Phase-Transition Studies in Polymesomorphic Compounds. 1. Density Studies in N-(p-n-Hexyloxybenzylidene)-p-n-butylaniline

N. V. S. Rao^{*†} and V. G. K. M. Pisipati[‡]

Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar 522 510, India (Received: April 15, 1982; In Final Form: August 17, 1982)

The density, ρ , of N-(p-n-hexyloxybenzylidene)-p-n-butylaniline (HBBA) is measured as a function of temperature from the isotropic liquid to the smectic-G phase. The compound is tetramorphic exhibiting three smectic phases S_{C} , S_{B} , S_{A} and a nematic phase. The changes in density across the phase transformations, and the calculated thermal expansion coefficients, confirm the order of the transitions as first order. The particular importance of the smectic-A to nematic transformation, which is of first order, is apparent from the density jump across the transition.

Introduction

Density studies in liquid crystals exhibiting polymesomorphism have been the subject of some discussion in the last two decades.¹⁻⁴ But detailed studies of density variation in polymesomorphic compounds are meager. The N-(p-n-alkoxybenzylidene)-p-n-butylanilines of the Schiff bases constitute a series of compounds exhibiting polymesomorphism.⁵⁻¹⁰ They transform from the crystalline solid to the isotropic liquid through different phases with each phase exhibiting a characteristic molecular arrangement. Each phase transformation involves a change in degree of order of the molecular arrangement, and the phases existing above and below the phase transformation are always stable enough in a thermodynamic sense to be observable for different ranges of temperatures by different techniques. Normally the transformations of solids to liquids are accompanied by the loss of rotational order. The liquid crystals exhibit different types of phases, i.e., nematic, smectic-A to smectic-I.¹¹ Hence, the transformations from one type to the other type of liquid crystalline phase or solid to liquid crystal phase involve positional disorder but not rotational disorder. The exhibition of different types of liquid crystalline phases is called polymesomorphism. Density studies by dilatometry in liquid crystals gained considerable importance in recent times because of its ease of measurement, low cost, and high precision, even though the filling of the sample through narrow-bore capillaries at high temperature is difficult.

Density studies give clear information regarding the nature of the phase transition and molecular ordering. Torza and Cladis¹² confirmed the smectic-A to nematic phase transition as first order in N(p-cyanobenzylidene)-p-n-octyloxyaniline (CBOOA), which was a subject of dispute. Demus et al.¹³ found a narrow range of blue phase existence (0.59 °C) between cholesteric and isotropic phases by density studies and confirmed the cholesteric-blue phase transition to be second order in cholesteryl myristate. Heat of transition studies suggest very small intermolecular force differences in mesophases as compared to solid crystalline phases: the heat of transition at the smectic-smectic or smectic-nematic or nematic-isotropic phase transformations is small when compared to solid-mesophase transformation. The pretranstional effects can be effectively inferred from such studies in the vicinity of phase transition.

Since the first report of the synthesis of low-temperature N-(p-n-alkoxybenzylidene)-p-n-alkylanilines by Kelker and Scheurle in 1969,⁵ various authors⁶⁻¹⁰ reported different types of work on these compounds, viz., synthesis, transition temperatures, characterization of the phases by different techniques such as differential scanning calorimetry, thermal microscopy, miscibility studies, and X-ray analysis. The reported differences in the observed phases, phase-transition temperatures, and order of the phase transitions prompted a detailed study in this homologous series.

The present work describes density studies with variation in temperature in N-(p-n-hexyloxybenzylidene)-p-nbutylaniline (HBBA). HBBA exhibits smectic-G, smectic-B, smectic-A, and nematic phases in between solid and isotropic phases with increasing temperature. The code letters for smectic phases of Demus et al.¹⁴ are followed. The transition temperatures observed through thermal microscopy are as follows:



N-(p-n-hexyloxybenzylidene)-p-n-butylaniline

Experimental Section

HBBA was prepared by condensation of *p*-*n*-hexyloxybenzaldehyde (0.1 mol) and *p*-*n*-butylaniline (0.1 mol) in refluxing absolute ethanol in the presence of a few drops of glacial acetic acid. After the reactants were refluxed for 4 h, the solvent was removed by distillation. The crude

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[†]Department of Chemistry.

[‡]Department of Physics.

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TABLE I: Density Values of HBBA at Different Temperatures

<i>T</i> , °C	ρ , gm/cm ³	<i>T</i> , °C	ρ , gm/cm ³	<i>T</i> , °C	ρ , gm/cm ³
88.0	0.943 37	75.5	0.95832	61.5	0.97712
87.0	0.94424	75.0	0.95901	61.0	0.97762
86.0	0.94511	74.5	0.95974	60.5	0.97811
85.0	0.94599	74.0	0.96043	60.0	0.97867
84.0	0.946 86	73.5	0.961 08	59.5	0.97929
83.5	0.94732	73.0	0.961 73	59.0	0.97993
83.0	0.94774	72.4	0.96257	58.5	0.98058
82.5	0.94820	72.0	0.96299	58.0	0.98137
82.0	0.94864	71.5	0.963 69	57.6	0.98245
81.5	0.94908	71.0	0.96438	57.5	0.98263
81.0	0.94949	70.5	0.96511	57.4	0.983 03
80.5	0.94990	70.0	0.96579	57.3	0.98364
80.0	0.95037	69.8	0.966 25	57.2	0.984.28
79.5	$0.950\ 84$	69.5	0.966 94	57.1	0.984 90
79.0	0.951 27	69.1	0.96794	57.0	0.98577
78.0	0.95270	69.0	0.96827	56.9	0.98657
77.9	0.95286	68.6	0.96962	56.8	0.98706
77.8	0.953 07	68.0	0.970 20	56.7	0.987 53
77.7	0.953 38	67.5	0.97079	56.6	0.98849
77.6	0.953 72	67.0	0.97137	56.5	0.98943
77.5	0.954 13	66.5	0.97193	56.4	0.99040
77.4	0.954 63	66.0	0.97242	56.2	0.99200
77.3	0.95515	65.0	0.97348	56.0	0.993 87
77.2	0.95551	64.5	0.973 97	55.9	0.99447
77.1	0.955 73	64.0	$0.974\ 50$	55.8	0.99506
77.0	0.955 93	63.0	0.97555	55.7	0.99566
76.5	0.956 91	62.5	0.97604	55.5	0.996 83
76.0	0.95765	62.0	0.97658	55.1	0.99876
				55.0	0 999 00

TABLE II: Comparison of Transition Temperatures of HBBA Reported

	transition temp, °C							
ref	solid-So	S SG-SB	$S_B - S_A$	S _A -N	N-I			
6	a	59.5	60.5	70.0	78			
7	34	57	58.5	69.5	77.5			
8	10	55.6	58	69	77			
9	32	57	58.5	69	76.5			
10	30	57.6	58.9	69.6	77.8			
present work	ь	56	58	69.1	77.3			

^a Room-temperature smectic phase. ^b Roomtemperature smectic phase, S_G .

HBBA was subjected to fractional distillation under reduced pressure and later recrystallized from absolute ethanol to give the pure compound.

A capillary pycnometer with a diameter of about 0.35 mm was used for density measurements. Two capillaries (40 cm) are arranged at the top of a bulb in a U shape. The amount of the sample within the dilatometer was about 4 g. The changes in the level of the liquid crystal were measured with a cathetometer to ± 0.01 mm. The absolute error in the density is ± 0.0001 g/cm³. The thermometer was calibrated in distilled boiling water. The permitted temperature control is ± 0.1 °C for a length of time ranging from 0.5 to 3 h. The maximum permitted heating or cooling rate is 4 $^{\circ}C/h$. The cooling rate in the present experiment is 2 °C/h.

Results and Discussion

Density values at different temperatures are presented in Table I. Our observed transition temperatures and other reported values are presented in Table II. Figures 1 and 2 show the variation of density with decreasing temperature where phase transitions are observed. Figure 3 illustrates the variation of thermal expansion coefficient α with temperature. The thermal expansion coefficient is calculated from the relation $\alpha = (1/V_n)(\Delta V/\Delta T)$, where V_n is the average molar volume for the temperature dif-





Figure 1. Variation of density, ρ (g/cm³), with temperature in S_g, S_B, and S_A phases in HBBA.



Figure 2. Variation of density, ρ (g/cm³), with temperature in nematic and isotropic phases in HBBA.



Figure 3. Variation of thermal expansion coefficient, α (°C⁻¹), with temperature in HBBA.

ference of ΔT and ΔV is the molar volume across the temperature of ΔT .

The compound exhibits a room-temperature smectic-G phase. Flannery and Haas⁶ reported that HBBA exhibits a room-temperature smectic-B phase. Patel⁷ reported that HBBA melts at 34 °C from solid to smectic phase and assigned it as the S_B phase. Smith et al.⁸ and Sorai et al.⁹ have not classified this phase. Leadbetter et al.¹⁰ identified this room-temperature phase as smectic-H, which is now abbreviated as smectic-G, from X-ray analysis. De Vries¹⁵

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and Meyer and McMillan¹⁶ reported that the smectic-G (formerly S_H) phase is ordered, having a tilted and welldefined three-dimensional lattice with hexagonally closepacked arrangement of molecules in the layers with translational and orientational order. The smectic-B phase was described as ordered, having orthogonal and two-dimensional hexagonally close-packed arrangement of molecules in the layers. It was also described as a translationally ordered phase with no orientational order. In the smectic-G phase the interlayer correlations exist; i.e., the adjacent layers are related by a simple translation along the long axes of the molecules with a tilted monolayer structure. In the smectic-B phase no interlayer correlations were established; however, bilayer stacking was reported. Recently X-ray studies¹⁰ indicated that the S_B to S_G transition involves a displacement of the molecules in the direction of their long axes such that adjacent planes are displaced by about 2 Å relative to each other. In addition, the S_B-S_G transition is accompanied by the disappearance of bilayer stacking and a simple translation along the long axes.

The discontinuity in density and the value of $\alpha = 96 \times$ 10^{-4} °C⁻¹ at the transition temperature T = 56 °C of the S_G-S_B transition suggests that there is an abrupt change in molecular structure. The change in density, which is large when compared to the changes in density across the other transitions, suggests a change in molecular arrangement. It is found that these observations are in good agreement with the X-ray studies. The thermal expansion coefficient and large change in density confirm the S_G-S_B phase transition as first order.

The transition at T = 58 °C is less prominent than the other transitions. This phase transition is more apparent in thermal expansion coefficient variation with temperature than the density variation with temperature. The phase transformation of S_A to S_B is explained as the increase in the number of nearest molecules while going from S_A to S_B . The random molecular distribution in the S_A phase becomes an ordered molecular distribution in the S_B phase.

The breadth of the smectic-A phase is about 11 °C. The transition at 69.1 °C, i.e., from nematic to smectic-A, is a first-order transition. The purposeful observation of this transition is to confirm the order of the transition. The value^{17,18} of $T_{\rm NA}/T_{\rm NI}$ of HBBA is about 0.98, which is far above the value of $T_{\rm NA}/T_{\rm NI} = 0.88$ predicted^{16,18} to be necessary for a first-order phase transition. In CBOOA¹² the value of $T_{\rm NA}/T_{\rm NI}$ is 0.93 for which second-order phase transition was reported by several authors¹⁸⁻²¹ by different techniques. However, volumetric study of the nematicsmectic-A transition of CBOOA confirmed¹² the first-order nature of the phase transition. Ultrasonic measurements in terephthal-4,4'-bis(butylaniline) (TBBA), $^{22} T_{NA}/T_{NI} =$ 0.92, also confirmed the first-order phase transition across the nematic to smectic-A transition. The salient features of the S_A -N transition are as follows: (1) At the nematic-smectic-A transformation the yellow opaque appearance of the nematic phase is transformed into the translucent appearance of the smectic phase. (2) The thermal expansion coefficient shows a maximum at the phase transition. The value of the thermal expansion coefficient in the S_A phase is lower than the value in the nematic phase. (3) The slope value in the smectic-A phase is smaller than the slope value in the nematic phase. It is apparent from the slopes that the change in degree of order in the smectic-A phase is small (0.8 to 0.85) in comparison to the change in degree of order in the nematic phase (0.4 to 0.8). Our ultrasonic results²³ also confirmed the first-order phase transition.

Our view is substantiated by other experiments reported earlier.^{8,24,25} Gasparoux et al.²⁴ carried out refractive index measurements in HBBA, and it is apparent from their results that the jumps in the refractive indices at the nematic to smectic-A transition suggest first-order transition. The reported heats of transition associated with this N-S_A phase transition are 0.54^8 and 0.38^{25} kcal/mol and strongly support a first-order transition. These values are relatively very high compared to the values reported for 4-n-octyl-4'-cyanobiphenyl (8CB) (0.047 kcal/mol),²⁶ 4-n-octyloxy-4'-cyanobiphenyl (80CB) (\sim 0.008 kcal/mol),²⁷ and CBOOA (0.02,²⁸ 0.013,²⁹ 0.006³⁰ kcal/mol). Leadbetter et al.²⁶ reported a first-order phase transition in 8CB by density studies while Kasting et al.³¹ reported a secondorder $N-S_A$ transition using heat capacity measurements. Armitage and Price³⁰ suggested a second-order S_A -N transition in CBOOA by volumetric studies and assigned the discontinuity at this transition observed in ref 12 to be due to small pretransitional effects. Several other authors reported second-order N-S_A phase transition in CBOOA, 8CB, and 80CB by different techniques³¹⁻³⁴ and all these compounds possess a strongly polar cyano group attached to one end of the molecule which gives rise to strong antiparallel correlation between neighboring molecules.³⁵ This in turn leads to a bilayer structure with interdigitated molecules in each bilayer in compounds exhibiting the smectic-A phase, and interestingly all these compounds possess a polar cyano group. Since HBBA is weakly polar compared with the cyano analogues, the strong antiparallel correlation may not exist and it is reported that the layer thickness in the smectic-A phase is slightly smaller than the molecular length.¹⁰ Hence, the nematic to smectic-A transition in weakly polar compounds, such as HBBA, is first order and probably is different from other polar compounds.

The isotropic–nematic phase transition is indicated by the sudden jump in density at 77.3 °C. The thermal ex-

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pansion coefficient and jump in density indicate first-order phase transformation. This transition is from the disordered molecular arrangement in isotropic liquid to the long-range molecular arrangement with orientational order in the nematic phase. The higher value of thermal expansion coefficient in the nematic phase than in the isotropic phase indicates the tendency of decreasing order with increasing temperature. The breadth of the nematic-isotropic transition is about 1 °C; the pretransitional effects are found to occur on both sides of the transition. The order parameter at the nematic-isotropic transition and the characteristics constant A from the Maier-Saupe table³⁶ are found to be 0.441 and 27.6 $\times 10^{-9}$ erg cm⁶, respectively. The order parameter value is in accordance with the theoretical predictions.

Acknowledgment. We are grateful to Prof. D. Premswarup and Prof. K. V. Jagannadha Rao for providing facilities. We are also grateful to U.G.C., New Delhi, for financial assistance.

Registry No. *N*-(*p*-Hexyloxybenzylidene)-*p*-butylaniline, 29743-11-1.

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