Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: D. L. Fishel & Prabhu R. Patel (1972): Thermotropic Liqid Crsytals II.: Transition Temperaturees and Mesophase Identifications for Some Anils, Molecular Crystals and Liquid Crystals, 17:2, 139-162

To link to this article: http://dx.doi.org/10.1080/15421407208083837

Molecular Crystals and Liquid Crystals. 1972. Vol. 17, pp. 139–162

Printed in Great Britain

Thermotropic Liquid Crystals II. Transition Temperatures and Mesophase Identifications for Some Anils

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Received September 11, 1971; *in revised form September* 21, 1971

Abstract—One hundred and seven compounds belonging to ten homologous series of aromatic anils were synthesized, purified and analyzed by differential thermal analysis and phase contrast microscopy. The freedom of starting materials from homologous impurities was confirmed by mass spectroscopic analyses. The transition temperatures and tentative assignments of mesophase class as determined by texture observations are presented; plots of transition temperatures *vs* carbon number are also given. An apparent correlation between monotropic behaviour and alkanoyloxy-substitution was observed. Many compounds are polymorphic and *p*-phenylenediamine derivatives demonstrate this to an extreme.

1. Introduction

Part of the synthetic effort at the Liquid Crystals Institute of Kent State University for the past few years has been directed toward preparing complete sets of certain homologous series of thermotropic liquid crystals. These compounds have been carefully purified by multiple recrystallization and analyzed; thermal transition data were obtained by both differential thermal analysis and phase

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contrast microscopy. In the interest of making these data generally available we are presenting the results of our work on ten series of anils without extensive accompanying qualitative comments relating thermal trends to structure.(1) It is our feeling that valuable correlations of these data with intermolecular structure will best be made by painstaking investigation with additional physical tools including precision calorimetry,(2) X-ray diffraction(3,4,5,6) molecular spectroscopy(7) and various nuclear resonance(8,9,10,11,12) as well as electron resonance techniques.(13,14) Some of this work is now being conducted at the Liquid Crystals Institute; we invite inquiries by other investigators.

2. Discussion

Appropriate comments regarding the synthesis of the anils and solvents employed for recrystallization are given in the Experimental Section. Analyses of the benzaldehyde and aromatic amine precursors for the anils by mass spectrometry were done to confirm the absence of homologous impurities. Molecular ions are absent from spectra of 4-*n*-alkanoyloxybenzaldehydes with side chains larger than C_5; cleavage at the aryl-oxygen bond occurs, followed or accompanied by rearrangement-fragmentation of the side chain to give a normal alkene and a highly stable $C_2H_4O_2$ ion at m/e 60. This latter ion is the base peak for homologues with a four carbon chain or larger. The *n*-alkene resulting from this rearrangement-fragmentation is produced in sufficient amount to be used as an indicator of the extent of homologous impurities for compounds with side chains larger than C_5, since its spectrum is always superimposed and is a part of the spectrum for the substituted benzaldehyde. The major fragmentation paths are given in Fig. 1.

A representative selection of the anils was submitted to elemental analyses to check purity and composition. Table 1 presents a summary of these analyses; in no case were there significant deviations from calculated values. One or two members of several series were reported in earlier days of activity in the field; these are footnoted in the respective tables of data.

The initial member of three series (Tables 2, 6 and 10) did not exhibit mesomorphic behavior. The tendency to monotropic

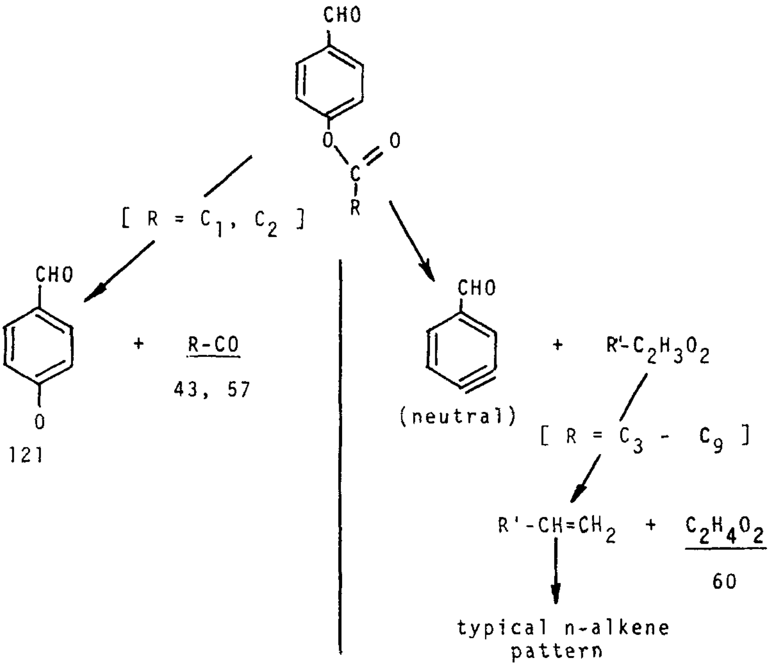

Figure 1. Major Electron-Impact (70 eV) Ion Fragmentation Pathways For 4-*n*-Alkanoyloxybenzaldehydes. Base peak ions are underlined.

TABLE 1 Elemental Analyses for Selected Mesomorphic Anils

Code Number[a]	Molecular Formula	C% Calc'd	C% Found	H% Calc'd	H% Found	N% Calc'd	N% Found
2–3	$C_{18}H_{19}O_2N$	76.84	76.89	6.80	6.58	4.98	4.99
3–4	$C_{21}H_{25}O_2N$	77.99	78.39	7.79	7.57	4.33	4.32
3–10	$C_{27}H_{37}O_2N$	79.56	79.68	9.15	9.17	3.44	3.30
4–4	$C_{19}H_{19}O_3N$	73.77	74.35	6.19	6.30	4.53	4.51
4–7	$C_{22}H_{25}O_3N$	75.19	75.31	7.17	7.23	3.99	3.89
6–3	$C_{21}H_{25}O_3N$	74.31	74.43	7.42	7.30	4.12	4.10
6–10	$C_{28}H_{39}O_3N$	76.85	76.99	8.88	8.75	3.20	3.19
7–7	$C_{26}H_{29}ON_3$	78.18	78.03	7.32	7.18	10.52	10.44
8–5	$C_{24}H_{23}O_2N_3$	74.98	75.07	6.01	6.10	10.90	10.93

(a) Code numbers are the Table and the variable substituent carbon-numbers (in Tables 2 through 8) separated by a dash.

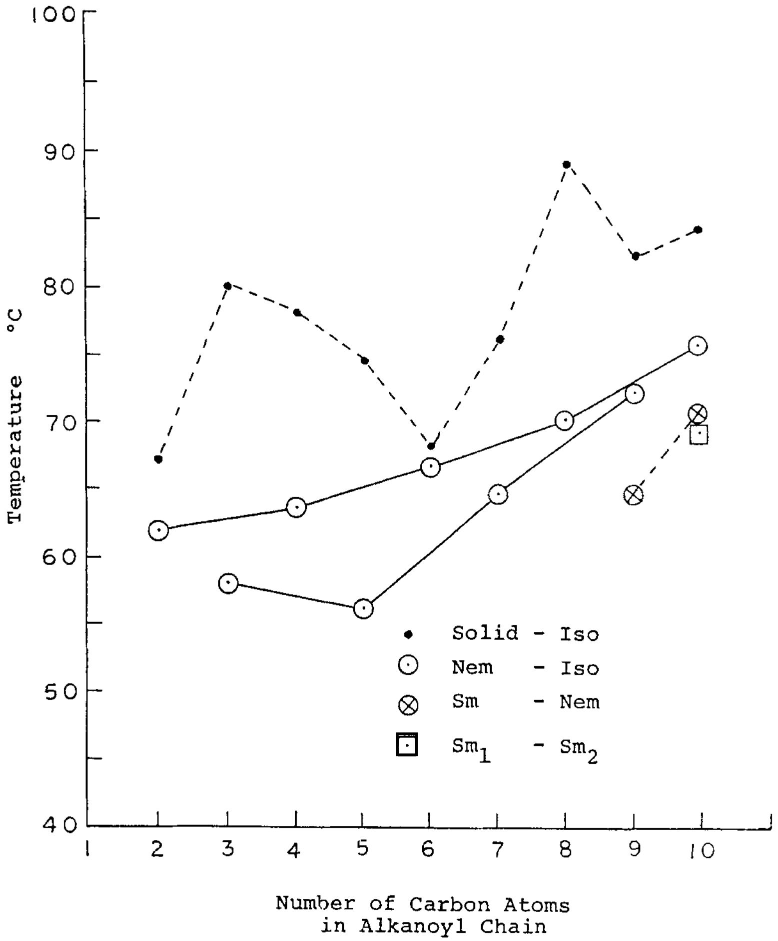

Figure 2. Transition Temperatures *vs* Chain Length For 4-*n*-Alkanoyloxybenzylidene-4′-ethylanilines.

behavior was observed to be particularly pronounced for 4-*n*-alkanoyloxybenzylidene derivatives (Tables 2, 3, 4 and 11); most compounds in these series show one or more monotropic transitions. This tendency does not appear limited to a particular mesophase. On the assumption of the most extended conformation for any given molecule in lower temperature condensed phases, each of these compounds would have a relatively strong dipole (the carbonyl group) transverse to the long molecular axis and which is not conjugated with the unsaturated aromatic system. This might enhance those intermolecular attractions which maintain the order of the crystalline lattice. Once melting has occurred, however, the relatively large molecule with multiple dipoles could adopt a number of stable intermolecular arrangements, differing from that in the crystalline lattice but with enhancement of the intermediate order of a mesophase. Considerable future effort will be required to unravel the structural and energetic details of this problem; the general trends noted here may be useful.

TABLE 2 Transition Temperatures for the 4-*n*-Alkanoyloxy-benzylidene-4′-ethylaniline Series

Alkanoyl	Temperature (°C) of transition to			
carbon number	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
C_2	—	—	—	67.0
C_3	—	—	(58.0)[a]	80.0
C_4	—	—	(63.5)	78.0
C_5	—	—	(56.0)	74.5
C_6	—	—	(66.5)	68.0
C_7	—	—	(64.5)	76.0
C_8	—	—	(70.0)	89.0
C_9	—	(64.5)[b]	(72.0)	82.0
C_{10}	(69.0)[b]	(70.5)[c]	(75.5)	84.5

[a] Values in parentheses indicate monotropy.
[b] Smectic B. [c] Smectic C.

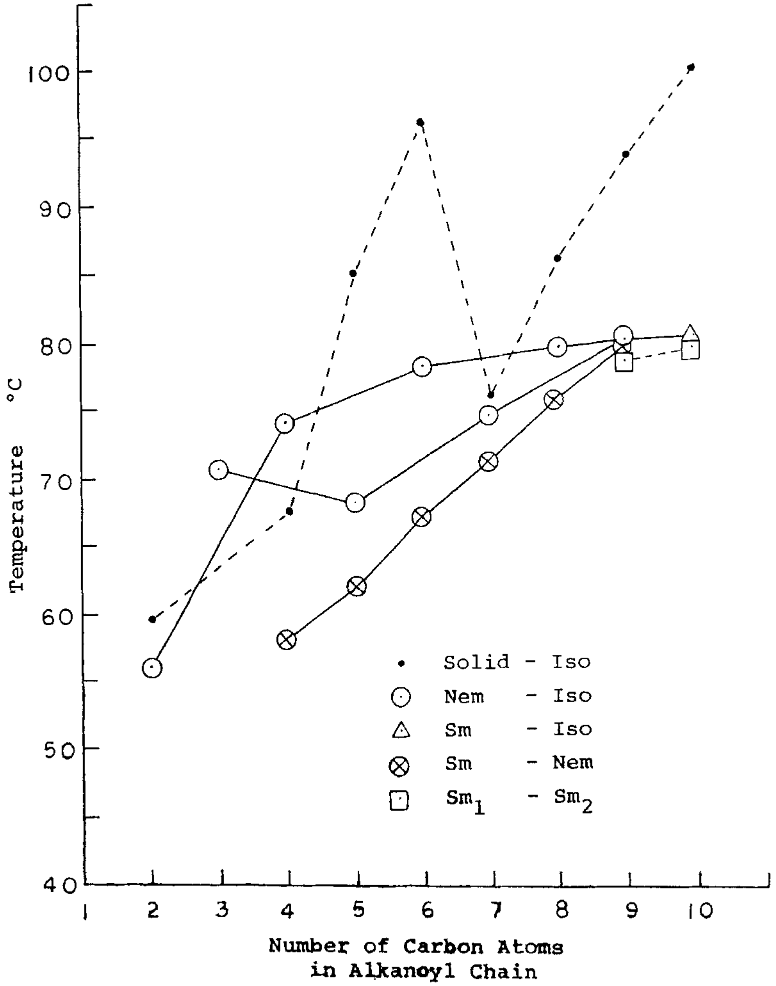

Figure 3. Transition Temperatures *vs* Chain Length For 4-*n*-Alkanoyloxybenzylidene-4′-*n*-butylanilines.

The nematic transition occurs at such elevated temperatures for compounds in the N,N′-di (4-*n*-alkanoyloxybenzylidene)-*p*-phenylenediamine series that decomposition was inevitable. The lower transition temperatures for these compounds were obtained by heating only to the nematic state, then cooling through each transition to establish reversibility. This series represents an extreme example of polymorphism, the heptanoyloxy- and octanoyloxy-derivatives demonstrating five different enantiotropic smectic mesophases as well as a nematic phase. Only the closely related bis(4′-*n*′alkoxybenzylidene)-1,4-phenylenediamines previously reported by Arora *et al.* of this laboratory[15] exhibits comparable polymorphism.

TABLE 3 Transition Temperatures for the 4-*n*-Alkanoyloxybenzylidene-4′-*n*-butylaniline Series

Alkanoyl carbon number	Temperature (°C) of transition to Smectic$_2$[a]	Smectic$_1$[b]	Nematic	Isotropic
C_2	—	—	(56.5)[c]	59.5
C_3	—	—	63.5	70.5
C_4	—	(58.0)	67.5	74.0
C_5	—	(62.0)	(68.0)	85.5
C_6	—	(68.0)	(76.0)	96.0
C_7	—	(71.0)	(74.5)	76.0
C_8	—	(75.5)	(79.5)	86.0
C_9	(79.0)	(79.5)	(80.0)	93.5
C_{10}	(79.5)	(80.0)	—	100.0

[a] Smectic 2 appear to be smectic B.
[b] C_4, C_5 and C_6 smectic 1 appear to be smectic A, C_7 and C_8 smectic 1 appear to be smectic B and C_9 and C_{10} smectic 1 appear to be smectic C.
[c] Values in parentheses indicate monotropy.

Transition temperatures obtained by DTA measurements were confirmed by examination of each compound by hot stage microscopy with polarized light; this also provided observations of texture for preliminary classification of mesophases by the Sackmann and Demus criteria.[5] These classes are specified in the footnotes to each table.

Figures 2 through 11 are plots of the transition temperatures *vs* the number of carbon atoms in the variable substituent for each series.

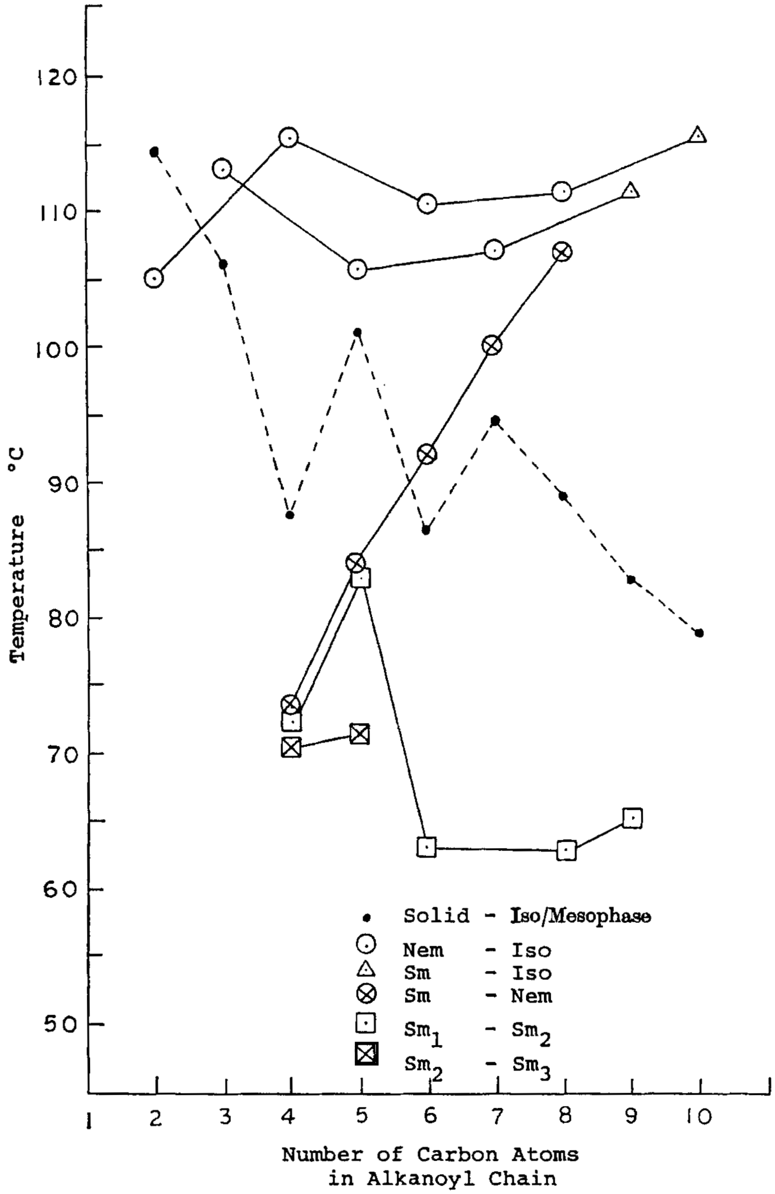

Figure 4. Transition Temperatures *vs* Chain Length For 4-*n*-Alkanoyloxybenzylidene-4′-aminoacetophenones.

These provide a convenient format illustrating the mesophase properties of any given compound at a glance and incidentally illustrate trends in the transition temperatures as a function of carbon chain length. These are generally typical of such plots; thus even-carbon homologues of either alkoxy- or alkanoyloxybenzylidene derivatives have higher mesophase-isotropic transition temperatures than neighboring odd-carbon homologues. Most mesophase-mesophase or mesophase-isotropic transitions fall on a smooth curve with change in carbon number whereas solid-mesophase transitions show relatively erratic rise and fall with carbon number.

TABLE 4 Transition Temperatures for the 4-*n*-Alkanoyloxybenzylidene-4′-aminoacetophenone Series

Alkanoyl carbon number	Temperature (°C) of transition to Smectic$_3$	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
C_2	—	—	—	(105.0)$^{(a)}$	114.5
C_3	—	—	—	106.0	113.0
C_4	(70.5)$^{(b)}$	(72.5)$^{(c)}$	(73.5)$^{(d)}$	87.5	115.5
C_5	(71.5)$^{(b)}$	(83.0)$^{(c)}$	(84.0)$^{(d)}$	101.0	105.5
C_6	—	(63.0)$^{(b)}$	86.5$^{(c)}$	92.0	110.5
C_7	—	—	94.5$^{(c)}$	100.0	107.0
C_8	—	(63.0)$^{(b)}$	89.0$^{(c)}$	107.0	111.5
C_9	—	(65.0)$^{(b)}$	83.0$^{(c)}$	—	111.5
C_{10}	—	—	79.0$^{(c)}$	—	116.0

(a) Values in parentheses indicate monotropy.
(b) Smectic B. (c) Smectic C. (d) Smectic A.

Smectic$_1$–smectic$_2$ transitions for several series (Figs. 4, 5 and 6) show the interesting phenomenon of passing through a minimum at chain lengths of about six carbon atoms; analogous transitions for both lower and higher members of these series are higher.

3. Experimental Methods

Analytical spectroscopic data were obtained on Perkin–Elmer Model 337 (infrared), Varian Associates Model A-60 (Pmr) and

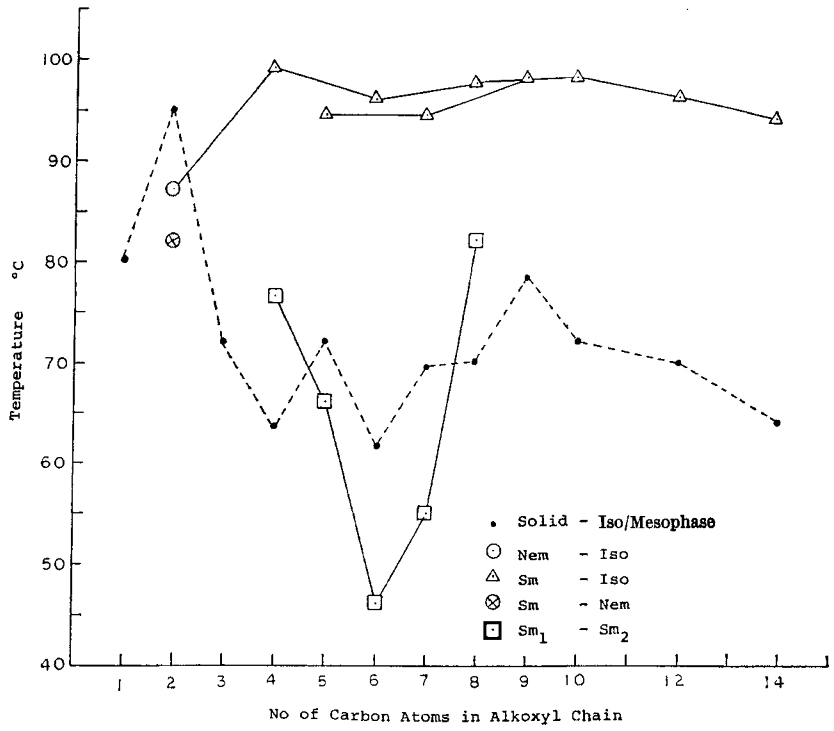

Figure 5. Transition Temperatures *vs* Chain Length For Ethyl 4-*n*-Alkoxybenzylidene-4′-aminobenzoates.

TABLE 5 Transition Temperatures for the Ethyl 4-*n*-Alkoxybenzylidene-4′-aminobenzoate Series

n-Alkyl	Temperature (°C) of transition to			
carbon number	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
C$_1$	—	—	—	80.0
C$_2$	—	(82.0)	(87.0)(a)	95.0(b)
C$_3$	—	—	—	72.0
C$_4$	63.5	76.5	—	99.0
C$_5$	(66.0)	72.0	—	94.5
C$_6$	(46.0)	61.5	—	96.0
C$_7$	(55.0)	69.5	—	94.5
C$_8$	70.0	82.0	—	97.5
C$_9$	—	78.5	—	98.0
C$_{10}$	—	72.0	—	98.0
C$_{12}$	—	70.0	—	96.0
C$_{14}$	—	64.0	—	94.0

(a) Values in parentheses indicate monotropy.

(b) Vorländer(17) reported: Solid $\xleftrightarrow{121.0}$ nem $\xleftrightarrow{129{\cdot}0}$ i.

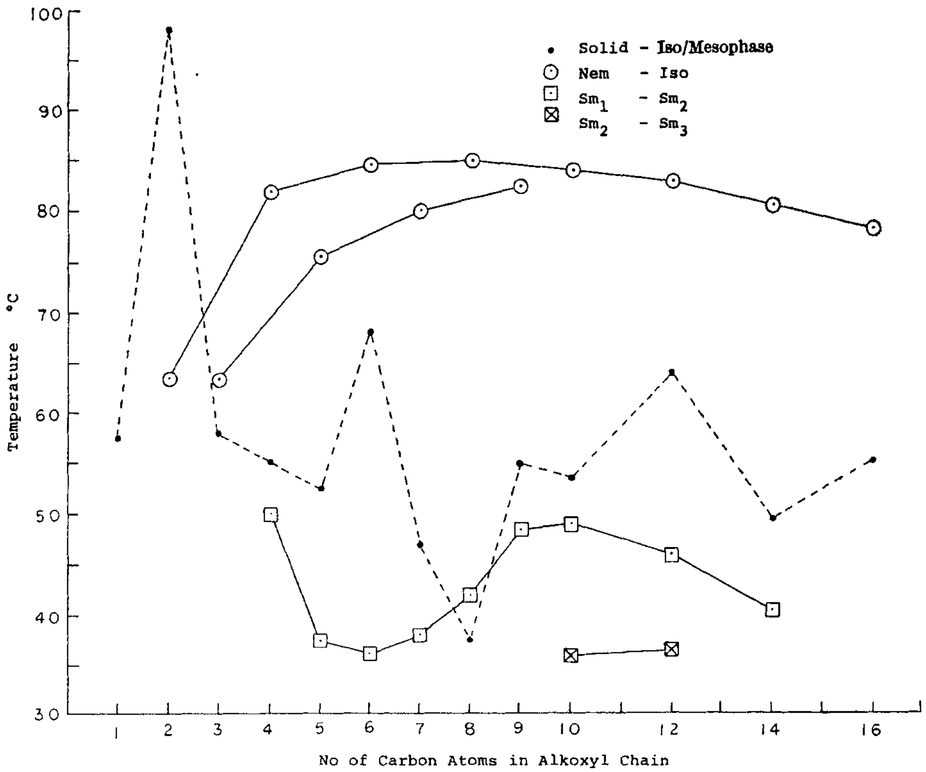

Figure 6. Transition Temperatures *vs* Chain Length For Butyl 4-*n*-Alkoxybenzylidene-4′-aminobenzoates.

TABLE 6 Transition Temperatures for the Butyl 4-*n*-alkoxybenzylidene-4′-aminobenzoate Series

n-Alkyl	Temperature (°C) of transition to			
carbon number	Smectic$_3$(a)	Smectic$_2$(b)	Smectic$_1$(c)	Isotropic
C_1	—	—	—	57.5
C_2	—	—	(63.5)(d)	98.0
C_3	—	—	58.0	63.5
C_4	—	(50.0)	55.0	82.0
C_5	—	(37.5)	52.5	75.5
C_6	—	(36.0)	68.0	84.5
C_7	—	(38.0)	47.0	80.0
C_8	—	37.5	42.0	85.0
C_9	—	(48.5)	55.0	82.5
C_{10}	(36.0)	(49.0)	53.5	84.0
C_{12}	(36.5)	(46.0)	64.0	83.0
C_{14}	—	(40.5)	49.5	80.5
C_{16}	—	—	55.0	78.0

(a) Smectic$_3$ appears to be smectic B.

(b) Smectic$_2$ phase is similar in appearance to a smectic A but with more lines of discontinuity.

(c) Smectic$_1$ state appears to be a smectic A.

(d) Values in parentheses indicate monotropy.

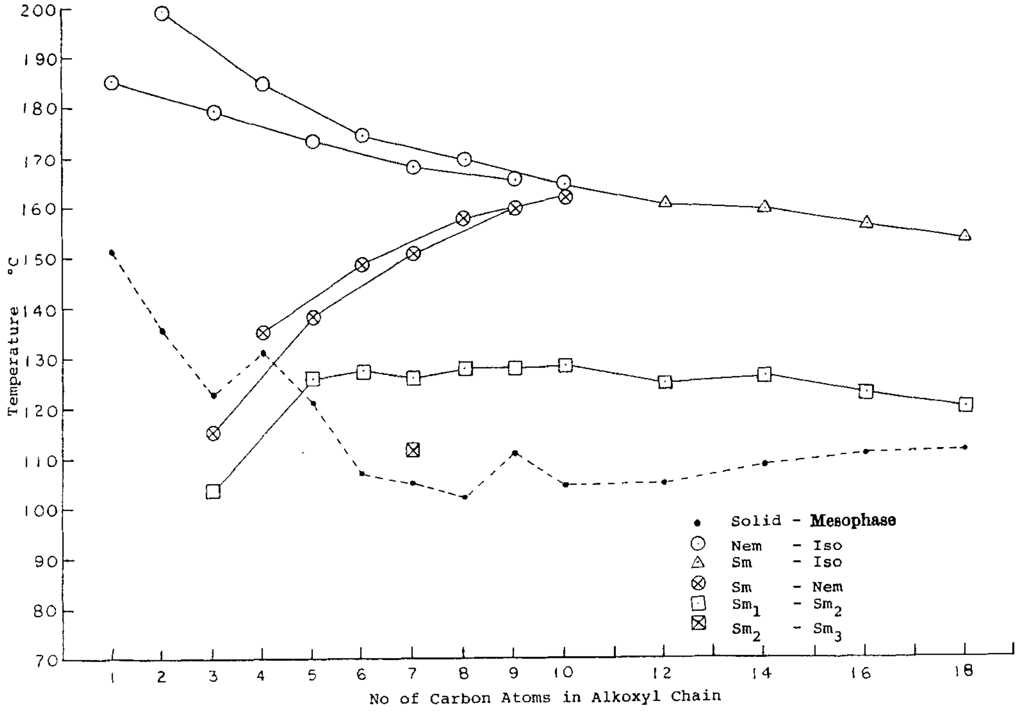

Figure 7. Transition Temperatures *vs* Chain Length For 4-*n*-Alkoxybenzylidene-4′-aminoazobenzenes.

TABLE 7 Transition Temperatures for the 4-*n*-Alkoxybenzylidene-4′-aminoazobenzene Series

n-Alkyl carbon number	Temperature (°C) of transition to				
	Smectic$_3$(a)	Smectic$_2$(b)	Smectic$_1$(c)	Nematic	Isotropic
C_1	—	—	—	151.0	185.0(d)
C_2	—	—	—	135.0	199.0(e)
C_3	—	(103.5)(f)	(115.0)(f)	122.5	179.0
C_4	—	—	131.0	135.0	184.5
C_5	—	121.0	125.5	138.0	173.0
C_6	—	107.5	127.0	148.0	174.0
C_7	105.0	111.5	125.5	150.5	167.5
C_8	—	102.0	127.5	157.5	169.0
C_9	—	111.0	127.5	159.5	165.0(g)
C_{10}	—	104.5	128.0	161.5	164.0
C_{12}	—	105.0	125.0	—	160.0
C_{14}	—	109.0	126.0	—	159.0
C_{16}	—	111.0	123.0	—	156.0
C_{18}	—	111.5	120.5	—	153.0

(a) The C_7 smectic$_3$ is similar to smectic 3 (modified smectic C).
(b) All smectic$_2$ to be smectic C.
(c) All smectic 1 appear to be smectic A.
(d) Vorländer and Schuster(18) reported.
(e) Stolzenberg(19) reported.
(f) Values in parentheses indicate monotropy.
(g) Weygand and Gabler(20) reported.

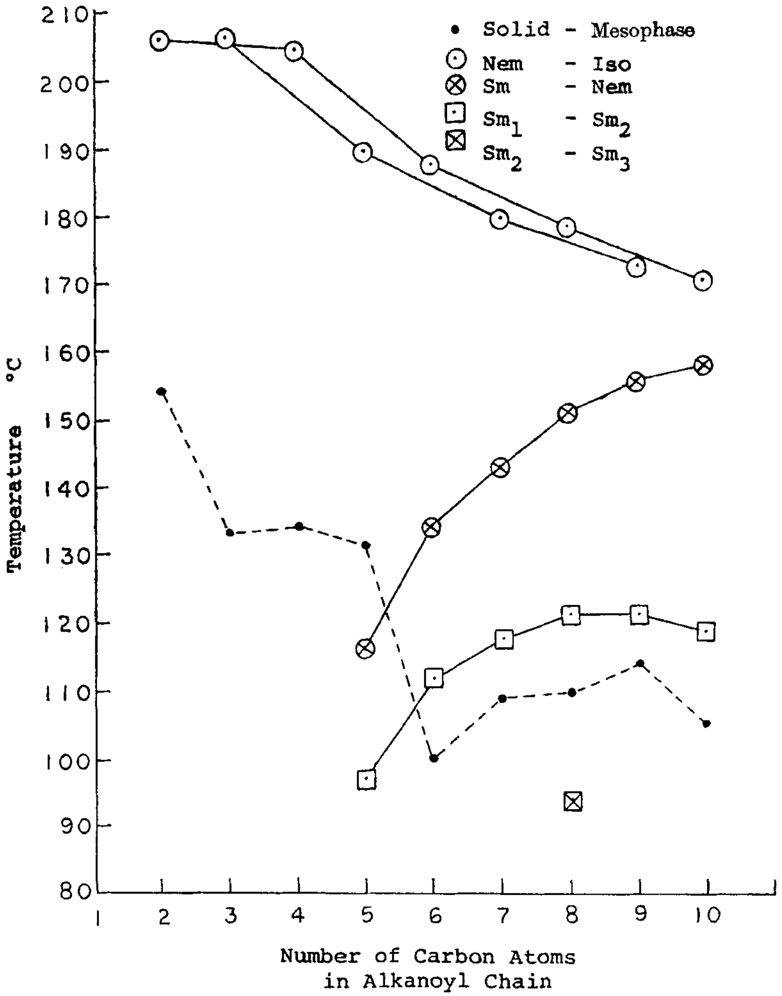

Figure 8. Transition Temperatures *vs* Chain Length For 4-*n*-Alkanoyloxybenzylidene-4′-aminoazobenzenes.

Associated Electronics Industries Model MS-12 (mass spectra) spectrometers. Elemental analyses were performed by Galbraith, Laboratories, Knoxville, Tennessee or Spang Laboratories, Ann Arbor, Michigan. Interphase transition temperatures were determined by differential thermal analysis and by phase contrast microscopy; instruments used were either a DuPont DTA 900 or DTA 920 and either a Leitz Ortholux polarizing microscope equipped with Mettler FP-2 heating stage or a Reichert Thermopan polarizing microscope equipped with a heating stage.

TABLE 8 Transition Temperatures for the 4-*n*-Alkanoyloxybenzylidene-4′-aminoazobenzene Series

Alkanoyl carbon number	Smectic$_3$[a]	Smectic$_2$[b]	Smectic$_1$[c]	Nematic	Isotropic
C_2	—	—	—	154.0	206.0
C_3	—	—	—	133.0	206.5
C_4	—	—	—	134.5	204.5
C_5	—	(97.0)	(116.5)[d]	131.5	189.5
C_6	—	100.0	112.0	134.0	187.5
C_7	—	109.0	118.0	143.0	179.5
C_8	(94.0)	109.5	121.0	151.0	178.5
C_9	—	114.0	121.0	155.5	172.5
C_{10}	—	105.0	119.0	158.5	170.5

[a] Smectic$_3$ for C_7 is assigned as Smectic B.
[b] Smectic$_2$ is tentatively assigned as Smectic C.
[c] Smectic$_1$ appears to be Smectic A.
[d] Values in parentheses indicate monotropy.

MATERIALS

Anil (Schiff's base) precursors were synthesized as described below or were purchased commercially, purified, and analyzed before use.

4-n-Alkoxybenzaldehydes were prepared by a modification of the Williamson synthesis reported for 2-*n*-butoxynitrobenzene.(16) An equimolar mixture of 4-hydroxybenzaldehyde, the respective alkyl bromide and anhydrous potassium carbonate was refluxed 24–48 hours in 2-butanone (70 ml/0.1 mole.). Water was added, the organic phase removed and the aqueous phase extracted with benzene.

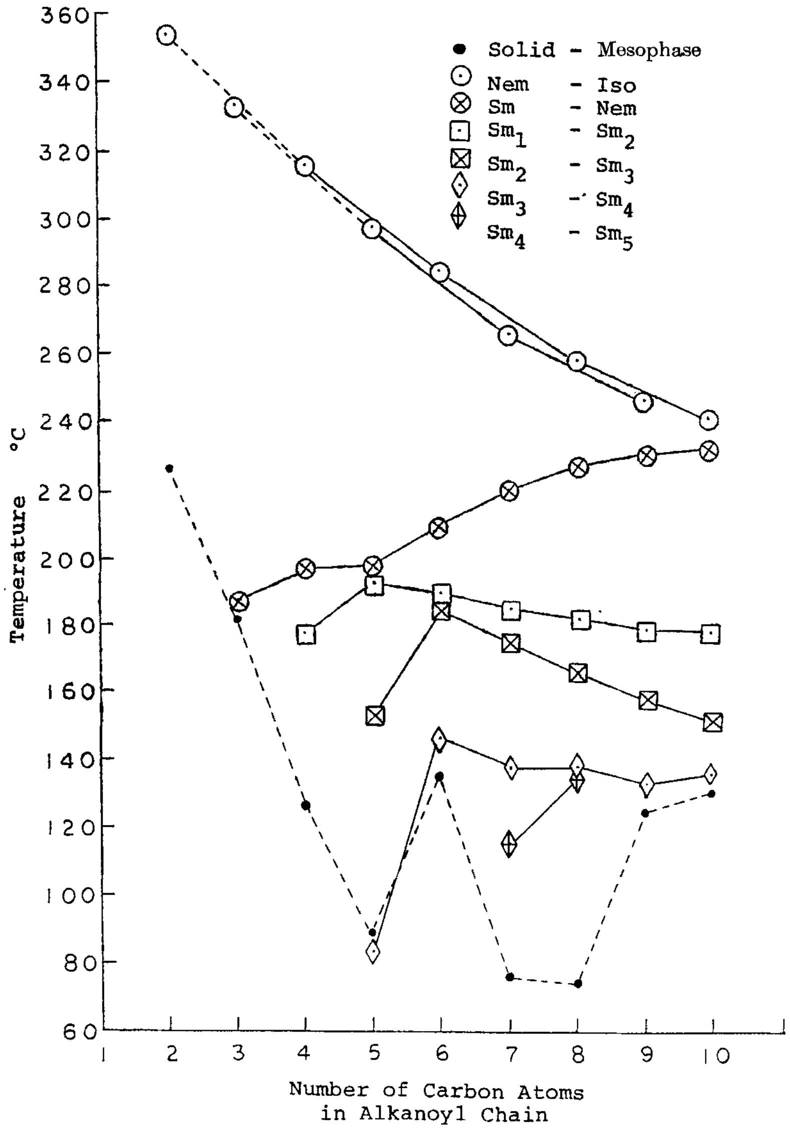

Figure 9. Transition Temperatures *vs* Chain Length For N,N′-*Bis*-(4-*n*-alkanoyloxybenzylidene-*p*-phenylenediamines.

The combined organic phase was washed with 15% sodium hydroxide and water, dried over sodium sulfate, stripped and distilled at reduced pressure. Yields ranged from 55–85%.

4-*n-Alkanoyloxybenzaldehydes* were prepared by the dropwise addition of the appropriate alkanoyl chloride to a stirred equimolar mixture of 4-hydroxybenzaldehyde and pyridine in benzene. The mixture was worked up after a brief reflux period in a manner similar to that for the 4-*n*-alkoxybenzaldehydes. Yields ranged from 50–70%.

TABLE 9 Transition Temperatures for the N,N′-Di-(*p*-*n*-alkanoyloxybenzylidene)-*p*-phenylenediamine Series

Alkanoyl carbon number	Smectic$_5$	Smectic$_4$	Smectic$_3$	Smectic$_2$	Smectic$_1$	Nematic	Isotropic†
C$_2$	—	—	—	—	—	225.0	> 315.0
C$_3$	—	—	—	—	181.0	187.0	> 315.0
C$_4$	—	—	—	126.0	177.0	196.5	315.0
C$_5$	—	(83.0)(a)	88.0	153.0	192.0	197.5	297.0
C$_6$	—	135.0	146.0	184.0	189.0	208.5	284.0
C$_7$	75.0	114.5	137.0	174.5	185.0	220.0	265.0
C$_8$	73.0	134.0	138.0	165.0	181.5	226.5	257.5
C$_9$	—	124.0	132.5	158.0	178.0	229.5	245.5
C$_{10}$	—	130.0	136.0	151.0	177.0	231.0	239.5

(a) Values in parentheses indicate monotropy.

† There is considerable decomposition at nematic-isotropic transition so transition temperatures are not reproducible within 1 °C range. It is best to check transition temperatures while heating and cooling up to smectic$_1$–Nematic point.

ANIL SYNTHESES, GENERAL PREPARATION

Equimolar quantities of the aldehyde and aniline (except for the use of two moles of the aldehyde for *p*-phenylenediamine derivatives) were mixed and refluxed in either benzene or absolute ethanol as the solvent. The resulting products were recrystallized several times from suitable solvents to constant transition temperatures. The compounds of the ethyl 4-*n*-alkoxybenzylidene-4′-aminobenzoate and the butyl 4-*n*-alkoxybenzylidene-4′-aminobenzoate series were first dissolved in ether and the ethereal solution

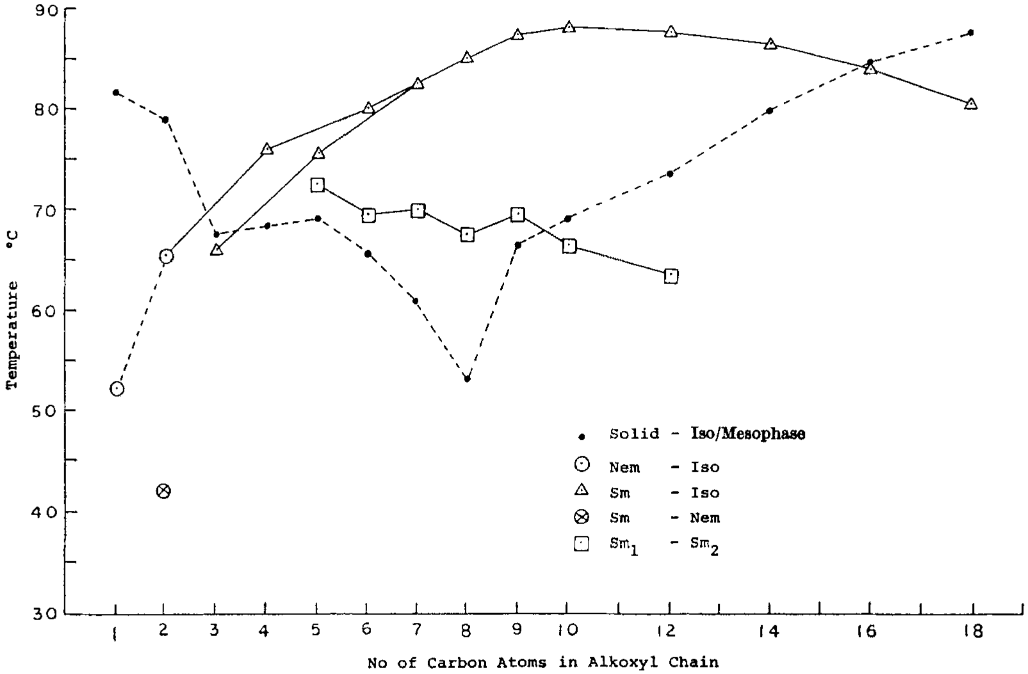

Figure 10. Transition Temperatures *vs* Chain Length For 4-*n*-Alkoxybenzylidene-2′-methoxy-5′-aminopyridines.

was washed with dilute sodium acid carbonate solution. The ether was evaporated and the product was crystallized from ethanol. Most of the compounds of the several 4-*n*-alkanoyloxybenzylidene anil series were recrystallized from methanol.

TABLE 10 Transition Temperatures for the 4-*n*-Alkoxybenzylidene-N-2′-methoxy-5′-aminopyridine Series

n-Alkyl carbon number	Temperature (°C) of transition to Smectic$_2$[a]	Smectic$_1$[b]	Nematic	Isotropic
C_1	—	—	—	81.5
C_2	—	(42.0)	(65.5)[c]	79.0
C_3	—	(66.0)	—	68.0
C_4	—	68.5	—	76.0
C_5	69.0	72.5	—	75.5
C_6	65.5	69.5	—	80.0
C_7	61.0	70.0	—	82.5
C_8	53.0	67.5	—	85.0
C_9	66.5	69.0	—	87.5
C_{10}	(66.5)	69.0	—	88.0
C_{12}	(63.5)	73.5	—	87.5
C_{14}	—	79.5	—	86.5
C_{16}	—	(84.0)	—	84.5
C_{18}	—	(80.5)	—	87.5

(a) All smectic 2 appear to be smectic C.

(b) C_2, C_3 and C_4 smectic 1 appear to be smectic B's; C_5 through C_{12} smectic 1 appear to be smectic A; C_{14}, C_{16} and C_{18} smectic 1 appear to be smectic C.

(c) Values in parentheses indicate monotropy.

Acknowledgements

We thank the United States Department of Defense for support of this work as part of an Air Force Office of Scientific Research Project under Contract Number F44620-69-C-0021. The mass spectrometer was purchased with a matching funds grant from the National Science Foundation; we appreciate the help of Mr. H. J. Eyman for mass analyses. We also thank Mr. Ying-yen Hsu for checking some of the transition temperatures and for preparing the figures.

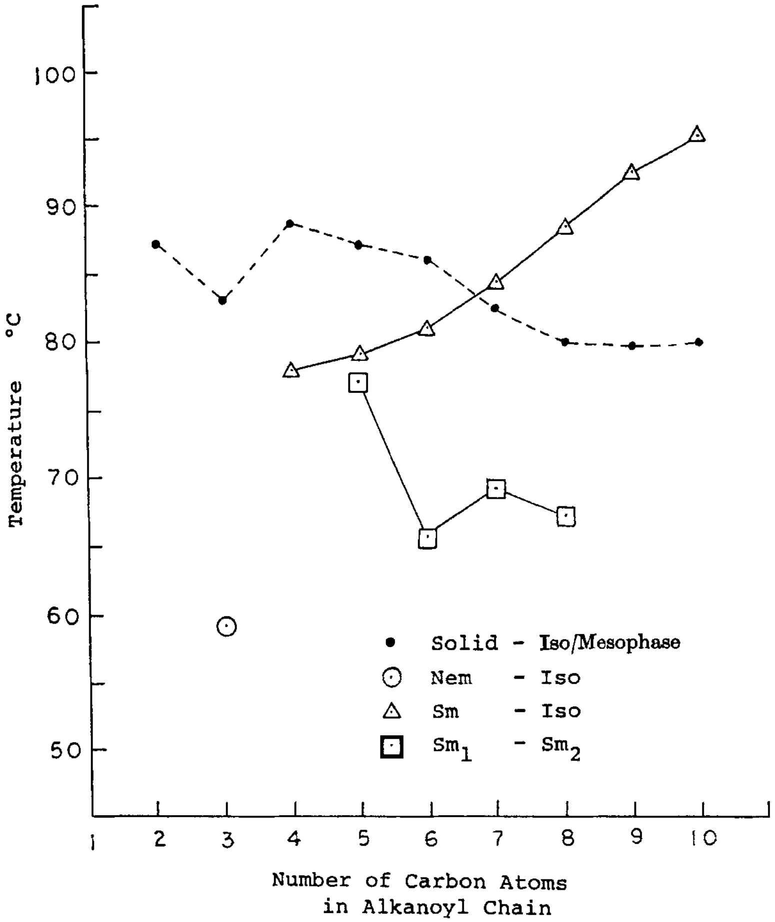

Figure 11. Transition Temperatures *vs* Chain Length For 4-*n*-Alkanoyloxybenzylidene-2′-methoxy-5′-aminopyridines.

TABLE 11 Transition Temperatures for the 4-*n*-Alkanoyloxybenzylidene-N-2′-methoxy-5′-aminopyridine Series

n-Alkyl	Temperature (°C) of transition to			
carbon number	Smectic$_2$[a]	Smectic$_1$[b]	Nematic	Isotropic
C_2	—	—	(49.5)[c]	87.0
C_3	—	—	(59.0)	83.0
C_4	—	(78.0)	—	88.5
C_5	(77.0)	(79.0)	—	87.0
C_6	(65.5)	(81.0)	—	86.0
C_7	(69.0)	82.5	—	84.5
C_8	(67.0)	80.0	—	88.5
C_9	—	79.5	—	92.5
C_{10}	—	79.5	—	95.0

[a] Smectic 2 appear to be Smectic C.

[b] C_4 smectic 1 appears to be smectic B; all other smectic 1 appear to be smectic A.

[c] Values in parentheses indicate monotropy.

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