Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Density studies in terephthalylidene-bis-*p*-*n*-alkylanilines

S. Lakshminarayana[a]; C. R. Prabhu[a]; D. M. Potukuchi[a]; N. V. S. Rao[a]; V. G. K. M. Pisipati[a]; D. Saran[b]
[a] Faculty of Physical Sciences, Nagarjuna University, India [b] Department of Physics, I. I. T., Kanpur, India

To cite this Article Lakshminarayana, S. , Prabhu, C. R. , Potukuchi, D. M. , Rao, N. V. S. , Pisipati, V. G. K. M. and Saran, D.(1993) 'Density studies in terephthalylidene-bis-*p*-*n*-alkylanilines', Liquid Crystals, 15: 6, 909 — 914
To link to this Article: DOI: 10.1080/02678299308036510
URL: http://dx.doi.org/10.1080/02678299308036510

LIQUID CRYSTALS, 1993, VOL. 15, NO. 6, 909–914

Density studies in terephthalylidene-bis-*p*-*n*-alkylanilines

by S. LAKSHMINARAYANA, C. R. PRABHU, D. M. POTUKUCHI, N. V. S. RAO and V. G. K. M. PISIPATI*
Faculty of Physical Sciences, Nagarjuna University,
Nagarjuna Nagar-522 510, India

and D. SARAN
Department of Physics, I. I. T., Kanpur-208 016, India

(*Received 19 November 1992; accepted 25 April 1993*)

The temperature dependence of density in terephthalylidene-bis-*p*-*n*-alkylanilines (TBAA5 and 6) is studied to investigate the phase transitions, associated volume jumps, order of the transitions, estimated pressure dependence of transition temperatures, and pretransitional effects. The compounds exhibit nematic, smectic A, smectic C, smectic F, smectic G and smectic H phases with higher clearing temperatures. The smectic A to smectic C transition, which is a fluctuation induced first order transition in TBAA9, is found to be a second order transition in TBAA5 and 6. The results are discussed in the light of other experimental reports. The estimated pressure dependence of transition temperatures along with the reported experimental P–T data are discussed. The N–S_A transition is first order in TBAA5 and 6. The studies across other transitions are also discussed.

1. Introduction

There has been considerable interest [1–3] in the experimental investigations of terephthalylidene-bis-*p*-*n*-alkylaniline series, popularly known as the TBAA series. The TBAA homologues exhibit a variety of mesophases with wide thermal ranges, namely, nematic, smectics A, C, F, T and G. Hence the study of phase transitions between thermally stable phases in such compounds can reveal:

(1) the influence of orientational critical thermal fluctuations on the order [4] of N–S_A transitions,
(2) the validity of theoretical predictions of two dimensional melting [5] of crystals (S_C–S_F transition) and
(3) the influence of the strength of relative coupling of long range orientational order (tilt) to the short range positional order (hexagonal) where the six-fold symmetry breaks down (S_C–S_F transition)

Here, we present the results of thermal microscopy (TM), and density investigations in the compounds terephthalylidene-bis-*p*-*n*-pentylaniline (TBAA5), and terephthalylidene-bis-*p*-*n* hexylaniline (TBAA6). The pressure dependence of transition temperatures are estimated from measured volume jumps and enthalpy data. The order of the phase transitions, in the light of the reported [1–4] experimental results in the TBAA series and other liquid crystalline compounds, is discussed.

---

* Author for correspondence.

2. Experimental

The compounds TBAA5 and TBAA6 were synthesized as reported [3] earlier. Thermal microscopy was carried out using a Hertel–Reuss Super Pan-II polarizing microscope equipped with a hot stage. The density investigations were carried out using a bicapillary pyknometer as reported [3] earlier. The absolute error of the density measurement was ±0·1 kg m^{-3} and the accuracy of the temperature measurement was ±0·2°C. The transition temperatures (in °C) by various methods, and enthalpy values (ΔH in J mol^{-1} and scan rate is 5°C min^{-1}) associated with various transitions are presented below.

Compound	Method	I–N	N–S_A	S_A–S_C	S_C–S_F	S_F–S_G	S_G–S_H
TBAA6	TM/°C	215·5	207·5	186·2	152·4	141·6	(64·5)
	Density/°C	207·8	199·6	178·2	146·4	136·2	
	DSC/°C	213·6	206·6	186·6	152·7	142·6	(64·6)
	ΔH/J mol^{-1}	1440	1540	70	4720	62	910
TBAA5	TM/°C	233·3	211	178·3	148·8		
	Density/°C	235	213·6	180	149·8	140·6	
	DSC/°C	231·5	210·5	178·5	148·7	130·8	(63·7)
	ΔH/J mol^{-1}	1530	1200		3660	95	1140

( ) denotes a monotropic transition (in cooling cycle).

3. Results and discussion

The variation of density (ρ), volume expansion coefficient (α) with temperature (T) for TBAA5 is shown in figures 1 and 2, respectively. The calculated density jump $(\Delta\rho/\rho) \times 100$, volume expansion coefficient peak value (α), pressure dependence of transition temperatures (dT_C/dp) from density and DSC data for TBAA5 and TBAA6 are presented in table 1.

3.1. *Isotropic–nematic [I–N] transition*

The large density jumps ($\Delta\rho/\rho$) and the volume expansion coefficient maxima computed from the data (see table 1) for TBAA5 and TBAA6 suggest the first order nature of the I–N transition. It may be noticed that the order of density jump is comparable to that of the observed jump [6] across the I–N transition in *n*O.*m* compounds. The relatively higher jump for the compound TBAA5 with an odd numbered alkyl end-chain (i.e. an odd number of carbon atoms in the chain) reflects the odd–even effect across the I–N transitions. The results are found to be in agreement with the body of data on other compounds as predicted by Marceljas model [6]. It is also noticed that the density slope increases from the isotropic to nematic phase (see table 2) which indicates the relatively closer packing of orientationally ordered molecules in the lower temperature nematic phase.

The pretransitional effects in the fluctuation dominated non-linear region (FDNLR) from the density data are estimated using the equation (as described in our earlier investigations of the 4O.m series [6]),

$$|\Delta\rho| \propto |\Delta T|^{1-\alpha_{\rm eff}}$$

which yielded the values of $\alpha_{\rm eff}$ as 0·427 (for $T > T_{\rm NI}$ and 1°C FDNLR), 0·27 (for $T < T_{\rm NI}$ 0·8°C FDNLR) for TBAA5 and 0·553 (for $T > T_{\rm NI}$ 1·6°C FDNLR), 0·389 (for

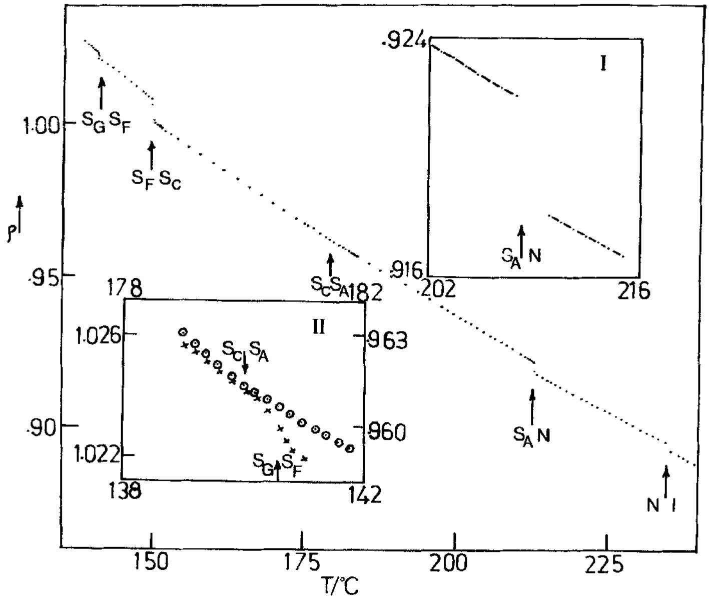

Figure 1. Density (ρ) variation with temperature (T in °C) in the compound TBAA5 (insets [I and II] indicate enlarged plots at the N–S_A, S_A—S_C and S_F–S_G transitions. In the inset II, the upper data points (⊙) correspond to the right and top axes; the lower data points (×) to the left and bottom axes.

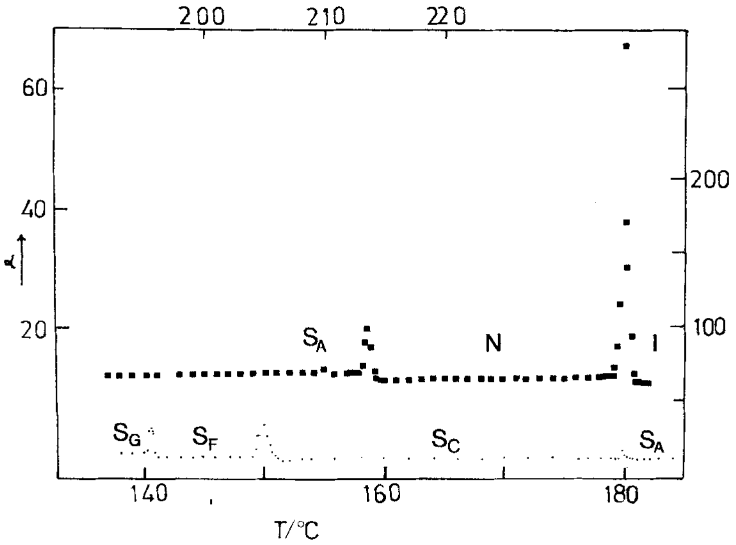

Figure 2. Volume expansion coefficient (α) with temperature (T in °C) for the compound TBAA5. The upper data points (■) correspond to the left and top axes; the lower data points (·) to the right and bottom axes.

Table 1. Density jump ($\Delta\rho/\rho \times 100$), volume expansion coefficient (α) peak value and pressure dependence of the transition temperature (dT_C/dp).

Compound	Transition	$(\Delta\rho/\rho)\times 100$	$\alpha/10^{-4}\,°\mathrm{C}^{-1}$	$dT_C/dp/\mathrm{K(kbar)}^{-1}$
TBAA5	I–N	0·356	67·12	56·05
	N–S_A	0·025	24·50	68·39
	S_A–S_C	0·021	13·47	
	S_C–S_F	1·660	242·9	37·58
	S_F–S_G	0·042	34·02	120·71
TBAA6	I–N	0·351	87·61	60·07
	N–S_A	0·08	30·81	12·73
	S_A–S_C	0·0003	12·22	
	S_C–S_F	0·505	114·59	21·33
	S_F–S_G	0·028	19·04	18·64

Table 2. Slope of the density curve ($d\rho/dt$) in the isotropic, nematic, smectic A, C, F and G phases.

Compound	$(d\rho/dt)_I$	$(d\rho/dt)_N$	$(d\rho/dt)_{S_A}$	$(d\rho/dt)_{S_C}$	$(d\rho/dt)_{S_F}$	$(d\rho/dt)_{S_G}$†
TBAA5	9·52	10·52	11·77	12·93	15·65	17·65
TBAA6	9·00	10·03	10·54	11·30	15·74	16·80

† $d\rho/dt$ in $10^{-4}\,\mathrm{g\,cc^{-1}\,°C^{-1}}$.

$T < T_{NI}$ 0·8°C FDNLR) for TBAA6 to suggest higher correlation lengths as are visualized from rapid growth of nematic like regions in the higher temperature side of the I–N transition, in spite of their longer thermal spans than on the lower temperature nematic side of it. The goodness of the fit is demonstrated through the χ^2 test. (The p values support the insignificant error in the hypothesis.)

The estimated pressure dependence of the I–N transition temperature from observed density and DSC data using the Clausius–Clapeyron equation is found to be remarkably higher than the reported values in nO.m and other compounds to indicate the steeper I–N interface in the P–T plane.

3.2. *Nematic–smectic A [N–S_A] transition*

Across the N–S_A transition, a relatively small density jump is observed. The volume expansion coefficient maxima suggests a weak first order N–S_A transition. The McMillan parameter (T_{NS_A}/T_{NI}) and the nematic thermal range values, respectively, are 0·958 and 21°C for TBAA5 and 0·983 and 7°C for TBAA6. The N–S_A transition in TBAA5 and 6 is found to be first order and is in agreement with the theoretical predictions. These results also support the hypothesis in which the McMillan parameter [4] had been used as an effective field variable in analysing the N–S_A tricritical point. It is also observed that the density jump, being higher for the odd numbered alkyl end-chain compounds across a I–N transition, is found to be of lower magnitude across a N–S_A transition. Similar trends of reverse order in density jumps are observed [6] in other homologous series of compounds exhibiting I–N and N–S_A transitions.

The pressure dependence of the N–S_A transition temperature (dT_{NS_A}/dp) estimated from density and DSC data is found to be remarkably higher in TBAA5 reflecting the effective role of higher temperature N–S_A pretranslational fluctuations. However, it is found to be lower in TBAA6.

3.3. *Smectic A–smectic C [S_A–S_C] transition*

The small $\Delta\rho/\rho$ and α values at the S_A–S_C transition indicate the second order continuous nature of this transition in agreement with the theoretical predictions. Furthermore, the density jump at the S_A–S_C transition for these compounds is found to be of the same order of magnitude in the body of data that is reported for compounds with a larger smectic C thermal range (and exhibiting a high temperature smectic A phase). It is apparent from the plots of density (i.e., ρ variation with temperature), that the increment of density is step-wise at the transition point rather than involving any smectic A–smectic C coexistence or smeared region. Although it is conceivable that fluctuations [3, 7–13] can convert an otherwise second order transition into a first order transition, there is absolutely no reason to believe that this effect is occurring here because of the wide range of the smectic A phase (33·6°C in TBAA5 and 21·4°C in TBAA6) or in the binary mixtures of compounds exhibiting large thermal ranges of the smectic A phase.

3.4. *Smectic–smectic F [S_C–S_F] transition*

The S_C–S_F transition is accompanied by large density jumps and volume expansion coefficient peak values, that support the first order nature of the transition. It may be noted that the large smectic C thermal ranges (30·2°C in TBAA5 and 31·8°C in TBAA6) are expected [14] to unlock the high temperature two-fold biaxial mode from the exponentially growing six-fold hexatic continuous symmetry, resulting into a second order transition (against the observed first order S_C–S_F transition) as in the case of two dimensional melting of crystals. Furthermore, a recent study [15] of TBAA5 discussed the S_C–S_F tricritical point where the order of the transition changes from second order to first order. The estimated pressure dependence of the S_C–S_F transition temperature of TBAA5 is found to be in agreement with the reported [3, 16, 17] smectic C to smectic F transition in TBAA7 and the smectic C to smectic I transition in TBAA9, 10 and 12, and the direct P–T data of TBAA10 by the metabolometer method. However, the value of the Clapeyron slope at the S_C–S_F transition in TBAA6 is found to be lower than S_C–S_F or S_C–S_I transitions involving a similar change of environment and symmetry, and might be due to the observed lower density jump across this transition.

3.5. *Smectic F–smectic G [S_F–S_G] transition*

The small density jump, volume expansion coefficient maxima and small ΔH values suggest the weak first order S_F–S_G transition. Across the S_F–S_G transition (which involves a change in bond orientational order, dimensionality, from two in S_F to three in S_G), the observed ΔH and $\Delta\rho/\rho$ values, (which are small but significant) are difficult to explain in the context of the higher ΔH and $\Delta\rho/\rho$ values for transitions involving no change in the structural dimensionality (namely, S_A–S_F, S_C–S_F and S_C–S_I transitions).

4. Conclusions

The N–S_A transition is found to be first order in the pentyl and hexyl homologues of terephthalylidene-bis-*p*-*n*-alkylanilines. The S_A–S_C transition is continuous, while the S_C–S_F and S_F–S_G transitions are found to be first order. The DSC data and density studies concurred in determining the order of the transitions.

Financial assistance is provided by CSIR and DST, New Delhi.

References

[1] Weigeleben, A., Richter, C., Deresch, J., and Demus, D., 1980, *Molec. Crystals liq. Crystals*, **59**, 329.

[2] Richter, L., Demus, D., and Sackmann, H., 1981, *Molec. Crystals liq. Crystals*, **71**, 269.

[3] Rao, N. V. S., Pisipati, V. G. K. M., Murthy, J. S. R., Bhaskar Rao, P., and Alapati, P. R., 1989, *Liq. Crystals*, **5**, 539, and the references therein.

[4] Potukuchi, D. M., Rao, N. V. S., and Pisipati, V. G. K. M., 1992, *Phase. Trans.*, **37**, 191, and the references therein.

[5] Brock, J. D., Birgeneau, R. J., Litster, J. D., and Aharony, A., 1989, *Physics Today*, July, p. 52.

[6] Rao, N. V. S., Potukuchi, D. M., and Pisipati, V. G. K. M., 1991, *Molec. Crystals liq. Crystals*, **196**, 71.

[7] Shashidhar, R., Ratna, B. R., Nair, G. G., Prasad, S. K., Bahr, Ch., and Heppke, G., 1988, *Phys. Rev. Lett.*, **61**, 547.

[8] Prasad, S. K., Raja, V. N., Rao, D. S. S., Nair, G. G., and Nuebert, M. E., 1990, *Phys. Rev.* A, **41**, 2479.

[9] Bahr, Ch., and Heppke, G., 1988, *Molec. Crystals liq. Crystals* B, **150**, 188; 1990, *Phys. Rev.* A, **41**, 4335.

[10] Goates, J. B., Garland, C. W., and Shashidhar, R., 1990, *Phys. Rev.* A, **41**, 3192.

[11] Liu, H. Y., Huang, C. C., Bahr, Ch., and Heppke, G., 1988, *Phys. Rev. Lett.*, **61**, 345.

[12] Alapati, P. R., Potukuchi, D. M., Rao, N. V. S., Pisipati, V. G. K. M., Paranjpe, A. S., and Rao, U. R. K., 1988, *Liq-Crystals*, **3**, 1451.

[13] Kumar, S., 1981, *Phys. Rev.* A., **23**, 3207.

[14] Goodby, J. W., and Gray, G. W., 1982, *Smectic Liquid Crystals—Textures and Structures* (Leonard Hill), p. 95.

[15] Noh, D. Y., Brock, J. D., Litster, J. D., Birgeneau, R. J., and Goodby, J. W., 1989, *Phys. Rev.* B, **40**, 4920.

[16] Alapati, P. R., Potukuchi, D. M., Rao, N. V. S., Pisipati, V. G. K. M., and Saran, D., 1987, *Molec. Crystals liq. Crystals*, **146**, 111.

[17] Rao, N. V. S., Pisipati, V. G. K. M., Alapati, P. R., and Potukuchi, D. M., 1988, *Molec. Crystals liq. Crystals* B, **162**, 119.