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A phase transition study for two homologues of the terephthalylidene bis-4-*n*-alkylanilines

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The variation of density with temperature across different phases for two homologues of the terephthalylidene bis-4-*n*-alkylaniline series (TBAA7 and TBAA9) was determined to locate the phase transitions. The temperature dependence of the thermal expansion coefficient and the estimated pressure dependence of the transition temperatures together with the reported experimental *P*–*T* data are discussed.

1. Introduction

In recent years interest has focussed on the smectic phases of liquid-crystalline compounds which possess layered structure in which the degree of order within the layer changes in a very subtle way from one smectic phase to another. The particularly interesting phase transitions are smectic C–smectic I, smectic C–smectic F and smectic I–smectic F. The terephthalylidene bis-4-*n*-alkylaniline [1, 2] homologous series provides an opportunity to study the nature of these phase transitions in a systematic way by different experimental techniques. These include X-ray [4, 5], differential scanning calorimetry (D.S.C.) [1, 3], volumetric [4, 6] and pressure studies [7–9]. We report here density studies for terephthalylidene-bis(4-*n*-heptylaniline) (TBAA7) and terephthalylidene-bis(4-*n*-nonylaniline) (TBAA9) homologues, which exhibit the phase sequences N–S_A–S_C–S_F–S_G–S_H and S_A–S_C–S_I–S_F–S_G, respectively.

2. Experimental

The density studies were carried out with a bicapillary pyknometer [10] containing a sample of approximately 3 ml. The diameter of the capillary was about 0·35 mm and the accuracy in the density measurements was $\pm 0{\cdot}1\,\mathrm{kg\,m^{-3}}$. The permitted cooling rate in the present experiment was $1°\mathrm{C\,h^{-1}}$. The pyknometer was filled with the sample in an inert atmosphere, keeping the pyknometer surroundings at a temperature of about 200–215°C.

The samples were prepared by the standard procedure and recrystallized from an absolute alcohol–benzene mixture until the observed transition temperatures were constant. The transition temperatures were determined using a polarizing microscope equipped with a heating stage. Special precautions were taken to prevent atmospheric hydrolysis, since the compounds of this homologues series are susceptible to decomposition at high temperature because of prolonged heating. The structural formula, the identified mesomorphic phases and the transition temperatures observed by thermal microscopy are presented in table 1.

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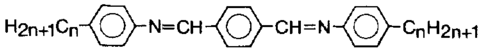
Table 1. Transition temperatures, density jumps, enthalpies and estimated dT_t/dP values across the transtions in TBAA7 and TBAA9.



	$n = 7$, TBAA7													$n = 9$, TBAA9												
	I		N		S_A		S_C		S_F		S_G		C	I		S_A		S_C		S_I		S_F		S_G		C
Transition temperature/°C		211·6		210		191·4		156·8		143		61·8			199		192·6		157·6		155·6		132·6		57·3	
$(\Delta\varrho/\varrho)$/per cent		0·48		0·57		—		0·73		—					1·00		0·13		1·00		0·11		—			
$\alpha_{max} \times 10^{-4}$		84		108		—		84		16					77		22		89		36		15			
ΔH/J mol^{-1}		2590		2730		200		4750		30					6680		550		5150		19		4			
(dT_t/dP)/K kbar^{-1}		47·9		53·5		—		33·1		—					41·5		63·1		39·1		—		—			

3. Results and discussion

The density in all the phases, except in the vicinity of the phase transitions, increases with decreasing temperature. No hysteresis was observed in the density during the heating and cooling cycles in the two compounds.

3.1. *Nematic–isotropic transition (TBAA7)*

The density jump ($\Delta\varrho/\varrho$ = 0·48 per cent) observed at the N–I transition is in good agreement with the body of data available in literature for this transition [11]. The significant density jump and the peak value of the thermal expansion coefficient confirm the first order nature of this transition. Pretransitional effects are found to occur on the nematic side of the transition.

An estimate of the pressure dependence of the transition temperature, dT_{NI}/dP (see table 1) at the nematic–isotropic transition is higher than the values obtained for other homologues for this transition [12].

3.2. *Smectic A–isotropic transition (TBAA9)*

The molar volume of TBAA9 in the isotropic liquid at T_{S_AI} + 5°C is 591·1 × $10^{-6}\,m^3\,mol^{-1}$. Assuming the additivity of molar volume in terephthalylidene-bis-4-*n*-alkylanilines the estimated methylene group contribution is 15 × $10^{-6}\,m^3\,mol^{-1}$ which is slightly lower than the contribution of the methylene unit to the molar volume of the isotropic liquid in other homologous series [13].

The smectic A–isotropic transition is accompanied by a significant density jump and a thermal expansion coefficient maxima indicating the first order nature of the S_A–I transition. The larger density jump across the transition than at the NI [11] or cholesteric–isotropic transitions [14] is due to the commencement of the smectic A phase, which has greater structural ordering than the nematic or cholesteric phases. The observed density jump is in agreement with the reported values across this transitions [6, 15]. The minimum [16] and maximum [14] values of density change ($\Delta\varrho/\varrho$) reported so far across the S_A–I transition are 0·35 and 2 per cent, respectively. The smaller value of $\Delta\varrho/\varrho$ for TBAA9, compared with TBAA10 (1·82 per cent), is due to the narrow temperature range of the S_A phase in TBAA10. Analogous results are observed [17] (for example TBAA7) at the smectic A–nematic transition for compounds exhibiting a narrow nematic phase. The material in the bulb was not homogeneous in the vicinity of the transition temperature, but rather appeared as two coexisting phases of isotropic and smectic phases separated by an interface for about 1·2°C. However, 90 per cent of the transformation is complete with in 0·2°C. Similar studies of coexistence of two phases of isotropic and smectic A are reported for TBAA8 [6] and TBAA10 [6] and for N-(4-*n*-nonyloxybenzylidene)4′-*n*-butylaniline and N-(4-*n*-octyloxybenzylidene)4′-*n*-butyl aniline [15]. The estimated value of (dT_{S_AI}/dP) from the molar volume change and heat of transition, namely 41·5 K $kbar^{-1}$ is found to be in agreement with the value of 42 K $kbar^{-1}$ estimated for TBAA8 [6] but lower than the value of 55·5 K $kbar^{-1}$ [7] for TBAA10 obtained from *P*–*T* data.

3.3. *Smectic A–nematic transition (TBAA7)*

The smectic A–nematic phase sequence is found to be present in the lower homologues of this series; however, the last compound to exhibit a smectic A–nematic transition in this series is TBAA7, with a narrow nematic range of 1·6°C. This transition is inferred with a density jump and a thermal expansion coefficient maximum. The smectic A–nematic density jump observed for TBAA7 is higher than those observed at the NI transition in this compound and the $S_A N$ transition in TBAA4 [18] (0·16 per cent) and the compounds N-(4-*n*-alkyloxy benzylidene)4′-*n*-alkylanilines [11] (the values for the nO.m compounds varied from 0·1 to 0·46 per cent). Further, the McMillan parameter $M = T_{S_A N}/T_{NI}$ ($T_{S_A N}$ = smectic A–nematic transition temperature and T_{NI} = nematic–isotropic transition temperature) is 0·997 and is far above the value of $M = 0{\cdot}88$ predicted to be necessary for a first order phase transition from the mean field theories of McMillan [19] and Kobayashi [20]. These observations indicate a first order $S_A N$ transition. The estimated pressure dependence of the $S_A N$ transition temperature from the Clausius–Clapeyron relation is in good agreement with the value estimated for TBBA (50·4 K kbar^{-1}) [18]. However, this value is greater than those found for this transition in nO.m compounds [21] from volume–enthalpy data.

3.4. *Smectic C–smectic A transition (TBAA7, TBAA9)*

The nature of the $S_C S_A$ transition in TBAA7 is found to be different from that in TBAA9. In TBAA7, as expected, a continuous change in density is observed with a change of slope at the transition, suggesting it to be second order in agreement with other results. However, in TBAA9 this transition is inferred by a small density jump with a noticeable value of α. Further, the heat of transition, ΔH, of 550 J mol^{-1} which includes the true latent heat associated with the transition besides the pretransitional heat of transition is much higher than the reported pretransitional heats of transition associated with second order transitions in liquid crystals [22]. These results suggest that the $S_C S_A$ transition is weakly first order. Our results concur with the observations from X-ray measurements for the TBAA series [3], viz. that the $S_C S_A$ transition changes smoothly from second order to first order as the alkyl chain length increases. Further, the density results for these compounds suggest a tricritical point where the phase transition changes from second order to first order in these homologous series, at or around TBAA8. However, our results differ from those obtained from D.S.C. and X-ray measurements [3] which find that the tricritical point occurs at TBAA5. The $dT_{S_C S_A}/dP$ value is found to be in agreement with the value for the compound TBAA10 [6].

3.5. *Smectic F–smectic C transition (TBAA7)*

The $S_F S_C$ transition is present in from the pentyl to the octyl homologue of this series. This transition is also found in the series of pyrimidine derivatives [23] and also in a few of the nO.m compounds [24]. The $S_F S_C$ transition is an example of an ordered to disordered tilted smectic transition. The results with a significant jump in density, and the maximum in the thermal expansion coefficient suggests a first order $S_F S_C$ transition. The density jump across this transition is higher than that across either the NI or the $S_A N$ transition in this compound. Pretransitional effects are found to occur on the higher temperature side (smectic C) of the $S_F S_C$ transition. The estimated value of ($dT_{S_F S_C}/dP$) is found to be smaller than that obtained for the higher homologue, TBAA8 [6].

3.6. *Smectic I–smectic C transition (TBAA9)*

The smectic I–smectic C phase sequence is found in TBAA9, TBAA10 and TBAA12 compounds. This phase transition is an example of another ordered tilted structure to disordered tilted structure in smectic–smectic transitions. The density jump across the $S_I S_C$ transition is found to be 1·0 per cent, complementing the higher transition enthalpy value [1]. This is in contrast to the density jumps observed for TBAA10 [6] and TBAA12 [25] even though the transition enthalpy values differ slightly in magnitude for the three compounds (see table 2). The thermal expansion coefficient, which is higher in the smectic C phase than the smectic I phase, indicates the closer molecular packing in the smectic I phase, leading to molecular rigidity. The density jump and the maxima of α confirm it as a first order transition.

Table 2. Density jumps, enthalpies and estimated dT_t/dP values across the smectic A–isotropic, smectic I–smectic C and smectic C–smectic A transitions.

	$(\Delta\varrho/\varrho)$/per cent	$\Delta H/\mathrm{J\,mol^{-1}}$	$(dT_t/dP)/\mathrm{K\,kbar^{-1}}$
Smectic A–isotropic			
TBAA8	0·9	5670	42
TBAA9	1·00	6680	41·5
TBAA10	1·82	7080	72·2 (55·5)
smectic I–smectic C			
TBAA9	1·0	6150	39·1
TBAA10	0·5	6310	21 (43·4)
TBAA12	0·29	6677	11·4 (42·5)
smectic C–smectic A			
TBAA7	—	200	—
TBAA8	—	260	—
TBAA9	0·13	550	63·1
TBAA10	0·39	1770	61 (71·4)

The estimated value of $dT_{S_IS_C}/dP$ is higher than the values obtained for the other two compounds TBAA8 and TBAA10 [6]. However, the values estimated for these three compounds from volume and enthalpy data are small compared with the values in parentheses obtained from P–T data (see table 2). Further, it should be mentioned that a comparison of the pressure dependence of the transition temperatures from the two methods, viz. volume–enthalpy data and P–T studies may not lead to realistic conclusions, due to the different experimental conditions in determining volume jumps and enthalpy values, depending on the rate of cooling or heating.

3.7. *Smectic F–smectic I transition (TBAA9)*

The D.S.C. measurements detected a small heat of transition which may be due to pretransitional effects. Thus, the $S_F S_I$ transition may be second order. However, the results for the density jump and the thermal expansion coefficient maxima suggest it to be a weak first order transition similar to that of the $S_C S_A$ transition for this compound. These results for this compound differ from those obtained for the higher homologues TBAA10 [6] and TBAA12 [25], which exhibited a second order $S_F S_I$ phase transition as inferred from the P–T data for TBAA10 [7].

3.8. *Smectic G–smectic F transition (TBAA7, TBAA9)*

Weigeleben [1] reported small enthalpy changes at the $S_G S_F$ transition for these two compounds, which is an indication of the second order nature of the transition. Our density measurements for both compounds showed no density jump but a change in slope indicating it as a second order transition in agreement with the reported enthalpy values. However, our results for TBAA7, 8 and 9 for this transition differ from the results obtained for 5O.6 [26] for which a small density jump is observed. In the higher homologues TBAA10 and TBAA12 the density measurements could not be carried due to the sample sticking to the walls of the pyknometer near the $S_G S_F$ transition in spite of repeated measurements with different cooling rates. The higher value of the thermal expansion coefficient in the smectic F phase than in the smectic G phase suggests a closer molecular packing in S_G than in S_F. Further, the change in slope at the transition in TBAA9 is larger than in TBAA7 and TBAA8. Further work is in progress to study this transition by high resolution measurements.

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