Mesomorphic Properties of Alkoxybenzylidene-aminoacetophenones

Sardari L. Arora, Ted R. Taylor, James L. Fergason
Liquid Crystal Institute
Kent State University
Kent, Ohio, 44240

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Abstract

As a part of the program to study the effects of unsymmetrical molecules on the formation of smectic phases, a number of 4-n-alkoxybenzylidene-4'-aminoacetophenones with a chain length in the alkoxy substituent from C_1, C_3 to C_{10}, C_{12} and C_{14} have been synthesized. All the homologs, with the exception of methoxy substituent, show mesophases as listed in Table I. Compounds for n-alkoxy chain length of C_3 to C_6 show an enantiotropic nematic and smectic 1 and a monotropic smectic 2. Compounds with a chain length of C_7 to C_9 exhibit an enantiotropic smectic 1 and a monotropic smectic 2. Other homologs with a chain length of C_{10}, C_{12} and C_{14} exhibit only an enantiotropic smectic 1. Both the smectic 2 and smectic 1 have a morphology identical to that of the classical smectic A of Sackmann and Demus.[4] Further, both the smectic phases show focal-conic structure and homeotropic form. No apparent change either in the mechanical or optical properties is observable at the transition temperature of these two phases. Experimental data on the phase transition temperatures differ from the previously reported work of Castellano et al.[1]

Compounds of alkoxybenzylidene-aminoacetophenone series are of special interest as many of them have a wide range of smectic phase A below 130°C. Four homologs of this series with C_1, C_2, C_4 and C_8 in the n-alkoxy chain length have been reported by Castellano et al.[1]

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(1) J. A. Castellano, J. E. Goldmacher, L. A. Barton and J. S. Kane, J. Org. Chem., 33, 3501 (1968).

Their observation of a nematic phase in 4-n-octyloxybenzylidene-4'-aminoacetophenone we believe to be in error. The only phase we observe between the melt and the isotropic liquid is a smectic phase. The possibility of a nematic phase in the aforementioned compound is, further, ruled out because no nematic phase is observed in the lower homolog with C_7 in the chain length. The absence of the nematic phase in these two compounds is further confirmed by our optical and differential thermal analysis studies.

EXPERIMENTAL SECTION

The phase transition temperatures were determined both by differential thermal analysis (Du Pont DTA 900) and with a Leitz Panphot polarizing microscope using a Mettler FP-2 heating stage. Melting points (solid-liquid or solid-liquid crystal transition) have been regarded as the transitions with the highest transition energy. These are also always the transitions that can most easily be supercooled, whereas supercooling in the case of liquid crystal transitions is negligible.

Monotropic liquid crystal transition temperatures observed below the melting points during the cooling operation of DTA thermograms were confirmed by reheating of the samples before crystallization. The assignments of the transition temperatures were confirmed by the polarizing microscope, except for the monotropic smectic 2 - smectic 1 transitions. The highest temperature smectic phase is always called smectic 1, the next lower one smectic 2, and so on. The transition temperatures for the various liquid crystal phases are listed in Table I. The error of the temperature measurements is estimated to be smaller than ±2°C. A plot of phase transition temperatures versus the number of carbon atoms in the alkyl chain is shown in Figure 1. For comparison, the data of Castellano, et al.[1] is shown by dotted lines.

4-aminoacetophenone was recrystallized from commercially available material.

4-n-alkoxybenzaldehydes were prepared from p-hydroxybenzaldehyde and various alkyl bromides either according to the method of our earlier publication[2] or by that of Weygand and Gabler.[3]

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(2) S. L. Arora, J. L. Fergason and A. Saupe, Mol. Cryst. and Liq. Cryst. (In Press, 1969)

(3) C. Weygand and R. Gabler, J. Prakt. Chem., 155, 338 (1940).

Alkoxybenzylidene-aminoacetophenones were prepared by refluxing equimolecular quantities of the 4-aminoacetophenone and the appropriate 4-n-alkoxybenzaldehyde in absolute alcohol for 5-6 hours. The product after isolation was recrystallized several times from appropriate solvents until the transition temperature remained constant.

The liquid crystal-liquid crystal transitions with the purified compounds were sharp and reversible. Differential thermal analysis gave on heating and on cooling, within a fraction of a degree, equal temperatures for these transitions.

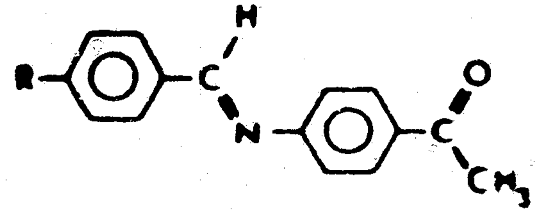

Table I. 4-n-alkoxybenzylidene-4'-aminoacetophenones

Compd.	Substituents	Transition temperatures, °C, from solid or preceeding liquid crystal state to:			Anal. %					
					Calcd.			Found		
		Smectic 1	Nematic	Isotropic	C	H	N	C	H	N
1	R= H_3CO	---	---	123 124.5^a	75.87	5.97	5.53	75.65	5.93	5.50
2	H_5C_2O	---	---	123^a ~~(118)^a~~	---	---	---	---	---	---
3	H_7C_3O	89.5 59.5	90.5	101	76.84	6.81	4.98	76.81	6.80	5.01
4	H_9C_4O	85 85^a 57.5^c	100.5 98^a	113 111^a	77.26	7.17	4.74	77.17	7.12	4.47
5	$H_{11}C_5O$	74 58^c	107.5	109	77.64	7.49	4.53	77.97	7.70	4.61
6	$H_{13}C_6O$	73.5 54^c	112.5	114.5	77.99	7.79	4.33	78.32	7.55	4.43
7	$H_{15}C_7O$	83 57^c	---	116	78.30	8.06	4.15	78.43	8.07	4.20
8	$H_{17}C_8O$	72 73^a 55^c	--- 117^{ab}	119 119^a	78.60	8.32	3.98	78.49	8.51	4.08
9	$H_{19}C_9O$	85 59^c	---	120	78.87	8.55	3.83	78.83	8.53	3.77
10	$H_{21}C_{10}O$	81	---	121	79.11	8.76	3.70	79.04	8.77	3.63
11	$H_{25}C_{12}O$	88	---	121	79.56	9.15	3.44	79.71	9.25	3.38
12	$H_{29}C_{14}O$	92	---	119	79.95	9.49	3.22	80.04	9.49	3.14

[a] Transition temperatures reported by Castellano, et al.[1] Value in parentheses is the monotropic nematic.

[b] Transition temperature for smectic 1-nematic by Castellano, et al.[1], and is wrong because no nematic phase is observed in this compound.

[c] Transition from monotropic smectic 2.

RESULTS

Of the eleven compounds synthesized by us in this series, the lowest homolog with C_1 in the alkyl chain shows no liquid crystalline phase. A nemtaic phase is observed in compounds with n-alkoxy chain lengths of C_3, C_4, C_5 and C_6 only. All other compounds from C_3 - C_{10}, C_{12} and C_{14} show an enantiotropic smectic 1 phase. Monotropic smectic 2 is observed in compounds with chain lengths of C_3 - C_9.

Smectic 1 shows the focal-conic texture typical of smectic A of Sackmann and Demus.[4] Monotropic smectic 2 appears to be identical with smectic 1, and it is not possible to distinguish this phase from smectic 1 by optical methods.

DISCUSSION

In Figure I, one observes an unusually marked alternation of the nematic-isotropic transition temperatures for odd and even numbers of carbon atoms in the alkyl chain of this homolog's series. The plot for even carbon chain homologs lies above that for odd carbon chain members. Further, this extent of alternation decreases as the chain length increases. The alternation of nematic-isotropic transition temperatures in such a series is similar to that found by Gray[5] in alkoxybenzoic acids and alkoxy Schiff bases.

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(4) H. Sackmann and D. Demus, Mol. Cryst., 2, 81 (1966).

(5) G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, London and New York (1962).

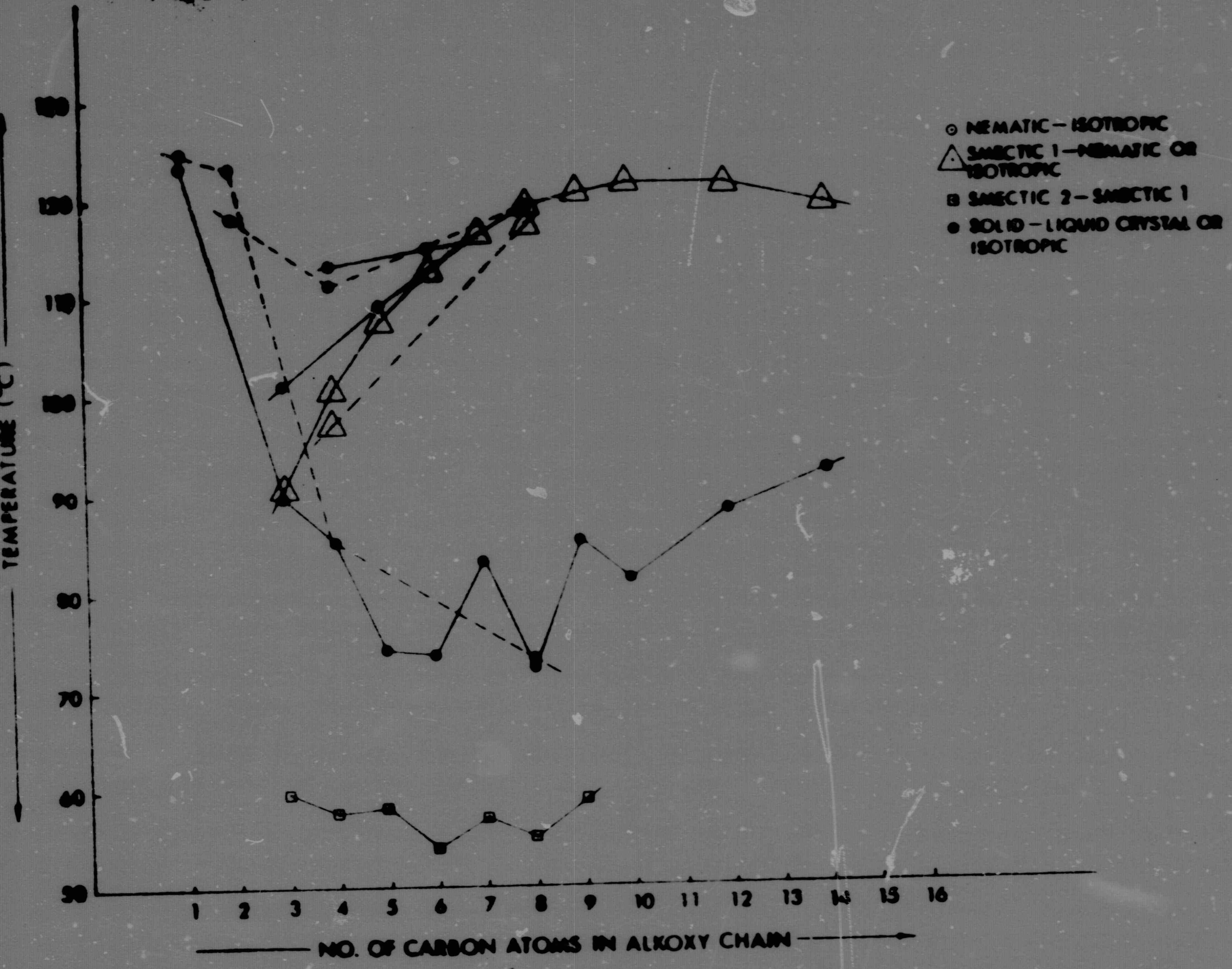
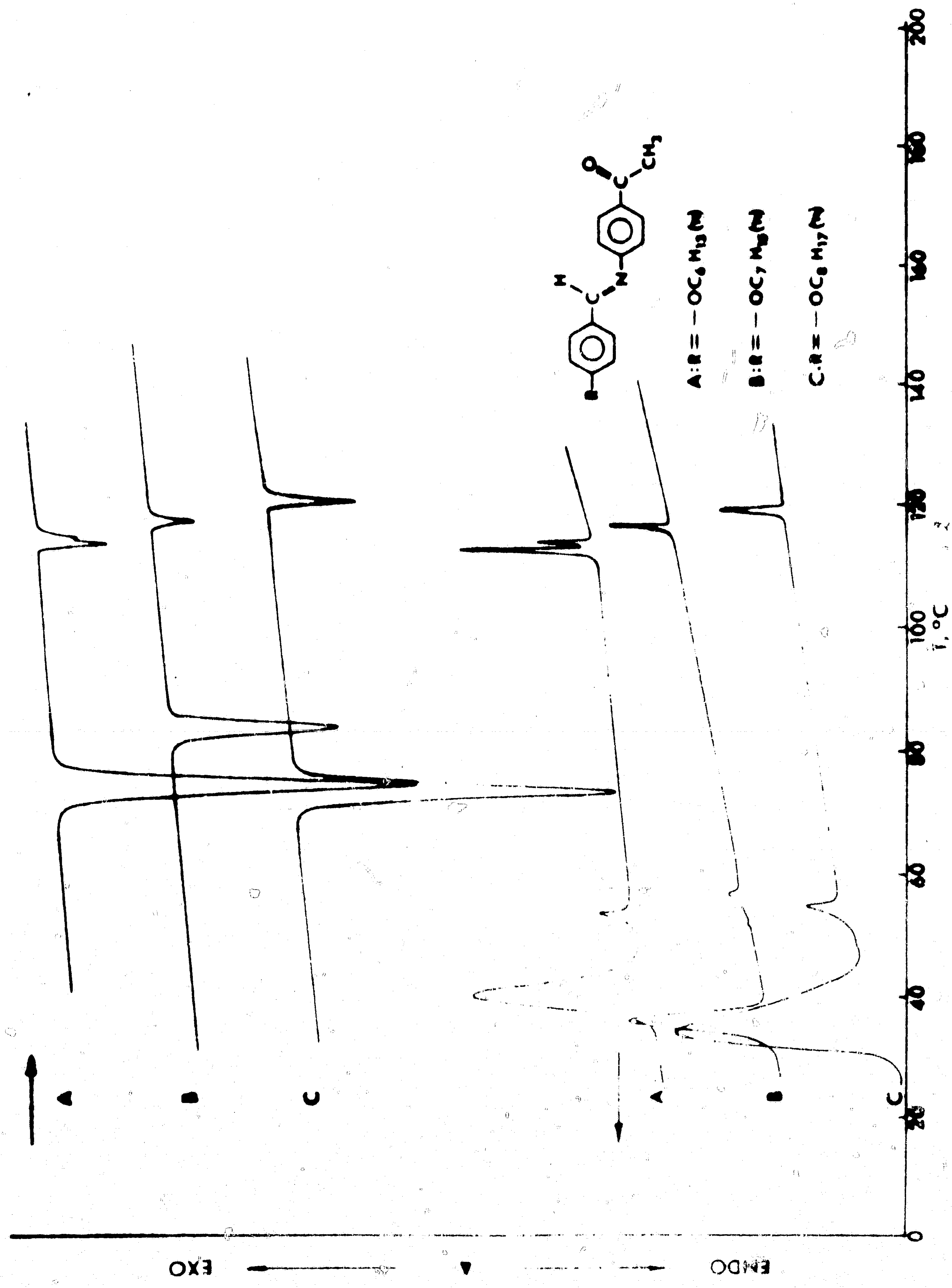

⊙ NEMATIC – ISOTROPIC
△ SMECTIC 1 – NEMATIC OR ISOTROPIC
⊡ SMECTIC 2 – SMECTIC 1
● SOLID – LIQUID CRYSTAL OR ISOTROPIC
TEMPERATURE (°C)
130
120
110
100
90
80
70
60
50
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
NO. OF CARBON ATOMS IN ALKOXY CHAIN

Fig 2

In Figure 1, the nematic isotropic phase curves for both odd and even alkyl chain homologs become coincident with the rising smectic-nematic transition curve at a point which lies below the point for the homolog with C_7 in the alkyl chain. When such a merging of the nematic-isotropic and smectic-nematic curves takes place, then it is well known that all other higher homologs above the merger do not show a nematic phase. This behavior is indeed observed in 4-*n*-heptyloxybenzylidene-4'-aminoacetophenone which does not exhibit a nematic phase but has only one enantiotropic smectic mesophase which passes directly into the isotropic liquid. Hence, on this basis, it is unlikely for C_8 to have a nematic phase when its predecessor homolog does not show such a phase.

The absence of a nematic phase in C_8 is further confirmed by our differential thermal analysis (DTA) of this compound. In Figure 2 the thermograms of homologs with alkyl chain length C_6, C_7 and C_8 are shown. An examination of these establishes one enantiotropic liquid crystal phase between the melt and isotropic liquid for C_7 and C_8. However, two enantiotropic mesophases are evident for C_6. Optical studies of these two mesophases indicate that the lower temperature phase is smectic and the higher temperature phase, nematic. Further, these two liquid crystal phases are separated from one another by a very narrow range. Optical studies of the single enantiotropic mesophase observed for C_6 and C_8 show this phase to be smectic A as defined by Sackmann and Demus.[4] In sum, our observations do not show a nematic phase for C_8 as reported by Castellano et al.[1]

In compounds with alkyl chain lengths C_3 - C_9, a previously unobserved[1] monotropic smectic 2 phase is observed. This phase is observed in cooling DTA thermograms as shown in Figure 2 for C_6, C_7 and C_8. Since smectic 2 is


A:R = —OC$_6$H$_{13}$(N)
B:R = —OC$_7$H$_{15}$(N)
C:R = —OC$_8$H$_{17}$(N)
R
H
C
N
C
O
CH$_3$
A
B
C
A
B
C
0
20
40
60
80
100
120
140
160
180
200
T, °C
EXO
ENDO

a supercooled state, it must be carefully distinguished from a transition to a solid. If the transition does represent a mesophase, the transition should be completely reversible. We, therefore, did make thermograms in which, after the smectic 1 - smectic 2 transition occurred on cooling, the DTA was reversed and the transition ran through on the heating cycle. In all cases, the transition was still present on heating, confirming our supposition that the transition did not represent crystallization.

Optically, monotropic smectic 2 appears to be identical to smectic 1, that is, smectic A. Within the limits of our optical measuring techniques, we can observe no change at the smectic 1 - smectic 2 transition temperature. There does appear to be a difference in viscosity between smectic 1 and smectic 2. If the relatively viscous smectic 2 is distorted by moving the cover slip, then on reheating there is flow near the smectic 1-smectic 2 transition temperature.

It is interesting to note that smectic 1 and smectic 2 cannot be classified according to the miscibility method of Sackmann and Demus.[4] Since both phases have identical optical textures, there would be no phase boundary due to miscibility. We recently encountered a similar situation during our studies on the smectic phases of the homologs of 4-n-alkoxybenzylidene-4'-aminopropiophenones[6] where an explanation is given for the unusual behavior of these apparently identical smectic phases

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(6) S. L. Arora, T. R. Taylor and J. L. Fergason, Paper submitted for Am. Chem. Soc. Sym. on Ordered Fluids & Liq. Crystals, Sept. (1969).

Acknowledgment

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