over, reflux was continued for 6 hours. It was allowed to cool, followed by extraction with ether to remove p-di-n-amyloxybenzene. The alkaline solution was acidified, extracted with benzene, benzene dried and distilled off. The residue, p-n-amyloxyphenol, was distilled under vacuum. Yield was approximately 35-40%(460) M.P.49°C.

(v) p-iso-Propoxyphenol

It was prepared as per 4(ii) of this section. After benzene was distilled off, the residue p-iso-propoxyphenol was distilled under vacuum. Yield was approximately 35-40%. B.P. 117°C (a) 4 mm.

(vi) p-iso-Butoxyphenol

It was prepared as per 4 (iv) of this section and after benzene was distilled off, distilled under vacuum. Yield was approximately 30-35 %, B.P. 230 °C.

(vii) p-iso-Amyloxyphenol

It was prepared as per 4(iv) of this section and after benzene was distilled off, distilled under vacuum. Yield was approximately 30-35 %, M.P. 45°C.

Melting points and/or boiling points almost agreed with those reported in literature (460) and are listed in Table 4.

5. p-Alkoxyphenyl-p'-n-alkoxycinnamates

p-Alkoxyphenyl-p'-n-alkoxycinnamates were synthesized by reacting trans-p-n-alkoxycinnamoylchlorides with p-alkoxyphenols.

Table 4

p-Alkoxyphenols (460)

p-Alkoxyphenol	M.P. °C	B.P. °C
p-Hydroxyphenetole	65-66	237-247
p-n-Propoxyphenol	56-57	-
p-n-Butoxyphenol	64-65	125 / 4 mm
p-n-Amyloxyphenol	48-49	-
p-iso-Propoxyphenol	-	117/4 mm
p-iso-Butoxyphenol	-	230
p-iso-Amyloxyphenol	45	155-8/20 mm

p-Alkoxyphenols (0.01 mole) were dissolved in dry A.R. pyridine (10.0 ml) and were added slowly to trans-p-n-alkoxycinnamoyl chloride (0.015 mole). The mixture was heated in waterbath with occasional stirring for an hour and poured into cold dilute hydrochloric acid. The precipitates were filtered and washed with water. The precipitates were then washed with cold dilute sodium hydroxide solution followed by water. The crude esters, of dark brown colour, were crystallized using ethanol or ethyl acetate : ethyl alcohol (10:90) mixture for some higher members. The melting points and transition temperatures are compiled in Table 5, 7, 9, 11, 13, 15 and 17. The elemental analysis conforms with the calculated ones. Yield is approximately 65 %.

6. m-Chlorophenyl-p'-n-alkoxycinnamates

m-Chlorophenyl-p'-n-alkoxycinnamates were synthesized by reacting trans-p-n-alkoxycinnamoyl chlorides with m-chlorophenol. m-Chlorophenol (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly to trans-p-n-alkoxycinnamoyl chloride (0.015 mole). The mixture was heated in water-bath with occasional stirring for an hour and acidified with cold dilute hydrochloric acid. The precipitates were filtered and washed with water. The precipitates were then washed with cold dilute sodium hydroxide solution followed by water. The esters, of dark brown color, were crystallized from ethanol or ethyl acetate:

ethanol (10:90) mixture. The melting points and transition temperatures are compiled in Table 19. The elemental analysis conforms with the calculated ones (Table 20). Yield is approximately 60 %.

7. O-Chlorophenyl-p'-n-alkoxycinnamates

O-Chlorophenyl-p'-n-alkoxycinnamates were synthesized and purified in the same way as m-chlorophenyl-p'-n-alkoxycinnamates in 6. The melting points and transition temperatures are compiled in Table 21. The elemental analysis conforms with the calculated ones (Table 22). Yield is approximately 60 %.

3.b. Study of the homologous series.

The study of the mesomorphic characteristics was carried out by polarizing microscope method.

Polarizing Microscope

A polarizing microscope equipped with hot stage comes handy for detecting multiple phases of a mesogen. A polarizing microscope with a Kofler heating stage has been used in the present study. Fig.5.

Slides of the compounds were prepared by one of the three different methods, (i) the substance is heated on a slide to a little more than the mesomorphic temperature and a cover slip is placed near the melt and moved towards the melt so that it

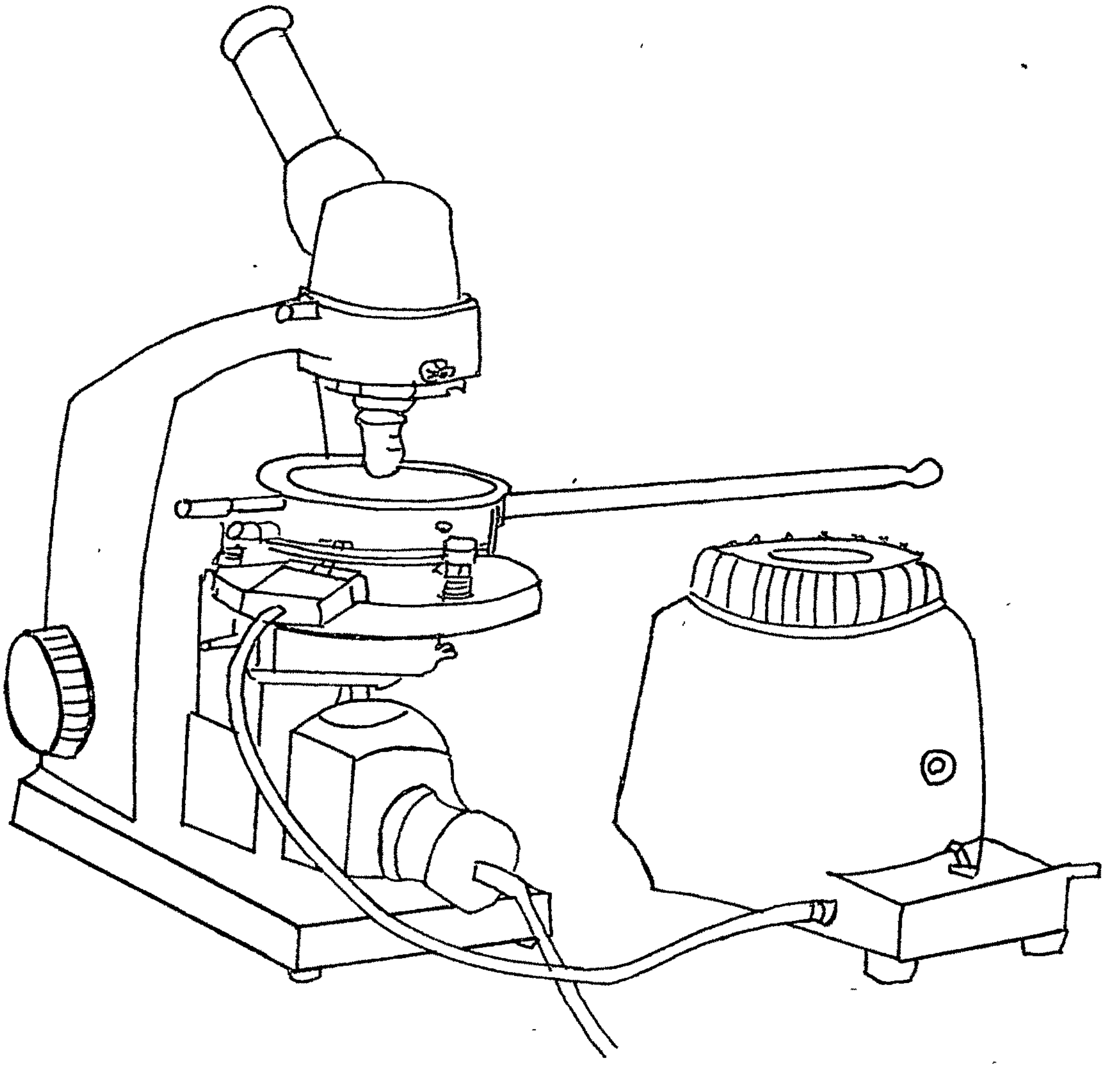

FIG. 5

POLARISING MICROSCOPE WITH KOFLER HEATING STAGE

Table 5

A-1 p-Ethoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	131	150
Ethyl	-	145	161
Propyl	-	126	145
Butyl	-	111	150
Pentyl	-	97	131
Hexyl	-	88	140
Heptyl	(72)	88	136
Octyl	(92)	99	133.5
Decyl	80	104	126
Dodecyl	86	109	122
Tetradecyl	86	109.5	116.5
Hexadecyl	90	108	113

Value in the parenthesis indicates monotropy

Table 6

A-1 p-Ethoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{18}H_{18}O_4$	72.48	6.04	72.78	6.20
Ethyl	$C_{19}H_{20}O_4$	73.08	6.41	72.83	6.66
Propyl	$C_{20}H_{22}O_4$	73.62	6.75	73.98	6.47
Butyl	$C_{21}H_{24}O_4$	74.12	7.06	74.36	7.22
Pentyl	$C_{22}H_{26}O_4$	74.58	7.34	74.78	7.18
Hexyl	$C_{23}H_{28}O_4$	75.00	7.61	75.23	7.45
Heptyl	$C_{24}H_{30}O_4$	75.39	7.85	75.16	7.95
Octyl	$C_{25}H_{32}O_4$	75.76	8.08	75.85	8.48
Decyl	$C_{27}H_{36}O_4$	76.42	8.49	76.36	8.52
Dodecyl	$C_{29}H_{40}O_4$	76.99	8.85	77.23	8.97
Tetradecyl	$C_{31}H_{44}O_4$	77.50	9.17	77.32	9.35
Hexadecyl	$C_{33}H_{48}O_4$	77.95	9.45	77.85	9.49

SERIES A-1

p-ETHOXYPHENYL-p'-n-ALKOXY CINNAMATES

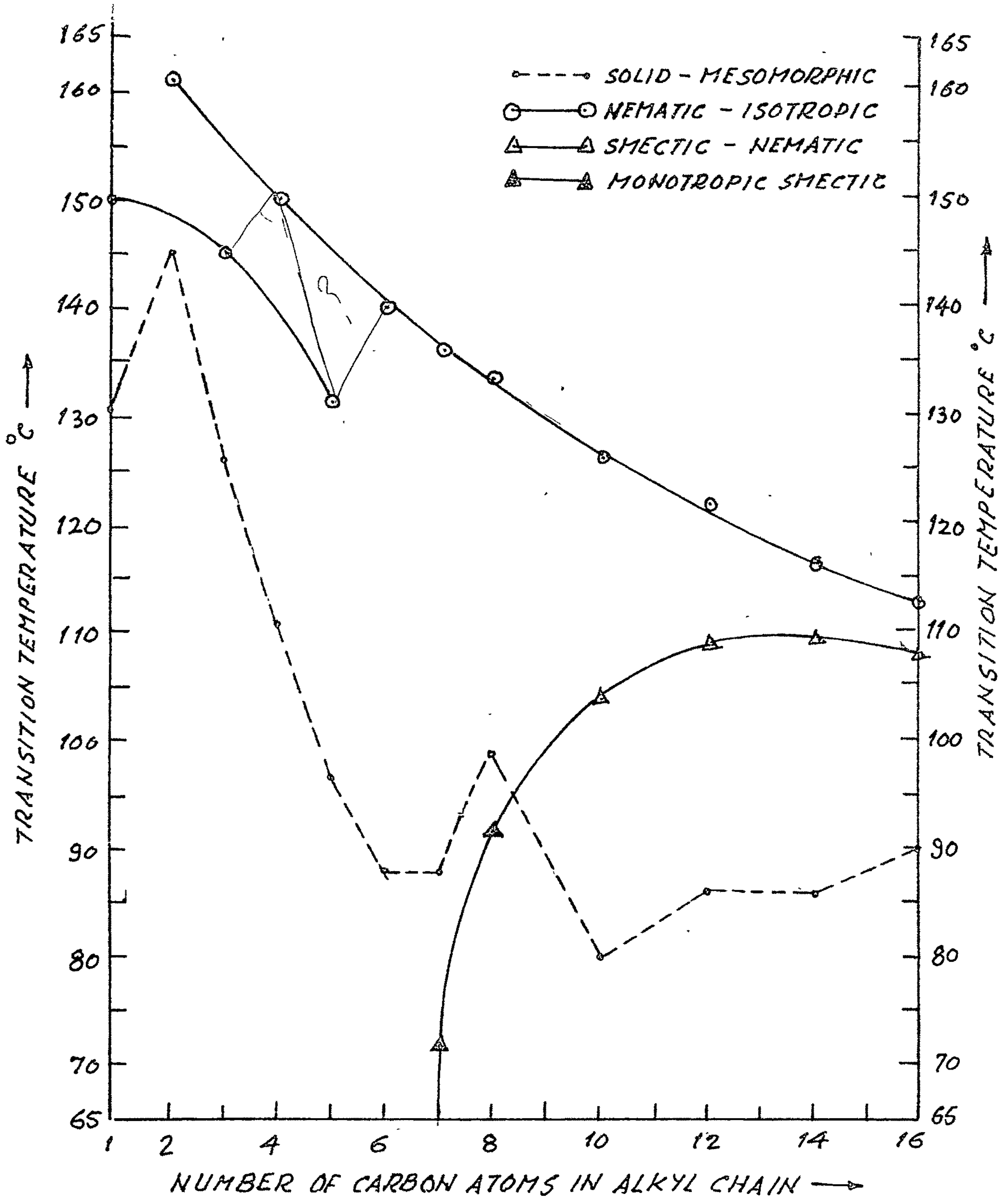

FIG. 6

Table 7

A-2 p-n-Propoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	(126)	127
Ethyl	-	125	144
Propyl	-	(127)	128
Butyl	-	110	137
Pentyl	-	102	124
Hexyl	-	98	130
Heptyl	(92)	94	127
Octyl	99	101.5	124
Decyl	78.5	102	116
Dodecyl	85	102	111
Tetradecyl	86	-	107
Hexadecyl	88	-	104

Value in the parenthesis indicates monotropy

SERIES A-2

p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

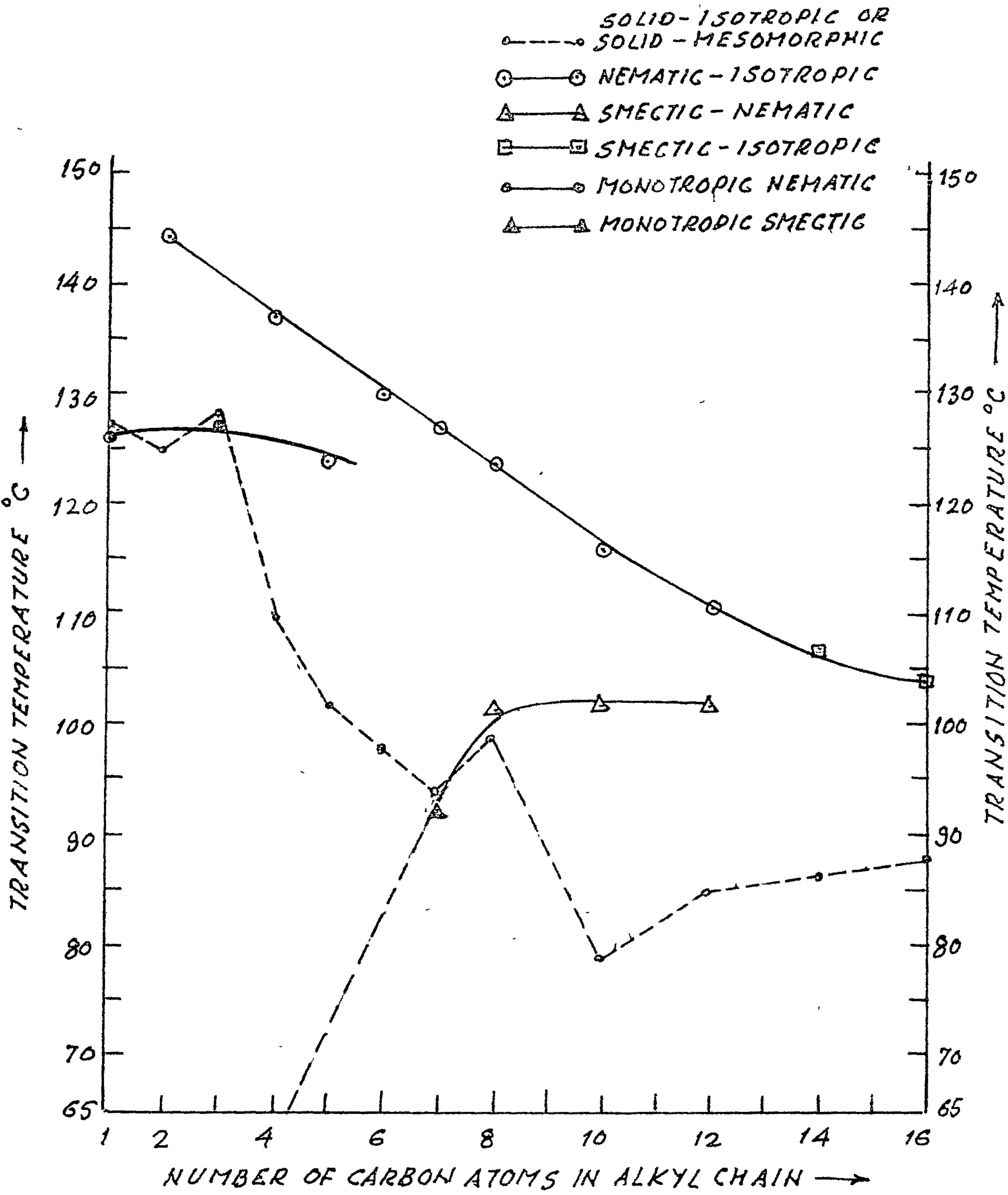

FIG. 7

Table 9

A-3 p-n-Butoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	95	132
Ethyl	-	109	146
Propyl	-	117	137
Butyl	-	117	141
Pentyl	-	111	138
Hexyl	-	105	133
Heptyl	-	103	127
Octyl	(94)	100	123
Decyl	83	107.5	115
Dodecyl	85	-	113
Tetradecyl	87	-	111
Hexadecyl	90	-	111

Value in the parenthesis indicates monotropy

Table 10

A-3 p-n-Butoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{20}H_{22}O_4$	73.62	6.75	73.78	6.56
Ethyl	$C_{21}H_{24}O_4$	74.12	7.06	73.90	6.86
Propyl	$C_{22}H_{26}O_4$	74.58	7.34	74.92	7.16
Butyl	$C_{23}H_{28}O_4$	75.00	7.61	75.36	7.75
Pentyl	$C_{24}H_{30}O_4$	75.39	7.85	75.53	7.56
Hexyl	$C_{25}H_{32}O_4$	75.76	8.08	75.50	8.31
Heptyl	$C_{26}H_{34}O_4$	76.10	8.29	75.90	8.48
Octyl	$C_{27}H_{36}O_4$	76.42	8.49	76.60	8.29
Decyl	$C_{29}H_{40}O_4$	76.99	8.85	76.87	8.39
Dodecyl	$C_{31}H_{44}O_4$	77.50	9.17	77.87	9.08
Tetradecyl	$C_{33}H_{48}O_4$	77.95	9.45	78.15	9.68
Hexadecyl	$C_{35}H_{52}O_4$	78.36	9.70	78.79	9.94

SERIES A-3

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

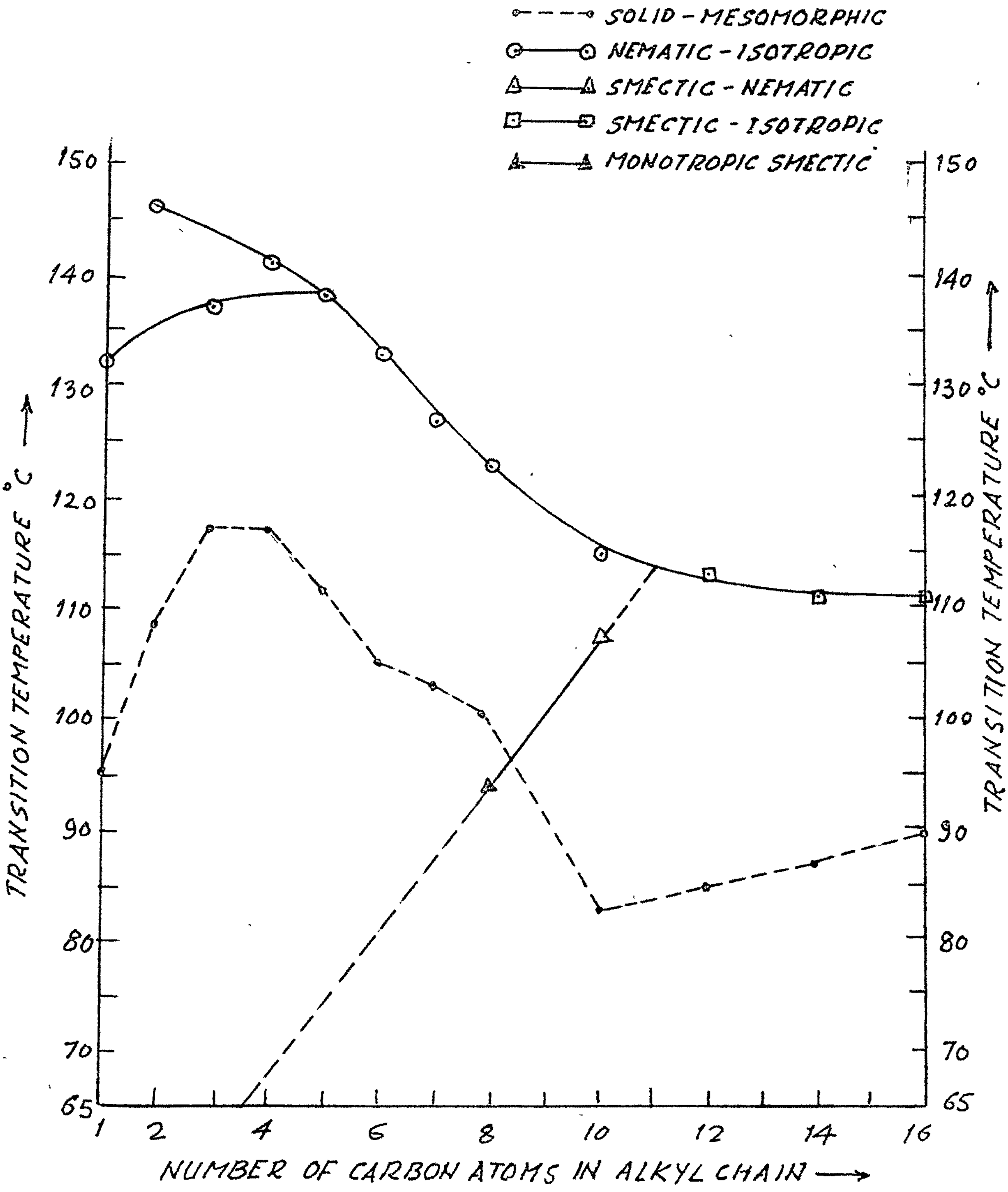

FIG. 8

Table 11

A-4 p-n-Amyloxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	82	127
Ethyl	-	91	135
Propyl	-	110	129
Butyl	-	111	135
Pentyl	-	105	127
Hexyl	-	97	131
Heptyl	(91.5)	95	125
Octyl	94	108	125
Decyl	82	109	117
Dodecyl	82	-	112
Tetradecyl	84	-	109
Hexadecyl	88	-	110

Value in the parenthesis indicates monotropy

Table 12

A-4 p-n-Amyloxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{21}H_{24}O_4$	74.12	7.06	74.03	7.41
Ethyl	$C_{22}H_{26}O_4$	74.58	7.34	74.75	7.15
Propyl	$C_{23}H_{28}O_4$	75.00	7.61	75.23	7.83
Butyl	$C_{24}H_{30}O_4$	75.39	7.85	75.26	7.75
Pentyl	$C_{25}H_{32}O_4$	75.76	8.08	75.36	8.26
Hexyl	$C_{26}H_{34}O_4$	76.10	8.29	75.93	8.09
Heptyl	$C_{27}H_{36}O_4$	76.42	8.49	76.92	8.67
Octyl	$C_{28}H_{38}O_4$	76.71	8.68	76.58	8.42
Decyl	$C_{30}H_{42}O_4$	77.25	9.01	77.19	9.31
Dodecyl	$C_{32}H_{46}O_4$	77.73	9.31	77.93	9.47
Tetradecyl	$C_{34}H_{50}O_4$	78.16	9.58	77.79	9.42
Hexadecyl	$C_{36}H_{54}O_4$	78.55	9.82	78.19	9.57

SERIES A-4

p-n-AMYLOXY PHENYL-p'-n-ALKOXY CINNAMATES

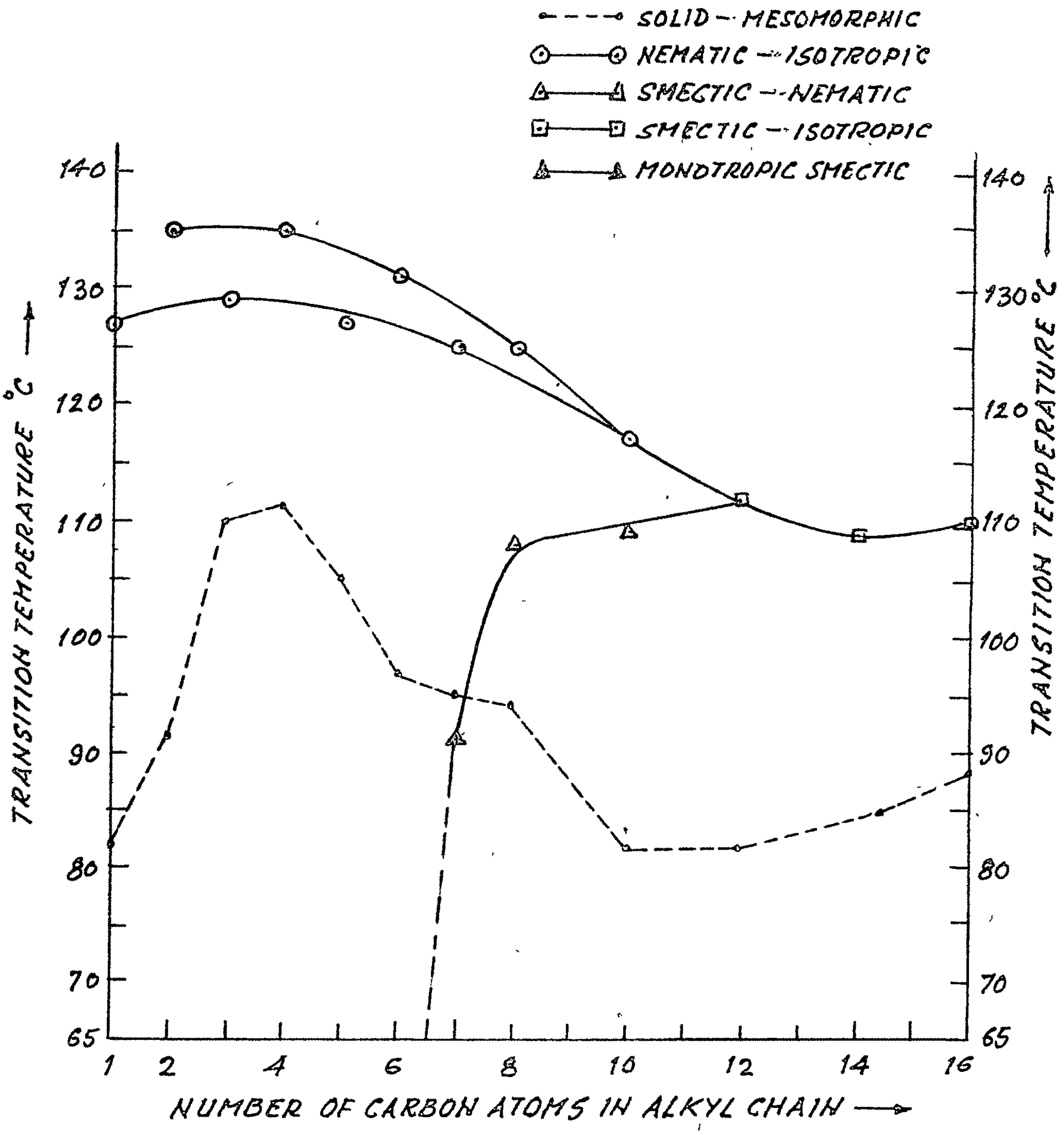

FIG. 9

Table 13

B-5 p-iso-Propoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	-	99
Ethyl	-	-	145
Propyl	-	(99)	109
Butyl	-	(109)	110
Pentyl	-	(98)	103
Hexyl	-	(103)	103
Heptyl	-	96	98.5
Octyl	82	87	99
Decyl	73	90	96
Dodecyl	84	-	94
Tetradecyl	83	-	91
Hexadecyl	82	-	89

Value in the parenthesis indicates monotropy

Table 14

B-5 p-iso-Propoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{19}H_{20}O_4$	73.08	6.41	72.88	6.67
Ethyl	$C_{20}H_{22}O_4$	73.62	6.75	73.95	6.49
Propyl	$C_{21}H_{24}O_4$	74.12	7.06	74.08	7.29
Butyl	$C_{22}H_{26}O_4$	74.58	7.34	74.79	7.22
Pentyl	$C_{23}H_{28}O_4$	75.00	7.61	75.25	7.58
Hexyl	$C_{24}H_{30}O_4$	75.39	7.85	75.50	7.60
Heptyl	$C_{25}H_{32}O_4$	75.76	8.08	75.92	8.00
Octyl	$C_{26}H_{34}O_4$	76.10	8.29	76.34	8.08
Decyl	$C_{28}H_{38}O_4$	76.71	8.68	76.51	8.98
Dodecyl	$C_{30}H_{42}O_4$	77.25	9.01	77.68	9.25
Tetradecyl	$C_{32}H_{46}O_4$	77.73	9.31	77.60	9.25
Hexadecyl	$C_{34}H_{50}O_4$	78.16	9.58	78.38	9.18

SERIES B-5

p- iso-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

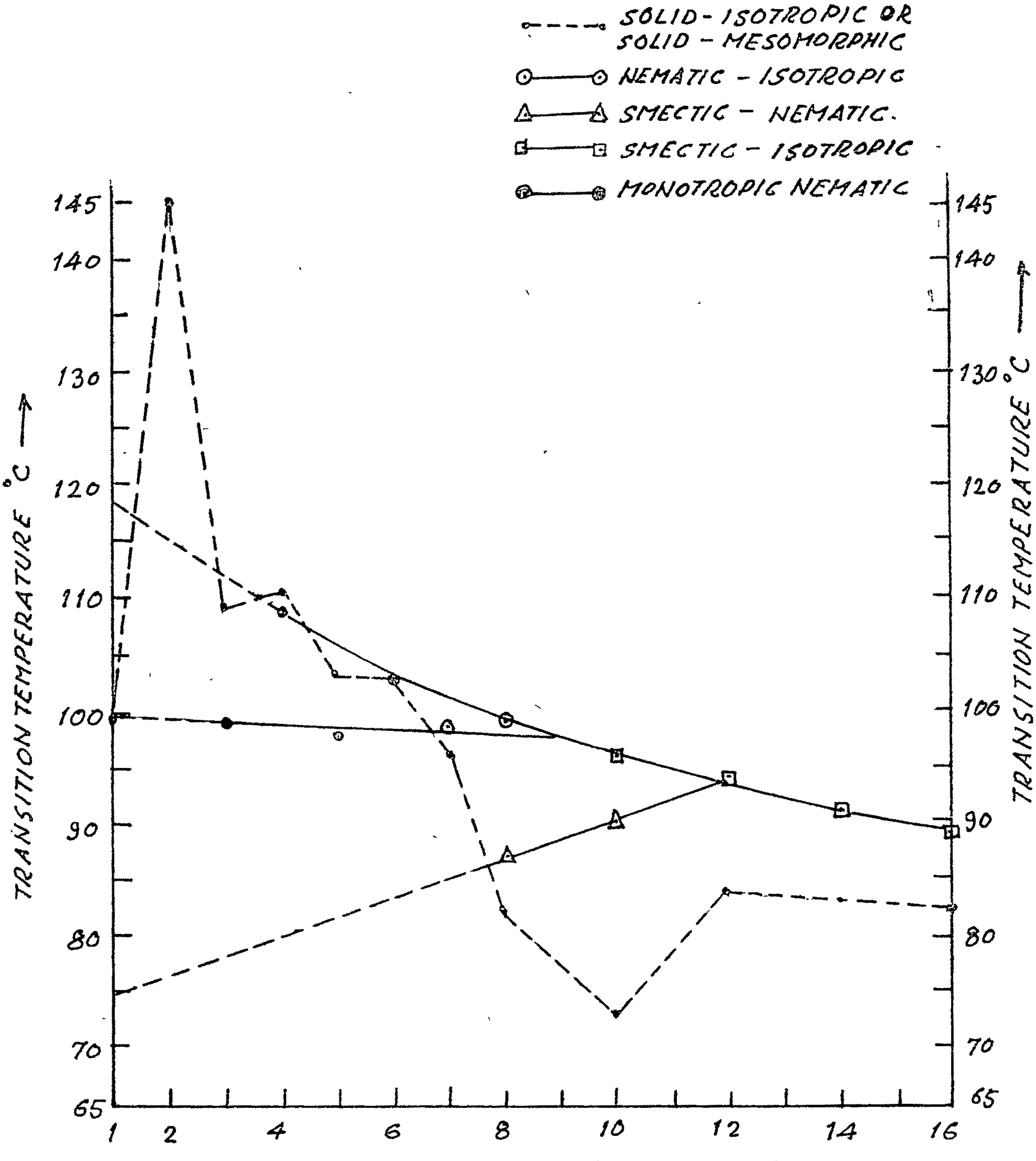

FIG.10

Table 15

B-6 p-iso-Butoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	-	128
Ethyl	-	-	139
Propyl	-	-	128
Butyl	-	(112)	115
Pentyl	-	(105)	109
Hexyl	-	(105)	110
Heptyl	-	108	115
Octyl	(99.5)	100	109
Decyl	92	-	103
Dodecyl	88	-	102
Tetradecyl	92	-	101
Hexadecyl	92	-	100

Value in the parenthesis indicates monotropy

Table 16

B-6 p-iso-Butoxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{20}H_{22}O_4$	73.62	6.75	73.56	6.97
Ethyl	$C_{21}H_{24}O_4$	74.12	7.06	74.36	7.12
Propyl	$C_{22}H_{26}O_4$	74.58	7.34	74.39	7.20
Butyl	$C_{23}H_{28}O_4$	75.00	7.61	74.86	7.83
Pentyl	$C_{24}H_{30}O_4$	75.39	7.85	75.50	7.65
Hexyl	$C_{25}H_{32}O_4$	75.76	8.08	75.66	8.27
Heptyl	$C_{26}H_{34}O_4$	76.10	8.29	75.87	8.03
Octyl	$C_{27}H_{36}O_4$	76.42	8.49	76.08	8.81
Decyl	$C_{29}H_{40}O_4$	76.99	8.85	76.93	8.65
Dodecyl	$C_{31}H_{44}O_4$	77.50	9.17	77.01	9.09
Tetradecyl	$C_{33}H_{48}O_4$	77.95	9.45	78.23	9.62
Hexadecyl	$C_{35}H_{52}O_4$	78.36	9.70	78.83	9.81

SERIES B-6

p-iso-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

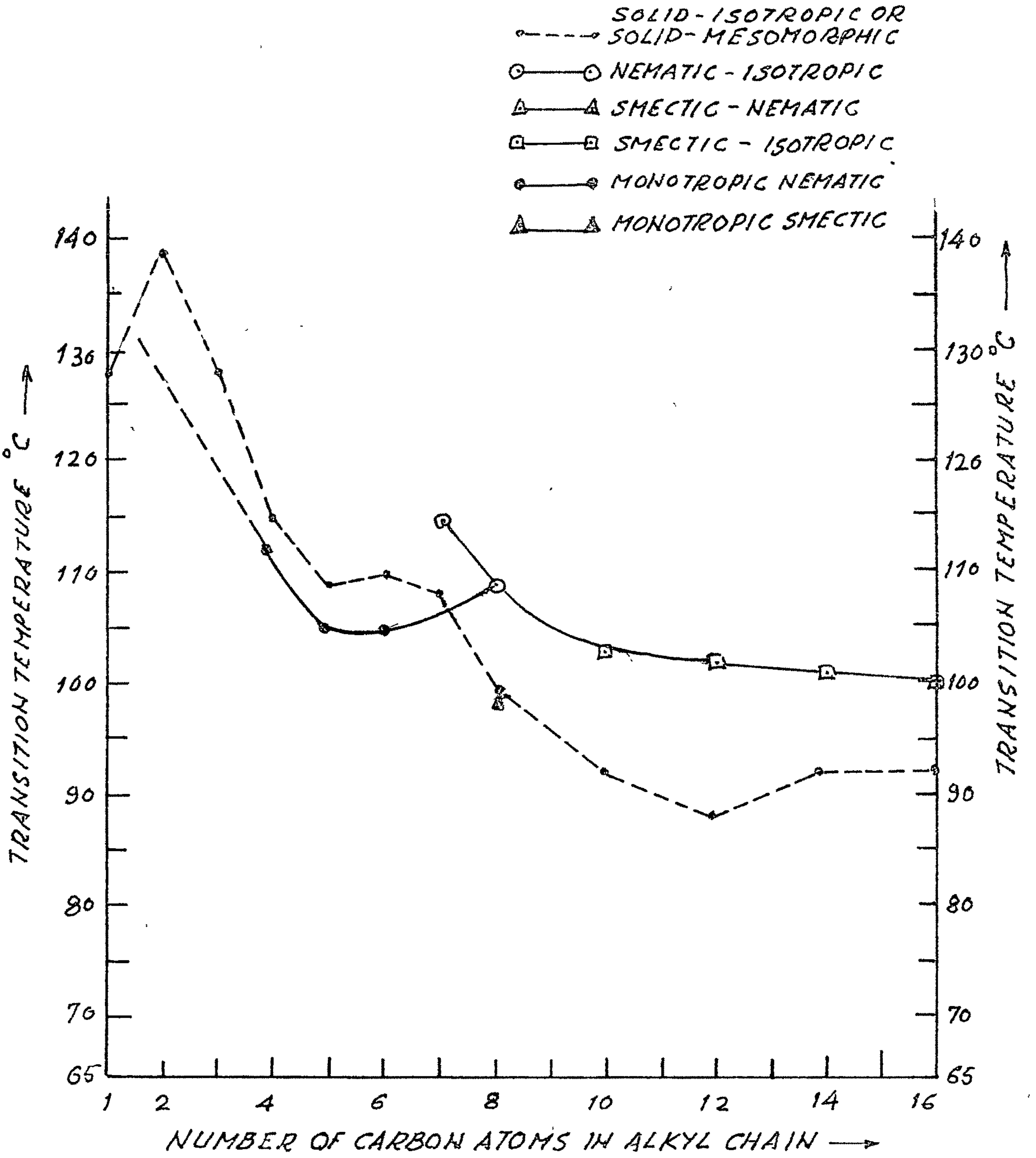

FIG. 11

Table 17

B-7 p-iso-Amyloxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	112	114
Ethyl	-	117	134
Propyl	-	113	117
Butyl	-	109	125
Pentyl	-	101	117
Hexyl	(95)	105	119
Heptyl	92	95	115
Octyl	89	98.5	112
Decyl	76	102	106
Dodecyl	71	-	105
Tetradecyl	70	-	105
Hexadecyl	69	-	106

Value in the parenthesis indicates monotropy

Table 18

B-7 p-iso-Amyloxyphenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{21}H_{24}O_4$	74.12	7.06	73.90	7.23
Ethyl	$C_{22}H_{26}O_4$	74.58	7.34	74.38	7.14
Propyl	$C_{23}H_{28}O_4$	75.00	7.61	74.80	7.87
Butyl	$C_{24}H_{30}O_4$	75.39	7.85	75.50	8.02
Pentyl	$C_{25}H_{32}O_4$	75.76	8.08	75.59	7.92
Hexyl	$C_{26}H_{34}O_4$	76.10	8.29	75.97	8.09
Heptyl	$C_{27}H_{36}O_4$	76.42	8.49	76.68	8.75
Octyl	$C_{28}H_{38}O_4$	76.71	8.68	76.32	8.61
Decyl	$C_{30}H_{42}O_4$	77.25	9.01	77.15	9.32
Dodecyl	$C_{32}H_{46}O_4$	77.73	9.31	77,43	9.21
Tetradecyl	$C_{34}H_{50}O_4$	78.16	9.58	77.98	9.92
Hexadecyl	$C_{36}H_{54}O_4$	78.55	9.82	78.98	9.71

SERIES B-7

p-iso-AMYLOXYPHENYL-p'-n-ALKOXY CINNAMATES

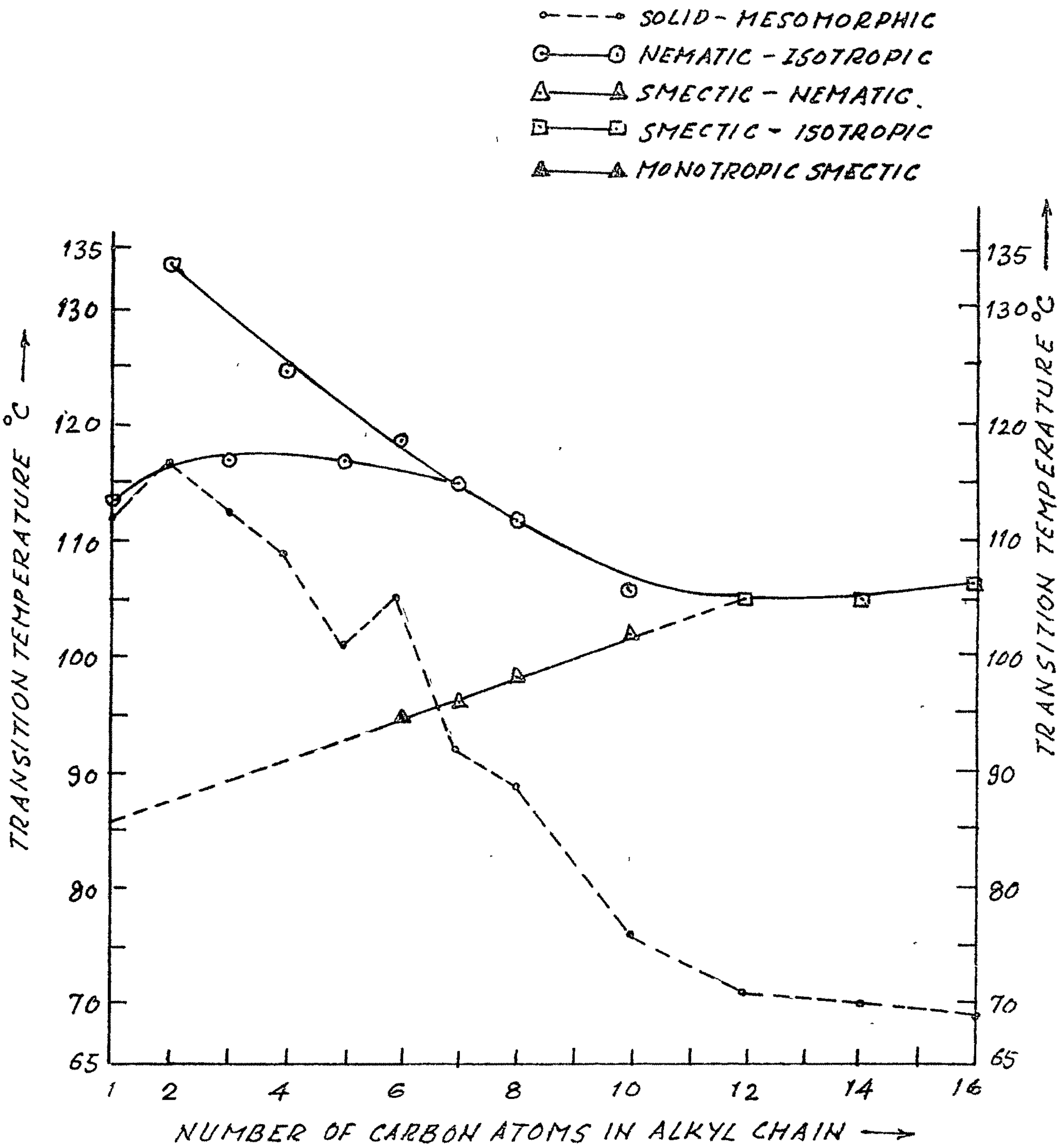

FIG. 12

Table 19

C-8 m-Chlorophenyl-p'-n-alkoxycinnamates

n-Alkyl group	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	-	-	100
Ethyl	-	-	116
Propyl	-	-	67
Butyl	-	-	57
Pentyl	-	-	82
Hexyl	-	-	73
Heptyl	-	-	54
Octyl	-	-	56
Decyl	-	-	55
Dodecyl	-	-	63
Tetradecyl	-	-	69
Hexadecyl	-	-	75

Table 20

C-8 m-Chlorophenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{16}H_{13}O_3Cl$	66.55	4.51	66.27	4.25
Ethyl	$C_{17}H_{15}O_3Cl$	67.44	4.96	67.68	5.01
Propyl	$C_{18}H_{17}O_3Cl$	68.25	5.37	68.42	5.09
Butyl	$C_{19}H_{19}O_3Cl$	68.99	5.75	68.89	5.91
Pentyl	$C_{20}H_{21}O_3Cl$	69.67	6.10	69.92	6.22
Hexyl	$C_{21}H_{23}O_3Cl$	70.29	6.42	70.36	6.50
Heptyl	$C_{22}H_{25}O_3Cl$	70.87	6.71	70.70	6.91
Octyl	$C_{23}H_{27}O_3Cl$	71.41	6.99	71.78	7.16
Decyl	$C_{25}H_{31}O_3Cl$	72.38	7.48	72.59	7.62
Dodecyl	$C_{27}H_{35}O_3Cl$	73.22	7.91	73.58	8.08
Tetradecyl	$C_{29}H_{39}O_3Cl$	73.96	8.29	74.05	8.63
Hexadecyl	$C_{31}H_{43}O_3Cl$	74.62	8.63	74.98	8.42

SERIES C-8

m-CHLOROPHENYL-p'-n-ALKOXY CINNAMATES

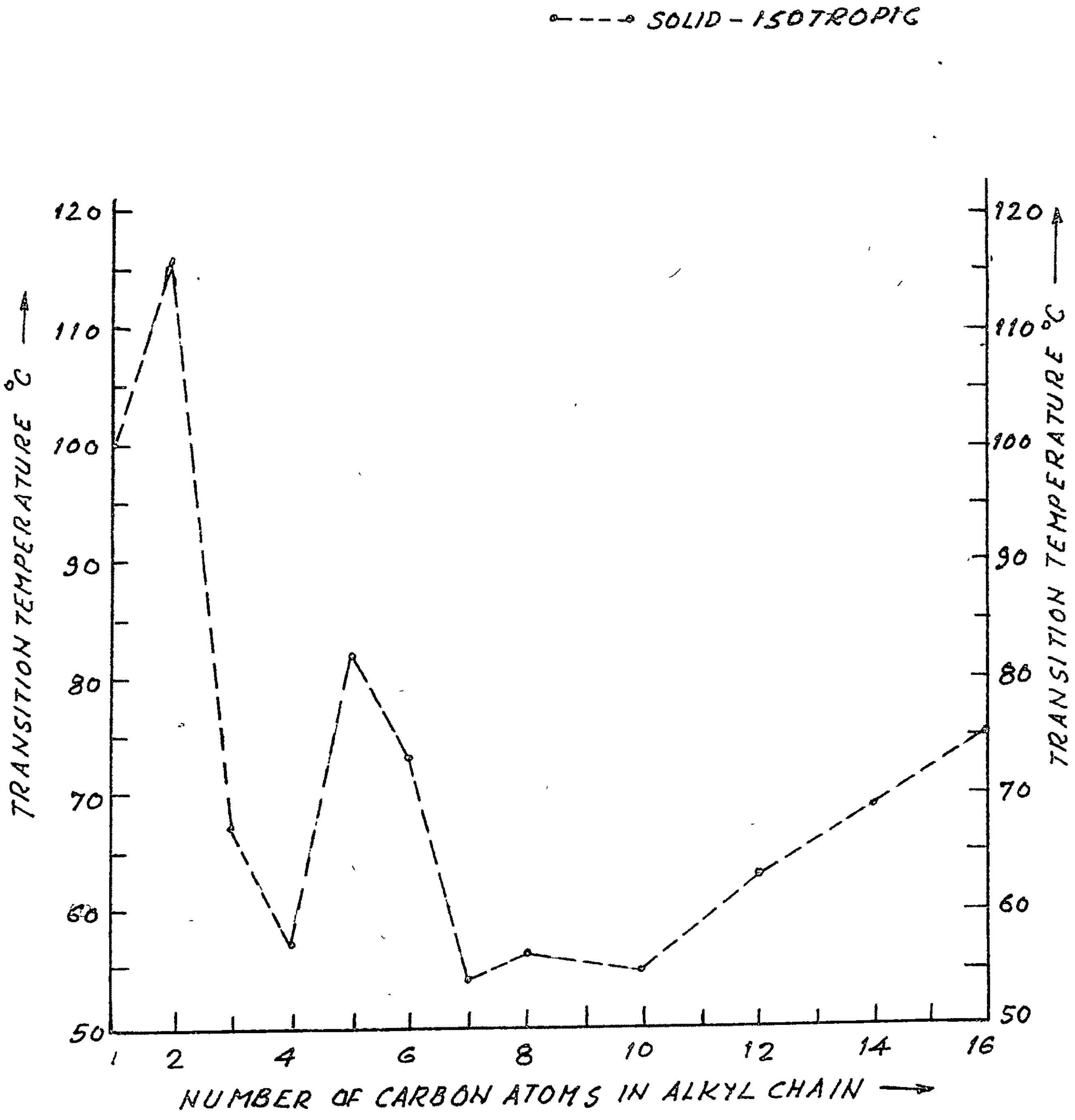

FIG. 13

Table 22

C-9 O-Chlorophenyl-p'-n-alkoxycinnamates

n-Alkyl group	Molecular formula	% Required		% Found	
		C	H	C	H
Methyl	$C_{16}H_{13}O_3Cl$	66.55	4.51	66.15	4.36
Ethyl	$C_{17}H_{15}O_3Cl$	67.44	4.96	67.60	4.89
Propyl	$C_{18}H_{17}O_3Cl$	68.25	5.37	68.42	5.50
Butyl	$C_{19}H_{19}O_3Cl$	68.99	5.75	69.15	5.69
Pentyl	$C_{20}H_{21}O_3Cl$	69.67	6.10	69.22	5.99
Hexyl	$C_{21}H_{23}O_3Cl$	70.29	6.42	70.19	6.56
Heptyl	$C_{22}H_{25}O_3Cl$	70.87	6.71	70.99	6.75
Octyl	$C_{23}H_{27}O_3Cl$	71.41	6.99	71.71	7.25
Decyl	$C_{25}H_{31}O_3Cl$	72.38	7.48	72.00	7.39
Dodecyl	$C_{27}H_{35}O_3Cl$	73.22	7.91	73.40	8.01
Tetradecyl	$C_{29}H_{39}O_3Cl$	73.96	8.29	74.32	8.46
Hexadecyl	$C_{31}H_{43}O_3Cl$	74.62	8.63	75.08	8.48

SERIES C-9

O-CHLOROPHENYL-p'-n-ALKOXY CINNAMATES

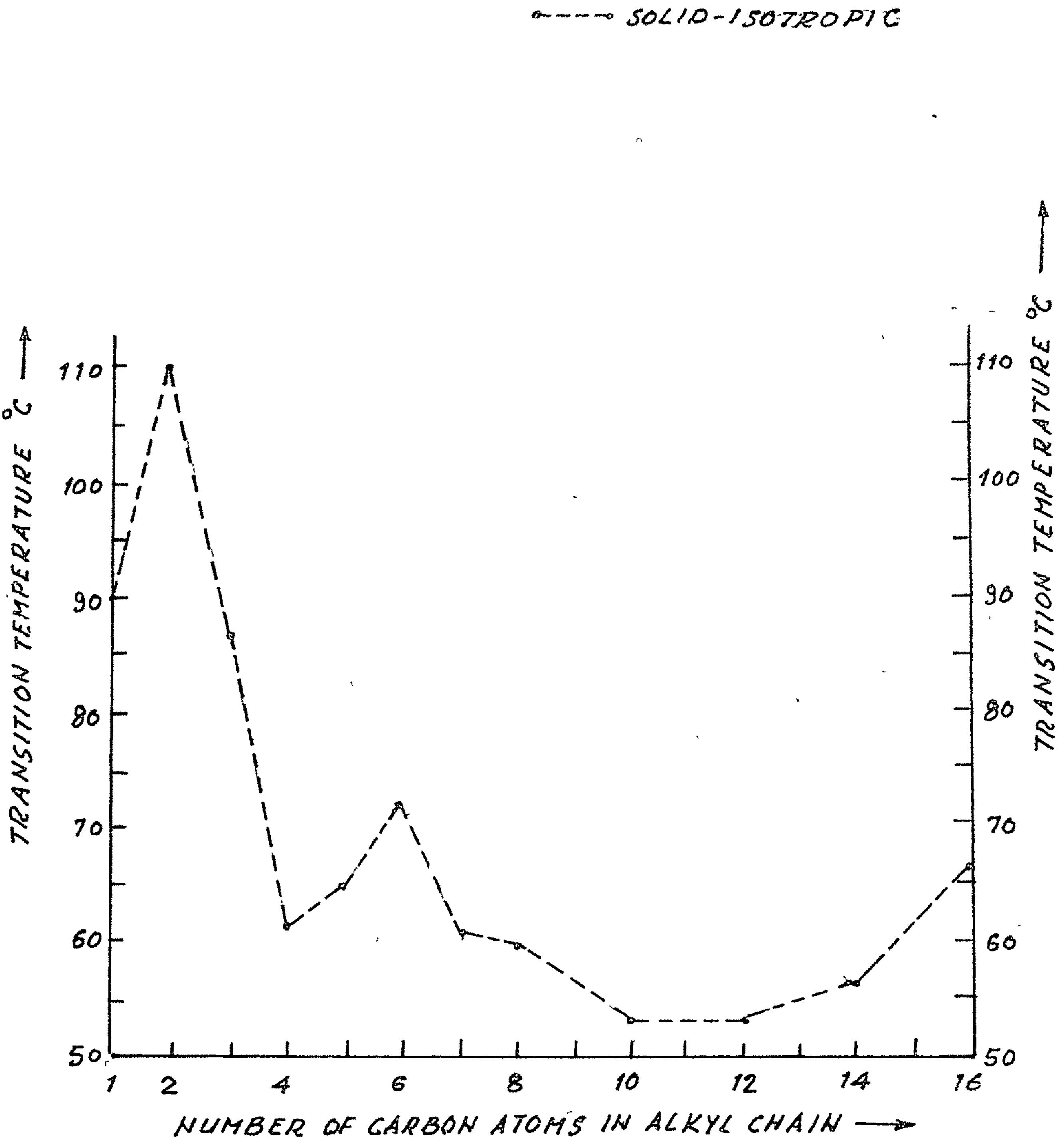

FIG. 14

just touches the melt. The melt slowly forms a thin layer between the slide and the coverslip, when the coverslip is further moved into the melt as required. When a complete thin layer is formed the slide is allowed to cool, (ii) the compound is heated up to the isotropic liquid point, then a coverslip is put in such a way that it just touches the melt. Push the coverslip into the melt slowly so that a complete thin layer is formed and then allowed to cool off,(iii) A few drops of the solution of the substance in a suitable solvent are placed on a slide and a coverslip is placed over it after the solvent is evaporated. By and large the slides are prepared by the second method. Meticulous care is taken while preparing a slide in order to get an almost uniform spread.

The prepared slide is then placed over the heating stage of the microscope. The switch is put on and the sample is heated at a slow rate, say 1°C per minute. The changing textures over the temperature ranges are carefully observed and characteristics of the phases are noted.

Accuracy of the heating device is checked by taking melting points or transition temperatures of very pure but known substances like benzoic acid, α -naphthol, succinic acid, p-azoxyanisoles, p-propionoxybenzal-p-phenetidine,p-anisal, p-phenetidine, p-azoxyphenetole etc.

Approximate transitions are initially determined by heating pretty fast, say about 5°C per minute and allowed to cool down until stable solid reappears. Once again the slide is heated at a highly regulated rate of say 1°C per minute from about 5°C below the expected transition points in order to measure the transition points accurately. A meticulous observation of the transitions, as the appearance of focal conic, plane, homeotropic and threaded structures of smectic and nematic phases under polarized light, ensured a great deal of accuracy. Formation of isotropic liquid is clearly marked by the field of vision becoming extinct in polarized light.

Appearance of focal conic texture with disappearance of cleavage lines of solid structure on heating is taken as solid-smectic transition. In order to confirm this change the slide was disturbed with the help of a spatula. The disturbed smectic texture can be seen indicating that it is not solid and that the transition has actually taken place. Solid-nematic change is observed on heating with the appearance of threaded texture sharply at a definite temperature. All enantiotropic transitions are clearly detected on cooling the isotropic liquid; the reverse transitions take place sharply at the same temperature or within ± 0.2 to ± 0.5°C. Separation of small droplets from the isotropic liquids, which coalesce to give rise to a threaded region - an unfailing characteristic of the nematic phase indicates isotropic - nematic transition. Isotropic-smectic transition is marked by appearance of batonnets which coalesce to form fine mosaic of focal conic pattern. A sharp variation in the texture from focal conic to threated texture while heating and exactly the reversed sequence on cooling clearly marks smectic-nematic change. The homeotropic textures of the smectic and nematic variety can easily be identified by disturbing the coverslip in almost extinct field of vision and observing the spark of light.

Monotropic transitions are determined by carefully observing the isotropic liquid as it cools slowly until batonnets of smectic phase or droplets of nematic phase appear. While observing monotropic phases, it was possible to raise temperature before crystallization occured, which caused disappearance of the mesophase at the same temperature at which it had appeared on supercooling. This type of operation confirmed not only the monotropic change but also the temperature at which it occured. All the compounds under study were observed continuously under polarizing microscope from their solid state to isotropic liquid condition on heating and from isotropic liquid to solid state on cooling ensuring confirmation of all the transitions and making it pretty sure that no transition gets escaped unnoticed.

All observations were repeated several times, in case of any doubt, the compounds were prepared and/or purified again by repeating crystallizations and then subjected to study under microscope afresh.

3.c. DSC study:

Du Pont 910 Differential Scanning Calorimeter was used for this study. Du Pont DSC cell is a plug-in-module for the Du Pont 990 Thermal Analyser. It is unique in that it makes use of a constantan disc as the primary means of heat transfer to the sample and reference positions and as an element of the temperature measuring thermoelectric junctions.

Thermal analysis (TA) in its broadest sense is the measurement of changes in physical or chemical properties of materials as a function of temperature. Regardless of what temperature dependent variable is under measurement (energy, weight, dimension etc.), the TA instruments have certain elements in common. The sample is placed in an environment, the temperature of which is regulated by some form of a temperature programmer. Changes in sample are monitored by an appropriate transducer which produces an electrical output, the analog of the chemical or physical change. The output is amplified electronically and applied to the read out device usually a potentiometric recorder.

DSC is a technique in which the difference in temperature (ΔT) between a sample and an inert reference material is recorded as a function of temperature (usually sample temperature). The area under the output curve is directly proportional to the rate of heat transfer ($\frac{da}{dt}$) at any given time. Two factors essential to the generation of quantitative energy data are (1) a controlled heat path into the sample and reference materials and (2) location of the temperature sensors external to the sample.

A silver heating block, a resistive wound heater and a closely coupled platinel control thermocouple are used to control the cell temperature. The block temperature is monitored by the control thermocouple and the appropriate amount of power is supplied to the heater as determined by the difference of signal between the control thermocouple and output of the 990 programmer. Heat from the block then rapidly flows through the constantan disc toward the sample and reference platforms. The primary means of heat transfer is through the disc, although some heat is transferred from the lid and walls of the cell through the atmosphere.

Temperature at the raised sample and reference platforms are monitored by chromel constantan thermocouples formed by the junction of the constantan disc with a chromel wire at each platform position. These junctions are centered on each platform. The difference signal between these two thermocouple junctions is fed to the amplifier in the 990 cell base module and then monitored on the Y-axis of the 990 x-y recorder. The sample platform also has an alumel-lead wire forming a chromel-alumel thermocouple junction. The output from this thermocouple is monitored on the 'T' axis of 990 x-y recorder after suitable cold junction compensation. Thus the Δq signal is determined by chromel-constantan thermocouple and the sample temperature is measured with a chromel-alumel thermocouple. A dummy alumel-wire is also welded to the reference platform for thermal balance.

Purge gas (nitrogen) is admitted to the sample chamber through an orifice in one block wall positioned midway between the two raised platforms on the left. The purge gas enters the 990 cell base module at the rear purge connection, passes into the DSC cell and preheated by circulation through the block before entering the sample chamber at block temperature. The best atmosphere exchange can be obtained when open or uncrimped sample pans are used. The vacuum and cool parts on the 990 cell base lead into opening in the DSC cell, although not directly into chamber.

The pan containing sample is placed on the forward raised platform and an empty reference pan (usually no additional inert material is needed) is placed on the rear raised platform. Since the mode of heat transfer is reproducible for a given atmosphere and the temperature transducer is not in the sample, the area under the peak (on a time-base plot) is proportional to the energy involved in the transition and the mass of sample.

The baseline of the DSC cell is very reproducible (empty pan vs empty pan) and can be compensated to obtain a level baseline over the temperature range of the cell. Adjustment is provided by the base-line slope control of the 990 cell base. Once optimum compensation is obtained, it should hold over the life of the cell.

Specifications of the Cell (DSC):

Temperature range : Room temperature to 600°C. Cooling accessory provides quench cooling to -180°C and programmed cooling to -120°C.

Cooling rate : 10°C/min

Sample Size : 0.1 mg to 100 mg

Sample pans : Aluminium open or hermetically sealed to three internal atmospheres.

Atmosphere : Atmospheric to 2 Torr, preheated dynamic gas purge (in excess of 100 ml/min.)

Cell volume : 2 ml

Temperature repeatability : ± 1°C

Differential thermocouple : Chromel-constantan

Sample thermocouple : Chromel-alumel

Control Thermocouple : Platinel

Calorimetric Sensitivity : 0.05 to 50 (mcal/sec/in)

Calorimetric precision : ± 1 % (based on metal samples)

Calorimetric Measurement:

Programming was started well below the onset temperature of the transition to be measured. This allowed the heating rate to stabilize at the set rate and permitted the sample and reference platforms to equilibrate. At a programming rate of 10°C/min, at least 20°C was allowed. For this stabilization other programming rates require proportionate allowances.

To reach the required starting temperature the following was meticulously observed:

(i) The required temperature on the starting temperature dial was fixed.

(ii) The program button was then pushed. The DSC cell heated at full voltage and the programmer was step up and held isothermally at the desired starting temperature.

(iii) When the programmer reached the starting temperature, the programme rate switch was checked. The limit temperature and mode was set as desired.

(iv) The heat or cool button was then pushed. Sample temperature was displayed on the y-axis.

Δ H Calculations using T-axis in Time Base:

The peak area was used to calculate Δ H, the heat of fusion, by substitution into the equation:

SERIES - A-1

p-ETHOXY PHENYL-p'-n-ALKOXY CINNAMATES

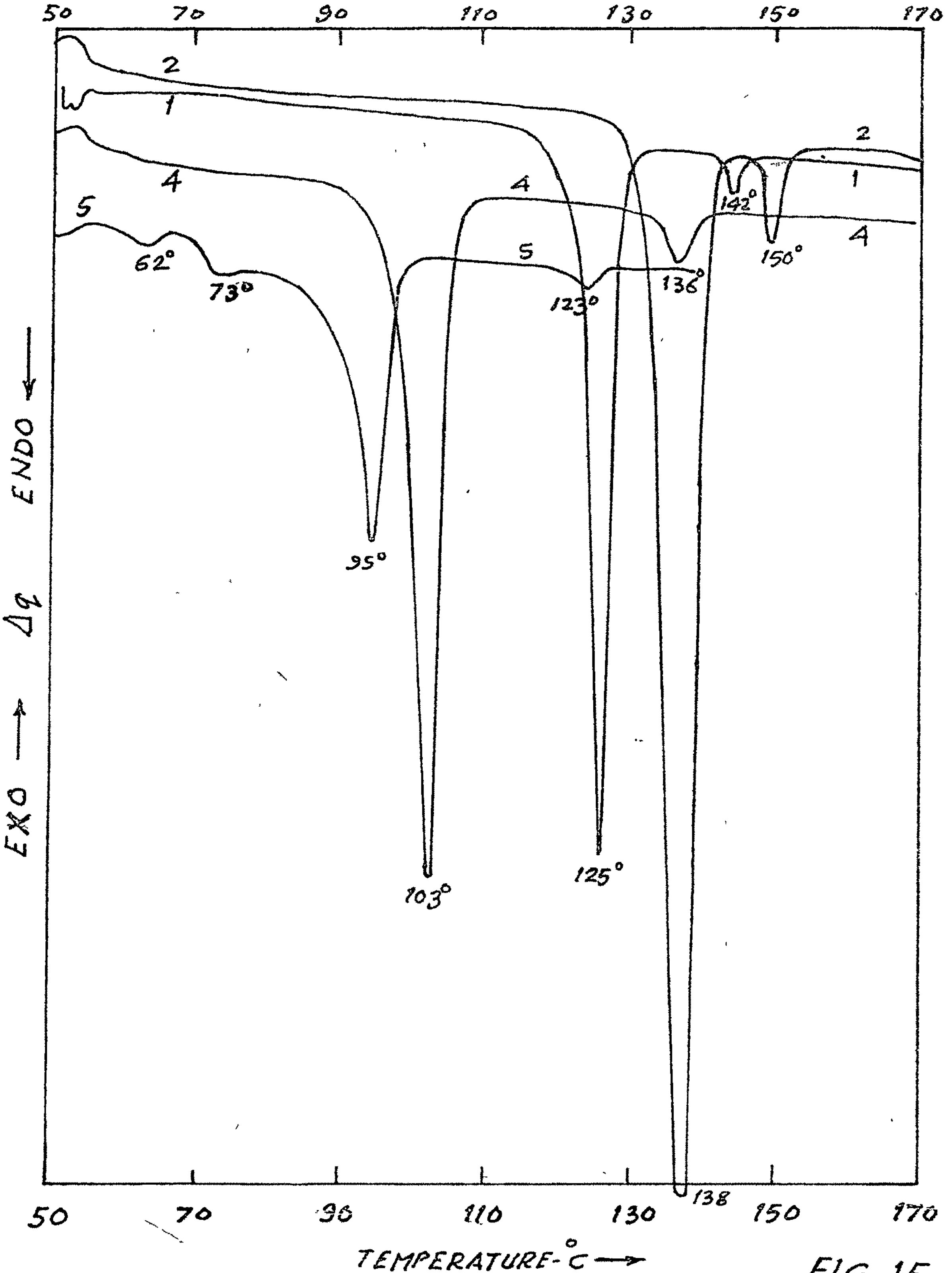

FIG. 15

SERIES - A-1

p-ETHOXY PHENYL-p'-n-ALKOXY CINNAMATES

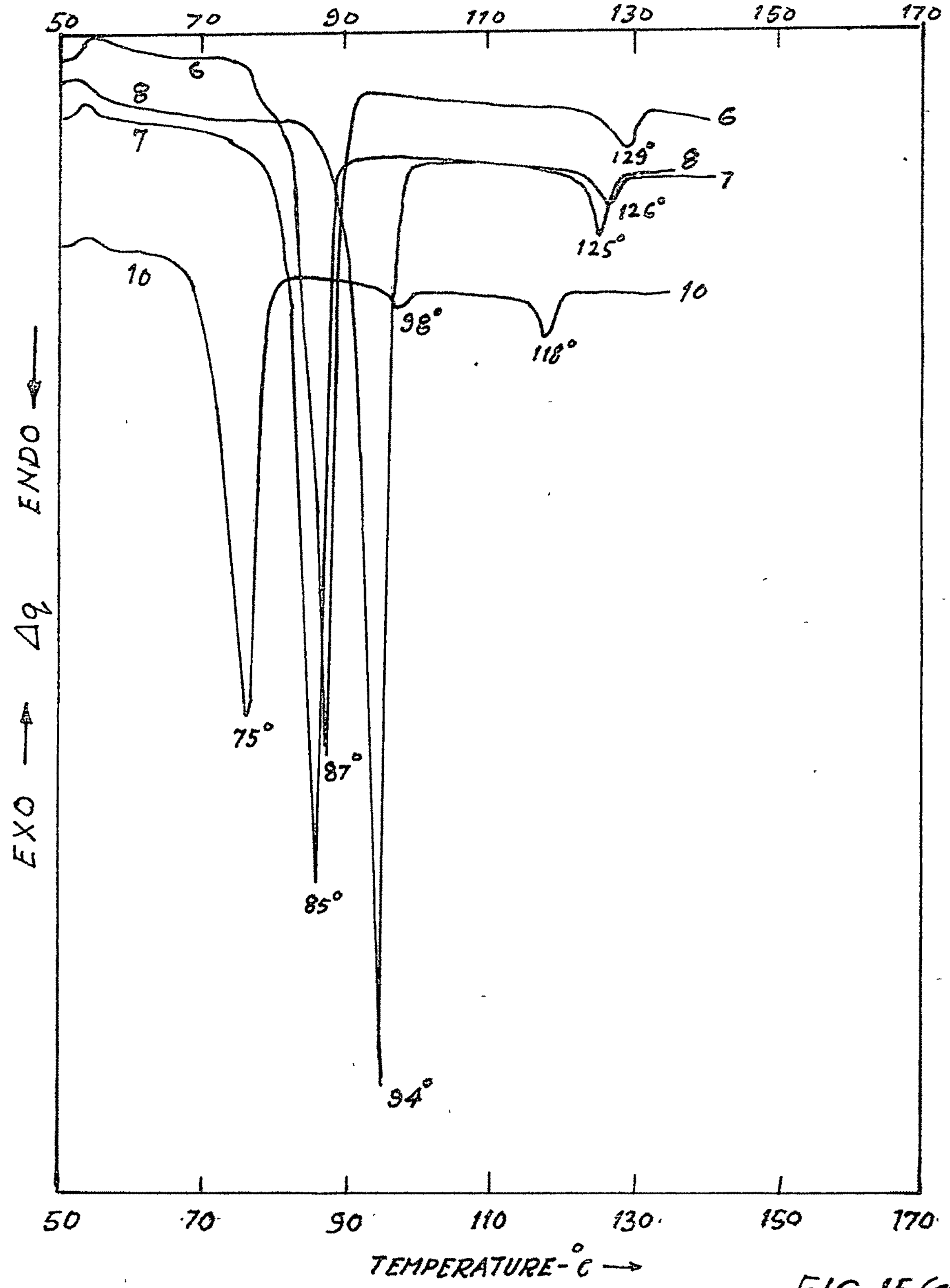

FIG. 15 (CONTD.)

SERIES A-1

p-ETHOXYPHENYL-p'-n-ALKOXY CINNAMATES

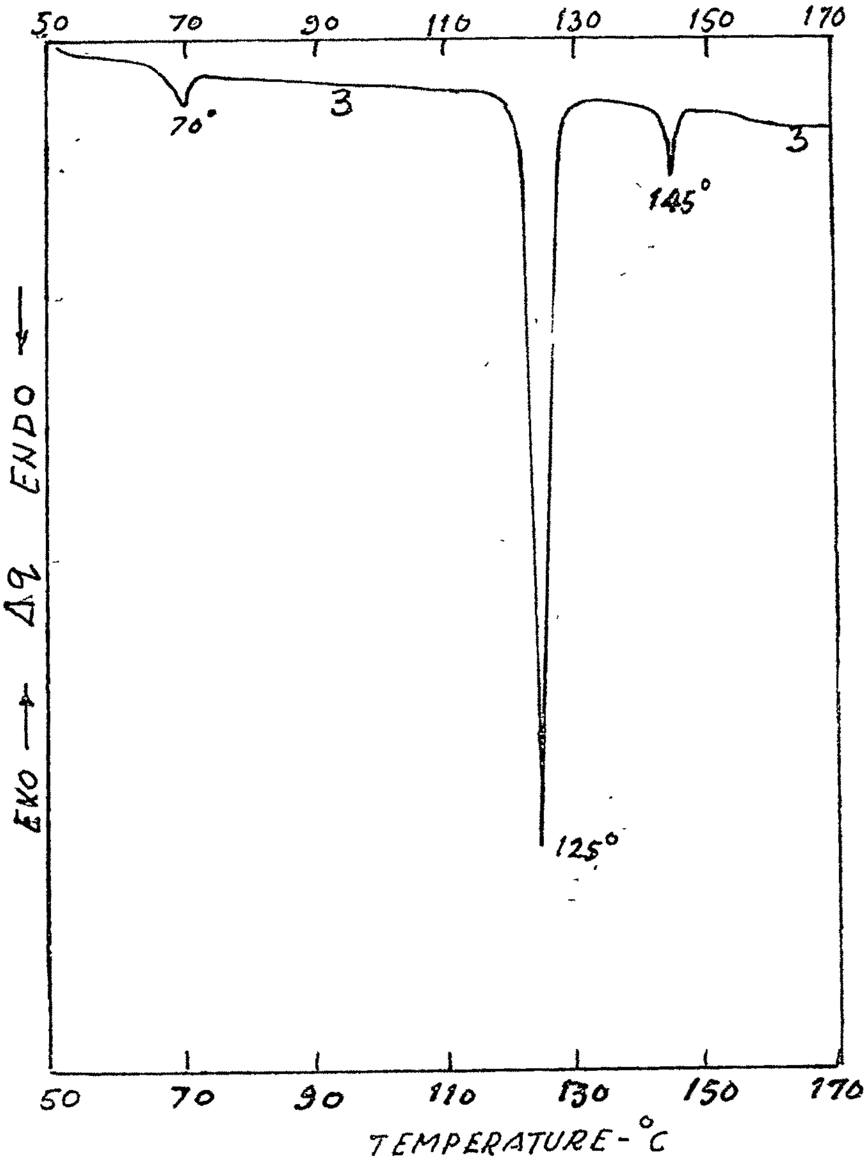

FIG. 15 (CONTD.)

SERIES A-2

p-n-PROPOXY PHENYL-p'-n-ALKOXY CINNAMATES

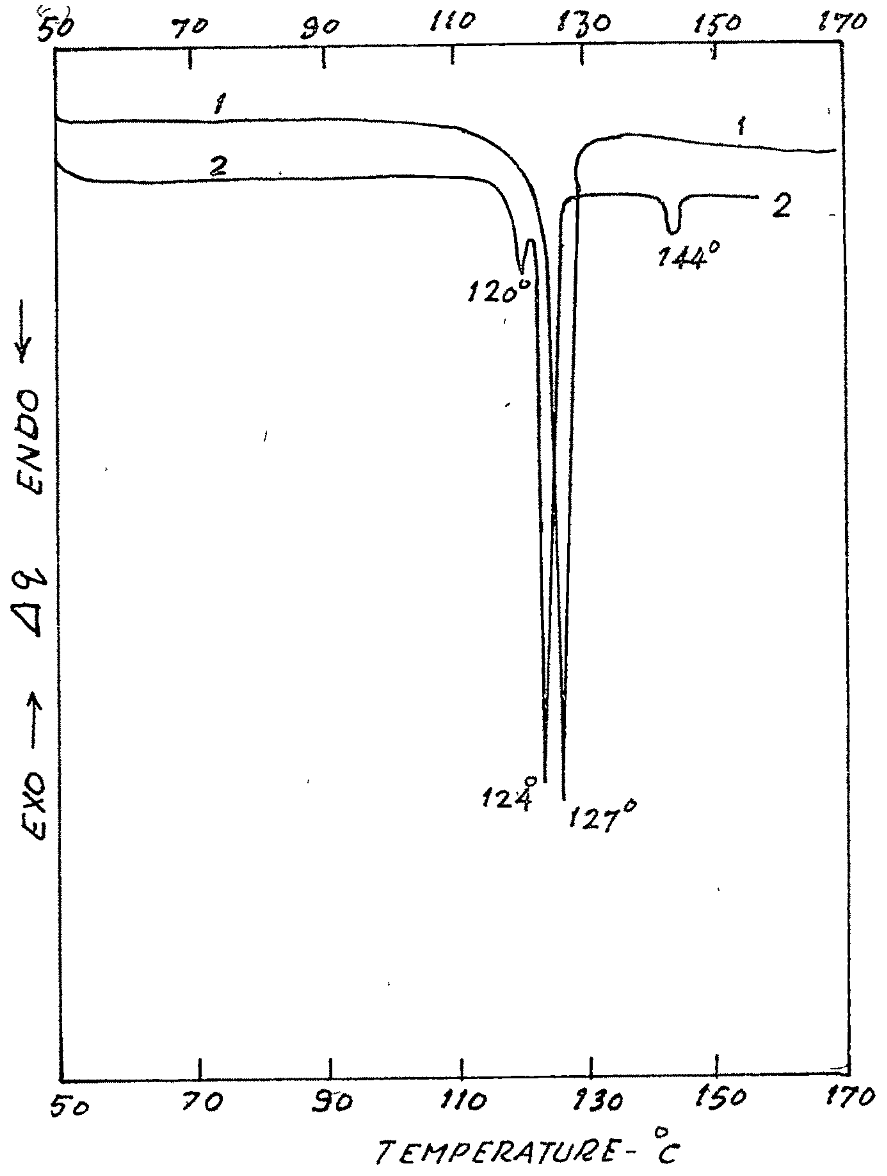

FIG. 16

SERIES A-2

p-n-PROPOXY PHENYL-p'-n-ALKOXY CINNAMATES

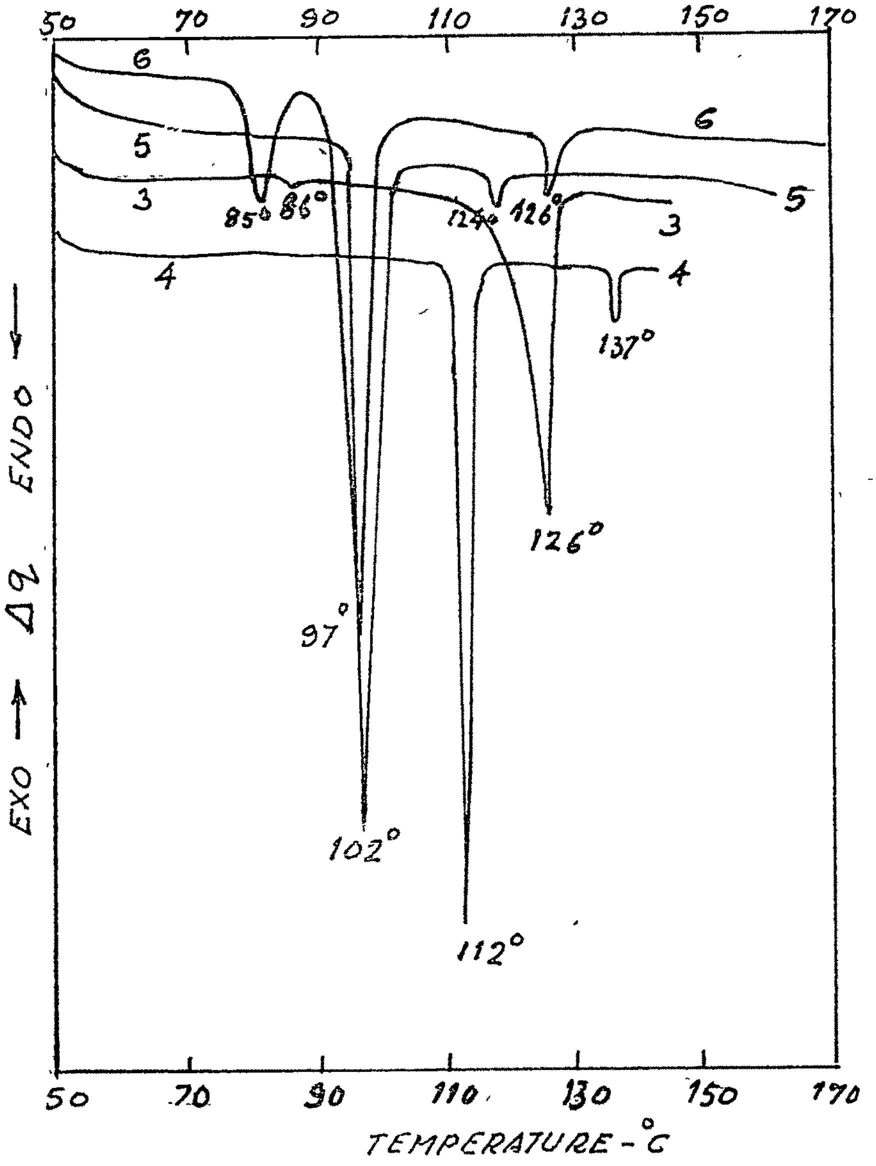

FIG. 16 (CONTD.)

SERIES - A-2

p-n-PROPOXYPHENYL-p'-n-ALKOXY CINNAMATES

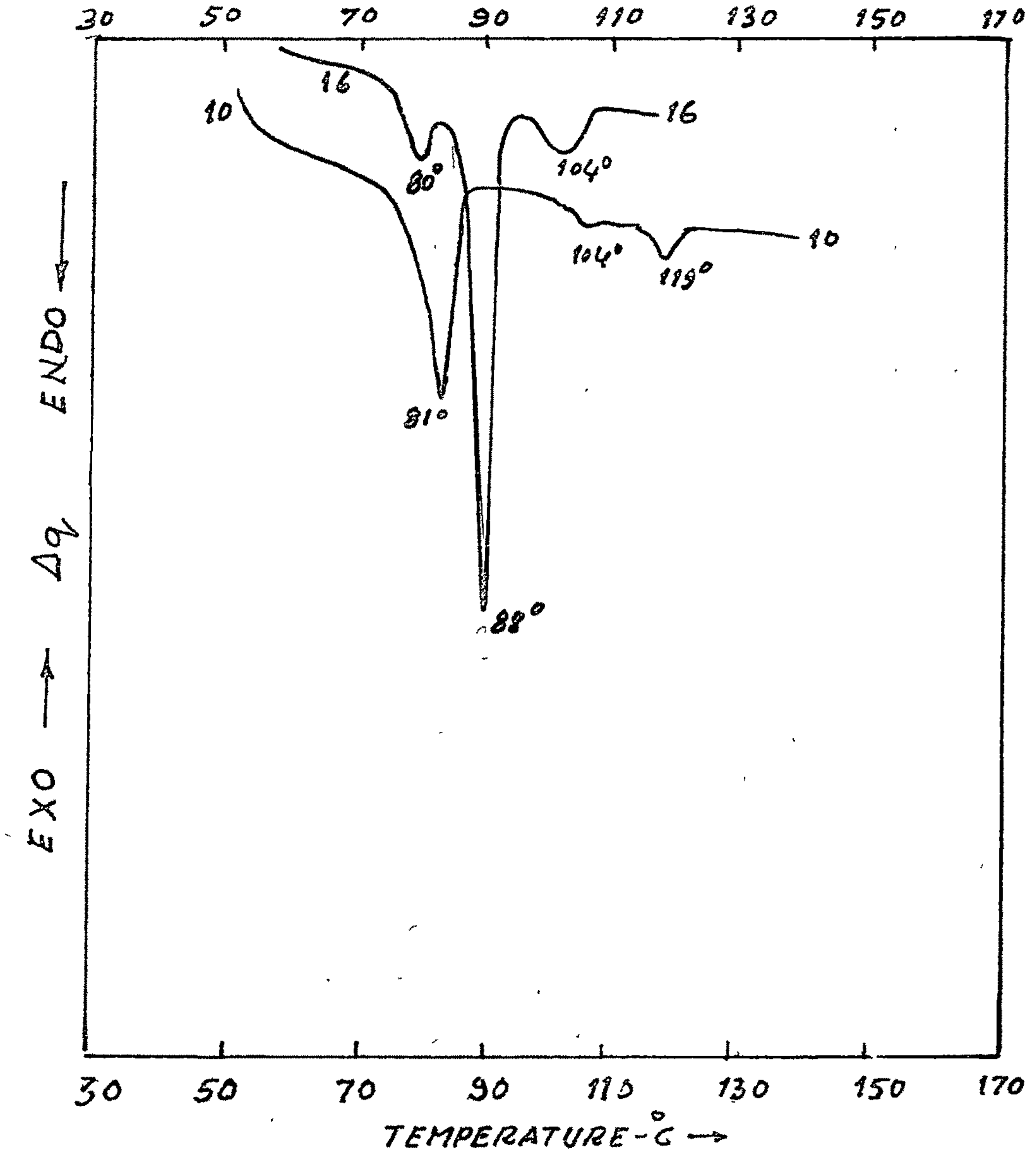

FIG. 16 (CONTD.)

SERIES A-3

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

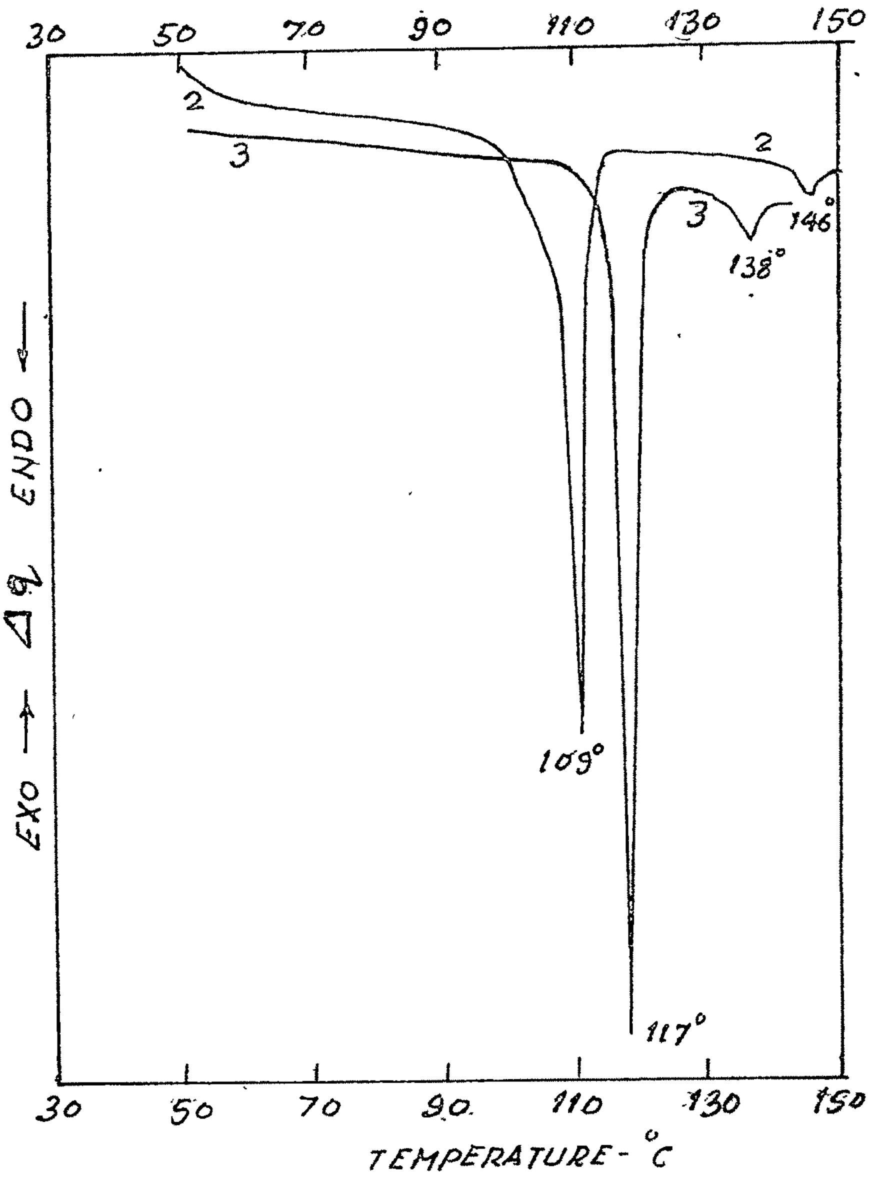

FIG. 17

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

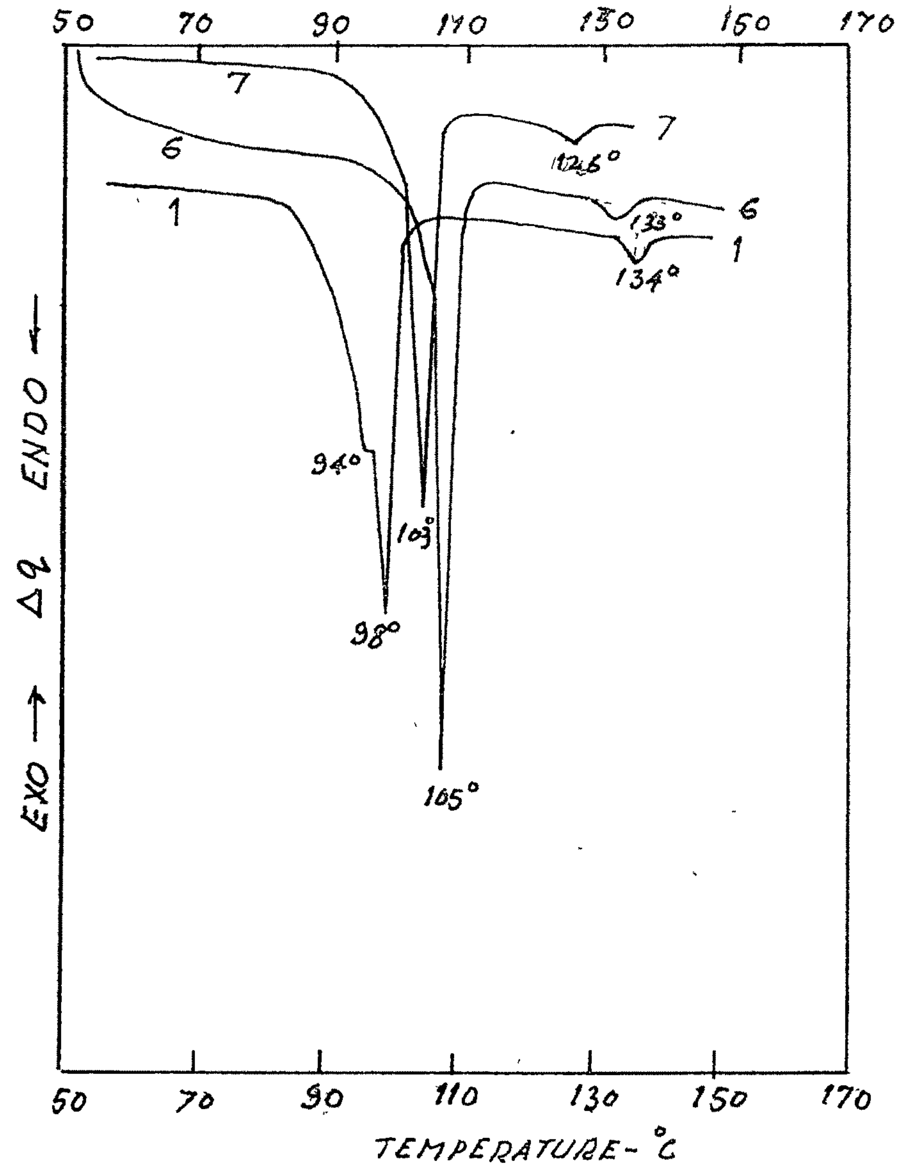

FIG.17 (CONTD.)

SERIES - A-3

p-n-BUTOXYPHENYL-p'-n-ALKOXY CINNAMATES

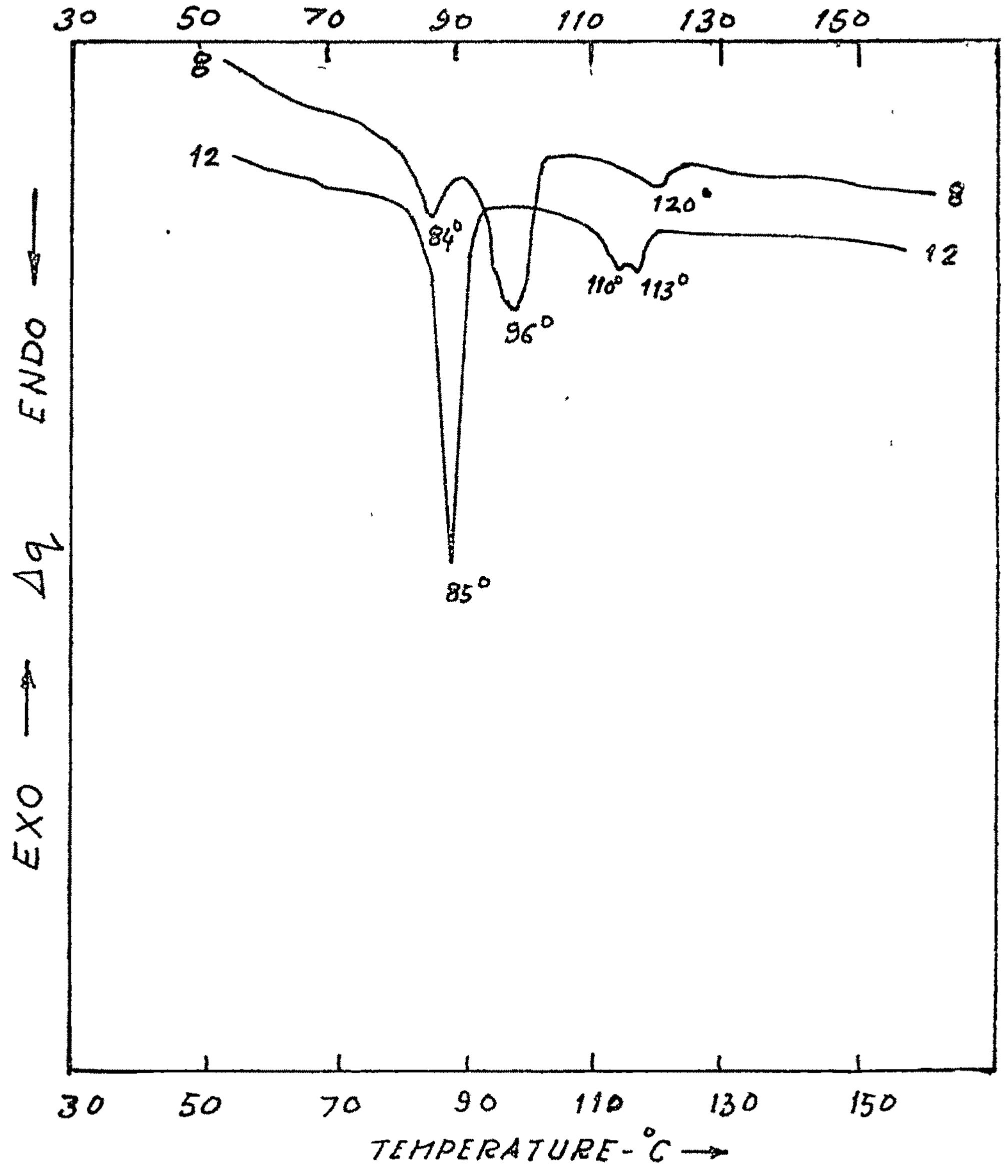

FIG. 17 (CONTD.)

SERIES A-3

p-n- BUTOXYPHENYL - p'-n-ALKOXY CINNAMATES

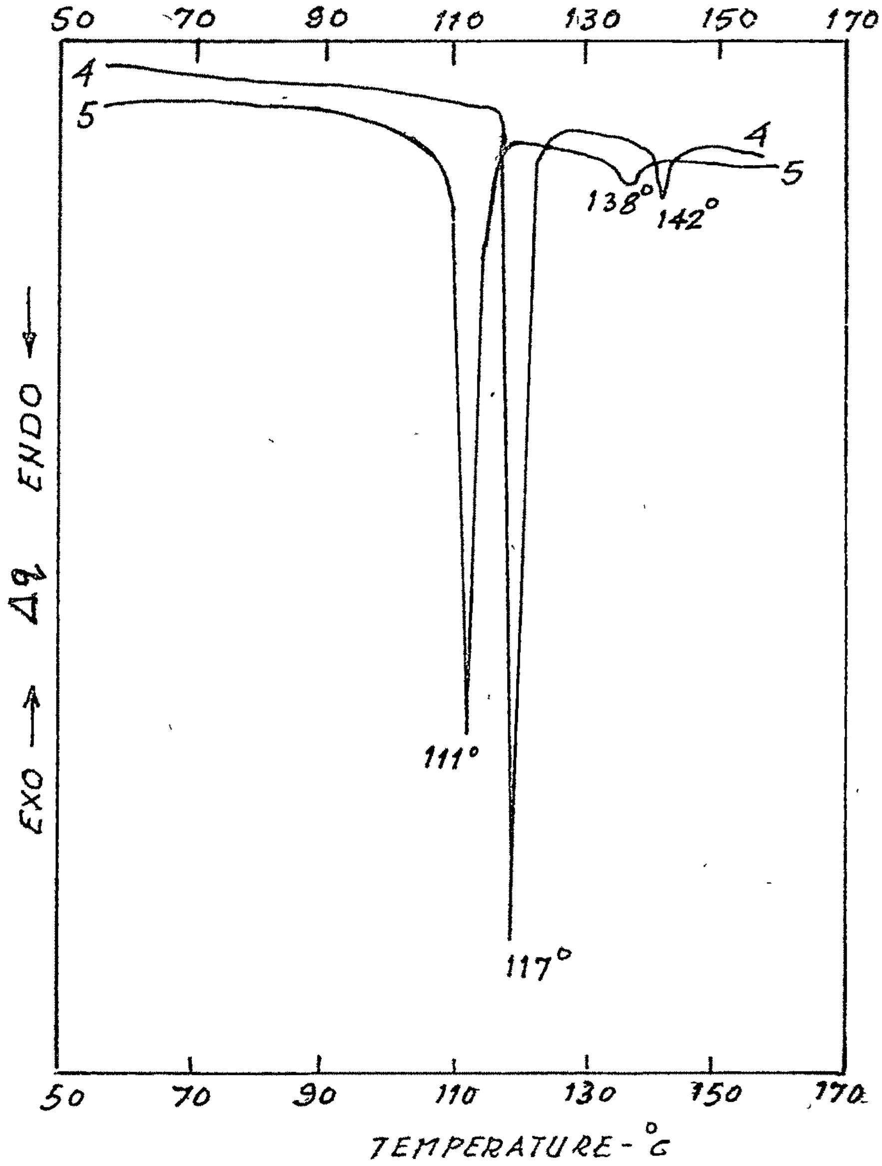

FIG. 17 (CONTD.)

$$\Delta H \text{ (mcal/mg)} = \frac{A}{m} (60 \times B \times E \times \Delta qs)$$

Where A = Peak area (sq.in.)/one inch area (sq.in.)

m = Sample mass (mgm)

B = Time base setting (min/in.)

E = Cell calibration coefficient at the temperature of the experiment

Δ qs = y-axis range (mcal/sec./in.)

The quantity (60 x B x E x Δ qs) is constant for any given set of instrument settings. This is used to convert area directly into heats of reaction.

3.d. Mixed Mesophases:

Study of mixed liquid crystal formation in binary systems, none, one or both components of which are liquid crystals, is as old as the discovery of liquid crystals. This study leads to revelation of structural characteristics and temperature and concentration conditions that are taken as conducive to liquid crystal formation besides helping generalizations concerning other factors responsible for exhibition of mesomorphism.

Mixed mesomorphism has also contributed recently to the applications of liquid crystals by way of widening the scope of utility of certain mesogens. For the mixed mesomorphic study some of the homologues which have been synthesized in this investigation, have been used for preparing the binary mixtures. The following binary systems have been investigated:

System 1.	p-Ethoxyphenyl-p'-n-heptyloxycinnamate p-Ethoxyphenyl-p'-n-octyloxycinnamate
System 2	p-Ethoxyphenyl-p'-n-decyloxycinnamate p-Ethoxyphenyl-p'-n-dodecyloxycinnamate
System 3	p-n-Propoxyphenyl-p'-n-Heptyloxycinnamate p-n-Propoxyphenyl-p'-n-octyloxycinnamate
System 4	p-n-Propoxyphenyl-p'-n-decyloxycinnamate p-n-Propoxyphenyl-p'-n-dodecyloxycinnamate
System 5	p-iso-Propoxyphenyl-p'-methoxycinnamate p-iso-Propoxyphenyl-p'-ethoxycinnamate
System 6	p-iso-Propoxyphenyl-p'-methoxycinnamate p-iso-Propoxyphenyl-p'-n-propoxycinnamate
System 7	p-iso-Propoxyphenyl-p'-ethoxycinnamate p-iso-Propoxyphenyl-p'-n-propoxycinnamate
System 8	p-iso-Propoxyphenyl-p'-n-butoxycinnamate p-iso-Propoxyphenyl-p'-n-amyloxycinnamate
System 9	p-iso-Propoxyphenyl-p'-n-hexyloxycinnamate p-iso-Propoxyphenyl-p'-n-heptyloxycinnamate
System 10	p-iso-Propoxyphenyl-p'-n-heptyloxycinnamate p-iso-Propoxyphenyl-p'-n-octyloxycinnamate
System 11	p-iso-Propoxyphenyl-p'-n-decyloxycinnamate p-iso-Propoxyphenyl-p'-n-dodecyloxycinnamate
System 12	O-Chlorophenyl-p'-n-butoxycinnamate m-Chlorophenyl-p'-n-butoxycinnamate

System 13 O-Chlorophenyl-p'-n-amyloxycinnamate
m-Chlorophenyl-p'-n-amyloxycinnamate
System 14 O-Chlorophenyl-p'-n-hexyloxycinnamate
m-Chlorophenyl-p'-n-hexyloxycinnamate
System 15 O-Chlorophenyl-p'-n-heptyloxycinnamate
m-Chlorophenyl-p'-n-heptyloxycinnamate
System 16 O-Chlorophenyl-p'-n-octyloxycinnamate
m-Chlorophenyl-p'-n-octyloxycinnamate

Preparation of Binary Mixtures:

Both components of the binary mixtures are accurately weighed in known proportions in clean and dry sample tubes. The total weight of the mixture taken is around 0.2 gm. The tube containing the mixture is immersed in an oil bath maintained at a temperature slightly higher than that at which the mixture melts. At the melting condition, the mixture is stirred thoroughly with a glass rod in order to obtain homogeneity. The tube is cooled by quenching it in a beaker containing cold water. The mixture solidifies almost instantly. The mixture is now taken out from the tube and then ground to a fine powder with the help of agate mortar and pastle. Mixtures of varying proportions are prepared and then studied under microscope.

3.e. Study of the mixed mesophases
Under Polarizing Microscope

Several binary mixtures with varying compositions have been examined under polarizing microscope with a view to study the

Table 23

Binary System No.1

(A) p-Ethoxyphenyl-p'-n-heptyloxycinnamate

(B) p-Ethoxyphenyl-p'-n-octyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	(72)	88	136
9.66	(75)	87	135
19.44	(77)	84	135
29.25	(79)	82	135
34.17	(80)	80	135
39.13	(80)	80	135
49.07	77	82	135
54.00	76	83	135
59.12	77	84	135
69.21	(87)	89	134
79.42	(89)	94	135
89.70	(91)	97	134
100	(92)	99	133.5

Value in the parenthesis indicates monotropy

SYSTEM - 1

p-ETHOXY PHENYL - p'-n-HEPTYLOXY CINNAMATE - (A)
AND
p-ETHOXY PHENYL - p'-n-OCTYLOXY CINNAMATE - (B)

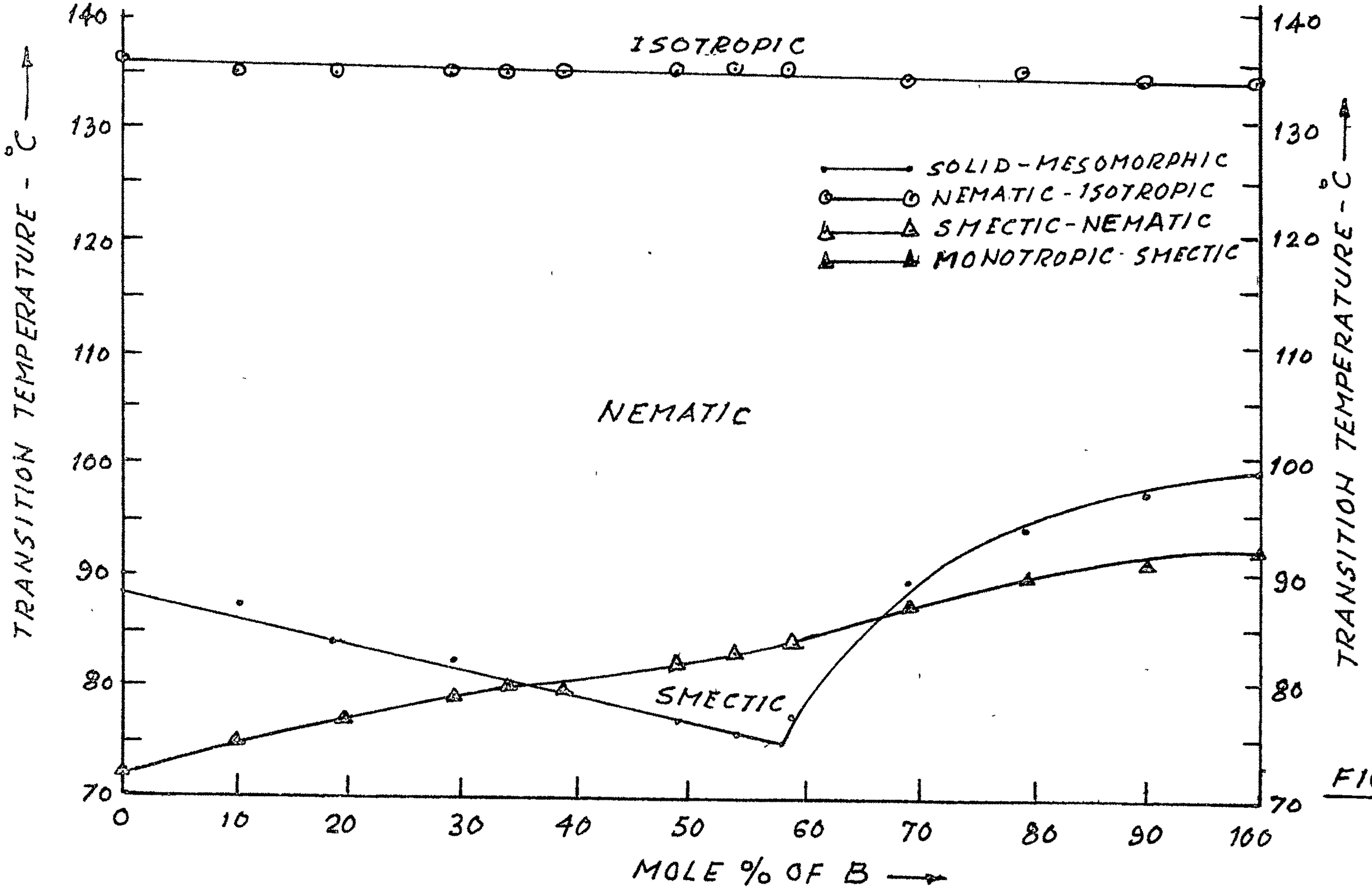

FIG. 18

Table 24

Binary System No.2

(A) p-Ethoxyphenyl-p'-n-decyloxycinnamate

(B) p-Ethoxyphenyl-p'-n-dodecyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	80	104	126
9.37	77	104	127
18.92	73	105	127
24.92	71	106	127
28.66	69	106	127
38.44	66	106	126
48.36	65	107	125
58.46	70	107	125
68.70	78	107	124.5
79.00	83	108	124
89.34	84	108	123.5
100	86	109	122

SYSTEM- 2

p-ETHOXY PHENYL-p'-n-DECYLOXY CINNAMATE - (A)
AND
p-ETHOXY PHENYL-p'-n-DODECYLOXY CINNAMATE- (B)

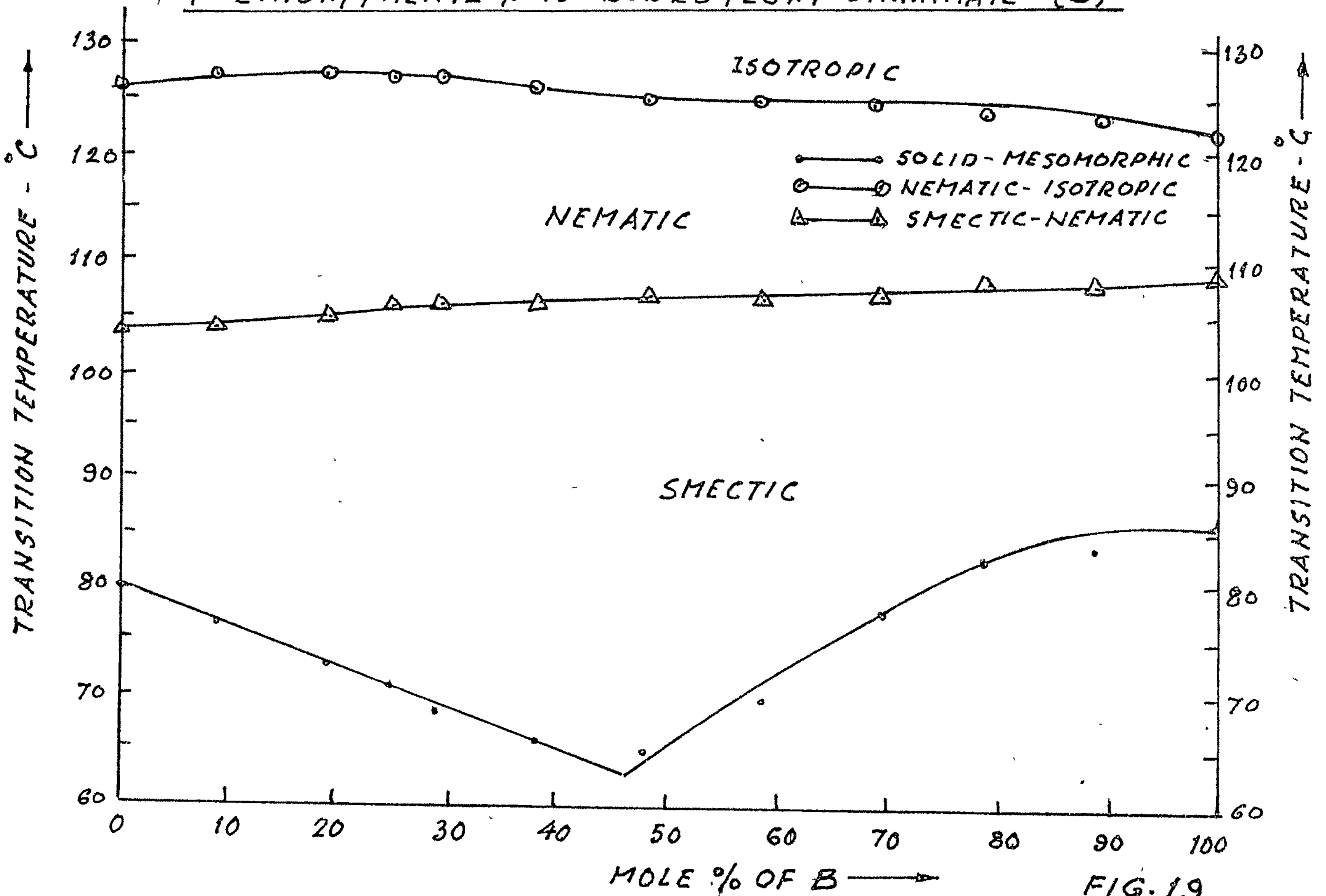

FIG. 19

Table 25

Binary System No.3

(A) p-n-Propoxyphenyl-p'-n-heptyloxycinnamate

(B) p-n-Propoxyphenyl-p'-n-octyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	(92)	94	127
9.72	(93)	93	126
19.54	91	94	126
27.00	89	96	126
29.17	89	96	126
34.59	88	97	126
36.66	87	97	126
39.09	87	97	126
49.16	87	98	125
59.03	87	100	125
69.30	85	100	125
76.07	87	101	125
79.39	93	101	125
89.72	97	102	125
100	99	101.5	124

Value in the parenthesis indicates monotropy

SYSTEM- 3

p-n-PROPOXY PHENYL-p'-n-HEPTYLOXY CINNAMATE -(A)

AND

p-n-PROPOXY PHENYL-p'-n-OCTYLOXY CINNAMATE-(B)

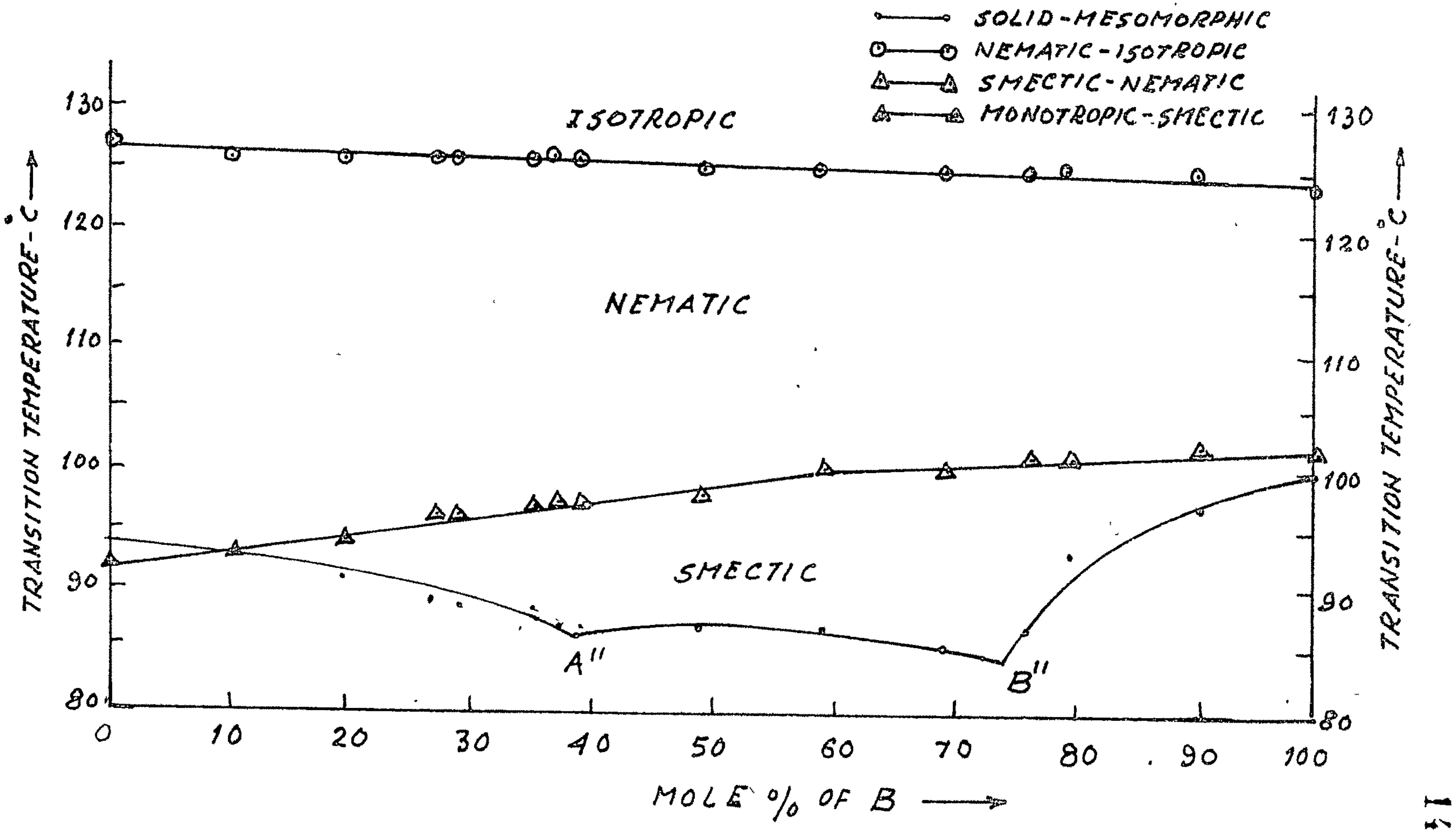

FIG. 20

Table 26

Binary System No.4

(A) p-n-Propoxyphenyl-p'-n-decyloxycinnamate

(B) p-n-Propoxyphenyl-p'-n-dodecyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	78.5	102	116
9.43	74.5	102	115
18.98	72	102.5	115
28.71	68	102.5	114.5
38.53	66	102	114
40.69	67	102	114
48.45	68	102	113
58.46	71	101.5	113
68.66	74	102	112
78.99	76	102	112
89.44	80	102	112
100	85	102	111

SYSTEM- 4

p-n-PROPOXY PHENYL - p'-n- DECYLOXY CINNAMATE - (A)

AND

p-n-PROPOXY PHENYL - p'-n-DODECYLOXY CINNAMATE-(B)

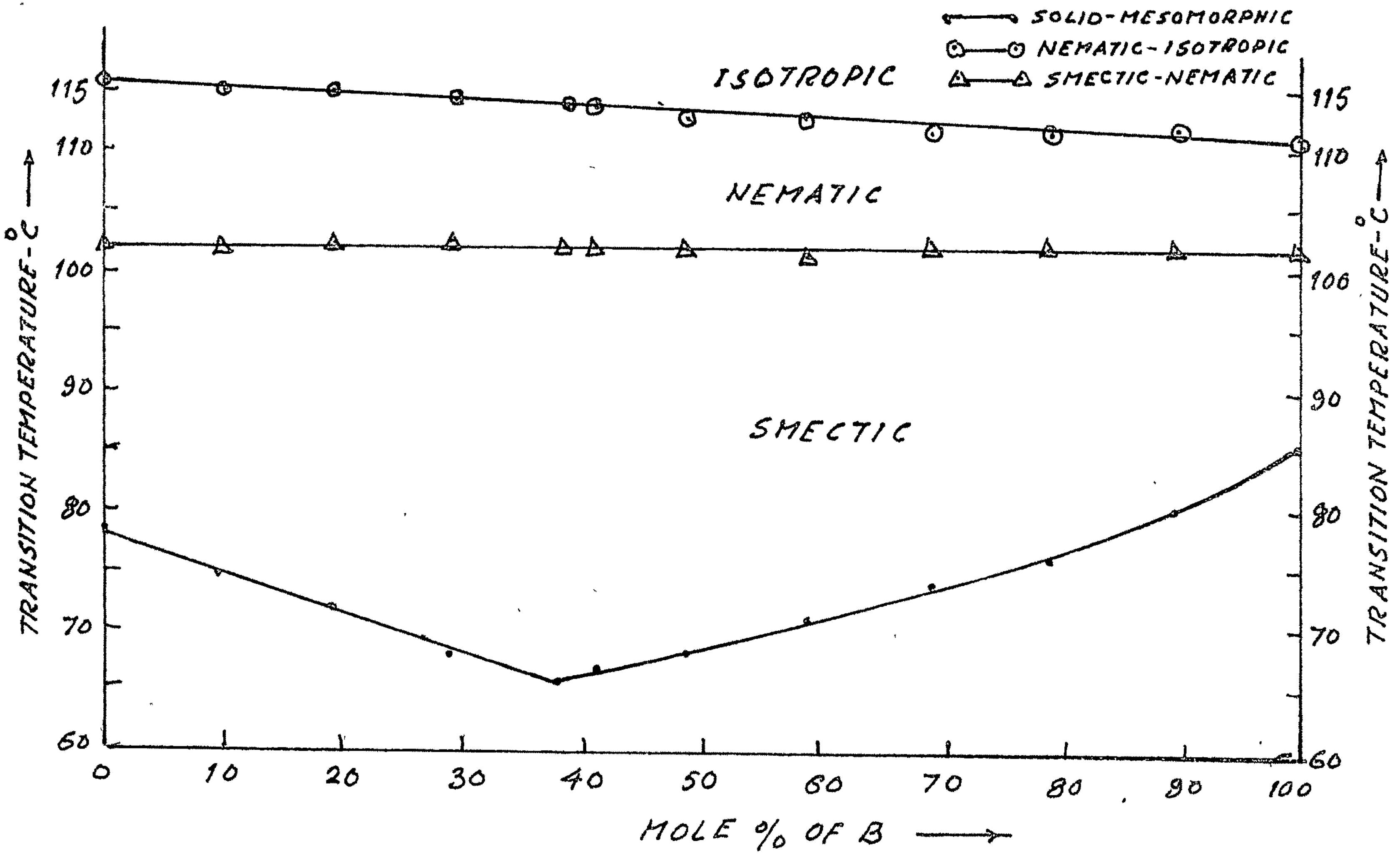

FIG. 21

Table 27

Binary System No.5

(A) p-iso-Propoxyphenyl-p'-methoxycinnamate

(B) p-iso-Propoxyphenyl-p'-ethoxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	99
8.77	-	95	96
9.59	-	95	96
18.02	-	94	101
19.26	-	93	102
28.41	-	98	113
29.09	-	98	114
38.92	-	112	120
48.88	-	118	125
58.94	-	125	133
65.20	-	127	132
69.04	-	131	136
79.25	-	138	141
89.62	-	138	143
97.40	-	-	142
100	-	-	145

SYSTEM-5
p-iso-PROPOXY PHENYL-p'-METHOXY CINNAMATE-(A)
AND
p-iso-PROPOXY PHENYL-p'-ETHOXY CINNAMATE-(B)

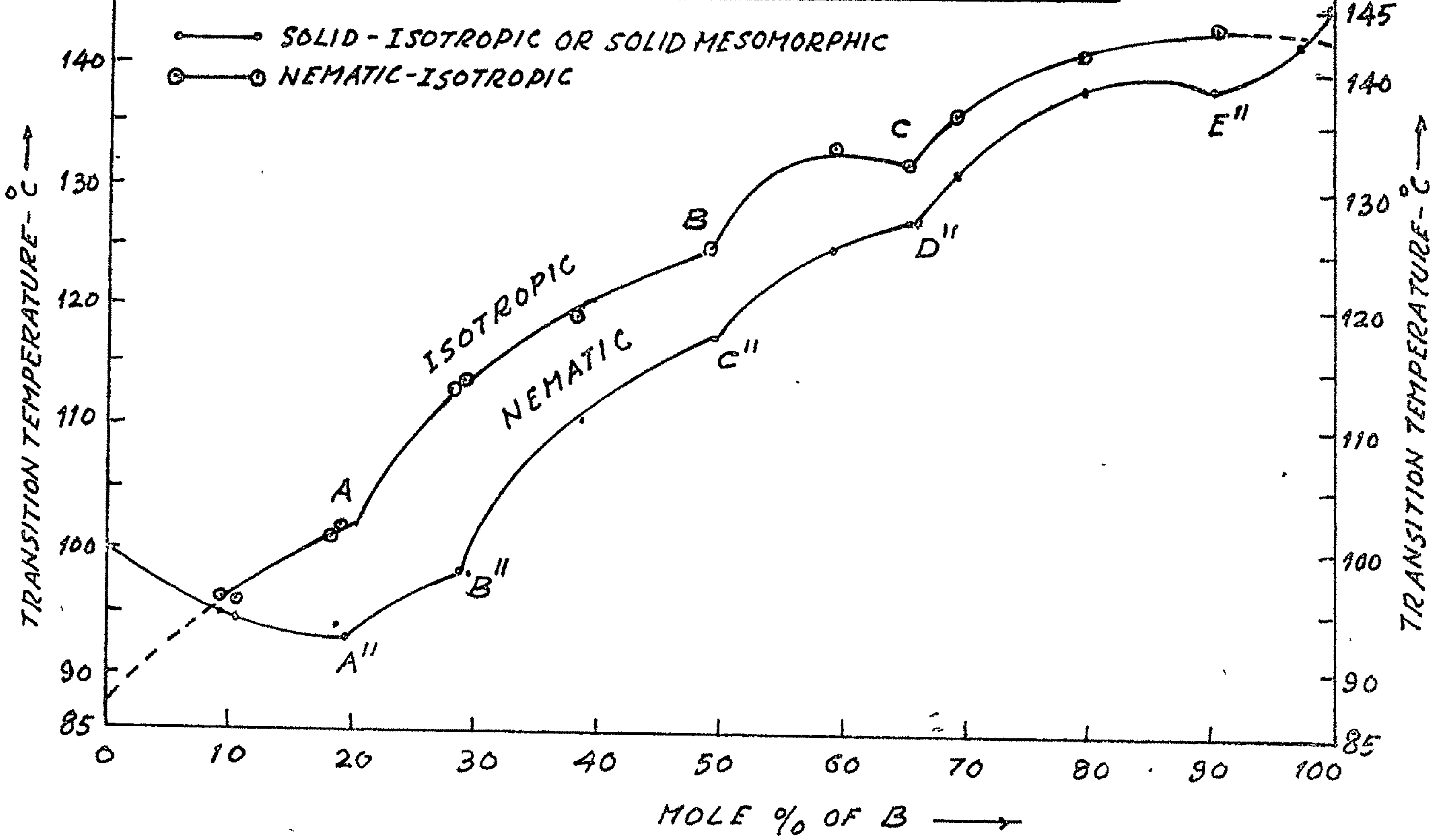

FIG. 22

Table 28

Binary System No.6

(A) p-iso-Propoxyphenyl-p'-methoxycinnamate

(B) p-iso-Propoxyphenyl-p'-n-propoxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	99
2.34	-	-	97.5
6.21	-	-	95.5
9.22	-	93.5	97
18.70	-	86	91
28.17	-	80	90
37.96	-	75	88
47.83	-	78	90
57.95	-	85.5	92
68.17	-	94	96
70.15	-	91	94
70.34	-	91	94
78.56	-	(96)	102
89.25	-	(97.5)	106
100	-	(99)	109

Value in the parenthesis indicates monotropy

SYSTEM-6

p-iso-PROPOXY PHENYL-p'-METHOXY CINNAMATE-(A) AND p-iso-PROPOXY PHENYL-p'-n-PROPOXY CINNAMATE-(B)

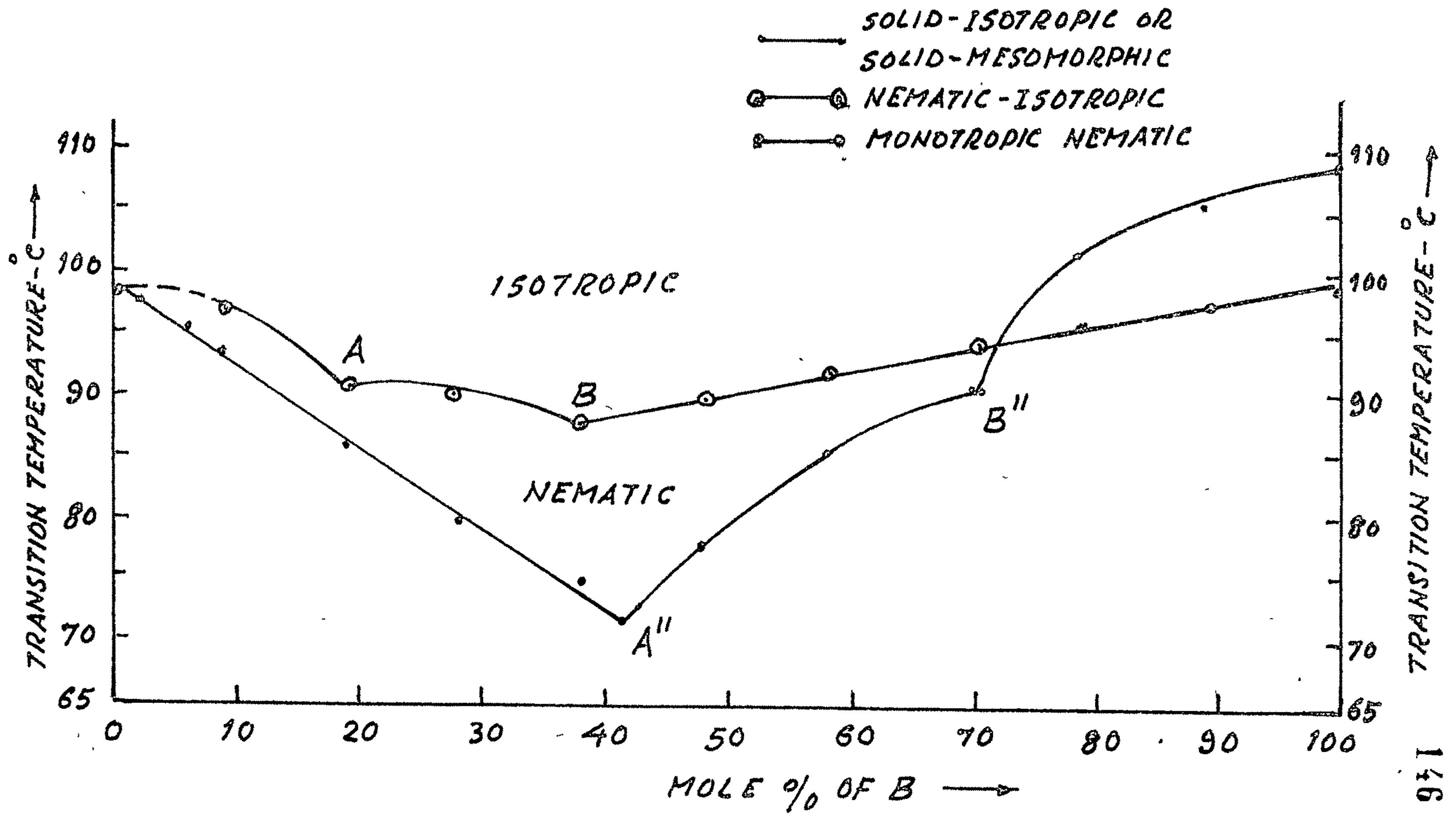

FIG. 23

Table 29

Binary System No. 7

(A) p-iso-Propoxyphenyl-p'-ethoxycinnamate

(B) p-iso-Propoxyphenyl-p'-n-propoxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	145
9.64	-	-	141
19.29	-	-	138
29.07	-	(109)	133
39.01	-	(108.5)	130
48.91	-	(107)	126
59.02	-	(105)	122
63.58	-	(103.5)	120
69.12	-	(104.5)	118
79.38	-	(104)	112
89.63	-	(102)	108
100	-	(99)	109

Value in the parenthesis indicates monotropy

SYSTEM-7

p- iso-PROPOXY PHENYL - p'-ETHOXY CINNAMATE - (A)

AND

p- iso-PROPOXY PHENYL - p'-n- PROPOXY CINNAMATE - (B)

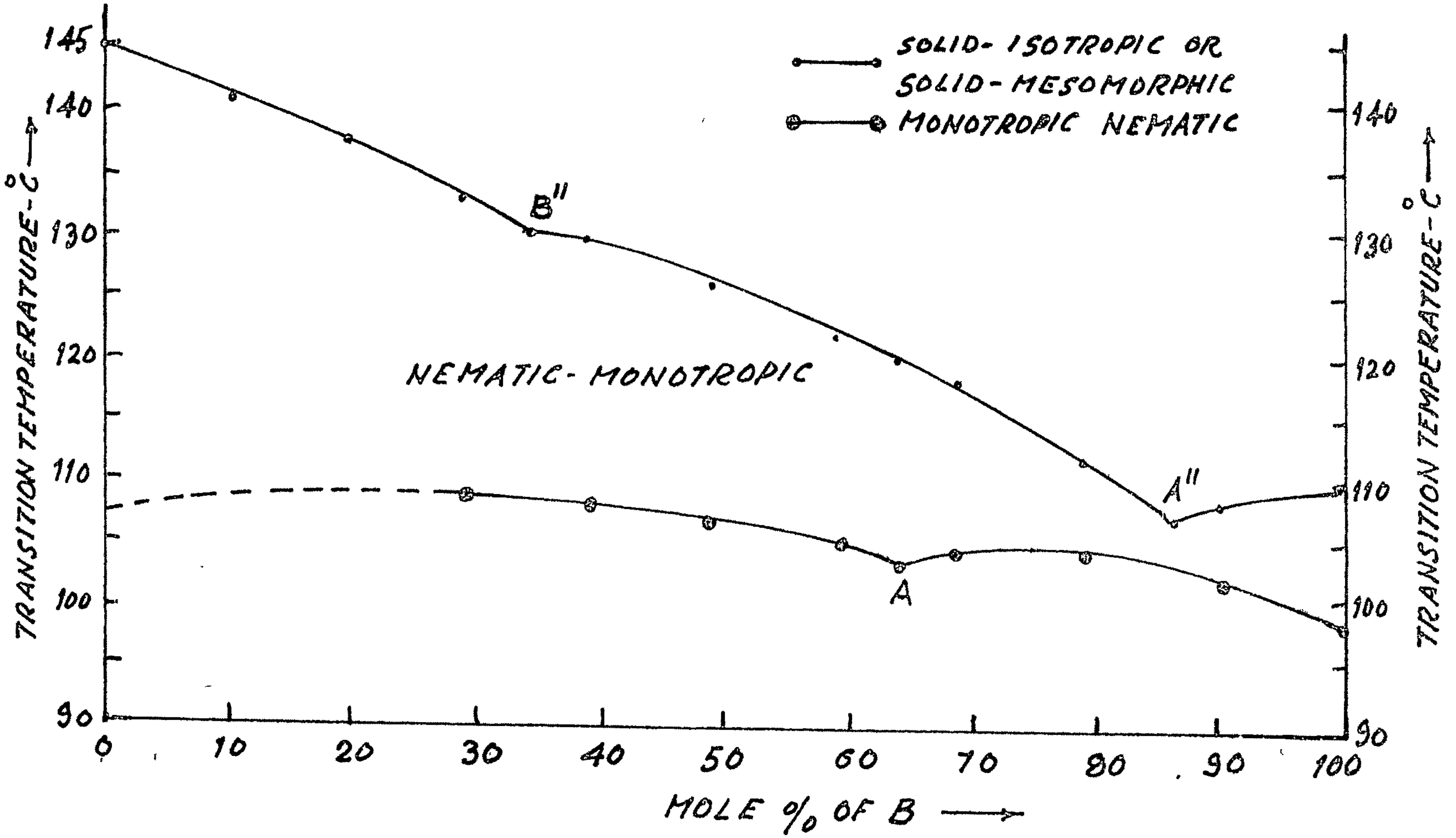

FIG. 24

Table 30

Binary System No.8

(A) p-iso-Propoxyphenyl-p'-n-butoxycinnamate

(B) p-iso-Propoxyphenyl-p'-n-amyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	(109)	110
9.65	-	(108)	109
19.54	-	(107)	108
28.95	-	(105)	106
35.36	-	(105)	105
39.13	-	(104)	105
49.17	-	(102.5)	104
58.95	-	(103)	104
68.95	-	(102)	103
79.25	-	(101)	103
89.85	-	(99)	103
100	-	(98)	103

Value in the parenthesis indicates monotropy

SYSTEM- 8

p-iso-PROPOXY PHENYL-p'-n-BUTOXY CINNAMATE - (A)
AND
p-iso-PROPOXY PHENYL-p'-n-AMYLOXY CINNAMATE - (B)

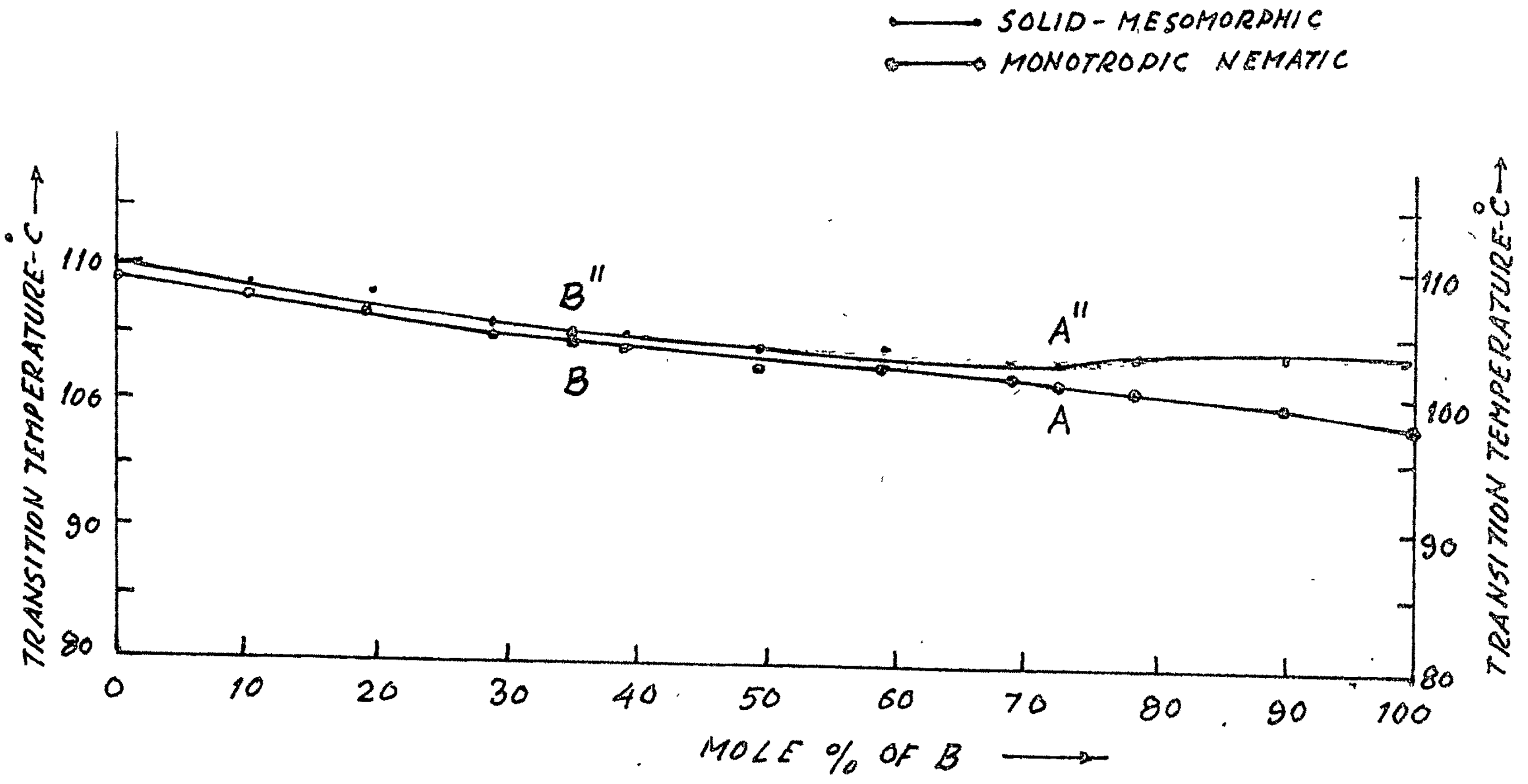

FIG. 25

SYSTEM- 9

p-iso-PROPOXY PHENYL-p'-n-HEXYLOXY CINNAMATE-(A)

AND

p-iso-PROPOXY PHENYL-p'-n-HEPTYLOXY CINNAMATE-(B)

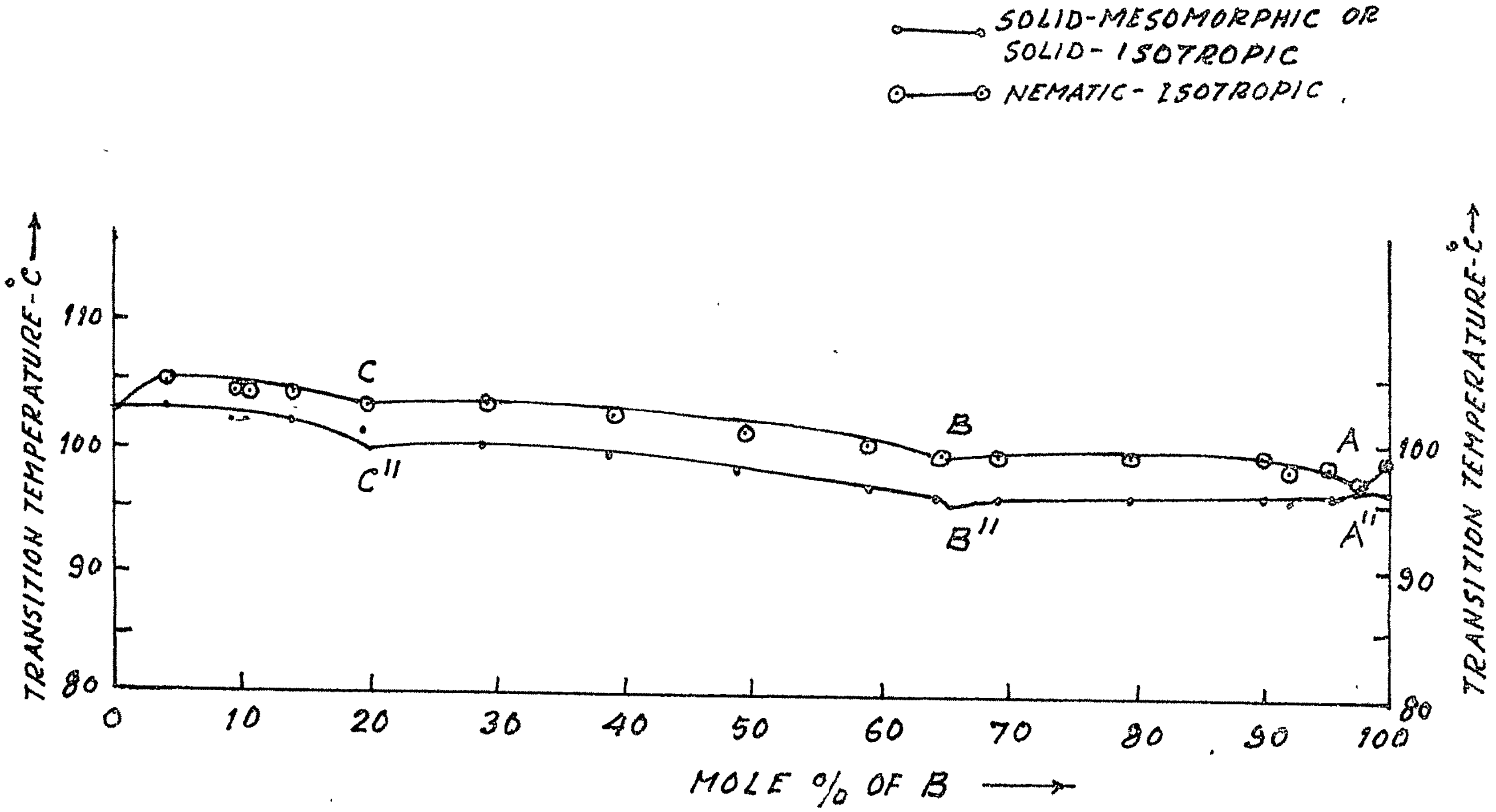

FIG. 26

Table 32

Binary System No.10

(A) p-iso-Propoxyphenyl-p'-n-heptyloxycinnamate

(B) p-iso-Propoxyphenyl-p'-n-octyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	96	98.5
9.63	-	94	98
19.31	-	91	97
29.38	-	88	98
39.13	(82)	86	99
49.07	(83)	83	99
58.97	80	84	99
69.35	78	84	99
79.20	76	84	100
90	75	85	100
100	82	87	99

Value in the parenthesis indicates monotropy

SYSTEM- 10

p-iso-PROPOXYPHENYL-p'-n-HEPTYLOXY CINNAMATE - (A)
AND
p-iso-PROPOXYPHENYL-p'-n-OCTYLOXY CINNAMATE - (B)

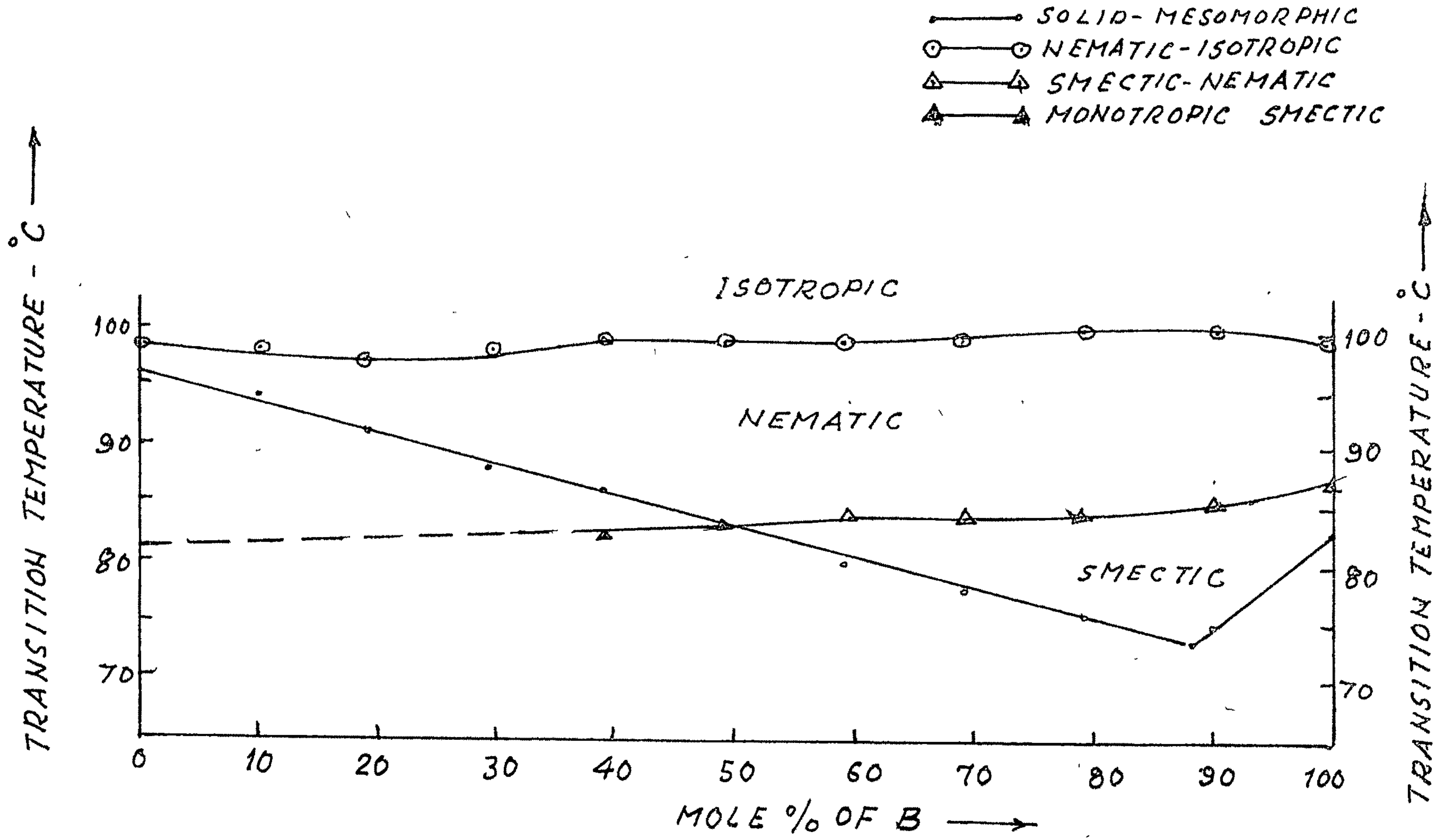

FIG. 27

Table 33

Binary System No.11

(A) p-iso-Propoxyphenyl-p'-n-decyloxycinnamate

(B) p-iso-Propoxyphenyl-p'-n-dodecyloxycinnamate

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	73	90	96
4.54	70	86.5	93
9.44	76	87	92
19.02	75	86	92
28.70	74	86	92
38.51	74	89	92
48.44	75	89	92
58.50	77	93	97
68.69	79	94	97
78.97	80	94	96.5
89.44	82	95	96.5
94.62	83	-	96
100	84	-	94

SYSTEM - 11

p-iso-PROPOXY PHENYL-p'-n-DECYLOXY CINNAMATE - (A)
AND
p-iso-PROPOXY PHENYL-p'-n-DODECYLOXY CINNAMATE - (B)

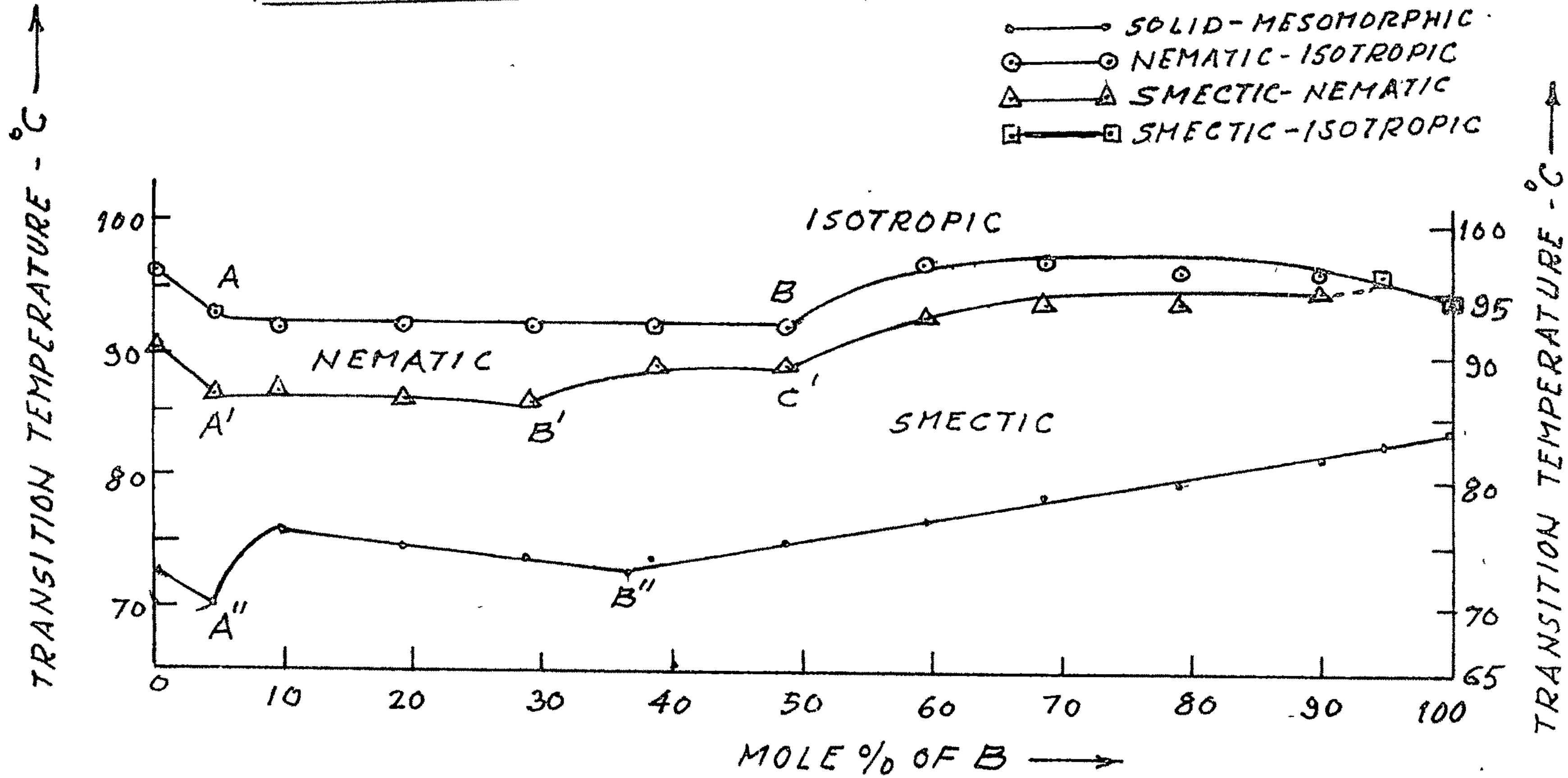

FIG. 28

Table 34

Binary System No. 12

(A) m-Chlorophenyl-p'-n-butoxycinnamate

(B) O-Chlorophenyl-p'-n-butoxycinnamate

Mole % of A	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	61
10.69	-	-	59
20.13	-	-	57
30.12	-	-	55
39.47	-	-	53
50.47	-	-	50
60.25	-	-	43
70.25	-	-	43
80.26	-	-	46
89.51	-	-	49
100	-	-	57

SYSTEM - 12

m-CHLOROPHENYL-p'-n-BUTOXY CINNAMATE- (A)
AND
O-CHLOROPHENYL-p'-n-BUTOXY CINNAMATE- (B)

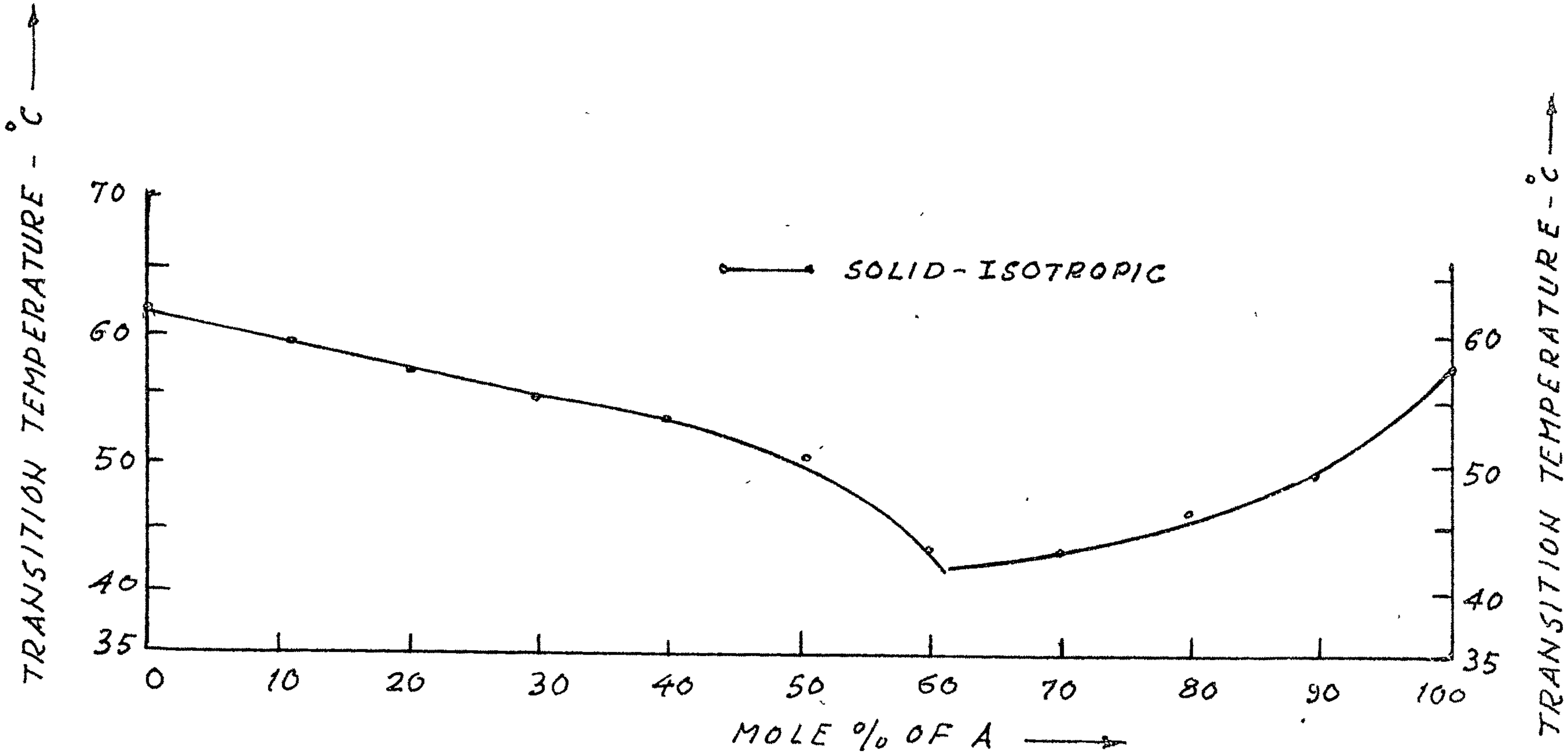

FIG. 29

SYSTEM - 13

m- CHLOROPHENYL - p'- n - AMYLOXY CINNAMATE - (A)

AND

O- CHLORO PHENL - p'- n - AMYLOXY CINNAMATE (B)

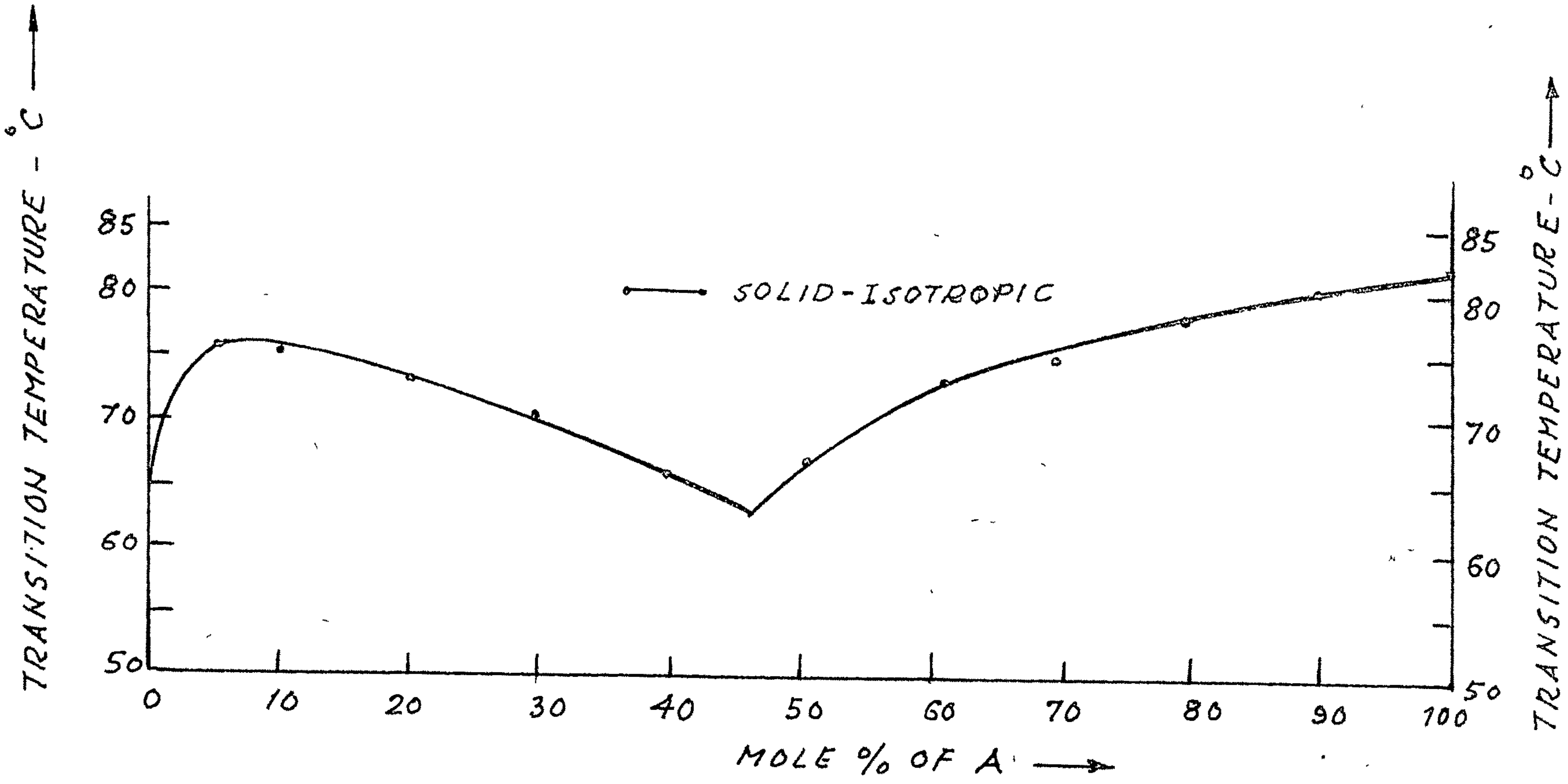

FIG. 30

Table 36

Binary System No.14

(A) m-Chlorophenyl-p'-n-hexyloxycinnamate

(B) O-Chlorophenyl-p'-n-hexyloxycinnamate

Mole % of A	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	72
10.59	-	-	70
20.30	-	-	67
30.04	-	-	65
39.86	-	-	60
49.83	-	-	60
59.62	-	-	63.5
70.05	-	-	68
80.53	-	-	70
90.23	-	-	72
100	-	-	73

SYSTEM- 14

m- CHLOROPHENYL-p'-n-HEXYLOXY CINNAMATE (A)
AND
O- CHLOROPHENYL-p'-n-HEXYLOXY CINNAMATE-(B)

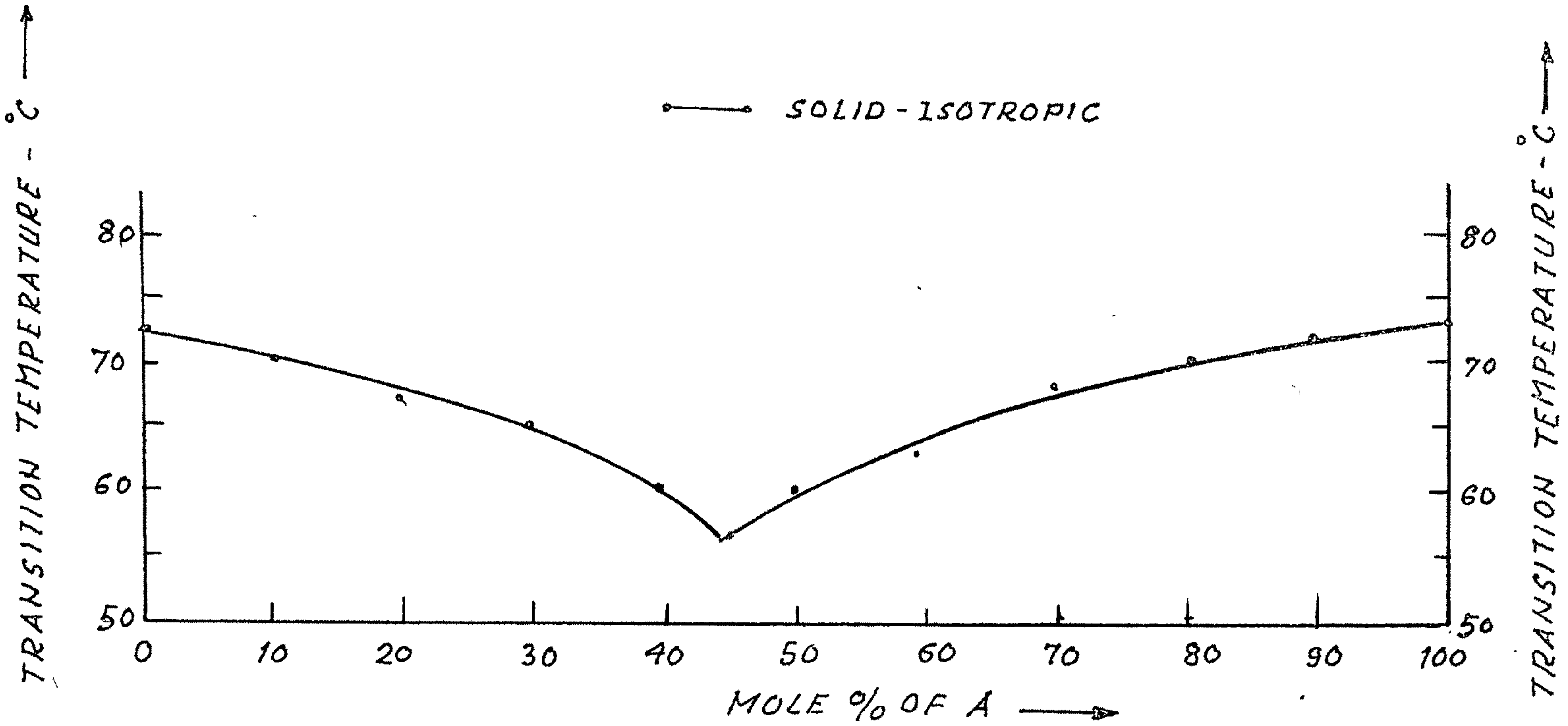

FIG. 31

Table 37

Binary System No. 15

(A) m-Chlorophenyl-p'-n-heptyloxycinnamate

(B) O-Chlorophenyl-p'-n-heptyloxycinnamate

Mole % of A	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	61
10.23	-	-	58
20.03	-	-	56
30.14	-	-	54
40.10	-	-	49
50.10	-	-	46
59.32	-	-	49
68.48	-	-	52
79.81	-	-	54
89.88	-	-	54
100	-	-	54

SYSTEM-15

m-CHLOROPHENYL-p'-n-HEPTYLOXY CINNAMATE- (A)
AND
O-CHLOROPHENYL-p'-n-HEPTYLOXY CINNAMATE- (B)

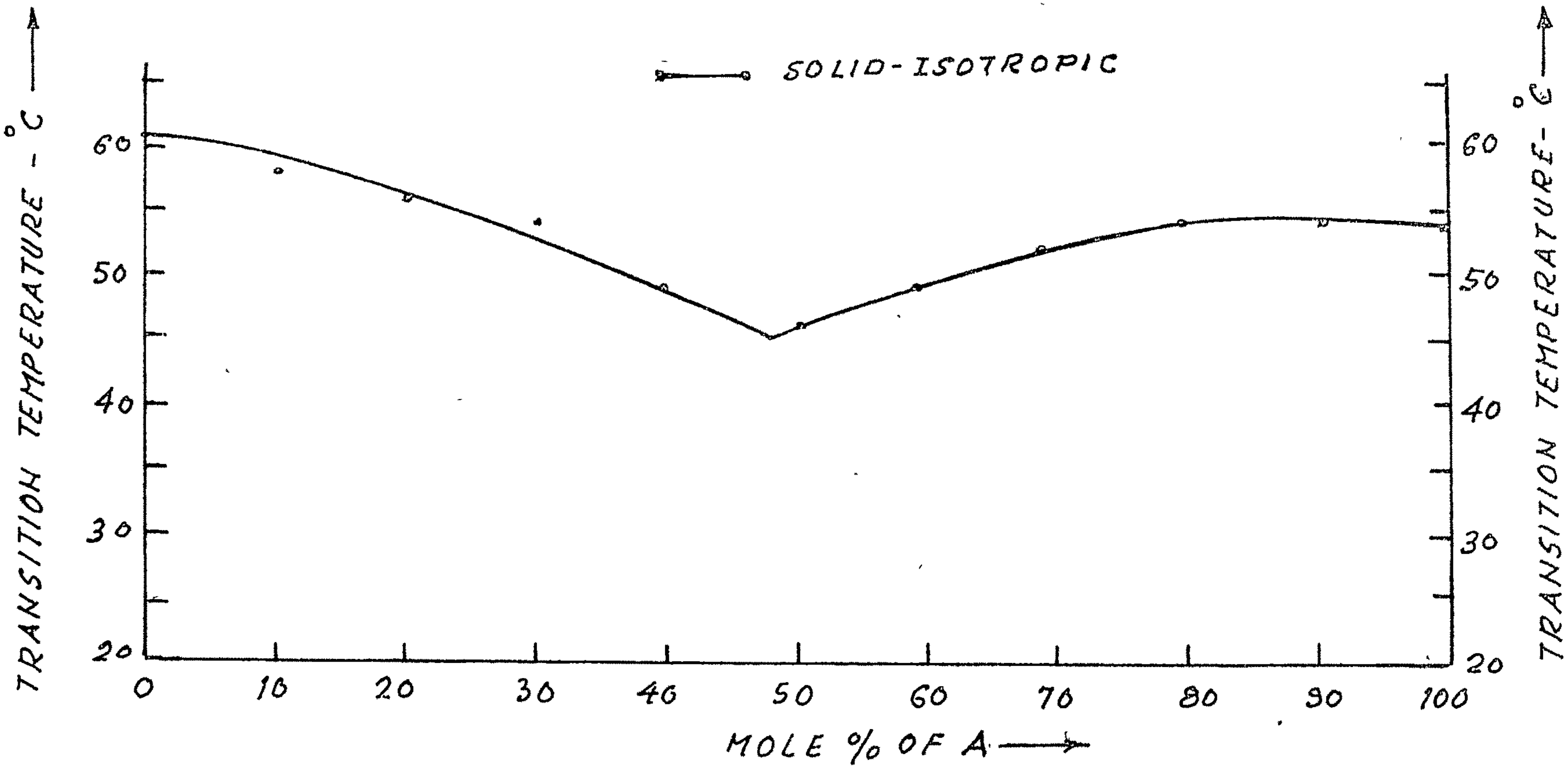

FIG.32

Table 38

Binary System No.16

(A) m-Chlorophenyl-p'-n-octyloxycinnamate

(B) O-Chlorophenyl-p'-n-octyloxycinnamate

Mole % of A	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0	-	-	60
9.37	-	-	59
19.59	-	-	57
27.63	-	-	56
39.89	-	-	53
49.92	-	-	48
59.77	-	-	44
70.43	-	-	43
79.16	-	-	50
89.80	-	-	54
100	-	-	56

SYSTEM- 16

m-CHLORO PHENYL-p'-n-OCTYLOXY CINNAMATE - (A)
AND
O-CHLORO PHENYL-p'-n-OCTYLOXY CINNAMATE - (B)

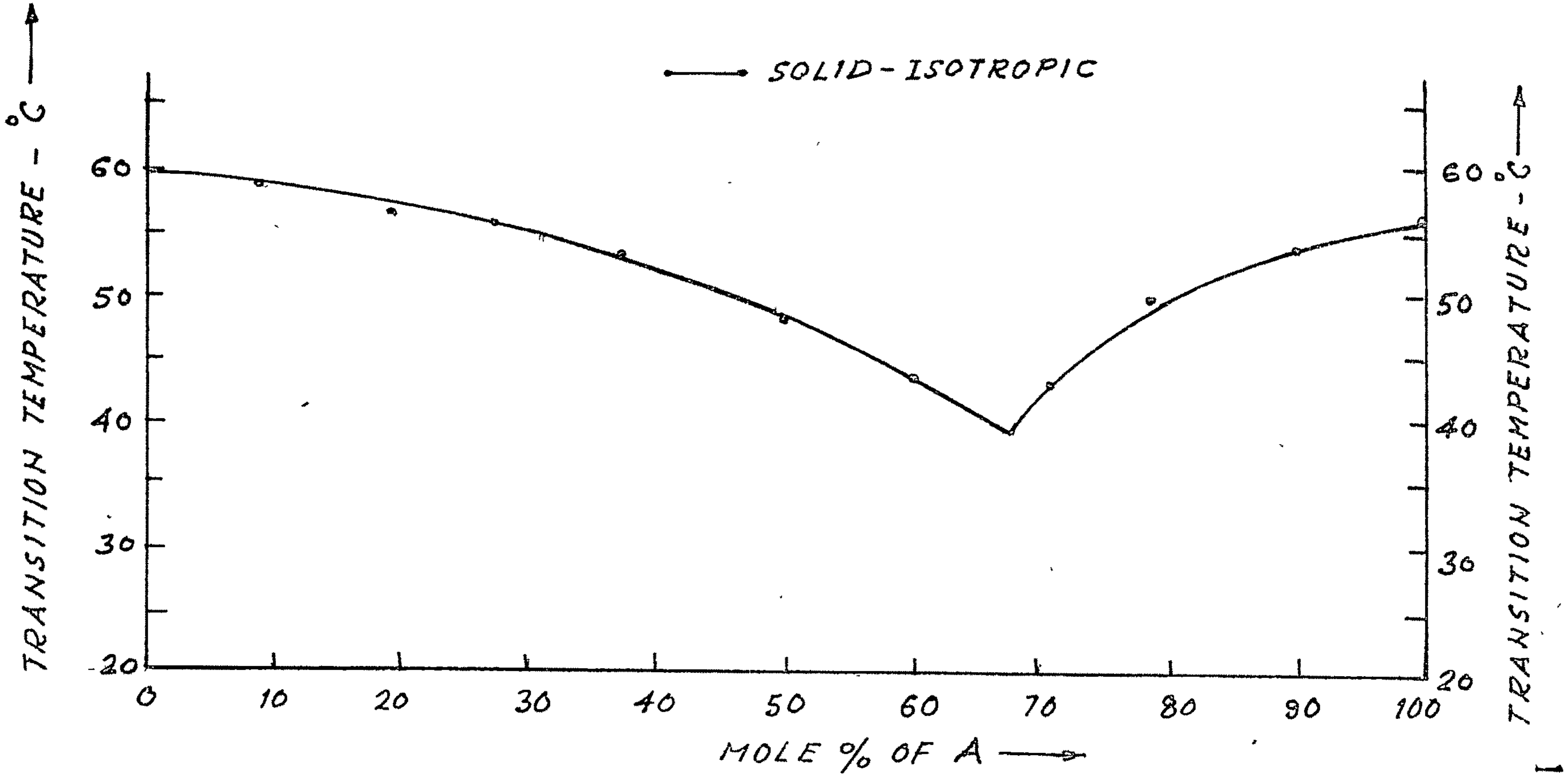

FIG. 33