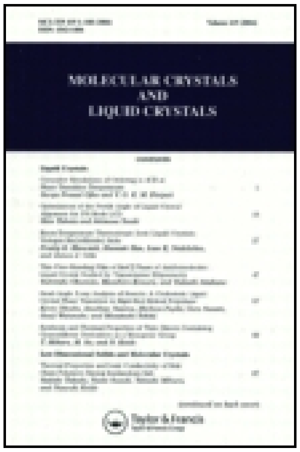

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Microscopic Textures and X-Ray Diffraction Patterns in Nematic Phases Occurring Above Smectic C Phases

Mary E. Neubert [a] & Adriaan De Vries [a]

[a] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242

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Microscopic Textures and X-Ray Diffraction Patterns in Nematic Phases Occurring Above Smectic *C* Phases

MARY E. NEUBERT and ADRIAAN DE VRIES
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

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Microscopic studies of the nematic phase in the 4-*n*-alkoxybenzoic acids have shown that the nematic-to-isotropic transition has a range ≧ 0.9° which is larger than the 0.2–0.3° range usually seen for this transition. This wide range was also observed in a variety of phenylbenzoates and thiobenzoates having smectic *C*-nematic transitions but was not observed for HOAB and the *bis*-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamines.

A subtle continuous textural change was observed in the middle of the nematic phase in most of the 4-*n*-alkoxybenzoic acids which have both a nematic and smectic *C* phase. This change was observed both on heating and cooling the sample and diminishes with increasing chain length until it is no longer observed in the C_{12} homolog. The nematic phases of a wide variety of other compounds with smectic *C*-nematic transitions were also studied, but these did not show this textural change within the nematic phase.

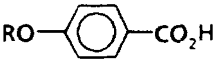
Plots of the effective molecular length versus temperature, obtained from x-ray diffraction data, showed a significant increase with temperature for the nematic phases of most 4-*n*-alkoxybenzoic acids. Such an increase has not been observed for other nematic phases occurring above smectic *C* phases, and it appears to be correlated with the textural change observed by us.

A study of the smectic *C*-nematic transitions in these compounds showed that this transition can also vary in width, with an intermediate texture being observed when the transition has a wide range.

Keywords: microscopic textures, 4-alkoxybenzoic acids, x-ray diffraction, smectic C phases, cybotactic nematics, phase transitions

INTRODUCTION

Recent reports of the observance of a smectic $A(S_A)$ like texture near the smectic $C(S_C)$ to nematic (N) transition $(S_C\text{-}N)$ in the 4-*n*-alkoxybenzoic acids *I*[1]



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and changes within the nematic phase itself observed in conductivity,[2] microscopy,[3] and depolarized Rayleigh scattering[3] studies have prompted this report on our observations of changes in microscopic textures and x-ray diffraction patterns within the nematic phases occurring above a S_C phase as well as texture changes occurring at the S_C-N transition in a variety of compounds.

Mesomorphic properties of the 4-*n*-alkoxybenzoic acids were reported as early as 1939[4] and revised in later studies.[5,6] This work established that many of the homologs in this series exhibit S_C-N transitions. Later, De Vries concluded from x-ray and microscopy data that N phases which occur directly above S_C phases have smectic C-like order and called these skewed cybotactic N phases.[7,8] A comparison of the x-ray diffraction patterns obtained by Chistyakov *et al.*[9] for 4-*n*-nonyloxybenzoic acid with the patterns obtained by De Vries[7] indicated that the N phase in this C_9 homolog is also a skewed cybotactic phase. Later, Blumstein and Patel[10] found a similar diffraction pattern for the C_8 homolog. Dutchak *et al.*[11] describe what appears to be short-range smectic C-like order for the C_6-C_{10} homologs. Most recently, De Vries *et al.*[12] observed the typical diffraction pattern of the skewed cybotactic nematic phase for the C_6, C_8, C_{10} and C_{12} homologs. X-ray studies of the S_C phases below these skewed cybotactic N phases indicated that they differed from those occurring below the S_A phase in that their tilt angles had little or no temperature dependence.[13]

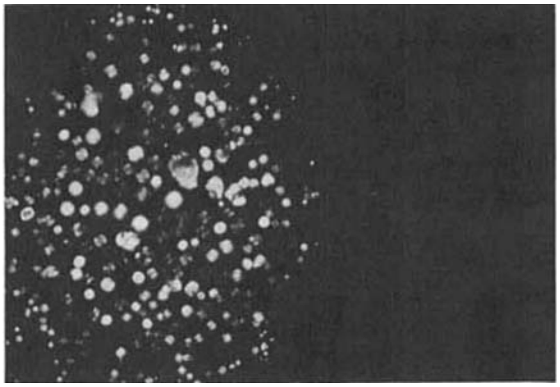
Until recently, there has been little indication in the literature that there were any differences in the microscopic texture for the nematic phase when it occurs above a S_C phase as compared to when there is no S_C-N transition, although the absence of pseudo-isotropic textures in the N phase above a S_C phase can be considered as an indication of a difference in textures of nematic phases.[8] In the first report on the microscopic studies of the chlorophenylenediamines 3 (see Table II for structure) an intermediate texture was reported to occur at the S_C-N transition,[14] and Demus and Richter mention this texture in their book on textures calling it transition bars and using 4-*n*-octyloxybenzoic acid as an example.[15] Other evidence for an intermediate state at the S_C-N transition can be found in the free surface studies of *bis*-heptyloxyazoxybenzene (HOAB) and the 4-*n*-alkoxybenzoic acids[16] and ESR studies which suggest that this state has a

S_A-like character.[17] The recent studies mentioned earlier support this S_A-like character in the 4-*n*-alkoxybenzoic acids[1] and also indicate that a change occurs within the *N* phase itself above the S_C-*N* transition.[2,3]

In determining the mesomorphic properties of a wide variety of new compounds by microscopy and comparing the textures observed with those seen for known compounds, we detected variations in both the *N*-*I* and S_C-*N* transitions as well as a textural change within the nematic phase of the 4-*n*-alkoxybenzoic acids.

MICROSCOPIC STUDIES

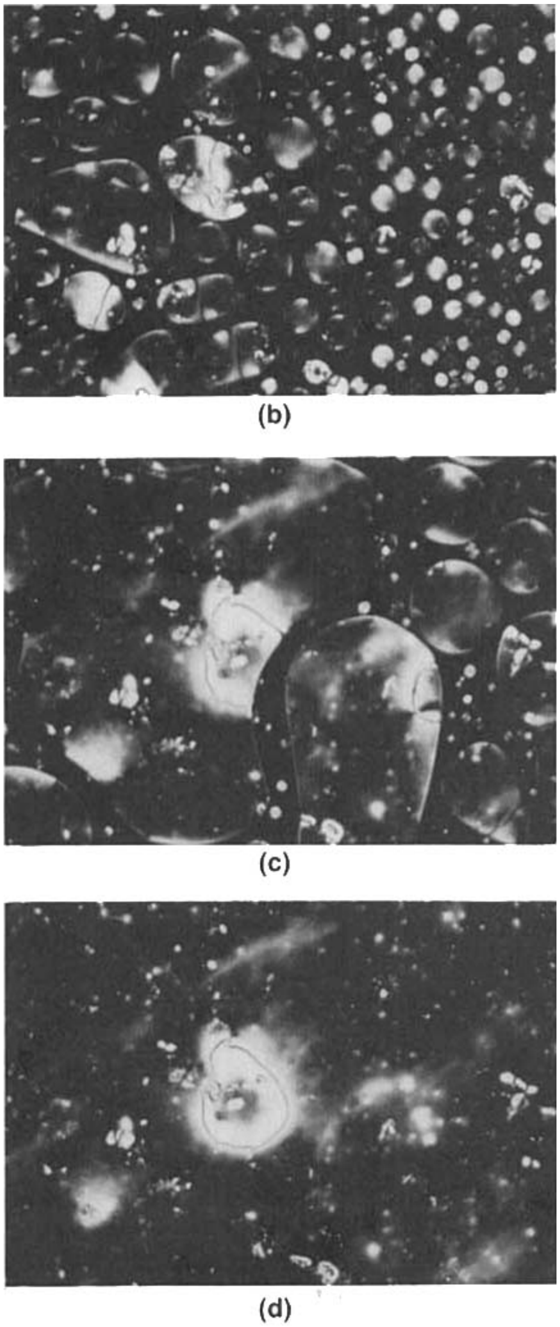
A typical example of the textures observed in the 4-*n*-alkoxybenzoic acids is presented for the C_8 homolog (8OBA) in Figure 1. Cooling the isotropic liquid at a rate of 2°/min causes droplets to slowly form (Figure 1a), grow larger (Figure 1b), and larger (Figure 1c) until they coalesce to form a typical *N* marble texture (Figure 1d). The formation of droplets at the *I*-*N* transition is not unusual but the width



(a)

FIGURE 1 Microscopic textures observed on cooling the isotropic liquid in 8OBA at 2°/min. See Color Plates I–IV

a. initial formation of *N* droplets (T = 145.2°).
b. growing *N* droplets (T = 144.6°).
c. growing and coalescing *N* droplets (T = 143.9°).
d. initial *N* marble texture (T = 141.9°).
e. *N* marble texture showing the haughty pig's head (T = 135.5°).
f. *N* texture at the beginning of the *N* textural change (T = 123.0°).
g. *N* texture near the *N* → S_C transition (T = 109.9°).
h. intermediate texture at the *N* → S_C transition (T = 105.3°).
i. S_C texture at the completion of the *N* → S_C transition (T = 103.6°).



(b)

(c)

(d)

Figure 1 (*continued*)

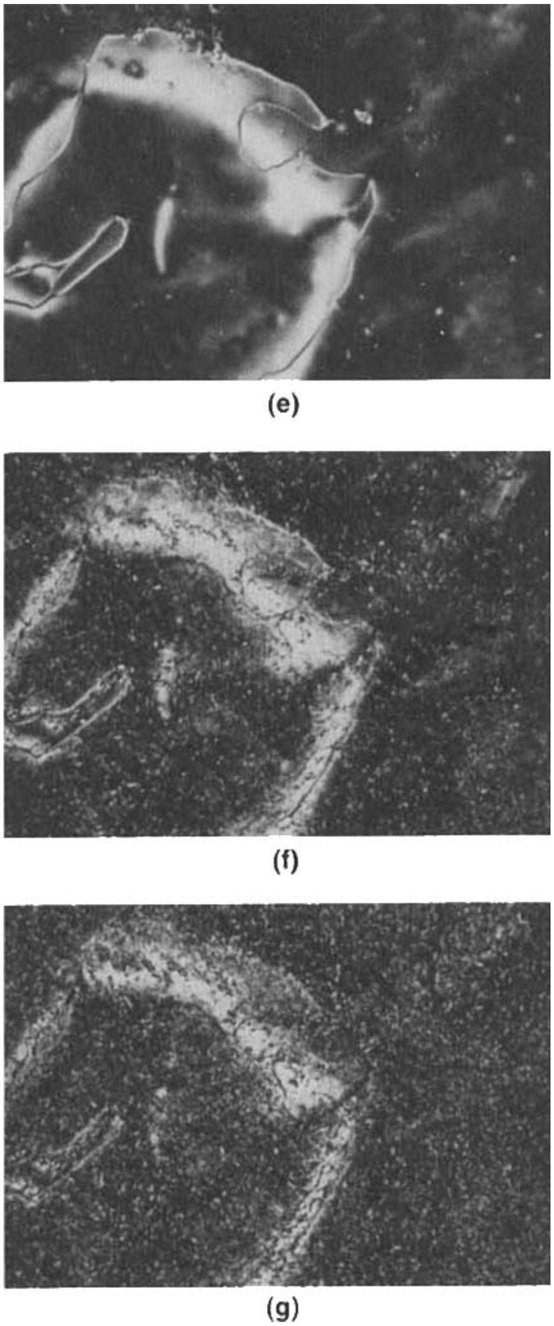
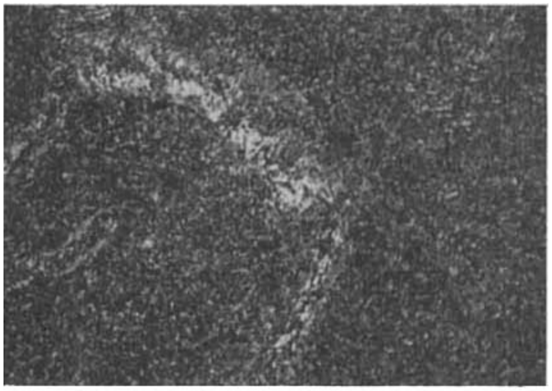
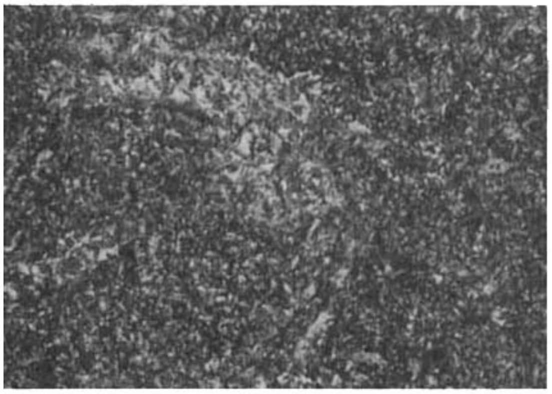


Figure 1 (*continued*)



(h)

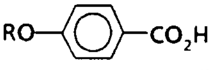


(i)

Figure 1 (*continued*)

of this transition in 80BA (≥0.9°) is larger than that observed in many mesogens (~0.3°). Usually such wide transitions are thought to be due to the presence of impurities. Samples of 80BA were repeatedly recrystallized and prepared by different methods but ranges ≤0.9° were not observed (Table I). Since it is difficult to imagine that so many samples were so impure as to give such wide transition ranges, it seems unlikely that the presence of impurities in the samples is the reason why the ranges are so wide. However, since acids can decarboxylate when heated, perhaps impurities were formed on heating these samples. Repeated heating and cooling was found to increase the transition ranges and lower the transition temperatures suggesting

TABLE I



Mesophase transition ranges (°C) for

R	Transition Range	
	S_C-N	N-I
C_6[a]	—	2.9
C_7	1.6	2.2
C_8	1.0	0.9
C_8[b]	0.3	0.9
C_8[c]	0.5	0.9
C_8[d]	0.3	1.6
C_9	0.9	0.7
C_{10}	3.0	2.7
C_{12}	1.2	2.7
C_{14}	—	3.5[c]

[a] All acids were obtained from Frinton Laboratories unless otherwise noted.
[b] This sample was prepared using the method described in Ref. 18.
[c] The preceding sample was recrystallized once from abs. EtOH.
[d] This sample was obtained from hydrolysis of the corresponding acid chloride.
[c] S_c-I transition.

that some decarboxylation occurs. To minimize this, samples of various homologs of the 4-alkoxybenzoic acids were placed on the heating stage~2° below the N-I transition and heated 2°/min. Although transition ranges were generally shorter than those observed with prolonged heating, none were <0.9°.

Wide transition ranges have also been observed in a variety of aromatic esters having S_C-N transitions but which cannot decarboxylate (Table II) and are prevalent enough in such mesogens to suggest that wide N-I transitions are characteristic of those which occur above S_C phases. However, there are many examples of N-I transitions occurring above S_C phases which are very sharp, such as those in HOAB *2* and the dianils *3* and wide transitions occur in some compounds that have no S_C phase such as the C_6 homolog of the acids *1*. The wide S_C-I transition in the C_{14} homolog indicates that a wide range is not just characteristic of N-I transitions. The sharp N-I transitions observed for the dianils *3* lends support to the idea that not all wide transitions are caused by the presence of impurities. Anils are known to slowly degrade at room temperature. Our dianil samples had set at room temperature for many years and were not recrystallized for these studies. Yet the N-I transitions were much sharper

TABLE II

Mesophase transition ranges in compounds with S_C-N transitions

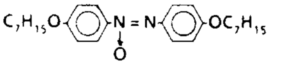
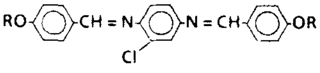
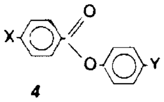
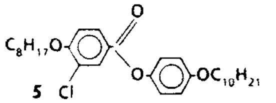
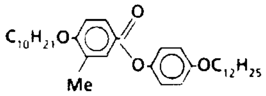
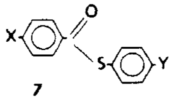
Compound[a]			TransitionRange (°C)[b]	
			S_C-N	N-I
 **2** HOAB	Sample #1[c]		3.1	0.3
	Sample #2[d]		2.4	0.4
 **3**	R[e]			
	C_9H_{19}		0.7	0.2
	$C_{12}H_{25}$		0.7	0.3
 **4**	X	Y		
	$C_9H_{21}O$	$OC_{10}H_{21}$[f]	0.5	0.1
	$C_8H_{17}O$	$OCOC_9H_{19}$	0.2	0.3
	$C_7H_{17}O$	C_5H_{11}	1.1	1.1
	$C_9H_{19}CO_2$	OC_5H_{11}	0.2	0.2
		OC_8H_{17}	0.1	0.1
	$C_7H_{15}CO_2$	$OCOC_9H_{19}$	0.4	1.0
 **5**			0.1	0.1
 **6**			0.3	0.1
 **7**	X	Y		
	$C_7H_{15}O$	C_5H_{11}[g]	0.1	0.1
	$C_8H_{17}O$	OC_7H_{15}	0.8	0.5
	$C_9H_{19}CO_2$	C_5H_{11}	0.2	0.4
		$C_{12}H_{25}$	0.4	0.3
		OC_7H_{15}	0.5	1.1
		$OC_{10}H_{21}$	0.9	1.9
 **8**	R[h]			
	C_4H_9		--	0.2
	C_5H_{11}		3.2	1.0
	C_7H_{15}		1.1	0.2
	C_9H_{19}		--	2.5[i]

Table II (*Continued*)

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[a] Many of these compounds are new. Detailed transition temperatures will be reported in subsequent papers.

[b] The transition range was taken from the temperature at which break-up of the texture began until it was completely converted to the second phase. Large color changes in the nematic phase, "scintillation" (vibration of the directors) and movement of the threads were not considered a break-up of the *N* texture.

[c] This sample was obtained from Eastman Kodak Company and recrystallized once from absolute EtOH.

[d] This sample was prepared using the method described in Ref. 19.

[e] These compounds were prepared using the method described in Ref. 20.

[f] Described in Ref. 21.

[g] Described in Ref. 22.

[h] Described in Ref. 23.

[i] $S_c \rightarrow I$ transition.

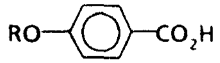
than those observed for the 80BA samples that were repeatedly recrystallized. One would expect the dianil to be considerably less pure than the acid yet the wide transition ranges suggest just the opposite is true. Additionally, from our work on the phenylthiobenzoates 7, we know that trace amounts of impurities have little effect on the width of the *N-I* transition.

To determine if these wide *N-I* ranges were a temperature or time effect, a sample of 80BA in which droplets had begun to grow in the isotropic liquid was kept at a constant temperature. The droplets continued to coalesce but did not grow until cooling was continued suggesting that the wide range is primarily a temperature effect.

Continued cooling of the plane nematic texture obtained from the isotropic liquid (Figure 1d) gave the one shown in Figure 1e (in this particular case) in which the threads have formed what can be imagined as a haughty pig's head with its floppy ear hanging over its face and its up-turned snout. Further cooling of this texture shows a gradual and continual change beginning at ~125° as shown in Figure 1e with increasing graininess on cooling and the outline of the pig's head becoming gradually very fuzzy as the N-S_C transition is approached (Figures 1f and 1g). This textural change in the *N* phase was also observed on reheating the sample but at slightly higher temperatures as shown in Table III, and correlates with the results reported in References 2 and 3. Since this change is initially very subtle, it is difficult to obtain accurately the starting temperature (or stopping on reheating) by microscopy. Thus, the temperatures recorded in Table III are only approximate values. This continuous change in the *N* texture is not always easily observed. However, it is more obvious when the *N* texture is fairly flat with few details and is best observed

TABLE III

Transition temperatures (°) for



R	Source[a]	Recrystallization Temperature (Cooling)	C-S_C	S_C-N	N Textural Change $N_S \rightleftharpoons N_N$ Cooling	N Textural Change $N_S \rightleftharpoons N_N$ Heating	N-I
C_4	A	139.9	-----	147.1-147.4	-----	-----	160.6-161.3
C_6	A	100.8	-----	100.1-104.9	120.6-118.0	129	144.6-148.3
	B	94.5	-----	101.8-105.0	128.2-126.5	137.4	149.0-151.5
C_8	C	97.0	100.2-100.9	107.4-107.7	125.5-117.4	132.4-135.2	145.6-147.8
	C,D	96.9	100.9-101.4	107.3-107.8	127.3-125.4	131.5-135.3	147.4-148.3
	A	95.5	99.5-100.5	106.1-107.0	130.6-126.9	130.7-135.9	145.6-147.4
	B	96.3	99.6-100.6	105.5-105.8	121.9-120.6	129.8-131.3	145.6-147.2
C_9	A	91.3	92.2-93.6	115.6-116.6	117.4-115.7	126.7	142.4-143.4
C_{10}	A	89.4	90.2-.94.6	113.4-116.8	126	132.8[b]	137.1-140.1
C_{12}	C,D	87.8	91.0-91.6	131.7-133.1	-----	-----	139.2-139.4
C_{14}	C,D	89.0	90.9-91.4	-----	-----	-----	131.5-135.0

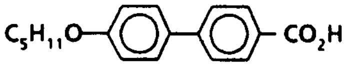
[a] A—Frinton Laboratories; B—hydrolysis of the corresponding acid chloride followed by recrystallization from absolute EtOH; C—hydrolysis of the methyl ester followed by one recrystallization from absolute EtOH, and D—recrystallized one more time.

[b] Textural changes within this nematic phase were very subtle and therefore accurate temperature data were difficult to obtain.

when there is some easily recognized arrangement of the threads (such as the pig's head in Figure 1) to aid one's memory and make the subtle changes more obvious. It is quite apparent when the *N* phase is cooled rapidly or when the sample is placed on the heating stage several degrees above the N-S_C transition and cooled.

This textural change within the *N* phase was observed in nearly all the 4-*n*-alkoxybenzoic acids. It seemed to weaken with increasing alkoxy chain length, being difficult to see in the C_{10} homolog and not observed in the C_{12} (Table III). It was not observed in the *N* phases of a variety of aromatic esters having S_C-N transitions (Table II).

A possible explanation for this subtle change within the *N* phase on approaching the N-S_C transition is that it indicates the skewed cybotactic character of the *N* phase in this temperature range, but this change was not observed in other compounds with known skewed cybotactic *N* phases such as HOAB *2* or the dianils *3*. Another possibility is that it is caused by the presence of different states of hydrogen bonding of the acid molecules but again no change was observed in the 4-*n*-alkylbenzoic acids which also form hydrogen bonded dimers. However, the alkyl acids have no S_C phase below the *N* phase. Possibly the textural change is a result of a combination of these two features. Therefore, other aromatic acids with N-S_C transition were considered. An attempt was made to study the biphenyl acid



but with its higher transition temperatures, this material sublimed too rapidly in the *N* phase coating the stage and microscope lenses to the point that careful observation of the *N* phase was not possible. This is also true of many of the other known acids which could be studied.

Continued cooling of the *N* texture in Figure 1g gave the intermediate texture (called transition bars by Demus†) at the N-S_C transition as shown in Figure 1h which gradually converts to a more typical marble-like S_C texture shown in Figure 1i. This intermediate texture broadens the S_C-N transition in the 4-*n*-alkoxybenzoic to as much as 3.0° in the C_{10} homolog (see Table I). Unlike the texture at the *I*-*N* transition, the intermediate texture continues to change at constant temperature. When cooling was stopped at the first appearance of the intermediate texture at 106.8° in this acid, the texture continued

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† We prefer not to call this texture transition bars to avoid confusion with the well known transition bars which occur in S_A and S_C to S_B transitions.

to change but the rate decreased with increasing time. Continued cooling to 106.6° increased this rate and completed the conversion to the S_C phase when the sample was kept at this temperature. These results suggest that the wide range in this transition is primarily a time effect. A study of this transition in a variety of other compounds (Table II) showed that it varies from being a wide range transition with the intermediate texture being obvious to one which is sharp and without an intermediate texture.

Another characteristic of the textures observed in N-S_C mesogens is that N homeotropic and S_C broken fan and schlieren textures are often difficult to obtain although usually these can be observed. However, none of these textures could be obtained in the 4-*n*-alkoxybenzoic acids despite repeated attempts to do so with many samples. These textures seemed easier to obtain with compounds that have sharp N-S_C transitions such as the esters *4* with $X = C_9$ or C_9CO_2 and $Y = OR$.

X-RAY DIFFRACTION STUDIES

Since the texture change observed in the N phase of the 4-alkoxybenzoic acids could be partly due to changes in its skewed cybotactic properties, we have done an extensive analysis of the x-ray diffraction patterns of these phases. Detailed results will be published elsewhere[12,24] but these are summarized here so that they can be correlated with the results from the microscope studies. The following correlations were observed:

1. Plots of effective molecular lengths (ℓ) versus temperature (t) for the acids (C_6,C_8,C_{10}) all showed a temperature region where ℓ increased sharply with t unlike the dianils which showed only a small increase in the C_6 homolog.[3,24,25] This steep increase was also not observed in p-*n*-hexyloxybenzylidene-*p*-aminobenzoic acid.[26] This suggests that the N phase in the 4-alkoxybenzoic acids differs from that in other compounds. The lack of observance of any N homeotropic and S_C schlieren or broken fan textures in these acids supports this difference.
2. The increasing difficulty in observing the N texture change in the 4-alkoxybenzoic acids with increasing chain length until it was not observed in the C_{12} homolog correlates with a decrease in the steepness of the ℓ versus t curves with increasing chain length.

3. At the average temperature for the N texture change (always slightly above the middle range), the largest increase of ℓ with t occurred with ℓ reaching its maximum value at this temperature in the C_{10} homolog.

4. The magnetically induced alignment in the N phase was less pronounced on fast heating than on fast cooling in 80BA[27] but not in HOAB[28] again suggesting that the N phase in the 4-alkoxybenzoic acids differs from that in other compounds.

DISCUSSION

The variations in microscopic textures observed both at the N-I and S_C-N transitions in a wide variety of compounds suggest that these transitions are not as simple as they are generally thought to be. Instead, there might be different types of N-I and/or S_C-N transitions, different types of structures for the mesophases or perhaps large pre-transition effects. The textural change observed within the N phase of the 4-*n*-alkoxybenzoic acids has been confirmed by our x-ray studies and by conductivity[2] and depolarized Rayleigh scattering studies.[3] The combined evidence suggests that the 4-*n*-alkoxybenzoic acids are rather unique possibly because of a combination of hydrogen bonding effects and skewed cybotactic nematic properties. It is hoped that this paper will stimulate discussions and research which will provide a better understanding of our observations.

EXPERIMENTAL

Microscope slides were washed with acetone and rubbed with a Kimwipe® in a direction parallel to the long side of the slide. The sample was placed on this slide and a cover slip added which had been treated in the same manner with the rubbed direction parallel to that of the slide. This slide was placed on a Mettler FP-2 heating stage on a Leitz Laborlux 12 Pol microscope (using polarized light) a few degrees below the clearing temperature. The sample was heated at 2°/min. to the isotropic liquid, cooled at 2°/min to the mesophase and reheated at 2°/min to obtain either the N-I or S_C-I transition temperature. The isotropic liquid was cooled again to the N phase and then continued at 2°/min to obtain the next transition at which point the sample was reheated at 2°/min to obtain the heating transition temperatures. Once all the transitions were clearly established, it was possible to proceed more rapidly from the N-I to the S_C-N transition using a faster cooling rate until a few degrees before the transition. This procedure to obtain the data in Table I was used to minimize the heating time and hopefully decomposition. All transition temperatures (°C) reported in the tables were obtained during a heating cycle. Independent runs were used to obtain different sets of data and therefore there are differences in the exact values recorded.

Photographs were taken using Ektachrome 160 film and a Leitz 35mm camera using a 10x objective and a 16x eyepiece. The sequence of photographs given in Figure 1 was taken without moving the slide and therefore is of the same area.

Experimental details of the x-ray studies will be given elsewhere.[12,24]

Acknowledgments

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