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J. P. Schroeder [a]

[a] Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, North Carolina, 27412, U.S.A.

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Liquid Crystals

VII. Smectic-Nematic Transition Temperature as a Function of Alkyl End Group Length in *p*-Phenylene Di-*p*-*n*-alkoxybenzoates[1]

J. P. SCHROEDER

Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, North Carolina 27412, U.S.A.

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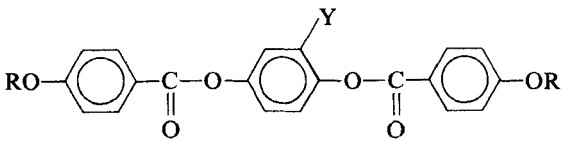
The Sm-N transition temperatures of the C_1–C_{12} homologs of some *p*-phenylene di-*p*-*n*-alkoxybenzoates were studied. For three homologous series of these esters (unsubstituted, methyl-substituted, and chlorosubstituted on the central phenylene ring), the transition temperature was found to decrease at first on ascending the series, pass through a minimum at the C_4 homolog, and then increase regularly. The data suggest that intermolecular attraction in the nematic and smectic mesophases and molecular order in the nematic mesophase increase modestly with increasing alkyl chain length, but molecular order in the smectic mesophase rises sharply on going from the C_1 to the C_4 homolog and then much more gradually. This would result in a large increase of ΔS transition relative to ΔH transition on first ascending the series and, therefore, a drop in the transition temperature $T = \Delta H/\Delta S$. From the C_4 to the C_{12} homolog, ΔH apparently increases faster than ΔS and T rises.

INTRODUCTION

Smectic mesomorphism is often observed in compounds with *n*-alkyl end groups, and the Sm-N or Sm-I transition temperature in an homologous series of such compounds ordinarily increases with alkyl chain length.[2] However, while methyl-*p*-phenylene di-*p*-methoxybenzoate (**1**, R = CH_3, Y = CH_3)



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is smectic,[3] its homologs in which R = C_6H_{13} – C_9H_{19} are not.[4] Smectic mesomorphism reappears in the C_{10} homolog and persists to increasingly higher temperatures with increasing alkyl chain length. Similar behavior has been observed for the homologous series **1**, Y = Cl[3] and **1**, Y = H.[4,5] The data suggest that, for these systems, the Sm-N transition point decreases as the homologous series is ascended from the methoxy ester, passes through a minimum, and then increases.[3] The objective of the work described in this paper was to test that possibility experimentally. The C_1–C_{12} homologs of the three systems were studied. Only a few of the smectic mesophases could be observed directly; the Sm-N transition temperatures of some others were estimated by extrapolation of data for binary mixtures of the compounds with their homologs.

EXPERIMENTAL SECTION

p-n-Alkoxybenzoic acids

The C_2–C_4 and C_6–C_8 acids were commercial products. The C_9–C_{12} acids were prepared by Williamson synthesis of the corresponding ethyl esters from ethyl *p*-hydroxybenzoate, K_2CO_3 and the appropriate *n*-alkyl bromide, followed by hydrolysis.[6] The crude products were recrystallized from 95% ethanol. The transition temperatures of the purified acids and literature values are:

Alkyl group	M. pt., °C	Sm-N pt., °C	N-I pt., °C	Literature
n-C_9H_{19}	94	117	143	94,117,143[7] 92,118,145[8]
n-$C_{10}H_{21}$	97	123	141.5	97,122,142[7] 97,125,143[8]
n-$C_{11}H_{23}$	96	128	138	96,129,140[8]
n-$C_{12}H_{25}$	93.5	131	137	95,129,137[7] 90,133,139[8]

The smectic mesophases of the four acids exhibit mottled, labyrinthine textures indicating that they are all of type C.

p-n-Alkoxybenzoyl chlorides

p-Anisoyl chloride and *p-n*-pentyloxybenzoyl chloride were purchased. The others were obtained from the corresponding acids by treatment with thionyl chloride.

p-Phenylene dibenzoates

Typically, a solution of 3–6 mmol hydroquinone (unsubstituted, methyl, or chloro) in 15 ml dry pyridine was added with stirring to a solution of 12 mmol alkoxybenzoyl chloride in 15 ml dry pyridine. After standing at least overnight, the mixture was poured with stirring into 150 ml water.[9] The precipitated crude ester was filtered, washed with water, and dissolved in 50 ml dioxane. After treatment at reflux with Norit A, the mixture was filtered hot, and the ester recrystallized twice from dioxane–95% ethanol. The transition temperatures of the products are given in Table I.

Preparation of mixtures and transition point determinations

The two components of the mixture (20–30 mg total) were weighed to the nearest 0.1 mg into a 10 ml beaker, melted by means of a heated silicone oil bath, and stirred until homogeneous. The melts were chilled in ice-water, and the resulting solid cakes broken up with a spatula. Transition temperatures were determined with a Reichert Thermopan polarizing microscope equipped with a Kofler micro hot stage which had been calibrated against pure substances having known melting points. Since many of the Sm-N transitions were monotropic and, therefore, required supercooling of the melt for their determination, the powder method[12] was used. By this technique, one or more of the separate droplets produced on melting will usually supercool much further than a single large drop of the same composition because seeding of neighboring material when crystallization begins is minimized. For each set of two compounds, the concentration of the one for which the virtual transition temperature was desired was increased in successive mixtures until the Sm-N transition could no longer be observed on cooling because of previous crystallization. The data are summarized in Figures 1–4.

Analyses

Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

RESULTS AND DISCUSSION

The C_1–C_{12} homologs of the systems **1**, Y = CH_3, Cl and H, were synthesized except for **1**, R = C_9H_{19}, Y = H. All 36 esters display nematic mesomorphism, but only 16 exhibit a smectic mesophase. An attempt was made to estimate the "virtual" Sm-N transition temperatures of the others by extrapolation of data from their binary mixtures.[13–17] The transition points of mixtures of the ester under investigation with a suitable second

TABLE I

p-Phenylene dibenzoates (**1**)[a]

R	Transition temperatures, °C[b] m pt.	Sm-N[c]	N-I	Lit. values	Ref.
Y = H					
CH_3	217.5	(175)	299	217, (178), 301	5
C_2H_5	235		296	226, 287	10
n-C_3H_7	180		254	175, 249	10
n-C_4H_9	153.5		243.5	153, 241	10
n-C_5H_{11}	143		220	145, 222	11
n-C_6H_{13}	126		208	124, 213	4
n-C_7H_{15}	122	(111)	199	122, (110), 199	4
n-C_8H_{17}	121	125	193.5	122, 126, 195	4
n-C_9H_{19}				128, 136, 186	4
n-$C_{10}H_{21}$	126	145.5	180	127, 147, 182	4
n-$C_{11}H_{23}$	109.5	151	174	111, 151, 175	4
n-$C_{12}H_{25}$	108	154.5	170	109, 156, 171.5	4
Y = CH_3					
CH_3	169	(123)	252	170, (126), 250	3
				166, (123), 252	5
C_2H_5	188	(118)	252		
n-C_3H_7	137		213		
n-C_4H_9	112.5		202		
n-C_5H_{11}	89.5		178		
n-C_6H_{13}	90		172	88, 172	4
n-C_7H_{15}	85		159	84.5, 160	4
n-C_8H_{17}	74		156	72, 156	4
n-C_9H_{19}	77		147	77, 148.5	4
n-$C_{10}H_{21}$	81	(58)	144	79.5, 144	4
n-$C_{11}H_{23}$	82,87[d]	(75)	138	82, (74), 138	4
n-$C_{12}H_{25}$	80	88	136	80, 88, 136	4
Y = Cl					
CH_3	165.5, 173.5[d]	(124.5)	253	166.5, (127.5), 254	3
				162, 252	5
C_2H_5	208, 211.5[d]		252		
n-C_3H_7	149		213		
n-C_4H_9	110.5		212		
n-C_5H_{11}	95		180		
n-C_6H_{13}	88		167.5	90, 169.5	3
n-C_7H_{15}	93		165		
n-C_8H_{17}	88		159		
n-C_9H_{19}	93.5		150		
n-$C_{10}H_{21}$	88.5	(47.5)	147		
n-$C_{11}H_{23}$	95	(71)	142		
n-$C_{12}H_{25}$	91.5	(87)	138		

[a] Satisfactory analytical data ($\pm 0.24\%$ or better for C, H and Cl) were reported for all new compounds listed in the table.

[b] Values for monotropic transitions (observed only on cooling) are in parentheses.

[c] The smectic mesophases of the methyl and ethyl homologs exhibit focal-conic fan textures (smectic A); those of the other homologs are grainy and/or labyrinthine (smectic C).

[d] Polymorphic.

Analytical data for Table I

Y	R	% C		% H		% Cl	
		Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
CH_3	C_2H_5	71.42	71.40	5.75	5.80		
	n-C_3H_7	72.30	72.35	6.29	6.38		
	n-C_4H_9	73.09	72.93	6.77	6.81		
	n-C_5H_{11}	73.79	73.93	7.19	7.00		
Cl	C_2H_5	65.38	65.22	4.80	4.90	8.04	8.24
	n-C_3H_7	66.59	66.52	5.37	5.46	7.56	7.71
	n-C_4H_9	67.67	67.80	5.88	5.88	7.13	7.06
	n-C_5H_{11}	68.63	68.79	6.33	6.50	6.75	6.70
	n-C_7H_{15}	70.27	70.19	7.11	7.00	6.10	6.30
	n-C_8H_{17}	70.98	71.16	7.45	7.50	5.82	5.94
	n-C_9H_{19}	71.62	71.52	7.75	7.67	5.56	5.79
	n-$C_{10}H_{21}$	72.21	72.07	8.03	7.93	5.33	5.36
	n-$C_{11}H_{23}$	72.76	72.52	8.29	8.24	5.11	5.34
	n-$C_{12}H_{25}$	73.26	73.37	8.52	8.56	4.91	4.98

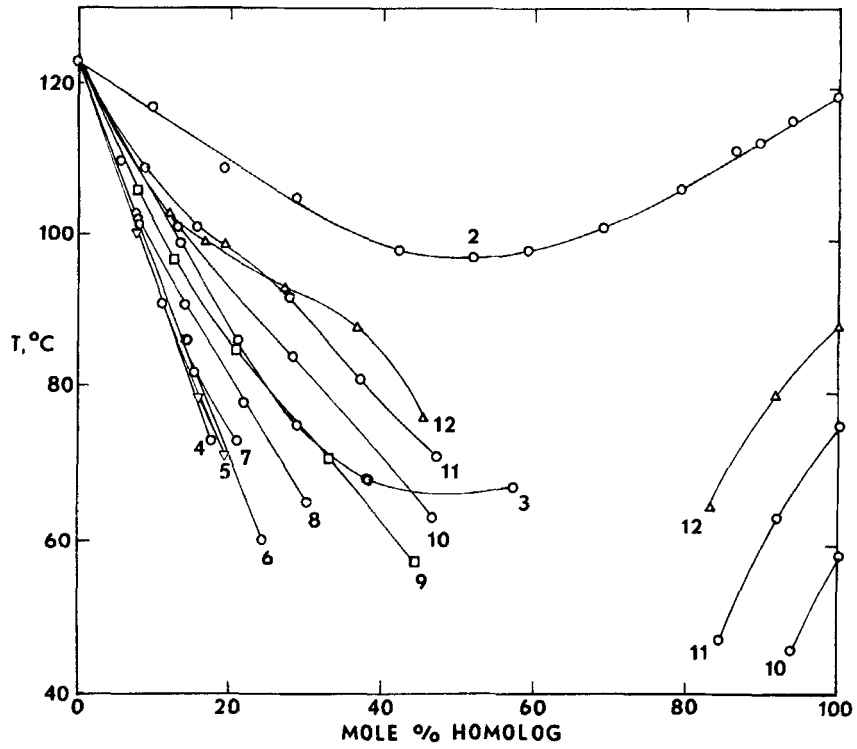
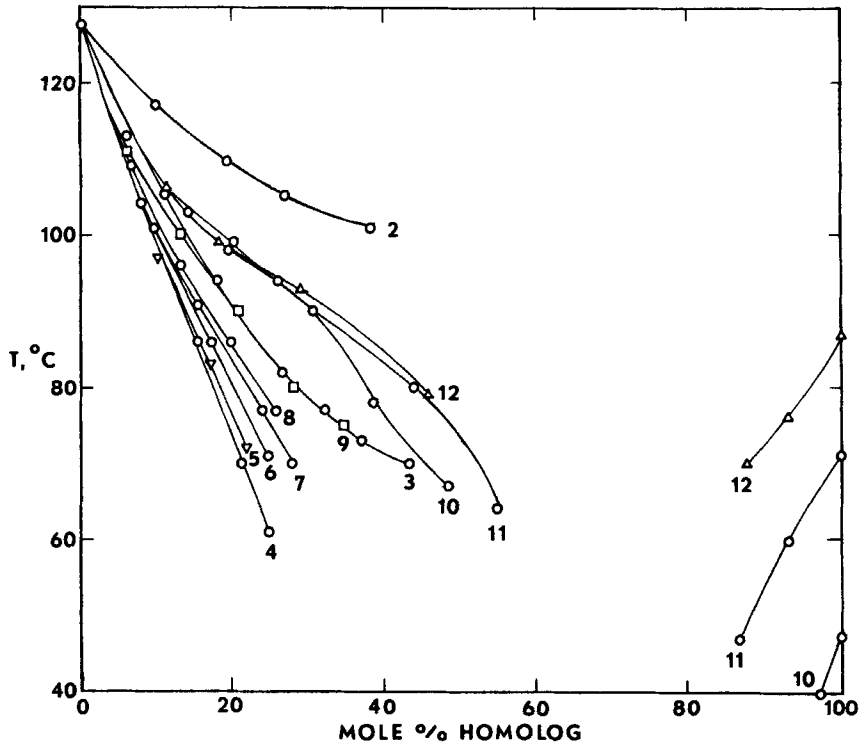


FIGURE 1



FIGURES 1 and 2 Plots of Sm-N transition temperatures of binary mixtures of **1**, R = CH_3, Y = CH_3 and **1**, R = CH_3, Y = Cl with their homologs vs. composition. (Curves labelled with number of carbon atoms in R of homolog).

component were entered on a temperature vs. composition plot, and the resulting curve extrapolated to 100% ester to obtain the desired value. As in all such methods, the confidence that can be placed in the result depends on the nature of the curve that is extrapolated, since success rests on the assumption that nothing peculiar happens in the region over which the extrapolation is done. A straight, or nearly straight, line is best, implying an uncomplicated variation of transition point with composition over the entire range. However, smoothly curved lines can be satisfactory, too. The greatest reliability is afforded when the curves for several different co-components extrapolate to the same value.

The general approach was to use homologous esters with relatively high Sm-N transition points and relatively low melting points as co-components. These should give the best opportunity for good compatibility (formation of homogeneous mixed liquid crystals—the optimum condition for extrapolation), and an observable Sm-N transition temperature (above the freezing

point). The first experiments involved mixtures of the methyl esters of the **1.** $Y = CH_3$ and $Y = Cl$ systems with their homologs (Figures 1 and 2). From the data for the C_2, C_3 and C_{10}–C_{12} compounds, the curves appear to be characteristically concave upward, but no points on the right hand side of the diagram could be achieved experimentally for the other homologs, so extrapolation to their virtual Sm-N transition points was impossible. The C_{12} curves display a point of inflection, starting off at low concentrations as if they would extrapolate to the known C_{12} transition points, and then dipping steeply downward at high concentration. The C_{11} and C_{10} curves have this feature also, but it is only slightly evident in the C_9 curves. This irregularity may be associated with poor compatability of the higher homologs with the more polar C_1 co-component, and the C_4–C_9 homologs probably have smooth, regularly concave curves like those of the C_2 and C_3 esters. If this is correct, the relative order of the transition points can be estimated from the portions of the curves that are available. For both systems, it appears to be $C_1 > C_2 > C_{12} > C_3 > C_{11} > C_{10} > C_9 > C_8 > C_7 > C_6 > C_5 > C_4$; i.e.,

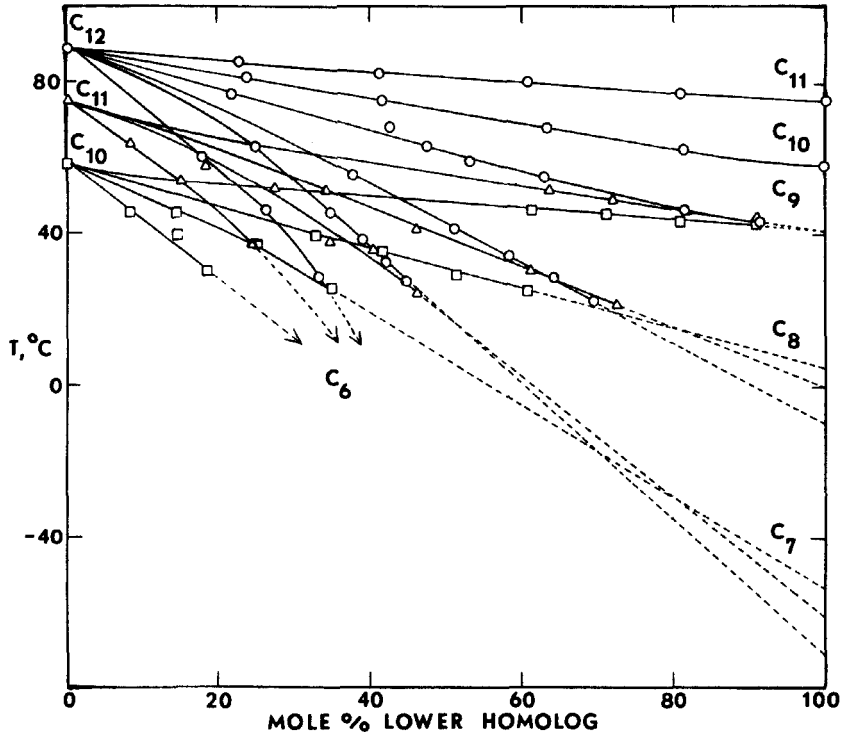
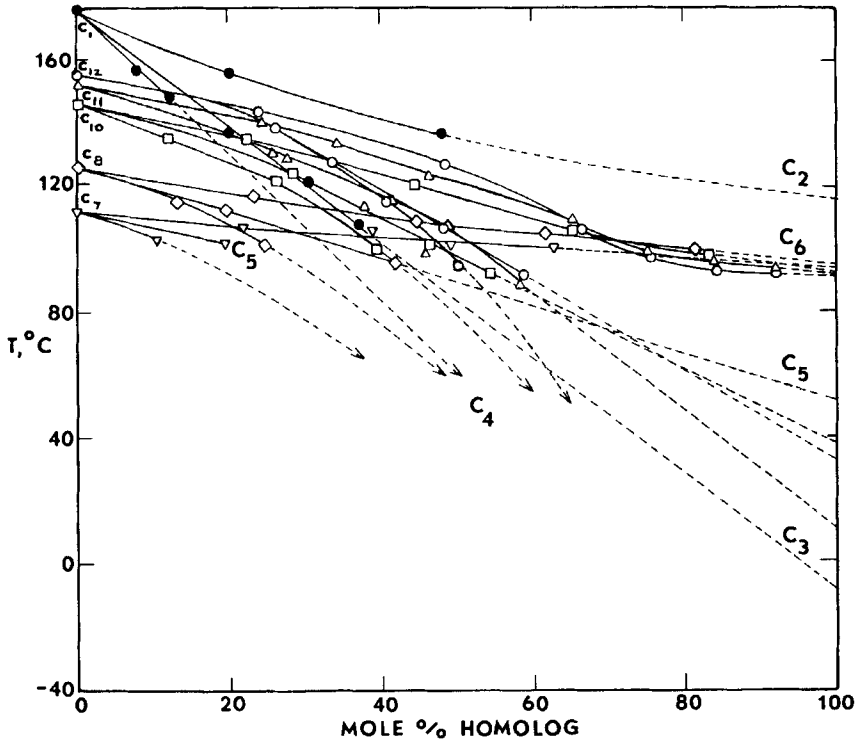


FIGURE 3



FIGURES 3 and 4 Plots of Sm-N transition temperatures of binary mixtures of **1**, Y = CH_3 homologs and **1**, Y = H homologs vs. composition. (Curves labelled at left and right with number of carbon atoms in R of homologs. Composition is mole % of homolog indicated on the right).

the Sm-N transition temperature decreases at first on ascending the homologous series, reaches a minimum at C_4, and then increases.

Attention was turned next to mixtures with neighboring homologs in an attempt to maximize compatibility, and, therefore, minimize curve irregularities. This approach gave better results. The curves are more nearly linear and, by employing three or more different curves for each compound, what are believed to be meaningful virtual transition temperatures were obtained for the C_7–C_9 homologs of **1**, Y = CH_3 (Figure 3) and the C_5 and C_6 homologs of **1**, Y = H (Figure 4). Much less trustworthy values for the C_2–C_4 esters of the latter system and the C_6, Y = CH_3 ester were also determined. The Sm-N points, both virtual and directly determined, are listed in Table II. The few available values for **1**, Y = Cl, are included, also, for comparison.

TABLE II
Smectic-nematic transition points of *p*-phenylene dibenzoates (**1**)

R	Sm-N transition temperature, °C[a]		
	Y = H	Y = CH_3	Y = Cl
CH_3	(175)	(123)	(124.5)
C_2H_5	(115)[b]	(118)	
n-C_3H_7	(−10)[b]		
n-C_4H_9	(−50)[b]		
n-C_5H_{11}	(40)[b]		
n-C_6H_{13}	(95)[b]	<(−100)[b]	
n-C_7H_{15}	(111)	(−60)[b]	
n-C_8H_{17}	125	(0)[b]	
n-C_9H_{19}	136	(40)[b]	
n-$C_{10}H_{21}$	145.5	(58)	(47.5)
n-$C_{11}H_{23}$	151	(75)	(71)
n-$C_{12}H_{25}$	154.5	88	(87)

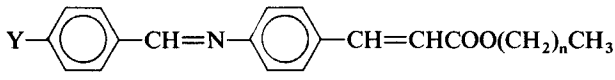
[a] Values for monotropic transitions are in parentheses.
[b] Approximate values obtained by extrapolation of data for mixtures with homologous esters.

The data for the **1**, Y = H system are in general agreement with the results (Figures 1 and 2) for the other two systems. The sequence of Sm-N transition points is: $C_1 > C_{12} > C_{11} > C_{10} > C_9 > C_8 > C_2 \simeq C_7 > C_6 > C_5 > C_3 > C_4$. The different positions of the C_2 and C_3 homologs in this sequence cannot be given much significance since the data for these compounds are admittedly tenuous. Another point that emerges from a study of Table II is the very low value indicated for the minimum Sm-N point in the Y = CH_3 system. If this does indeed occur at C_4, it must be well below −100°C. In any event, the C_4–C_{12} portions of all three homologous series behave "normally" in that the Sm-N transition temperature increases steadily with increasing length of the *n*-alkyl end group.[18] This has been rationalized in the literature by means of a thermodynamic argument.[5,19] The relationship $\Delta H = T\Delta S$ holds at the transition, so that an increase in the transition temperature T with chain length indicates an increase of $\Delta H/\Delta S$. ΔH and ΔS reflect the changes in intermolecular forces and in mesophase order, respectively, on passing from smectic to nematic liquid. With successive additions of CH_2 units to the *n*-alkyl end groups, intermolecular attractive forces increase in both mesophases, but more so in the more highly ordered, less mobile smectic liquid, resulting in an increase in ΔH with chain length. There is also an increase in ΔS as chain extension contributes more additional order to the well organized smectic "lattice"

than to the relatively open molecular arrangement of the nematic mesophase. The enthalpy effect predominates, and the net result is an increasing transition temperature T.

The "abnormal" behavior in the **1**, Y = H, CH_3 and Cl esters, then, is the decrease in T on ascending the series from the methyl to the C_4 homolog. There is every reason to believe that the ΔH and ΔS of the Sm-N transition both increase with increasing length of the terminal alkyl group here, also. However, the observed decrease in T suggests that the entropy effect predominates in the lower parts of the homologous series. This is plausible. It has been remarked earlier[1b,20] that the *p*-phenylene dibenzoate molecular system shows a strong tendency to form stable nematic mesophases irrespective of the end groups. It is logical to suppose that all of the nematic mesophases of a given **1** series have similar degrees of molecular order. On the other hand, the order in the smectic liquids may well increase rapidly on going from the C_1 to the C_4 homolog as the lengths of the two terminal alkyl groups increase by a factor of four, resulting in a rapid rise in ΔS. The accompanying increase in ΔH would not be expected to be as rapid because the lateral intermolecular attractive forces that must be overcome in the Sm-N transition are largely provided by the powerful dipoles in the central aromatic ester moiety, which is common to all homologs, and only marginally by the weak Van der Waals attractions between adjacent alkyl end groups. In sum, it is believed that intermolecular attraction in both the nematic and smectic mesophases, and the molecular order in the nematic mesophases increase regularly but not dramatically on ascending all three homologous series, while the molecular order in the smectic mesophases increases markedly on passing from the C_1 to the C_4 homolog. Thus, the entropy effect predominates in the C_1–C_4 region and T decreases. From C_4 on, the smectic mesophases are all highly ordered, intermolecular attraction increases more rapidly in the smectic mesophases with each addition of CH_2 than in the nematic, the enthalpy effect predominates, and T rises.

There is apparently only one other report of minima in plots of Sm-N transition temperature vs. terminal alkyl chain length. Gray and Harrison[21] have described shallow minima for *n*-alkyl *p*-methoxy- and *p*-acetoxybenzylideneaminocinnamates (**2**) that occur at about the same R length (C_4–C_5).



2a, Y = CH_3O

b, Y = CH_3COO

Again, these are aromatic esters with strong lateral dipoles so the same explanation could apply. Perhaps the relative shallowness of the minima reflects the smaller effect from homolog to homolog of only one terminal alkyl group rather than two.

There are several further observations that can be made. Dewar and Griffin[5] studied the series, **1**, R = CH_3, Y = H, CH_3, and the halogens, and found that the N-I transition temperatures of the substituted esters are substantially lower than that of the unsubstituted ester. They proposed that the bulky substituent limits molecular mobility in the nematic mesophase, resulting in a significant decrease in entropy and a small increase in intermolecular attraction. As a consequence, there is a relatively large increase in ΔS_{N-I}, a smaller increase in ΔH_{N-I}, and the transition temperature is lowered. They also concluded that the same argument should apply with even greater force to Sm-N transitions. The present work certainly supports their comments on both counts. Comparing like homologs, one is struck by the close correspondence of the N-I transition temperatures of the methyl- and chloro-substituted esters, in which the substituents are of similar size, and by the fact that these values are much lower (32–47°) than those of the analogous unsubstituted esters (Table I). As for the Sm-N transition temperatures, where values are available (Table II) there is, again, a close agreement between comparable methyl- and chloro-substituted esters, and these are very much lower than the values for the analogous unsubstituted esters. (The lone exception is **1**, R = C_2H_5, Y = H, which makes this extrapolated estimate even more suspect.)

Note also that the methoxy homologs in the three ester series and the ethoxy homolog in the Y = CH_3 series exhibit smectic A mesomorphism, whereas the long alkoxy homologs exhibit smectic C mesophases. Griffin[22] has suggested that the minima in the Sm-N transition temperatures at C_4 may represent the intersection of a descending Sm_A-N curve and an ascending Sm_C-N curve as alkyl chain length is increased. This proposal is consistent with the observation that the mixed smectic mesophases from which the extrapolated transition temperatures in Table II were obtained are type C for the Y = CH_3 C_6–C_9 homologs and for the Y = H C_5–C_6 homologs. These extrapolated transition temperatures, along with those for higher homologs, give smooth ascending curves when plotted vs. alkyl chain length. It is reasonable to assume that the extrapolated values are for Sm_C-N transitions. On the other hand, the mixed smectic mesophases for the Y = H C_2 homolog are Sm_A. The situation is less clear for the Y = H C_3 and C_4 homologs, C_3–C_{11} and C_3–C_1 mixtures exhibit Sm_C and Sm_A mesomorphism, respectively; blends of C_4 with C_7–C_{12} are Sm_C while those of C_4 and C_1 are Sm_A. However, when the resulting extrapolated values are plotted vs. alkyl chain length, the C_3 point is obviously on the "Sm_A" curve

and the C_4 point on the "Sm_C" curve. Both are near the intersection of the curve extensions, which occurs at about $-120°C$. No monotropic Sm_A-Sm_C transitions were observed for either pure compounds or mixtures, but these data raise the possibility that the C_1–C_3 homologs would exhibit such transitions if super-cooling of the Sm_A mesophases to the required very low temperatures could be achieved experimentally.

Acknowledgments

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References

1. (a) This work was supported by grants from the Research Council of the University of North Carolina at Greensboro. (b) Previous paper in this series: D. C. Schroeder, and J. P. Schroeder, *J. Org. Chem.*, **41**, 2566 (1976). (c) N, Sm and I are abbreviations for nematic, smectic and isotropic, respectively.
2. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press, New York, 1962).
3. D. W. Bristol and J. P. Schroeder, *J. Org. Chem.*, **39**, 3138 (1974).
4. S. L. Arora, J. L. Fergason, and T. R. Taylor, *J. Org. Chem.*, **35**, 4055 (1970). The C_{10} homolog was also reported to be non-smectic in this paper, but A. C. Griffin (private communication) and I (see Table I) have found that it displays a monotropic smectic mesophase.
5. M. J. S. Dewar and A. C. Griffin, *J. Amer. Chem. Soc.* **97**, 6662 (1975).
6. M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).
7. G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179 (1953).
8. A. J. Herbert, *Trans. Faraday Soc.*, **63**, 555 (1967).
9. In some instances, an emulsion was produced here, and NaCl was added to induce flocculation.
10. M. J. S. Dewar and R. S., Goldberg, *J. Org. Chem.*, **35**, 2711 (1970).
11. S. A. Haut, D. C., Schroeder, and J. P., Schroeder, *J. Org. Chem.*, **37**, 1425 (1972).
12. W. R. Young, I. Haller, and A. Aviram, *Mol. Cryst. Liq. Cryst.*, **15**, 311 (1972).
13. A. Bogojawlenski and N. Winogradow, *Z. Phys. Chem.*, (Leipzig) **60**, 433 (1907); **64**, 299 (1908).
14. R. Walter, *Chem. Ber.*, **58B**, 2303 (1925).
15. J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, 4617 (1954); 4305 (1955).
16. M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).
17. J. S. Dave and R. A. Vora in *Liquid Crystals and Plastic Crystals*, G. W. Gray and P. A. Winsor, eds. (Ellis Horwood, Ltd., Chichester, 1974), vol. 1, p. 155, ff.
18. Reference 2, Chapter 9.
19. E. M. Barrall II and J. F. Johnson in *Liquid Crystals and Plastic Crystals*, G. W. Gray and P. A. Winsor, eds. (Ellis Horwood, Ltd., Chichester, 1974), vol. 2, pp. 261 and 264.
20. J. P. Schroeder and D. W. Bristol, *J. Org. Chem.*, **38**, 3160 (1973).
21. G. W. Gray and K. J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971).
22. A. C. Griffin, private communication.