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High-resolution x-ray measurements of the smectic phases of terephthal-bis-(4*n*)-alkylanilines

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High-resolution x-ray measurements (error ~200–400 ppm) of smectic layer spacing *d* of six homologs (TB3A–TB8A) of terephthal-bis-(4*n*)-butylaniline (TBBA) have been made as a function of temperature. In the smectic-*C* phase, the exponent of the tilt angle for TB3A and TBBA has a value close to 1/3, implying critical behavior. For higher homologs the smectic-*A* to -*C* transition becomes weakly first order. Two new effects, asymmetry of the Bragg reflections in the smectic-*C* phase due to layer undulations in the bulk sample, and existence of domains with different values of *d* in smectic-*H* and lower-temperature phases, were observed. The jump in *d* at the smectic-*C* to -*F*/*H* transition and its variation in the *H* phase with temperature are strongly dependent on the size of the molecule. In the smectic-*H* phase the molecular tilt (also measured by conoscopy) for TB8A decreases with decreasing temperature in contrast to other homologs. However, the (110) spacing (measured with error less than 50 ppm) of the smectic-*H* phase increases with temperature for both TB5A and TB8A. The smectic-*F* phase of TB8A was, for the first time, detected by miscibility with TB7A.

I. INTRODUCTION

TBBA has six different liquid-crystalline phases. It was the first compound to exhibit the smectic-*C* (Sm-*C*) phase characterized by a temperature-dependent tilt, and the smectic-*H* (Sm-*H*) phase. The de Gennes[1] and McMillan[2] theories of the Sm-*C* phase and the extension of McMillan's[3] theory to the lower-temperature phases generated interest and resulted in extensive experimental investigations of these phases of TBBA. Surprisingly enough, the other homologs of TBBA attracted little attention until recently. Some of them have been reported to have new smectic phases.[4-7] The study of the mesophases of these homologs can give information about the change of properties of the mesophases with the changing length of the alkyl chain. The comparison of similar phases of different homologs can help us gain insight into the orientation of molecules and molecular motions in these phases.

In this paper we report the results of our investigations of this homologous series by microscopy, differential scanning calorimetry (DSC), miscibility, conoscopy, and high-resolution x-ray measurements of the layer spacing *d* of the smectic phases. We also report two new effects observed: undulations in the Sm-*C* phase and the formation of domains with different layer spacings in the Sm-*H* and lower-temperature phases.

II. APPARATUS

A three-crystal x-ray diffractometer was used to measure the layer spacing. The diffractometer, as shown in Fig. 1, has two polished [(111)-face] germanium crystals Ge1 and Ge2 that act as monochromator and analyzer, respectively. The rocking curves of these crystals have full width at half-maximum (FWHM) of less than 50 sec of arc. The position of Ge2, mounted on a 2θ ring, can be measured with an accuracy of 1/1000 of a degree. The Mettler FP-52 hot-stage *H* rest on the table *A*. The table *A* and ring *B* can be simultaneously rotated by θ and 2θ angles, respectively. *S*1, *S*2, and *S*3 are slits. The orientation of *H* with respect to *A* can be varied and measured with an accuracy of 0.25 degree. This enabled us to measure the rocking curves of liquid-crystalline phases, which are a measure of the mosaicity of the smectic planes. We used Cu$K\alpha$(1.541 78 Å) radiation and a NaTlI scintillation counter as the detector. The sample holder is shown as the inset in Fig. 1. The sample, 1.5 mm thick and about 12 mm in diameter, is

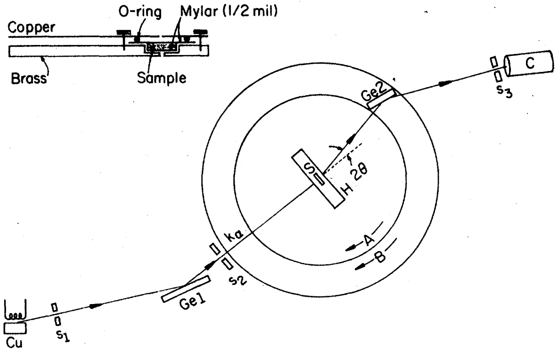

FIG. 1. Experimental set up for x-ray diffraction. *S* is the sample holder, *S*1, *S*2, and *S*3 are the slits, Ge1 and Ge2 are the Germanium crystals used as monochromator and analyzer, Cu is the source of x rays, *C* is the NaTlI scintillation counter. The sample holder is shown as the inset.

TABLE I. Transition temperature (°C) and change in entropy[a] (R_0). R_0=1.986 Cal/K Mol.

		Crystalline		Mesophases						
Compound		C1	C2	Sm (?)	Sm-H	Sm-F	Sm-C	Sm-A	Nematic	Isotropic
	Heating		108.4–109^b							
TB3A			0.475R_0		110.0		144.0	158.3	185.6	260.1
	Cooling	85.3^b	104.7		0.223R_0		1.98R_0	Not detected	0.071R_0	0.189R_0
		1.103R_0	0.493R_0							
	Heating				111.2					
TB4A					6.029R_0		144.2	172.2	199.5	235.3
	Cooling			71.1^b	85.8^b		1.128R_0	Not detected	0.222R_0	0.347R_0
				0.146R_0	0.379R					
	Heating				71.0					
TB5A					5.987R_0	139.8	149.2	179.4	212.3	233.9
	Cooling			52.9^b	60–61	0.026R_0	0.954R_0	0.014R_0	0.296R_0	0.372R_0
				Very large	0.574R_0					
	Heating									
TB6A					58	143.8	154.0	188.0	209.0	216.2
	Cooling				0.173R_0	Not detected	0.820R_0	Not detected	0.26R_0	0.27R_0
TB7A					57.6	144.5	157.6	190.9	209.7	212.6
					5.556R_0	Not detected	1.436R_0	0.034R_0	0.588R_0	0.498R_0
	Heating				56.1^b					
TB8A					13.08R_0	140.2	157.4	193.0		202.4
	Cooling				43.6^b	Not detected	1.538R_0	0.108R_0		1.546R_0
					13.996R_0					

[a] Error in entropy change ~10%.

[b] Transition temperature obtained from DSC thermograph, other temperatures from microscopy.

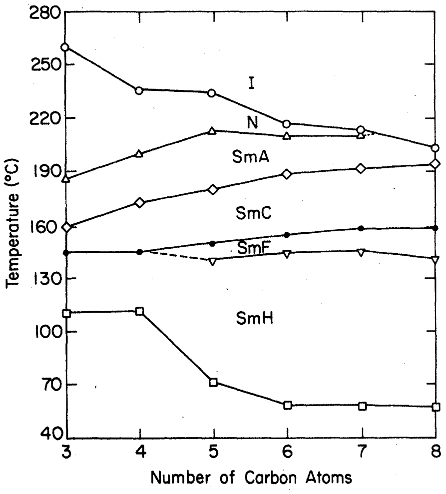

FIG. 2. Variation of the transition temperatures with the number of carbon atoms in alkyl chain.

held between two 0.5 mil thick Mylar sheets. The sample holder slides tightly into the hot stage. The temperature accuracy is 0.1° and 0.2° between 0–100 °C and 100–200 °C, respectively. A magnetic field of 4.5 KG was used to align samples.

III. EXPERIMENTAL DETAILS

TBBA and its five homologs were synthesized using the method of Taylor *et al.*[8] Terephthaldehyde and alkylanilines were acquired from Fluka and Aldrich. The compounds were recrystallized from ethanol and then from a mixture of benzene and hexane, until the transition temperature agreed with the published[4-7] values. The transition temperatures were determined from changes in the characteristic texture of the mesophases observed under a polarizing microscope. The heat of mesomorphic transitions was calculated from the thermographs obtained by the Perkin Elmers DSC-1B machine, calibrated with indium.

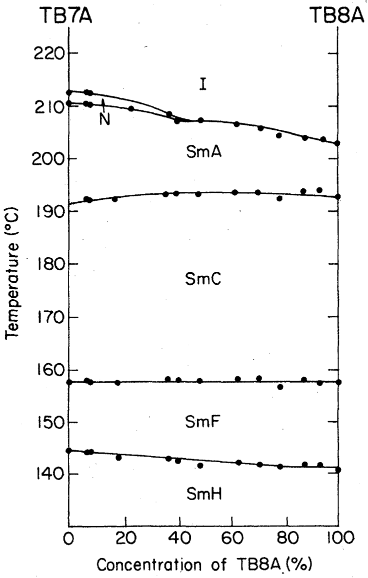

FIG. 3. Miscibility of TB8A and TB7A.

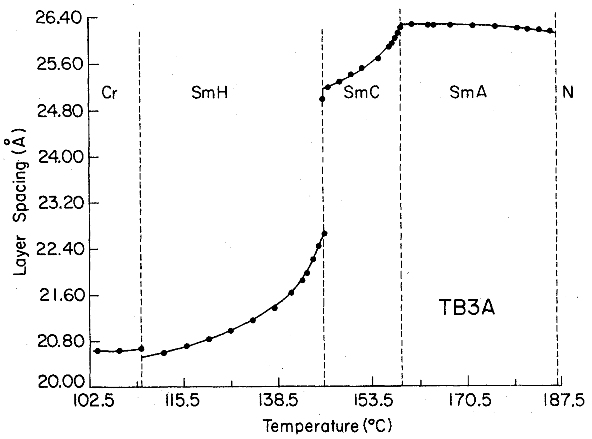

FIG. 4. Layer spacing of the smectic phases of TB3A as a function of temperature. The line joining the points is a guide to the eye.

For x-ray measurements, degassed samples were used so that the effects of moisture and oxygen absorbed in the sample could be minimized. The hot stage was put in a magnetic field and the sample heated to the nematic (isotropic) phase. The temperature was then lowered to the Sm-*C* phase and the field turned off. The hot stage was transferred to the diffractometer table. The sample alignment thus obtained is par-

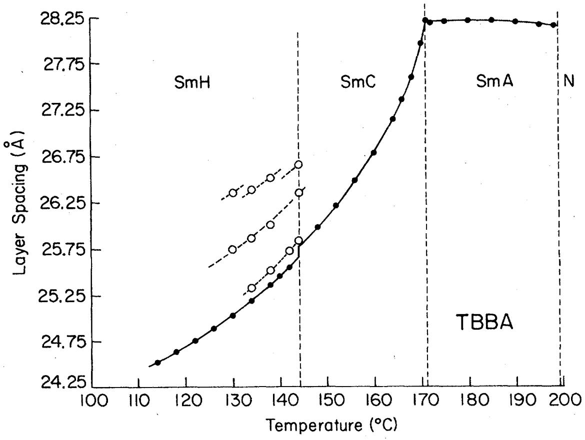

FIG. 5. Layer spacing of the smectic phases of TBBA as a function of temperature. Filled circles are from the main Bragg peak; open circles are from weaker reflections corresponding to the domains with differ layer spacings.

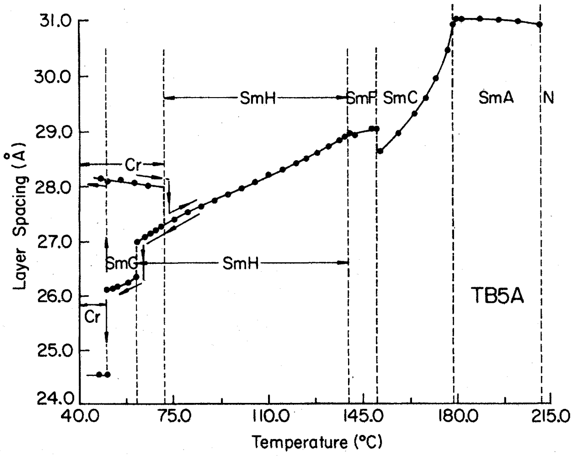

FIG. 6. Layer spacing of the smectic phases of TB5A as a function of temperature. The arrows show the direction of the temperature change. While cooling the monotropic smectic-*G* phase is observed.

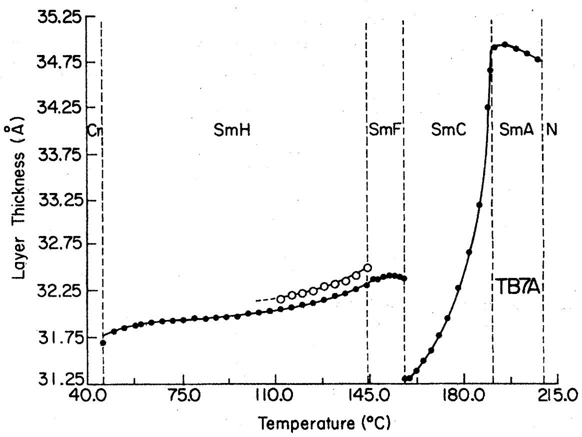

FIG. 8. Layer spacing of the smectic phases of TB7A as a function of temperature, shown by filled circles. The open circles are calculated from the strongest peak corresponding to a different value of *d*.

tially preserved through different mesophases as long as the sample is not heated back to the nematic (isotropic) phase, or cooled down to the crystalline phase. The rocking curves of the Sm-*A* phase had their FWHM between 1.8 to 2.5° for different samples.

After aligning the sample with respect to the x-ray beam, the profile of the Bragg reflection from the smectic layers was recorded at different temperatures. A Lorentzian curve was fitted to this profile to determine the position of the peak. The error in the measured value of *d* is ~200–400 ppm and for the (110) spacing less than 50 ppm.

These compounds decay very rapidly at high temperatures. The Sm-*A* to Sm-*C* transition temperature T_{ac} is most sensitive to the decomposition. We used fresh samples to take the data below and above T_{ac}. The transition temperatures were determined optically after every run and the data rejected if T_{ac} differed by more than 0.5° from the actual value. Our results were reproducible, the maximum difference between any corresponding data points of the different runs being less than 0.2%.

IV. RESULTS AND DISCUSSION

The results obtained from microscopy and DSC are summarized in Table I, and agree with those of Nuebert[7] and Sakagami.[5] The variation of the transition temperatures with the length of the alkyl chain is shown in Fig. 2. The miscibility

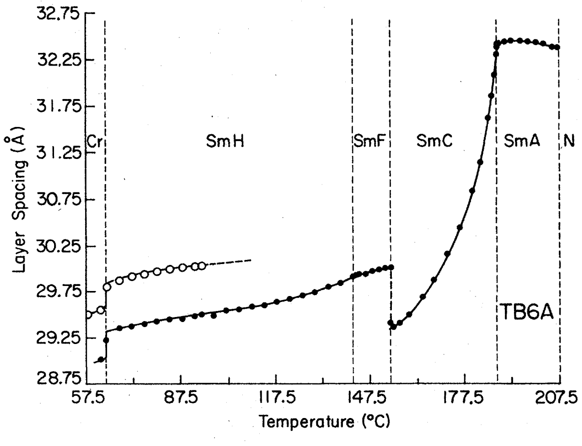

FIG. 7. Layer spacing of the smectic phase of TB6A as a function of temperature, shown by filled circles. The open circles correspond to the strongest peak from the domains with different layer thickness.

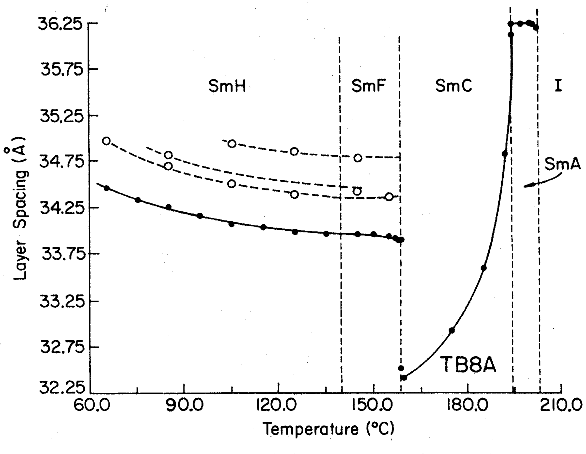

FIG. 9. Layer spacing of the smectic phase of TB8A as a function of temperature shown by filled circles. The open circles show the different values of *d* observed for different domains.

TABLE II. Straight-line fit to Sm-A phase.

Compound	Intercept [$d(0)$ [a]] Å	Slope Å/°C
TB3A	27.04	−0.0049
TB4A	28.67	−0.0026
TB5A	31.38	−0.0028
TB6A	32.99	−0.0029
TB7A	36.56	−0.0086
TB8A	36.72	−0.0025

[a] Intercept at $T = 0\,°\mathrm{C}$.

experiments on TB5A with TB6A and TB6A with TB7A yielded the same results as those of Sakagami[5] and Leadbetter.[6] From the miscibility of TB7A with TB8A, shown in Fig. 3, we found that TB8A also had a smectic-F (Sm-F) phase between 157 and 140 °C. The smectic phase between Sm-C and Sm-H reported for TB3A by Nuebert[7] was not detected in the DSC. However, the layer spacing d as measured by x-rays decreased rapidly for the first 2° below the Sm-C phase. This can give the illusion of a phase change. We were unable to see any sharp change in the texture at 2° below the transition from the Sm-C to the lower-temperature phase. The layer spacing d, obtained from x-ray diffraction experiments on TB3A-TB8A is shown in Figs. 4–9.

A. Smectic A

In the Sm-A phase, the layer spacing increases slowly with decreasing temperature. This is attributed to the stiffening of the end chains due to their reduced thermal motion. The values of the intercepts $d(0)$ and the slopes of straight line fits to the Sm-A data are given in Table II. TB8A has no nematic phase and TB7A has a nematic region of only 2°. The modification of the order parameter causes d to decrease more rapidly near the Sm-A to nematic (isotropic) transition for these two compounds. Near the Sm-A to Sm-C transition we also see a decrease of d as a pretransition effect. Figure 10 shows the even-odd effect on the calculated change in the molecular length and the measured change in Sm-A layer thickness with the change in the number of carbon atoms in the alkyl chain.

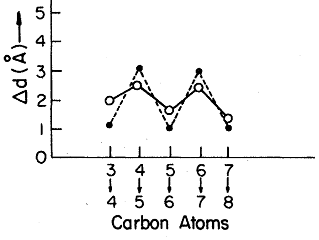

FIG. 10. The change in layer thickness of the Sm-A phase as the number of C atoms in alkyl chain is changed. This illustrates the even-odd effect. Open circles correspond to the measured change in d and filled circles to calculated change in the length of the molecule in transconfiguration.

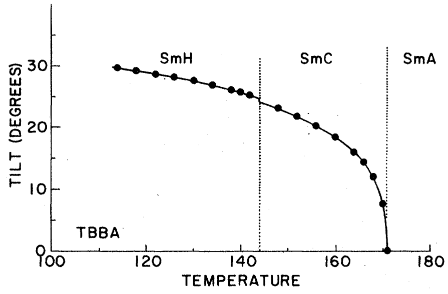

FIG. 11. The variation of the tilt angle in the smectic-C and -H phases of TBBA, calculated from the measured value of d.

B. Smectic C

In the Sm-C phase all six compounds have a temperature-dependent tilt angle. The variation of the tilt angle with temperature in the smectic phases of TBBA, calculated from the measured value of d, is shown in Fig. 11. The jump in tilt at the Sm-C to Sm-H transition is finite. We fitted a function

$$d(T) = d_{ac}\cos[a(b-T)^{\beta}]$$

to the data points in the Sm-C phase, where d_{ac} is the value of layer thickness in the Sm-A phase near the Sm-A to Sm-C transition. The values of the parameters a, b, and β are listed in Table III. β decreases with the number of C-atoms in the alkyl chain as shown in Fig. 12. β has a value close to $\frac{1}{3}$, for TB3A and TBBA, suggesting that we have critical behavior at the second-order transition.[1] Safinya[9] *et al.* have measured this exponent for the Sm-A to -C transition of $8\bar{S}5$ and found it to be $\sim\frac{1}{2}$, i.e., mean fieldlike. Their measurements are closer to the transition than

TABLE III. Parameters from the fit to the Sm-C phase.

Compound	a	Parameters b (°C)	β	d_{ac} [a] Å
TB3A	0.128	159.200	0.33	26.24
TB4A	0.148	171.010	0.32	28.22
TB5A	0.162	178.050	0.28	30.86
TB6A	0.187	187.525	0.25	32.42
TB7A	0.220	190.540	0.22	34.87
TB8A	0.258	194.001	0.17	36.23

[a] Measured value of d just above T_{ac}.

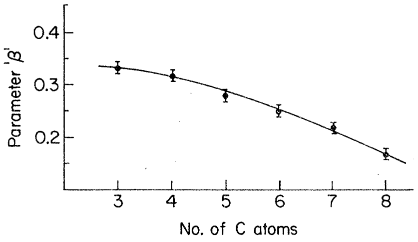

FIG. 12. Value of the parameters β from the fit to the Sm-C phase as a function of C atoms in alkyl chain.

ours, which is probably the reason for the difference in the values of β. The values of β are smaller for the higher homologs. Also, the heat of this transition for TB8A is 0.1 Kcal/Mol as compared to 0.03 for TB7A, 0.01 for TB5A, and is unmeasurably small for TB3A and TBBA. These two observations show that this transition becomes weakly first order for TB5A and the higher homologs. In fact the first two points below T_{ac} for TB8A were observed at the same temperature. This coexistence of Sm-A and Sm-C further strengthens our conclusion that this transition is weakly first order for the higher homologs (TB5A–TB8A).

C. Smectic *F*

At the Sm-C to Sm-F/H transition d makes a jump, downwards for TB3A and TBBA, and upwards for the others. A plot of this jump and the heat of transition against the number of carbon atoms in the alkyl chain is presented in Fig. 13. The magnitude of the jump seems to be correlated to the heat of transition. In the Sm-F phase (for TB5A–TB8A), d stays almost unchanged. There is no abrupt change in d at the Sm-F to Sm-H transition. The (110) reflection, due to the hexagonal ordering of the Sm-H phase, disappears at the transition to the Sm-F phase. This suggested lack of long-range order within the smectic-F plane. A similar conclusion has been drawn by Benattar *et al.*[10]

D. Smectic *H*

In the Sm-H phase the layer spacing decreases (except for TB8A). The decrease is larger for smaller members of the homologous series. For TB8A the d increases slowly but the effect (0.006 Å/° C) is considerably bigger than the thermal change (0.0025 Å/° C). This indicates a possible decrease in the tilt of the molecules, unlike other compounds. To check this we measured the (110) spacing of the hexagonal ordering inside the smectic plane for TB5A and TB8A. For both of them the (110) spacing was found to be proportional to the temperature as shown in Fig. 14. For TB8A, the change in the orientation of the sample holder, as measured on the roking scale (Fig. 15) indicates that the tilt angle stays constant for about 20–30°C below the Sm-C to Sm-F transitions and decreases at lower temperatures. The net decreases in tilt from 155 to 60° C is 2 to 3°. This is in agreement with the calculated value (2.7°) from

$$\text{Tilt angle} = \arccos[d(T)/d(0)] \ .$$

The calculated tilt angle is also shown in Fig. 15. In order to make direct observations of the tilting of the molecules, conoscopic measurements were made. We used an objective with n.a. 1.25(95X), suitable for measuring angles up to 55°. The conoscopic patterns obtained in the reflection mode were identical to those of Niessen and denOuden.[11] The isogyres became very diffuse at lower temperatures making it difficult to determine the distance between two

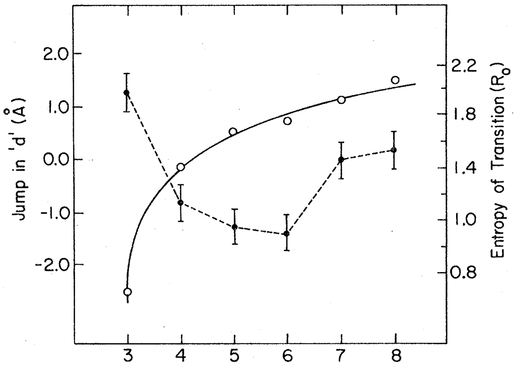

FIG. 13. The jump in the value of d (open circles) and the entropy change at the Sm-C to Sm-F/H transition (filled circles with error bars) versus the number of C atoms in the alkyl chain.

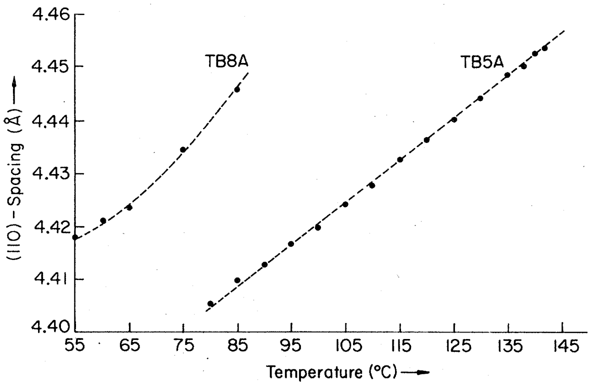

FIG. 14. (110) spacing of the Sm-H phase of TB5A and TB8A as a function of temperature. The lines are drawn as a guide to the eye.

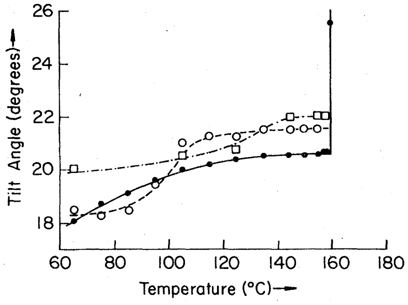

FIG. 15. Variation of the tilt angle with temperature in the Sm-H phase of TB8A. The filled circles are calculated from the measured d; the open circles and squares, from the difference in the readings of the rocking scale. The lines are drawn as a guide to the eye.

of them or their points of intersection. Also the experimental setup did not permit good temperature regulation. Our results, shown in Fig. 16, in spite of large errors indicate decrease of tilt upon cooling in the Sm-H phase.

E. Two new observations

(i) During the x-ray measurements we observed that, for all members of the series, the Bragg peak in the Sm-C phase become increasingly asymmetric with the decrease of temperature. At lower temperatures it developed secondary peaks on one sides, as shown in Fig. 17. (ii) In the Sm-H phases we detected the existence of small domains with different values of the layer spacing. The values of d, for most of such domains detected for TBBA and TB8A and only the ones with most intense Bragg reflection for TB6A and TB7A, are shown in Figs. 5 and 7–9 by the open circles and dotted lines. The d for these domains behaves in similar fashion to the main peak with temperature. Similar observations have been reported by Doucet *et al.*[12] in the smectic phases of n-(alkoxybenzylidene)-p-n-alkylanilines (70.7, 70.5, and 50.7) and by Brownsey[13] in the case of cyano compounds. The x-ray photographs of the Sm-H phase of TB5A by Leadbetter[14] also show finer structure of the Bragg spots but it has been overlooked.

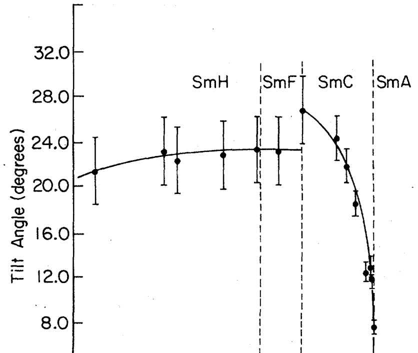

FIG. 16. Tilt angle as a function of temperature in the Sm-C, -F, and -H phases ot TB8A measured by conoscopy in the reflection mode.

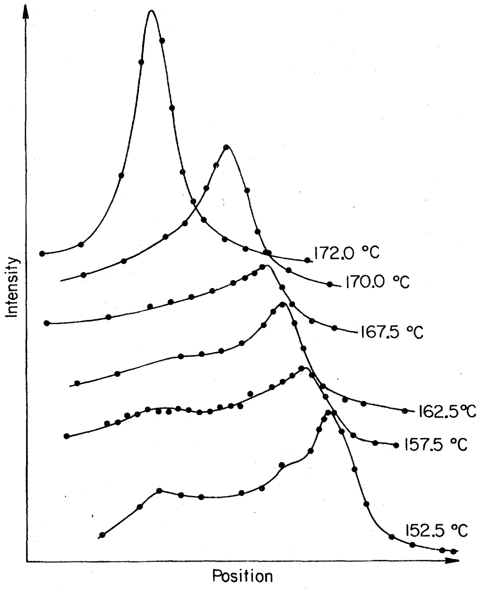

FIG. 17. The growth of asymmetry and development of secondary peaks in the Bragg reflections from the Sm-C phase of TB5A as the temperature is lowered.

Our explanation for the asymmetry of the diffraction spots is as follows. With the decrease of temperature, the tilt of the molecules with respect to the layer normal increases, thus causing the decrease in layer thickness. This requires that the number of layers increase to fill the space. The additional layers have to move in from the boundaries via the motion of dislocations and this takes finite time. As a result the layers bend to fill the space and d no longer has a symmetric distribution. This is similar to the undulation[15] effect that is observed when the distance between two surfaces, with the Sm-A[16] phase between them, is increased. The asymmetric spread in d shows up as a spread on the smaller angle side of the diffraction peak. The undulations were also observed in the microscopic texture as sets of parallel lines, similar to those reported by Johnson,[17] thus supporting our explanation. Therefore, the asymmetry is definitely due to the layer undulations. As the sample is further cooled, the sample divides itself into domains of different spacings. This phenomenon is similar to spinodal decomposition in metal alloys. These domains seem to have different molecular conformations frozen in them producing different values of d.

V. CONCLUSION

We have characterized the various mesophases of the different homologs of TBBA and have determined their transition temperatures and changes in entropy. We found that four of them (TB5A–TB8A) exhibit the Sm-*F* phase in addition to Sm-*A*, -*C*, and -*H*. TB8A has no nematic phase. We have concluded that the Sm-*A* to Sm-*C* transition for higher homologs becomes weakly first order. It is of great interest to look at this transition in still higher homologs and make more careful x-ray and calorimetric measurements closer to the transition in order to determine the exponents. Unfortunately the TBBA series is not suitable for such measurements due to their fast deterioration at high temperatures. Some suitable homologous series should be picked for such a study. Also we have observed the asymmetry in the Bragg reflections of the Sm-*C* phase of these compounds due to layer undulations. The study of Bragg reflections from compounds with fixed (temperature-independent) tilt in the Sm-*C* phase would be interesting. In the Sm-*H* (and lower-temperature phases) the existence of domains with different d is intriguing. The study of the formation of such domains as a function of the cooling rate and their growth (decay) with time could reveal more about their nature and possibly about nucleation processes in liquid-crystalline and similar systems.

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