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The Preparation and Mesomorphic Properties of the Homologous Series of Terephthal-*bis*-*n*-Alkylaniline†

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The C_1–C_8 and C_{10} members of the homologous series of terephthal-*bis*-*n*-alkylaniline (including TBBA) have been prepared by the condensation of 4-alkylanilines with terephthaldehyde. Synthesis of the anilines was achieved through a Friedel–Crafts acylation of acetanilide followed by a Wolff–Kishner reduction. Interphase transitions between solid, mesomorphic and isotropic phases were studied by hot-stage microscopy and DTA. The nematic phase was observed in the C_1–C_7 homologs, the smectic A and C phases in the C_3–C_{10} compounds and the smectic H(B) phase in the C_2–C_{10} homologs. An additional smectic phase with a mosaic texture was observed in the C_5 homolog and some unexplained anomalies were found in the phase transition behavior of the C_2 and C_3 compounds. A study of the textures of the smectic C phases as a function of temperature indicated that all these phases have a temperature dependent tilt angle. Relationships between structure and mesomorphic properties as well as with thermodynamic data are discussed and a comparison made with compounds of similar structures reported in the literature.

INTRODUCTION

A considerable number of research efforts have been directed towards the study of the smectic phases of TBBA (scheme 1, R = n-C_4H_9 in 3). This has been due primarily to the presence of two types of smectic phases which initially had not been observed in other mesomorphic compounds. TBBA was the first compound reported to have a smectic C phase with a temperature dependent tilt angle.[1] Since then, this tilt angle has been measured as a function of temperature by optical microscopy,[1,2] dilatometry,[3] x-ray

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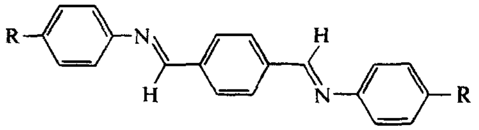
crystallography,[3–5] nmr[6] and esr[7] spectroscopy, neutron diffraction[8] and magnetic torque.[9] A smectic B phase, often called a smectic H, in TBBA[10] in which the molecules are tilted in the layers in a hexagonal packing was also first observed in TBBA and has been studied by x-ray crystallography[4,11–15] and nmr.[16]

McMillan's proposal that the smectic C phase in TBBA occurs when the rotation around the molecular axis "freezes out" and allows the "outboard" dipole moments to cause the molecules to tilt within the smectic layers,[17] generated a great deal of research designed to study the molecular motions in TBBA to determine the validity of this theory. The observation of the presence of more highly ordered phases below the smectic H(B) phase[18] increased the interest in studying these molecular motions in attempts to determine whether these phases were liquid crystals, plastic crystals or crystals. The extension of McMillan's theory to smectic B and H phases[19] and discussions by de Vries on the structures of these phases[14,20] increased this interest so that the molecular motions in TBBA have been studied by nmr[6,21–26] and Raman[27–31] spectroscopy and neutron[32–39] and x-ray[40] diffraction.

With such a tremendous interest in studying the smectic phases in TBBA, it seems surprising that these same studies have not been performed on the other homologs of terephthal-*bis*-*n*-alkylanilines. In fact, only two other homologs, the C_1 and C_8, have been reported in the literature (see Table I).[41] Thus, it seemed of interest to prepare and study the homologs C_1–C_8 and C_{10} for a variety of reasons. Our first interest was in determining if the other homologs exhibited a temperature dependent tilt angle in the smectic C phase or if TBBA was unique in this respect. During the course of this investigation, we not only found such smectic C phases in these compounds but also in the simple Schiff bases, phenyl benzoates and phenyl thiobenzoates

TABLE I

Terephthaldehyde analogs (alkyl anils)[a]



R	S?	S_G?	S_H	S_C	S_A	N	I
C_1						190	265
C_4	(52)	(68)	113.0	144.0	172.5	199.6	236.5
C_8			64	157	192		202

[a] Ref. 41.

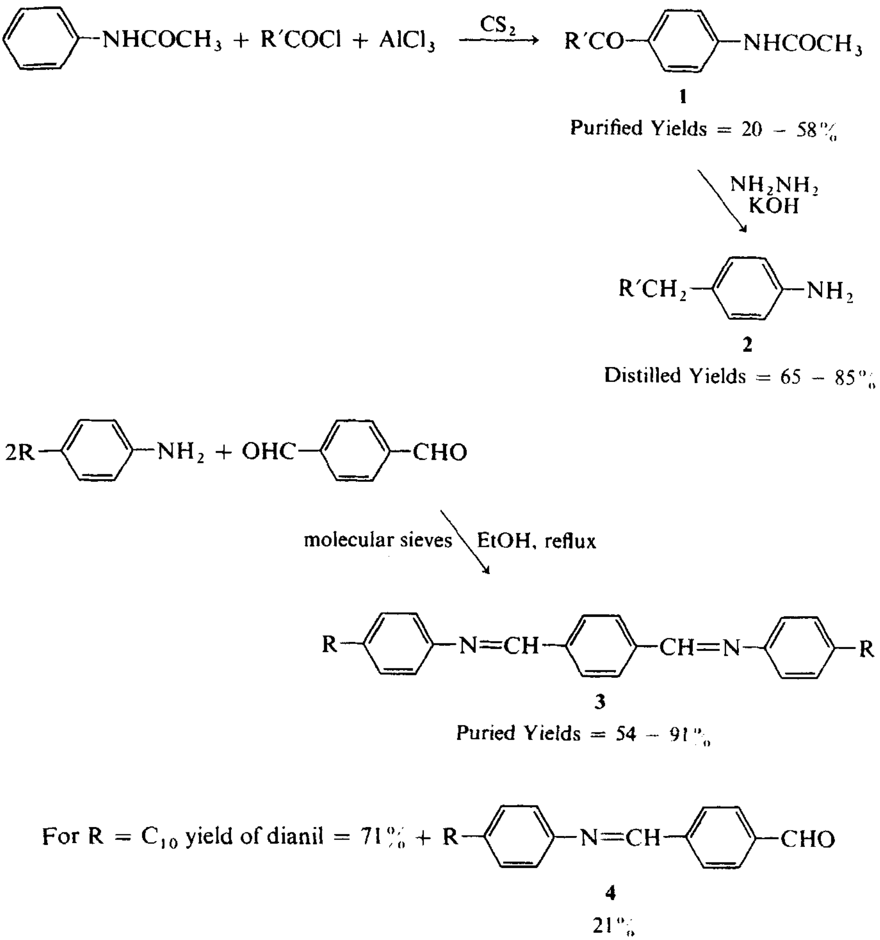
indicating that this is not a unique type of smectic C phase.[42] We also wanted to look at the homologous series as a whole to determine how the mesophases changed with various chain lengths, if mesophases which differed from those found in TBBA occurred in the other homologs and if the smectic H(B) phase could be observed in these homologs; perhaps as the only smectic phase so that it could be studied independent of the influence of other smectic phases. Equally important was our desire to make this homologous series available for further physical studies with the hope of being able to resolve some of the existing controversies on the structures of the various smectic phases.

PREPARATION

These terephthal-*bis*-*n*-alkylaniline homologs were prepared by the reaction sequence outlined in scheme 1. A friedel-Crafts acylation of acetanilide in refluxing carbon disulfide with a large excess of aluminum chloride and of the acid chloride according to Hsu's procedure[43] gave the desired ketone **1**. Although the crude yields appeared to be high, this material contained a compound of lower solubility than that of the ketone. This compound could be separated from the ketone by extracting the crude material with either chloroform or ethyl acetate; the by-product being insoluble but it has not yet been identified. A maximum yield of 58% of the ketone **1** was obtained in this manner. Recently, this reaction has been studied more extensively at room temperature and in different solvents but the reported yields are lower.[44] A Wolff-Kishner reduction of the ketone gave the desired aniline **2**. Examples of the experimental procedures which gave the best results are given in the experimental section. More recent results indicate that the yield of the aniline might be improved if a continuous liquid-liquid extraction were used to remove the aniline from the reaction mixture; especially with the shorter chain length anilines. The ketone **1** can also be reduced by catalytic hydrogenation[42,44] and the amide hydrolyzed to the desired aniline.[44]

Reaction of the aniline **2** with terephthaldehyde in absolute ethanol but using molecular sieves in place of the usual acid catalyst gave the desired compounds **3** in good yields (see Table II). However, when $R = C_{10}H_{21}$, a mixture of the desired dianil **3** and the monoanil **4** was isolated. These could be separated by recrystallization but the monoanil has not yet been obtained sufficiently pure to determine if it also shows mesomorphic properties. Recent results indicate that at least with the C_4 and C_5 homologs neither an acid catalyst nor molecular sieves are needed for the reaction to go and elimination of the sieves makes the work-up of the reaction easier since the product can then be obtained simply by collecting the crystals which are

SCHEME 1 Synthesis of terephthal-*bis*-*n*-alkylaniline homologs



formed on cooling the reaction mixture. Results obtained in using molecular sieves in the synthesis of dianils of 2-chloro-4-phenylenediamine indicate that when condensation fails to occur when molecular sieves are used, that it can be achieved by using a few drops of acetic acid in place of the sieves.[42] Thus, a good yield of the C_{10} dianil could probably be achieved using this method rather than the procedure given here. Although Table II indicates that some of the homologs can be recrystallized from ethanol, usually the addition of a solvent in which the material is more soluble is preferred. Chloroform, ether, or ethyl acetate have been used successfully.

TABLE II

Terephthal-*bis*-*n*-alkylanilines

R	Purified yield (%)	Recrystallization solvent
C_1	89.8	2:1 $CHCl_3$, EtOH
C_2	91.1	1:1 Et_2O, EtOH
C_3	79.4	EtOH
C_5	54.0	EtOH
C_6	81.6	1:1 Et_2O, EtOH
C_7	59.0	EtOH
C_8	61.4	2:1 Et_2O, EtOH
C_{10}	71.0	3:10 $CHCl_3$, EtOH

MESOMORPHIC PROPERTIES

The transition temperatures and the mesophases involved in these compounds were studied by a combination of hot-stage microscopy and DTA. Mixture studies have not yet been performed; identification of the various smectics was done by comparing their microscopic textures with those seen in TBBA and should not be considered as absolute. Conoscopic studies on homeotropic regions supported these assignments, i.e., the smectic A was uniaxial whereas the smectic C, H(B) and the unknown smectic ($R = C_5H_{11}$) were all biaxial. Considerably more physical studies would have to be done to determine the actual structure of these phases. A plot of transition temperatures *versus* chain length is presented in Figure 1 and the data given in Table III. This data indicates that the following mesophases were observed for the various chain lengths:

Mesophase	R
N	C_1–C_7
S_A, S_C	C_3–C_{10}
$S_{H(B)}$	C_2–C_{10}

Although there is a definite indication that the smectic A phase would be lost when $R > C_{10}H_{21}$ (the mesophase range becomes very short), there is no indication that this would occur with the smectic C and H(B) phases. The homologs with $R > C_{10}$ were not studied because of the difficulty in preparing and isolating the longer chain-length anilines.

Microscopic studies of the smectic C phases indicated that all of these phases have a temperature dependent tilt angle as shown by the continuous change in either the schlieren or the fan texture with temperature. In Figure 2a is shown the fan texture for the smectic C phase near the $S_C \rightarrow S_A$ transition for the C_6 homolog. On cooling, this texture undergoes a continuous

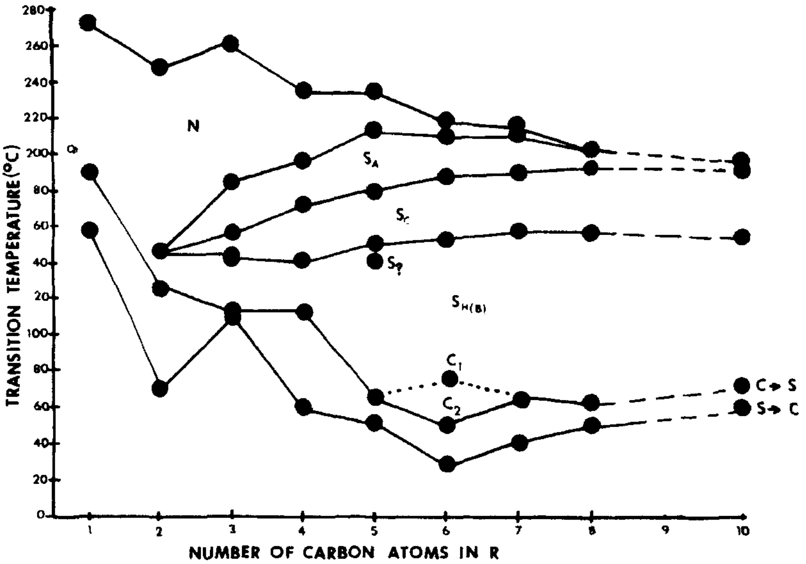
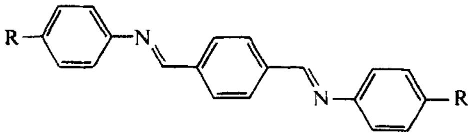


FIGURE 1 Transition temperatures versus alkyl chain length for



change until the fan texture for the smectic C phase near the $S_C \rightarrow S_{H(B)}$ transition appears as in Figure 2b. Further cooling gave the mosaic texture of the smectic H(B) phase as shown in Figure 2c. Changes in the birefringence colors also occur as the sample thickness changes with the tilt angle as can be seen in Figures 2a and 2b. The presence of a temperature dependent tilt angle in the smectic C phase was also confirmed for the C_5 and C_6 homologs by studying the change in layer thickness with temperature using x-ray crystallography.[45]

The two most interesting homologs proved to be those in which $R = C_3H_7$ and C_5H_{11}. The C_3 homolog showed an unusual short range transition between the smectic C and the smectic H(B) phases on cooling as shown in Figures 3a–3f. At *ca.* 144°, the smectic C texture (Figure 3a) undergoes a sharp transition to the texture shown in Figure 3b. Within *ca.* 2°, this texture gradually undergoes subtle changes and then at *ca.* 142° sharply converts to the mosaic texture of the smectic H(B) phase shown in Figure 3c. This intermediate texture could not be observed when the smectic H(B) phase was reheated since the textures became less well defined and more homeo-

TABLE III

Transition temperatures (C)[a] for

R	C_2-C_1[b]	C[b]	$S_{H(B)}$	$S_?$	S(?)	S_C	S_A	N	I
C_1		(159)						189.8– 190.1	272.2– 272.4
C_2		(70)	126					149.3– 149.7	248
C_3	87*	(109)*	108.7– 109.3		142.1	144– 145	157.8– 158.3	184– 185.7	260.2
C_4		(59.8)	111.2– 112.3			142.7– 143.9	171.2	197.8– 198.6	235.2– 235.3
C_5		(52.1)	65.1– 66.0	140.2– 140.5		149.7– 150.2	179.6	213.5– 213.9	233.6– 234.8
C_6	38*	(27.3)	70			154.6	187.4– 188.1	209.8– 210.2	217– 217.3
C_7		(41.4)	61*			158– 158.4	190.4– 191.3	210.4– 210.8	212.6– 213.1
C_8		(51.0)	63			157.6– 157.8	193.5– 193.7		202.6– 202.8
C_{10}		(58.0)	72*			151.0– 152.1	188.6– 189.0		191.0– 191.4

[a] All transition temperatures were determined by optical microscopy unless indicated by a (*). These were determined by DTA. Details are given in the experimental section.

[b] C = crystallization temperature, C_2 and C_1 = two different crystal forms.

tropic. It was also not observed in the other homologs. Conceivably, this intermediate texture could be caused by the presence of an additional short range smectic phase, by paramorphosis i.e., the fan texture of the smectic C phase is retained into the smectic H(B) phase until it cools enough to become a mosaic texture or by a pretransitional effect in the texture similar to the "transition bars" often seen to precede a smectic B phase.[46]

Continued cooling of the smectic H(B) phase caused subtle changes to occur in the mosaic texture as shown in Figures 3d–3f. Unlike the other homologs in this series, it was difficult to determine microscopically when crystallization occurred. The DTA curve (Figure 4) shows two peaks in the cooling curve near the melting transition (109°) suggesting that the sample crystallizes in the region of 100°. Reheating the cooled sample showed an additional peak at 87° (not seen microscopically) believed to be a crystal-to-crystal transition.

In the C_5 homolog, an additional sharp, enantiotropic transition was observed microscopically between the smectic C and the smectic H(B) phases as shown in the sequence of photographs presented in Figures 5a–5c.

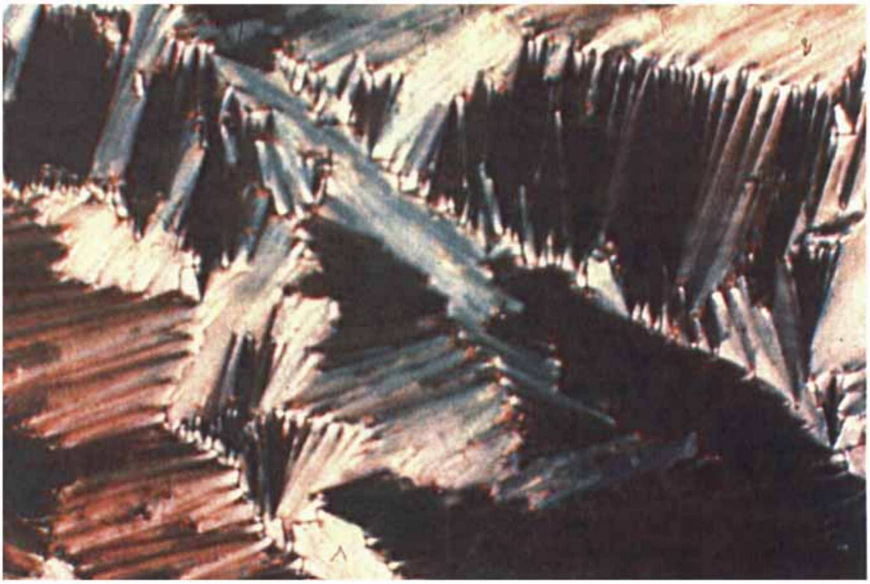


FIGURE 2a Smectic C phase near the $S_C \rightarrow S_A$ transition for R = C_6H_{13}, T = 183.6

FIGURE 2b Smectic C phase near $S_C \rightarrow S_{H(B)}$ transition, T = 159.1 .

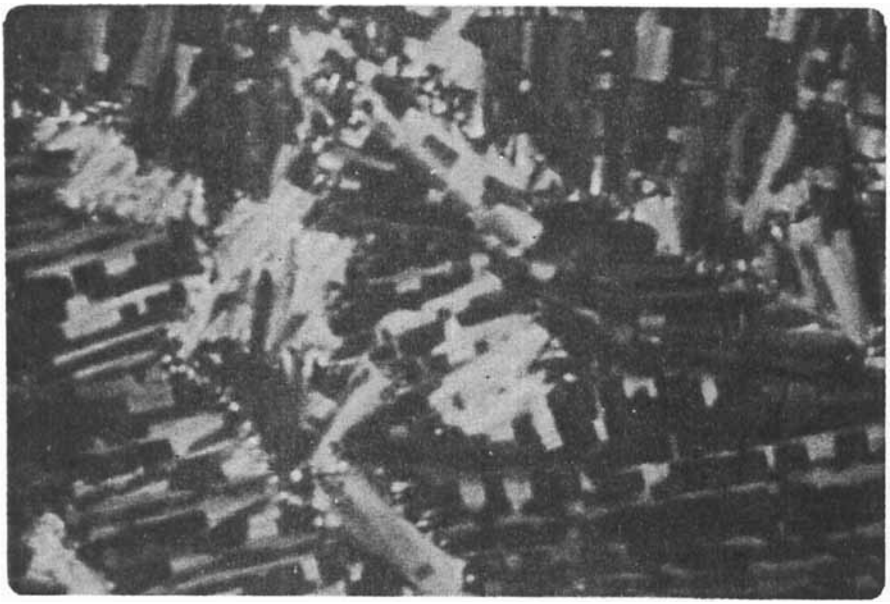


FIGURE 2c Smectic $S_{H(B)}$ phase, T = 152.9°.

FIGURE 3a Smectic C phase near the $S_C \rightarrow S_{H(B)}$ transition.

FIGURE 3b Intermediate state, T = 143.6°.

FIGURE 3c Smectic H(B), T = 140.7°.

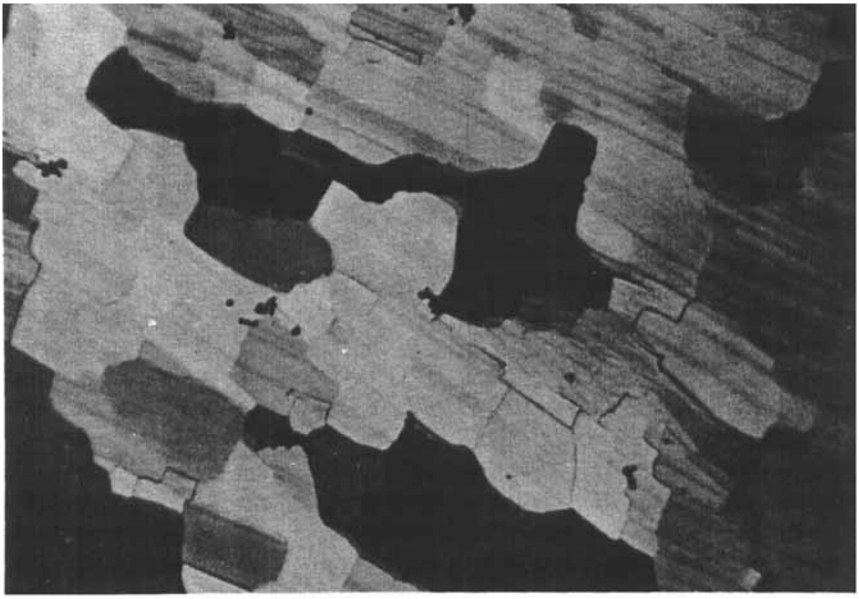


FIGURE 3d T = 99.6°.

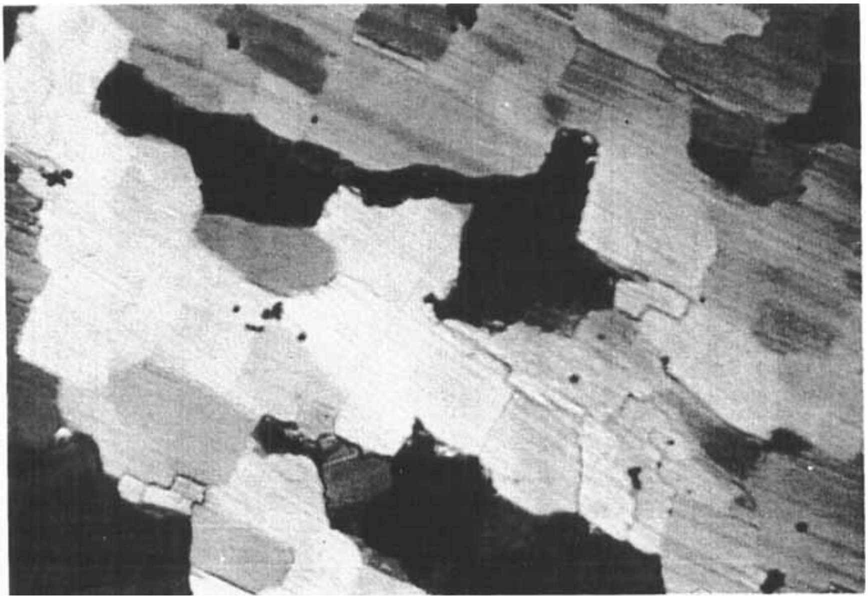


FIGURE 3e T = 97.9°.

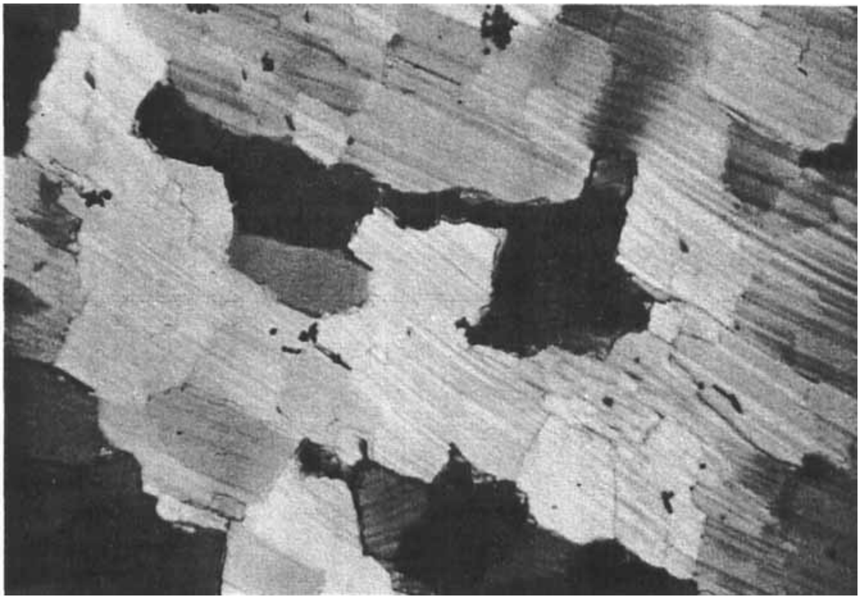


FIGURE 3f T = 29.3°.

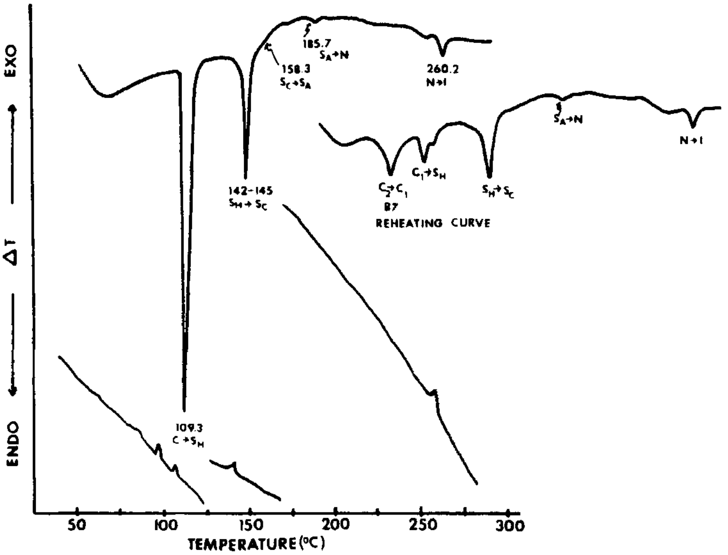
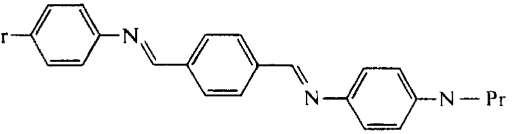


FIGURE 4 DTA curve for n-Pr

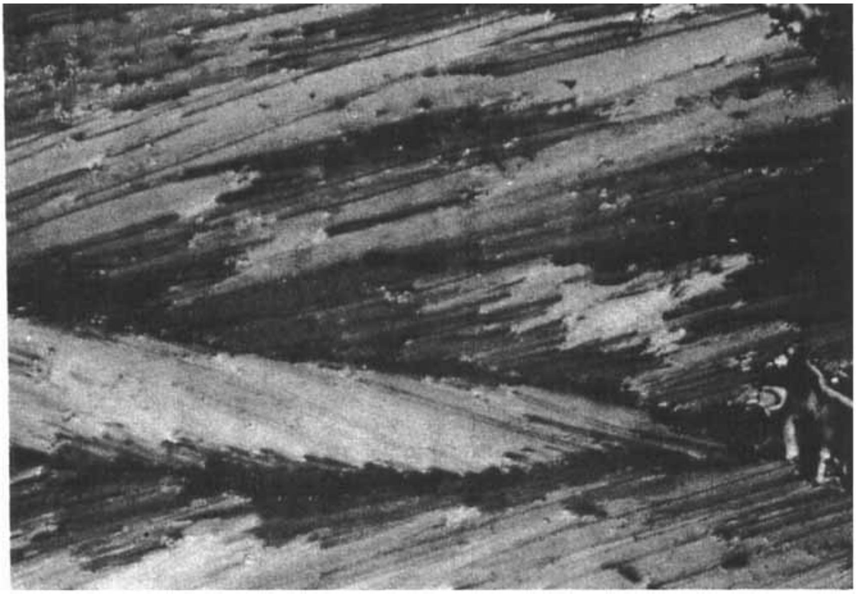


FIGURE 5a Smectic C phase near the transition to the unknown smectic for R = C_5H_{11}, T = 155.0°.

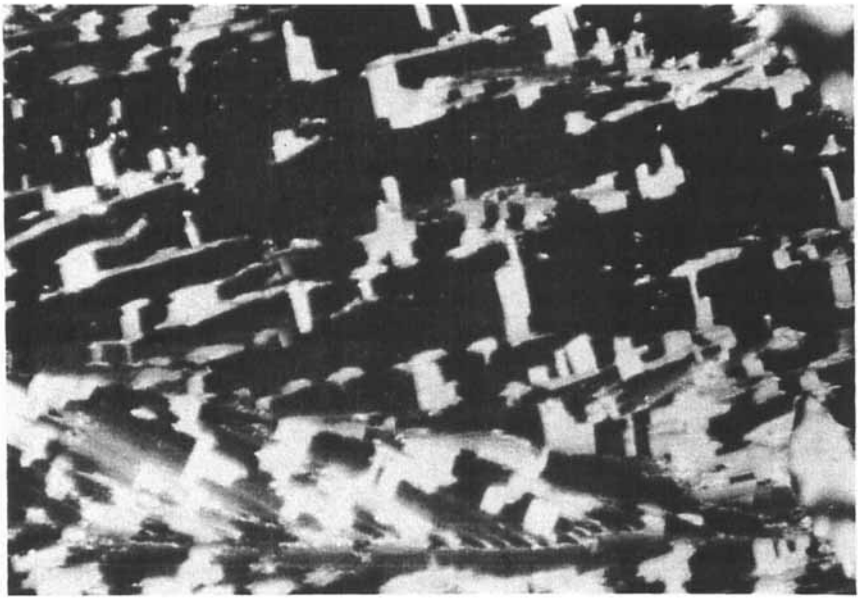


FIGURE 5b Unknown smectic, T = 148.6°.

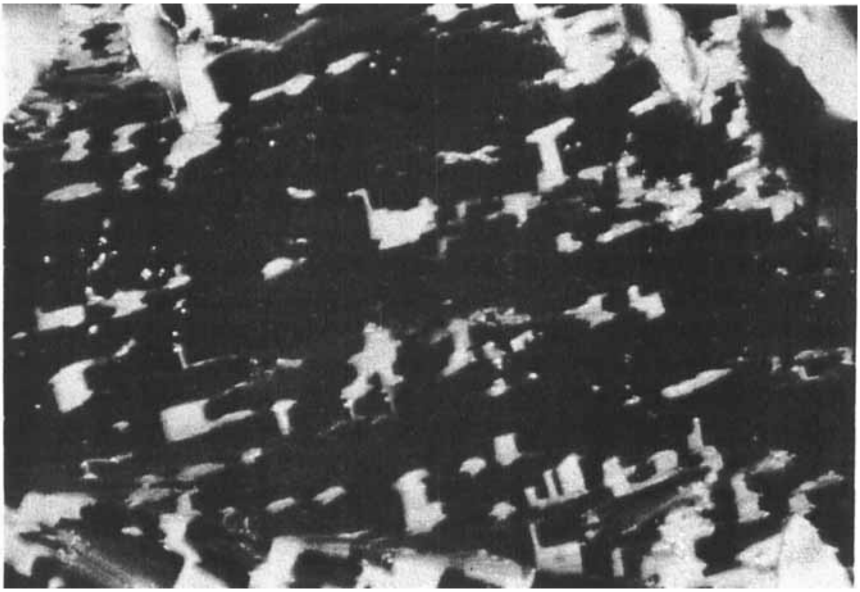


FIGURE 5c "Smectic H(B)", T = 140.0°.

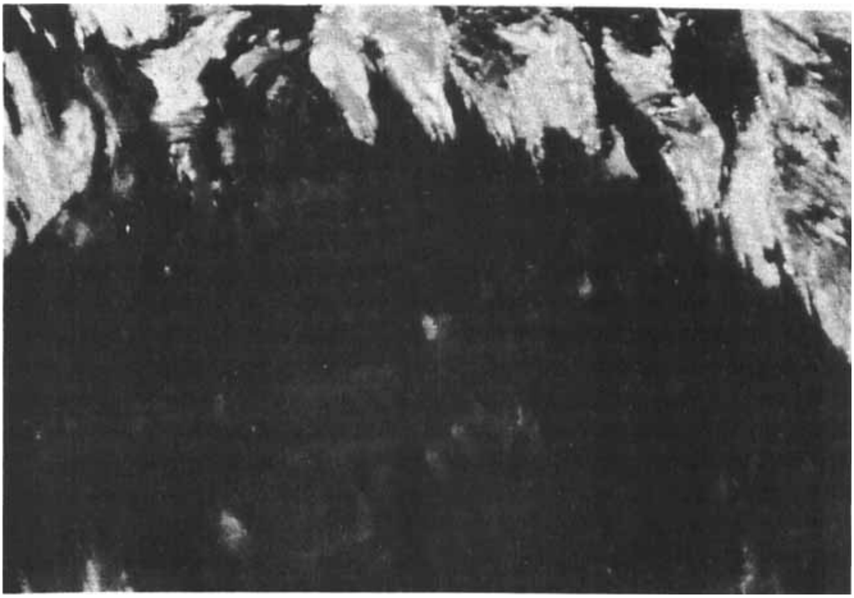


FIGURE 5d Crystals, T = 54.4°.

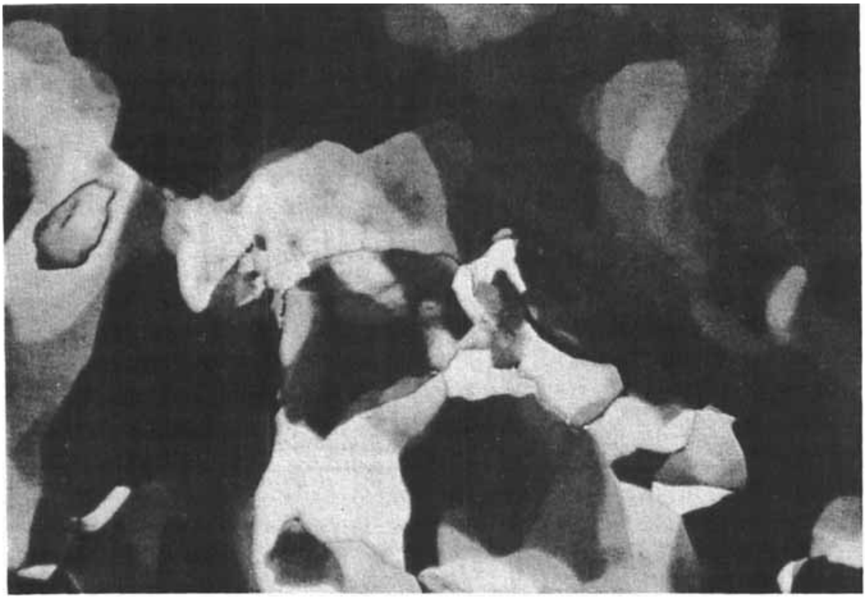


FIGURE 5e "Smectic H(B)" on reheating, T = 133.2°

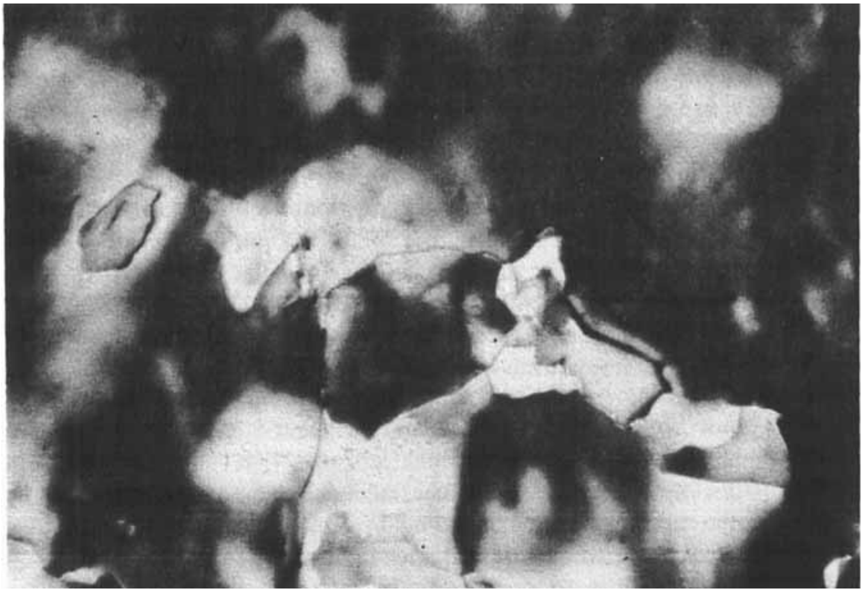


FIGURE 5f Unknown smectic on reheating, T = 143.2°.

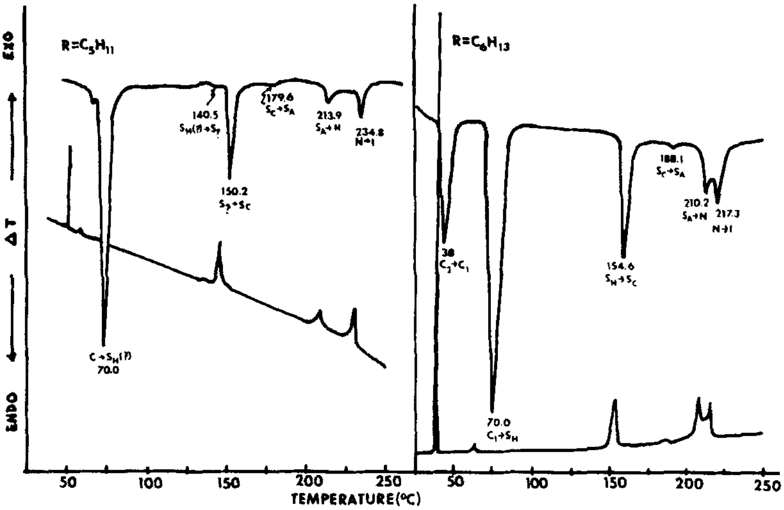
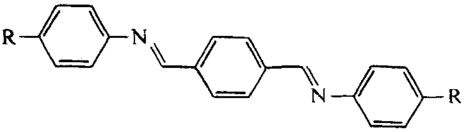


FIGURE 6 DTA curves for



Since both the unknown smectic (Figure 5b) and the smectic H(B) (Figure 5c) have mosaic textures, this assignment of smectic type is arbitrary since our data does not really determine which phase has the smectic H(B) structure or even if either one does.

The DTA curve (Figure 6) shows only a shoulder at 140.5° where the $S_{H(B)} \rightarrow S_?$ transition occurs microscopically. This would suggest that a second order transition is involved but the sharp change which is observed in the microscope does not support this explanation. The smectic phase range is short and our DTA heating rate of 30° per minute is probably too fast to pick up this transition. Continued cooling of the smectic H(B) phase led to an obvious sharp transition to crystals (Figure 5d). When these crystals were reheated, the mosaic textures of the two lower temperature smectic phases were more obvious (Figures 5e and 5f).

In the C_2 homolog, we have indicated that only a $S_{H(B)}$ phase occurs below a nematic phase but changes occur within this smectic phase which indicate another smectic phase might be present. In Figure 7a, is shown the mosaic texture of this smectic phase near the smectic to nematic transition. On cooling, subtle changes occur as shown by Figure 7b until at *ca.* 143° an obvious (and reversible on heating) change takes place as shown in Figure 7c. Subtle changes continue to occur on further cooling until the material crystallizes at 72° (Figures 7d–7f). No transition was observed at 143° in

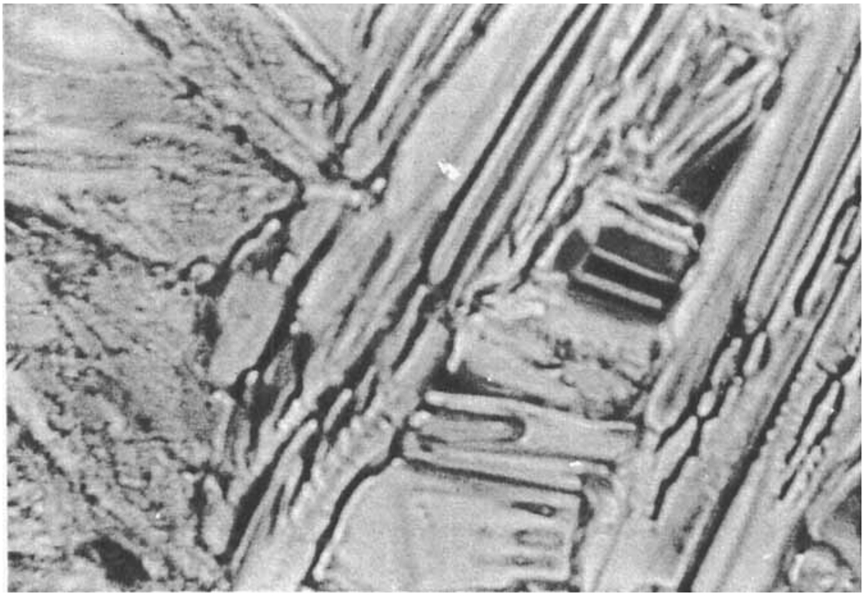


FIGURE 7a Smectic H(B) phase near $S_{H(B)} \rightarrow N$ transition for $R = C_2H_5$, $T = 148.1°$.

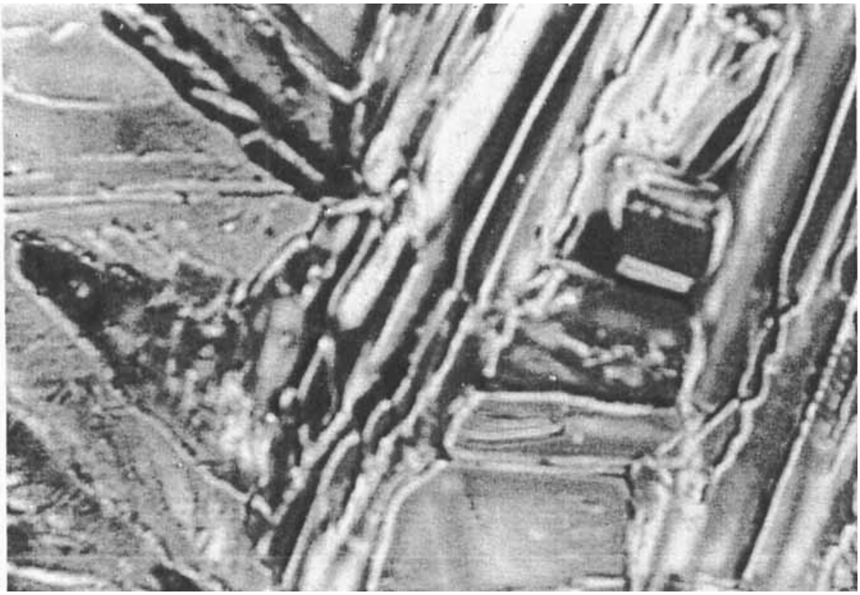


FIGURE 7b Smectic H(B) at $T = 146.0°$.

FIGURE 7c Smectic phase at T = 142.0°.

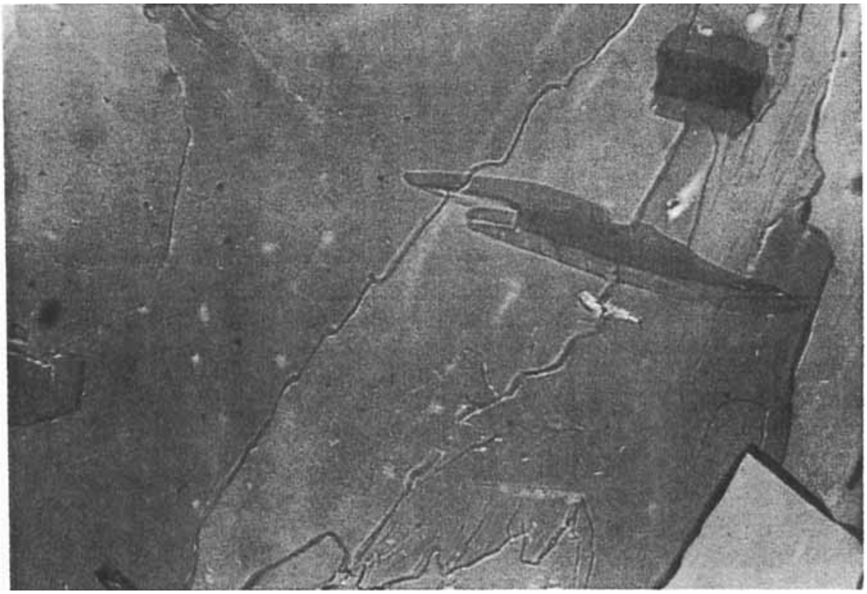


FIGURE 7d Smectic phase at T = 134.9°.

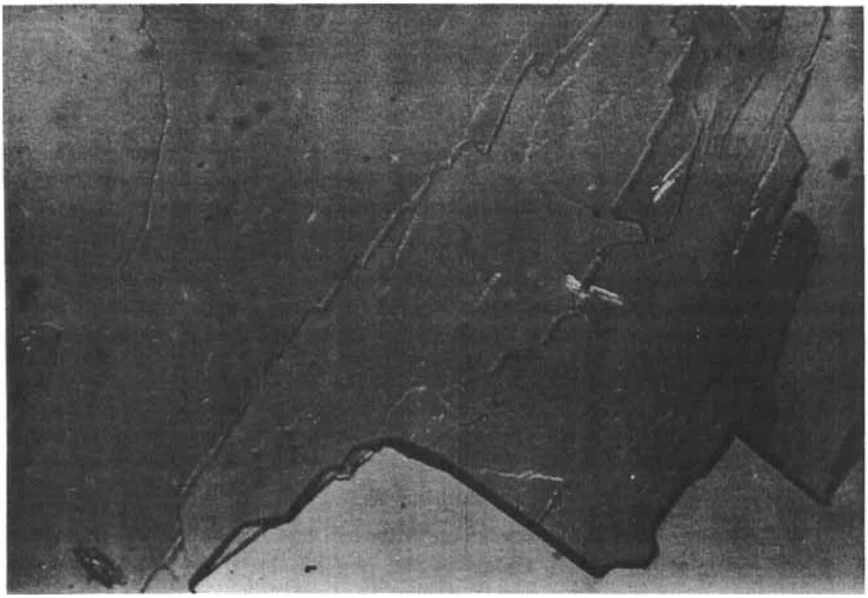


FIGURE 7e

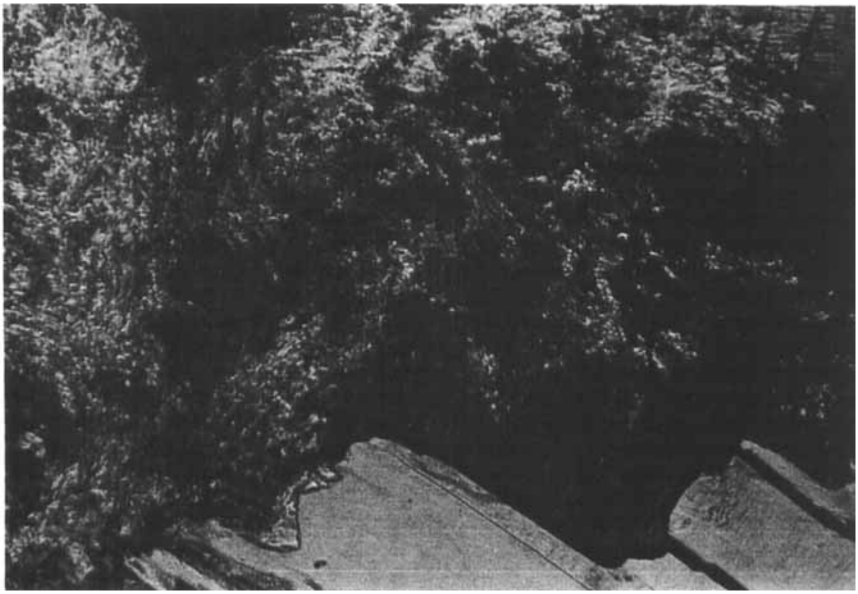


FIGURE 7f Crystals, T = 72.0°.

the DTA curve of this material. This transition is not quite as sharp as the additional one observed in the C_5 homolog making it difficult to say if two smectic phases are involved here. The gradual textural changes could be caused by a change in the tilt angle of the molecules in the smectic phase as observed in the smectic C phase or perhaps the phase observed at 143° is another crystalline phase. If the latter is true, it is a crystalline phase which does not supercool. It is interesting to note that in this C_2 homolog, the smectic C texture was not observed whereas it was in the C_3 homolog but with the unusual sharp transition to the short range texture seen in Figure 3b occurring between this smectic C and the smectic H(B) phase.

Usually, cooling of the smectic H(B) phases in these compounds caused subtle and continuous changes in the textures to occur. No sharp transitions could be observed by DTA or microscopic observations but changes in textures could be seen in comparing photographs taken at various temperatures. Possibly, these subtle changes are due to the tilt angle continuing to change with temperature in the smectic H(B) phase. This has been shown to occur in TBBA to the extent of *ca.* 5° (compared to *ca.* 28° for the smectic C phase) over the temperature range of the smectic H(B) phase by neutron

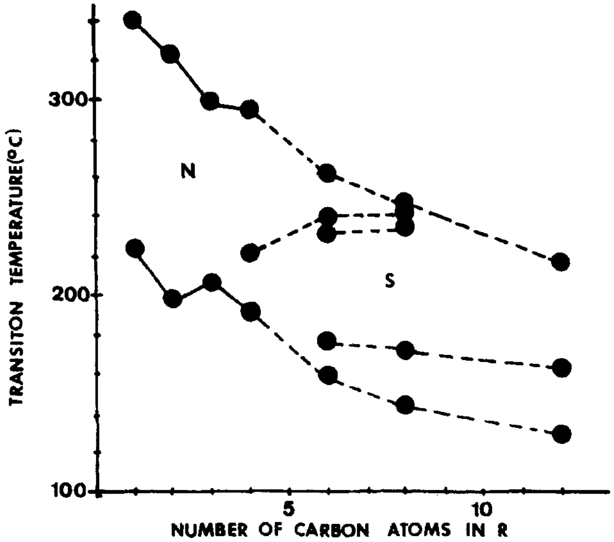
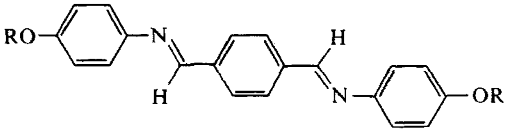


FIGURE 8 Terephthaldehyde analogs (alkoxy anils):



diffraction studies.[8] Or perhaps, there are additional more highly ordered smectic phases between the smectic H(B) and the crystalline phase as found for TBBA[18] but not observed by our methods.

The microscopic textures observed for the C_6 homolog (Figures 2a–2c) were typical of those seen in all homologs with R > C_5 and no additional unusual features were observed. However, a crystal-to-crystal transition at 38° was observed in the DTA curve (Figure 6) for the C_6 homolog which was not seen in the microscope textures.

It is interesting to compare the plot of transition temperatures *versus* chain length for these terephthal-*bis*-*n*-alkylaniline homologs (Figure 1) with those for the known corresponding alkoxy analogs in Figure 8[47] and the alkyl and alkoxy anil derivatives of phenylenediamine given in Table IV[48] and Figure 9.[48] As would be expected, the alkoxy analogs in both series have higher transition temperatures than the corresponding alkyl compounds. The data available for the alkoxy terephthalaniline analogs is too scattered to say much except that smectic polymesomorphism occurs in the longer chain-length compounds. In the phenylenediamine anil derivatives, only chain lengths through R = C_5H_{11} have been reported for the alkyl analogs

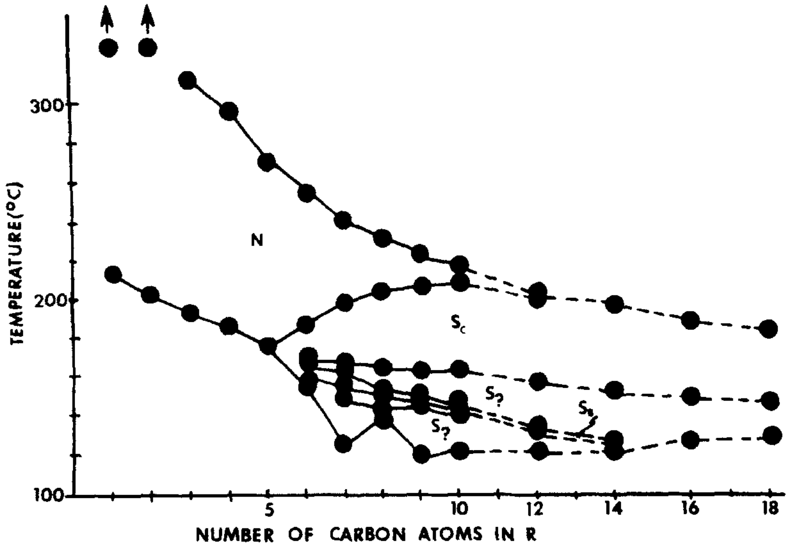


FIGURE 9 Phenylenediamine analogs (alkoxy anils)

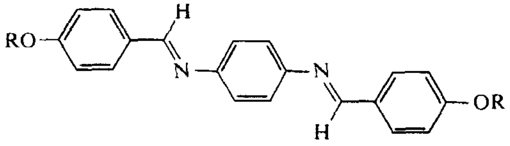
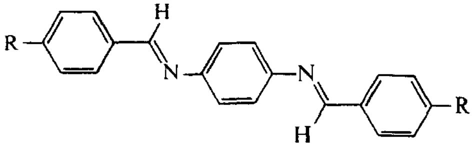


TABLE IV

Phenylenediamine analogs(alkyl anils)[a]



R	N	I
C_1	196	270
C_2	152	219
C_3	125	247
C_5	122	207

[a] reference 48

and these show only nematic properties. When $R = C_1$–C_5 in the alkoxy compounds, again only nematics are observed but enough data is available to show that smectics begin to appear at $R = C_6$ and that extensive polymesomorphism occurs with longer chain lengths. Many of these smectics have not yet been identified. In contrast to the phenylenediamine anils, the smectic phase first appears when $R = C_2$ in the terephthalalkylaniline series indicating a greater tendency towards mesomorphism in this series. It is not clear from the structures of these two compounds why this should be true. The electronic factors, such as dipole moments, should be essentially the same and both structures seem to have the same capability of being planar. This would suggest that the packing of the molecules in the liquid crystal phases might be the determining factor. The determination of the packing in the crystalline phases of these compounds by x-ray crystallography might be useful. Recently, the crystalline structure of TBBA has been reported and the molecules shown to be non-planar[49] but unfortunately, the crystalline structure of a member of the phenylenediamine dianil series has not yet been determined to be used for comparison.

THERMODYNAMIC DATA

Plots of the enthalpy and entropy changes *versus* the alkyl chain length for the crystal to mesophase transition are shown in Figure 10. A definite minimum occurs near $R = C_7$ followed by a sharp rise at $R = C_8$.[50] This suggests that the crystal structure involved in this transition changes at this point and that the change in molecular order for this transition is greater for the longer chain compounds than for the shorter ones. Perhaps, the longer chains are more flexible in the mesophase than in the crystalline state. This

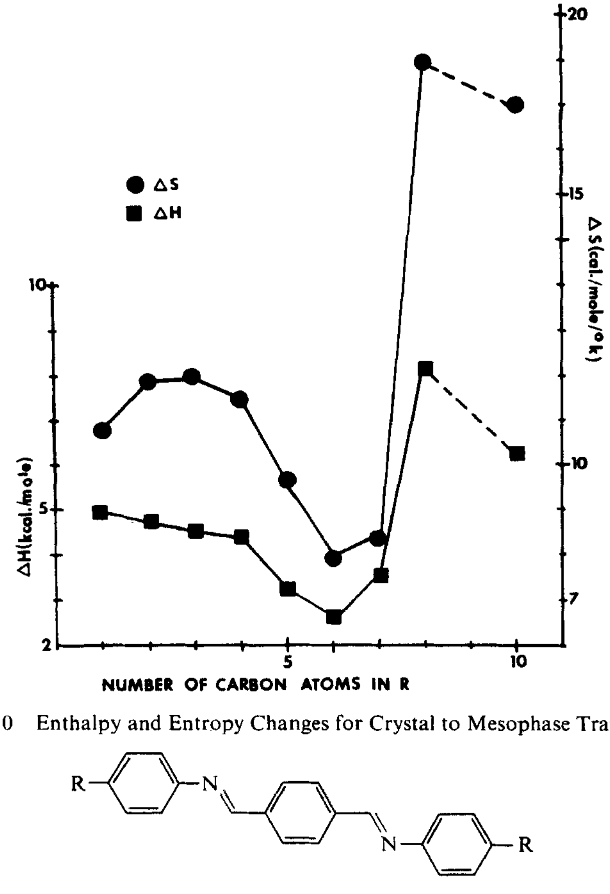
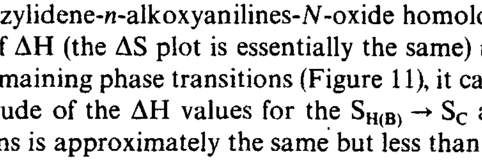


FIGURE 10 Enthalpy and Entropy Changes for Crystal to Mesophase Transitions for



type of curve has also been found for the 4,4′-dialkoxyazoxybenzene and the 4-*p*-*n*-alkoxybenzylidene-*n*-alkoxyanilines-*N*-oxide homologous series.[51]

In the plots of ΔH (the ΔS plot is essentially the same) *versus* alkyl chain length for the remaining phase transitions (Figure 11), it can be seen that the order of magnitude of the ΔH values for the $S_{H(B)} \rightarrow S_C$ and the N → I or $S_A \rightarrow I$ transitions is approximately the same but less than that observed for the ΔH values for the C → M transitions (Figure 10). This suggests that the change in order which occurs in the $S_{H(B)} \rightarrow S_C$ transition is of the same order of magnitude as that occurring in the N or $S_A \rightarrow I$ transitions and that the order in the smectic H(B) phase is probably closer to that found in a smectic C phase than that found in the crystalline structure. A minimum occurs in both these curves when $R = C_6$ suggesting that in this homolog, these transitions involve less of a change in order than in the other homologs.

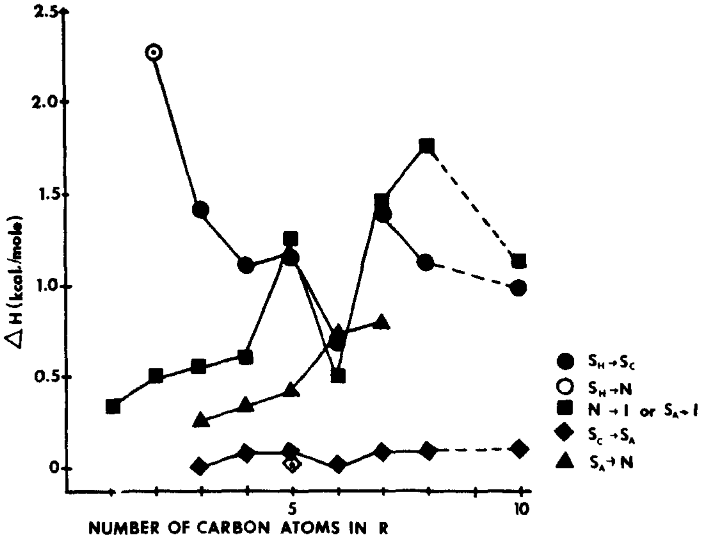
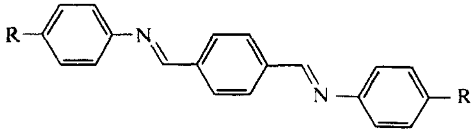


FIGURE 11 Enthalpy change as a function of alkyl chain length for



The ΔH values for the $S_A \rightarrow N$ transitions are somewhat less than those for the $S_H \rightarrow S_C$ and N or $S_A \rightarrow I$ transitions and increase with increasing chain length. This again could be an indication of the increasing disorder found in the more flexible longer chains in the higher temperature mesophase. The values for the $S_C \rightarrow S_A$ transitions are essentially zero which supports the second order nature of these transitions.

CONCLUSIONS

The terephthal-*bis*-*n*-alkylaniline homologs with alkyl chain lengths C_1–C_8, C_{10} have been prepared and their mesomorphic properties studied. The smectic C phase was observed in the C_3–C_{10} homologs and showed a temperature dependent tilt angle. A mosaic texture believed to be the $S_{H(B)}$ phase was observed in the C_2–C_{10} homologs and an additional mosaic texture was found in the C_5 compound. Anomalies, still unexplained, were seen in the C_2 and C_3 homologs. DTA data showed some interesting relationships between the types of phase transitions observed but better thermal data is needed to study the phases below the smectic H(B) phase than can be obtained by DTA analysis.

EXPERIMENTAL

Toluidine, 4-ethylaniline, acetanilide, the acid chlorides and other reagents and solvents used were purchased from commercial suppliers and not purified before use. Tlc data was obtained using Analtech silica gel GF-2.5 × 10 cm Uniplates® (250 μ) with iodine and UV light as detectors. A Perkin-Elmer Model 700 (ir), a Varian A-60 (nmr) and an Associated Electronics Industries Model MS-12 (mass spec.) instruments were used as analytical tools.

Transition temperatures were obtained using a Leitz–Wetzler ortholux polarizing microscope equipped with a calibrated FP-2 hot stage and a Du Pont 900 DTA instrument at a heating rate of 30°/min, the minimum rate we could use and obtain a good curve. Because of the limitations of this DTA instrument, good cooling curves were not obtained and the thermal data should not be considered complete at this point. This instrument was calibrated using the inorganic standards provided with this equipment.

In order to obtain good fan textures for microscopic studies, both the slide and cover slip were washed with acetone and wiped clean with a tissue by rubbing in a direction parallel to the plate. The sample slide was placed on the hot-stage near the temperature of the isotropic phase and cooled at *ca.* 2°/min. in order to obtain well-defined textures. Once a transition occurred, the sample was reheated at a rate of 2°/min to obtain the more accurate heating transition temperature and then cooling resumed to the next lower temperature phase. The sample was cooled in this manner to room temperature and then reheated to determine if the transitions were enantiotropic. Usually, a sample could not be taken through more than one such cycle without achieving homeotropic or less well-defined textures. Also, decomposition and sublimation tended to occur while the sample was in the nematic phase.

The photographs presented in this paper were taken using the Leitz microscope's 35 mm camera, Kodak High Speed Ektachrome Indoor or Tri-X film and with a 6x microscope objective and 10x eyepiece using crossed polarizers. All pictures shown for a series of phase transitions for a particular compound were taken without moving the sample slide so as to maintain the same area as much as possible. All photographs were taken during a cooling cycle unless otherwise noted and without reheating so as to maintain good fan textures in which even small changes could be observed.

4-*n*-Pentanoylacetanilide 1 (R = C_4H_9)

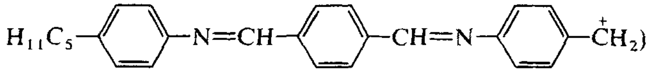
To a stirred mixture of acetanilide (135 g, 1.00 mole) and valeryl chloride (291 g, 2.41 moles) in 800 ml CS_2 was slowly added in small portions, anhyd. $AlCl_3$ (534 g, 4.00 mole) and the reaction mixture refluxed for 4 hr. After removal of the CS_2 by distillation, the pot residue was poured onto crushed ice, the precipitate collected, washed with H_2O (3x 700 ml), dried overnight in a hood and then over P_2O_5 in *vacuo* to give 425 g of crude product: mp 110–122° and ir ($CHCl_3$) 3320 (weak, NH), 1675 (strong; amide plus ketone C = 0) cm^{-1}. This material was extracted with $CHCl_3$ (2.2 l.) and the insoluble material removed by filtration. The $CHCl_3$ layer was extracted with 5% KOH (2 × 3 l.), washed with H_2O (3 × 3 l.), dried (Na_2SO_4), charcoaled, filtered and concentrated to dryness (Rotovap) to give 258 g (71.0%) of impure ketone. This material was recrystallized from 2 l. of a 1:1 mixture of EtOAc and ligroine (b.p. 60–90°) followed by a second recrystallization from a mixture of EtOAc (1 l.) plus ligroine (700 ml)[52] to give 209 g (57.6%) of the purified ketone, 1 (R = *n*-C_4H_9): mp 135–136° (lit.[53] mp 132–133°); tlc (EtOAc) showed one spot with R_f = 0.48 (acetanilide R_f = 0.47); ir (nujol) 3335 (weak NH), 1695 (strong ketone C=O), 1660 (more intense amide C=O) and 1600 (strong Ar) cm^{-1}; nmr ($CDCl_3$) δ8.2 (s, 1, NH), 7.88, 7.52 (2d, 4, *J* = 9 Hz, Ar*H* $A_2'B_2'$ pattern), 2.90 (t, 2, *J* = 7 Hz, CH_2CO), 2.18 (s, 3, $COCH_3$) and 1.9–0.7 (m, 7, 2CH_2 and CH_3) and mass spectrum (70 ev) *m/e* 219 (M+).

4-*n*-Pentylaniline, 2 (R′ = C_4H_9)

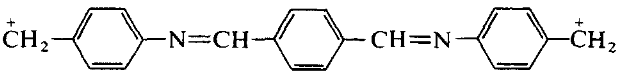
To a stirred mixture of 4-*n*-pentanoylacetanilide (209 g, 0.95 mole) and KOH (228 g, 3.27 moles) in triethylene glycol (1.7 l.) was added 97+ % hydrazine (166 g, 5.04 moles) and the mixture refluxed for 5 hr with a Dean-Stark trap to remove water. The contents of the trap were added to the cooled reaction mixture and this material extracted with Et_2O (4 × 1.6 l.) The Et_2O extract was washed with H_2O (2 × 1.0 l.), dried (Na_2SO_4), filtered and the solvent removed (Rotovap) to give 152 g (98.1%) of crude material. Distillation of this liquid gave 139 g (89.6%) of the aniline 2 (R′ = C_4H_9): bp 120° (2.5 mm) [lit[54] bp 96° (0.7 mm)]; tlc (EtOAc) showed one spot with R_f = 0.63 (starting material R_f = 0.53); ir (film) 3355 (broad, medium NH_2), 3220 (weak, NH_2), 1620 (strong Ar) and no carbonyl absorptions at 1695 and 1660 cm^{-1}; nmr (CCl_4 δ6.75 (d, 2, *J* = 8.0 Hz, ArH ortho to NH_2), 6.34 (d, 2, *J* = 8.0 Hz, ArH ortho to CH_2), 3.23 (s, 2, NH_2), 2.40 (d, 2, *J* = 7.0 Hz, ArCH_2) and 1.82–0.65 (m, 9, C_4H_9).

Terephthal-*bis*-pentylaniline, 3 ($R = C_5H_{11}$)

To a stirred mixture of terephthaldehyde (2.1 g, 15 mmoles) and molecular sieves (3.1 g, Linde ≠ 4A, 8 × 12 beads or 1/16″ pellets[55]) in abs. EtOH (50 ml) was added dropwise 4-*n*-pentylaniline (5.0 g, 31 mmoles). The reaction mixture was stirred with refluxing for 2.5 hr, poured into boiling abs. EtOH (300 ml) to obtain a solution. Et_2O or $CHCl_3$ can be added to maintain a solution, if necessary. This hot solution was filtered to remove the sieves, cooled to 5° and the yellow crystals collected to give 4.5 g (70%) of the crude product. Recrystallization twice from abs. EtOH gave 3.5 g (54%) of the dianil 3 ($R = C_5H_{11}$): capillary mp (Hoover-Thomas apparatus, corrected) ~137–235°; ir ($CHCl_3$) 1620 (intense Ar), 1600 (medium, CH=N) cm^{-1} and no C=O or NH_2 absorptions; nmr (CCl_4) δ8.33 (s, 1, C*H*=N), 7.84 (s, 4, terephthaldehyde Ar*H*), 7.02 (s, 8, aniline Ar*H*) 2.38–2.72 (t, 2, $J = 6$ Hz, CH_2Ar), 0.68–1.88 (m, 6, CH_2) and 0.90 (s, 3, CH_3) and mass spectrum (70 ev) *m/e* 424 (M+),

367 (M − 57, ),

318 (metastable peak from m/e = 367),

311 (M − 114, ),

216 (metastable peak from m/e = 311) and 219 (M-205, base peak).

When $R = C_{10}H_{21}$, the reaction mixture was poured into hot $CHCl_3$ to give 5.5 g (91%) of the crude material. This was shown to contain two materials by tlc ($CHCl_3$, Et_2O) which showed two spots with $R_f = 0.63$ and 0.76 (starting aldehyde $R_f = 0.54$, starting aniline $R_f = 0.48$) and by ir ($CHCl_3$) which showed an aldehyde C=O absorption at 1700 cm^{-1}. Recrystallization twice from a mixture of 60 ml $CHCl_3$ and 200 ml abs EtOH gave 4.3 g (71%) of the pure dianil, 3 ($R = C_{10}H_{21}$): capillary mp ~96–193°; ir ($CHCl_3$) showed no aldehyde absorption and tlc ($CHCl_3$, Et_2O) showed only one spot with $R_f = 0.84$.

Tlc and ir analysis indicated that both the dianil and the material with $R_f = 0.63$ were present in the recrystallization filtrate. Enough separation of this unknown compound from the dianil was achieved by recrystallization from i-PrOH to determine that it was monoanil, 4 ($R = C_{10}H_{21}$) although tlc indicated that some dianil was still present: ir ($CHCl_3$) 1698 (intense aldehyde C=O), 1620 (medium, Ar) and 1600 (medium, C=N); nmr (CCl_4) δ9.92 (s, 1, C*H*O), 8.38 (s, 1, C*H*=N), 7.87 (d, 4, $J = 2$ Hz, terephthaldehyde Ar*H*), 7.04 (s, 4, aniline Ar*H*), 2.58 (m, 2, ArCH_2), 1.26 (s, 6, CH_2), 0.89 (s, 3, CH_3) and mass spectrum (70 ev) *m/e* 349 (M+).

Acknowledgements

The samples of TBBA, 4-*n*-propylaniline and 4-*n*-octanoylacetanilide provided by D. L. Fishel's group were greatly appreciated. We are indebted to W. J. Mayer for the DTA curve for the C_6 homolog, to T. F. Longo, Jr. for mass spectral data, to R. B. Moreland for nmr data and to the National Science Foundation for financial support under grant numbers GH-34164X and DMR-74-13173.

Note added in proof

Since our paper was submitted for publication, a study of the C_5–C_7 homologs has been reported.[56] Our transition temperature data agrees quite well except that we did not observe the reported S(III) phase in the C_6 and C_7 homologs or the monotropic S(V) phases in the C_5 and C_6 homologs. This could be due, in part, to our use of the less sensitive DTA instrument and more reliance on changes in microscopic textures for determining phase changes.

We prefer not to accept the concept that the two enantiotropic smectics below the smectic C phase in the C_5 homolog are both smectic B phases without considerably more physical data being collected. The controversy over the classification of the $S_{B(H)}$ phase in TBBA is, in our opinion, not yet completely resolved. Based on microscopic texture studies alone, we found that this series of compounds exhibits more complex sequences of phase transitions than any of those we have seen in a wide variety of other mesomorphic compounds. These studies suggest to us the possibility of the existence, in at least some of the homologs, of a series of phase transitions from the crystalline state which shows a slowly decreasing order in the phases in such a manner that it might be difficult to state at some point as to whether a phase is a smectic or a crystalline one. This is, of course, just speculation at this point.

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