PHYSICAL REVIEW A VOLUME 38, NUMBER 8 OCTOBER 15, 1988

Specific-heat study of first-order smectic-A to smectic-B (hexatic) transitions in n-alkyl-4′-n-pentanoyloxy-biphenyl-4-carboxylates

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(Received 18 March 1988)

A recently synthesized and characterized homologous series of liquid-crystal compounds (n4COOBC) is shown by high-resolution ac microcalorimetry experiments (on the $n=3,6$ homologs) to most likely exhibit smectic-A to smectic-B (hexatic) (SmB_H) phase transitions exclusively. This is in partial contrast to earlier tentative assignments, based on low-resolution calorimetry, x-ray, and microscopy studies, which had crystal smectic-B (SmB_x) for $n=4-8$ and SmB_H for $n=3$ and 9. The SmA-SmB_H thermal anomalies reported here exhibit strong fluctuation contributions but are clearly first order. Experimental results are compared with the extensively characterized n-alkyl-4′-alkoxy-biphenyl-4-carboxylates (nmOBC's) and discussed in the context of Goodby's empirical molecular structure rules for the existence of the SmB_H, and in the context of a generic phase diagram (SmA, SmB_x, SmB_H) recently predicted by Aharony *et al.* The latter illustrates the physical content of our earlier suggestion that short-range hexagonal positional order is responsible for ubiquitous tricriticality of the SmA-SmB_H phase transition.

I. INTRODUCTION

A new homologous series of liquid-crystal compounds, the n-alkyl-4′-n-pentanoyloxy-biphenyl-4-carboxylates (n4COOBC, $n=1-12$), recently synthesized and characterized by Surrendranath *et al.*[1] exhibited smectic-A to smectic-B transitions for $n=3-9$. The smectic-B phases for $n=3,9$ were tentatively assigned[1] as hexatic SmB phases[2] (SmB_H) based on microscope and low-resolution x-ray studies: whereas for $n=4-8$ the crystal B phase (SmB_x) was tentatively assigned.

High-resolution ac microcalorimetry studies of the $n=3,6$ compounds reported here strongly suggest that n4COOBC compounds with $3 \leq n \leq 9$ exhibit SmA-SmB_H transitions exclusively.

The molecular structure (see Fig. 1) of the n4COOBC series is a small modification of the nmOBC series (n-alkyl-4′-alkoxy-biphenyl-4-carboxylates) synthesized and studied by Goodby[3] and rich in continuous SmA-SmB_H transitions. The modification, involving a change from alkoxy to acyloxy, is designed to weaken the lateral dipole moment of the molecule which, according to the empirical criteria of Goodby,[3] should shift behavior from hexatic toward crystal phase.

The results reported here indicate that the SmB_H phase persists in spite of the weakened lateral dipole. However the SmA-SmB_H thermal anomalies are much stronger than those in the nmOBC series which are believed to be continuous.[4] Indeed they are clearly first order but with strong fluctuation enhancement of the heat capacity. This is interesting because it is consistent with the generic phase diagram (Fig. 2) recently suggested by Aharony *et al.*,[5] which predicts that a change in the molecular interaction that moves continuous SmA-SmB_H transitions toward SmA $-$SmB_x transitions, will merely yield first order SmA-SmB_H transitions, as observed, if the change is too small. Thus the nmOBC materials, which apparently show continuous but nearly tricritical behavior,[5] would lie near and to the left of the tricritical point whereas the n4COOBC materials lie clearly (but not far) to the right of it and still on the SmA-SmB_H portion of the line (see Fig. 2). If this scenario, which assumes Goodby's empirical rules and Aharony *et al.* qualitative theoretical analysis, is correct, it means that the range of lateral dipole moment strength spanned by these two homologous series is insufficient to produce materials which are (1) far enough to the left of the tricritical point (i.e., insufficiently strong lateral dipoles) to exhibit simple critical behavior or (2) far enough to the right

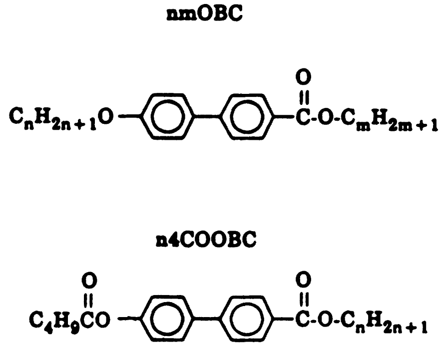

FIG. 1. Molecular structure of n4COOBC and nmOBC.

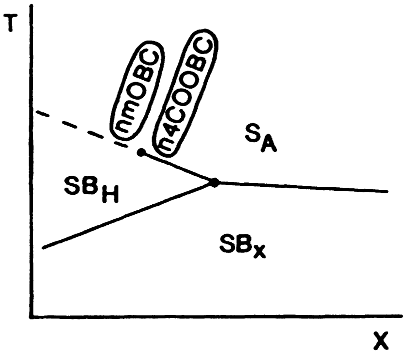

FIG. 2. The generic phase diagram discussed in paper schematically showing regions covered by *nm*OBC and *n*4COOBC.

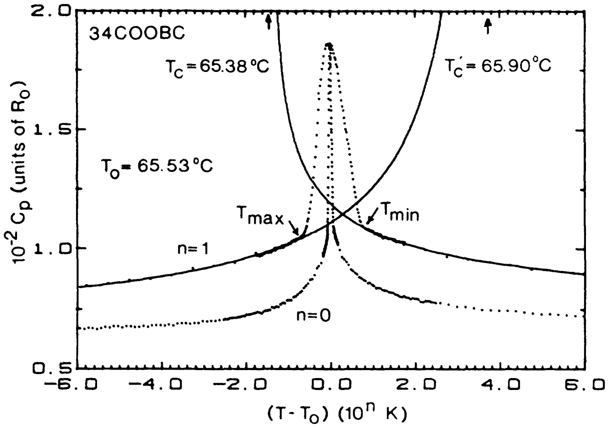

FIG. 3. Heat-capacity data for 34COOBC. An expanded plot of the data is also shown with a solid line plotted through it indicating the best fit to the data. $T_{\max}$, $T_{\min}$, T_c, and T_c' are also indicated on the graph.

(insufficiently weak lateral dipoles) to exhibit the SmB_x phase. Although the experimental evidence is not entirely convincing, and it is unlikely that lateral dipoles alone are at work, these results do suggest that continued synthetic efforts aimed at extending the physically accessible region of Fig. 2 are in order, and should be paralleled by high resolution microcalorimetry and x-ray experiments.

II. EXPERIMENTAL

The materials used in this study were purified by normal recrystallization procedures and by preparative high-pressure liquid chromatography (HPLC). Area ratio analysis of analytical HPLC data indicated that the samples were ~99.9% pure. The specific heats were measured by an ac microcalorimetry technique described elsewhere[6] and used extensively in liquid-crystal phase transition studies. The accuracy is probably not better than 20%; however, the heat-capacity resolution is approximately 0.5% for sample size in the range 50–150 mg. The temperature resolution of the data reported here is 0.005 K, being determined by the amplitude of the ac temperature oscillations.

III. RESULTS AND DISCUSSION

Experimental results are shown in Fig. 3 for 34COOBC and in Fig. 4 for 64COOBC. These figures clearly show sharp breaks in the slope of the experimental specific heat data just above and below the peak temperature (see arrows labeled $T_{\max}$ and $T_{\min}$). We attribute these breaks to narrow two-phase regions which are likely due to a small residual impurity concentration or to structural defects (perhaps induced by layer thinning or warming through the SmA-SmB_H transition[7]) coupled with the first-order character of the transition. The existence of the two-phase region casts serious doubts on the meaningfulness of the data between the arrows because the ac microcalorimetry technique is not adiabatic.

The data outside the arrows were fit to simple power laws of the form

$$C_p = At^{-\alpha} + B, \tag{1}$$

where

$$t \equiv (T - T_c)/T_c \tag{2}$$

and all parameters (A, α, T_c, B) were allowed to adjust. The results are given in Table I. The curves through the data in Fig. 3 are the best fits of the data and are quite good as the χ^2 values and the figures themselves indicate. Because the transition is first order the constraints $T_c = T_c'$, $B = B'$, $\alpha = \alpha'$, taken collectively or in any combination, are unjustified and indeed destroy the quality of the fits. The first-order character of the transition also makes the regions within ~0.2–0.5 K of the transition physically inaccessible (see Figs. 3 and 4 and $T_{\min} - T_c$ and $T_c' - T_{\max}$ in Table I) so the data span only a little more than a decade of reduced temperature. Therefore,

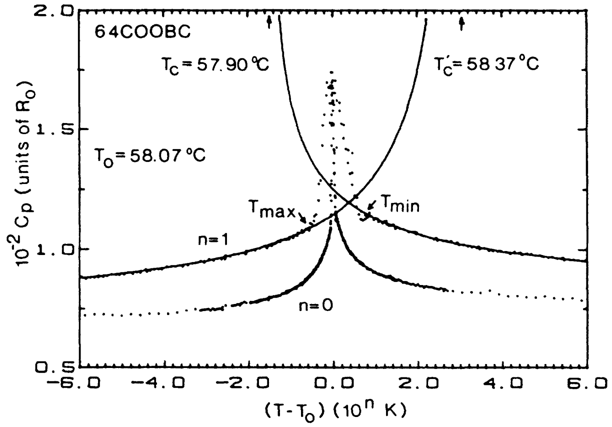

FIG. 4. Heat-capacity data for 64COOBC. An expanded plot of the data is also shown with a solid line plotted through it indicating the best fit to the data. $T_{\max}$, $T_{\min}$, T_c, and T_c' are also indicated on the graph.

TABLE I. Results of the fits for 34COOBC and 64COOBC. Primed quantities are for fits below the transition and unprimed quantities are for fits above the transition.

	$A(R_0)$ (A')	$B(R_0)$ (B')	α (α')	T_c(°C) (T_c')	$T_c - T_{\min}$ (K) $(T_{\max} - T_c')$	χ^2 $(\chi')^2$
34COOBC	2.3±0.24	60.1±0.53	0.42±0.02	65.38±0.012	0.22	0.82
	(0.13±0.025)	(62.7±0.30)	(0.87±0.04)	(65.90±0.025)	(0.45)	(1.23)
64COOBC	1.4±0.17	69.3±0.5	0.48±0.02	57.90±0.012	0.24	1.67
	(0.23±0.031)	(67.19±0.3)	(0.76±0.03)	(58.37±0.016)	(0.37)	(1.61)

the tabulated values of α and α' should be taken as only qualitatively correct, i.e., one can say they are strongly positive.

The close similarity of the heat-capacity anomaly in these two materials ($n=3,6$) and the strong fluctuation contributions make it very likely that these are SmA=SmB_H transitions and suggest that such a transition is common to this series for $3 \le n \le 9$.

Note that the asymmetry of the transitions is the reverse of that at a normal, continuous λ-like transition. It is interesting, but not understood, that a much weaker asymmetry is present in 65OBC, where the anomaly is in fact very nearly symmetric.[7,8] The anomaly reverts to the usual asymmetry (and is rapidly weakened) as PP5CC (4-propionylphenyl-trans-(4-n-pentyl)-cyclohexane carboxylate) is added to 65OBC.[7] Thus it appears that the asymmetry is in the reverse sense in materials exhibiting strong SmA-SmB_H thermal anomalies and in the usual sense in those exhibiting weak thermal anomalies. Considering that 65OBC may be near a tricritical point[4,7] it is tempting to speculate that this reversal in the sense of the anomaly is related to the crossover from first order to critical with nearly symmetric tricritical point anomalies. One must resist such a temptation because impurity renormalization almost certainly affects 65OBC/PP5CC thermal anomalies,[7] a technical problem which is under investigation.

The tricriticality versus criticality problem[4,7] that has plagued the SmA-SmB_H transition since its discovery remains an important unsolved problem in liquid-crystal physics. Our only direct contribution to that problem here is to note that the range of intermolecular interactions spanned by materials studied to date may be extremely narrow, as pointed out in the discussion of Fig. 2.

In earlier work[7] we presented what we consider to be quite compelling empirical evidence that coupling between short-range hexagonal positional order (SRHPO) and hexatic bond orientational order (BOO), is a good candidate for tricriticality in the nmOBC series. That reasoning has been extended here, augmented by Goodby's criteria,[3] and aided by the illustrative use of Aharony *et al.* phase diagram, to explain the first-order character of the n4COOBC SmA-SmB_H transitions. The resulting picture is not only empirically consistent but is also consistent with our current theoretical understanding of the SmA-SmB_H transition; e.g., as reflected in the model of Bruinsma and Nelson (BN).[8]

SRHPO and BOO are explicitly coupled in the BN free energy through an expression of the form

$$F_c = \frac{1}{2}\int_{\Lambda_0 < q < \Lambda_1} d^2q\{A(\mathbf{q}) + B(\mathbf{q})\,|\Psi_0|\cos 6[\theta(\mathbf{q})-\theta_0]\} \times |\rho(\mathbf{q})|^2 , \tag{3}$$

where

$$\Psi_0 = |\Psi_0|\,e^{i6\theta_0} \tag{4}$$

is the complex (XY-like) BOO parameter and $\rho(\mathbf{q})$ is the Fourier component of intralayer density at wave vector $\mathbf{q}$. $A(\mathbf{q})$ is the inverse density susceptibility at wave vector $\mathbf{q}$ and $B(\mathbf{q})$ measures the $\mathbf{q}$-dependent coupling between SRHPO and BOO. This form is valid when the spatial range of SRHPO is small compared with that of BOO. It ignores interlayer coupling. The domain of integration in Eq. (3) spans the diffuse peak of the in-plane x-ray structure factor $\sim \langle\, |\rho(q)|^2 \rangle$.

In the absence of a term in the free-energy coupling positional and bond orientational order there would be no diffuse sixfold symmetric x-ray signature for the SmB_H phase, contrary to experimental evidence.[2,9] Therefore, the x-ray signature of the SmB_H phase in all systems studied to date and the strong increase in the in-plane positional correlation length at the SmA-SmB_H transition[2,9] imply that Eq. (3) or a comparable form is necessary to explain known SmB_H phenomenology.

It is straightforward and illuminating to integrate out the short-range density fluctuations, $\rho(\mathbf{q})$. This leads to a renormalization of the coefficients of the SmB_H Landau model[8]

$$F = r\,|\Psi_0|^2 + u\,|\Psi_0|^4 + \cdots , \tag{5}$$

where

$$r = r_0(T - T^*) \text{ and } u > 0 . \tag{6}$$

The corrections are of the form

$$F_c = F_0 + \sum_n \alpha_n\,|\Psi_0|^{2n} . \tag{7}$$

F_0 is a term independent of Ψ_0 and

$$\alpha_n = \frac{-1}{2\pi}\int_{\Lambda_0}^{\Lambda} q\,dq \left[\frac{(2n-1)!!\,b_{(q)}^{2n}}{2^{n+1}nn!}\right] < 0 , \tag{8}$$

where

$$b(\mathbf{q}) = B(\mathbf{q})/A(\mathbf{q}) . \tag{9}$$

Note that corrections are negative at all orders in $|\Psi_0|^2$; resulting in an elevated transition temperature $(T_c = T^* - \alpha_1/r_0)$ and a reduced fourth power coefficient $(u + \alpha_2)$, where

$$\alpha_1 = -\frac{1}{8\pi}\int_{\Lambda_0}^{\Lambda_1} b^2(\mathbf{q})q\,dq \tag{10}$$

and

$$\alpha_2 = \frac{-3}{64\pi}\int_{\Lambda_0}^{\Lambda_1} b^4(\mathbf{q})q\,dq \ . \tag{11}$$

The negative contribution, α_2, that F_c makes to the fourth power coefficient [Eq. (11)] can drive an otherwise continuous transition discontinuous or, at least, toward tricriticality. Therefore, it is important to be reminded that $A(\mathbf{q})$, the denominator of $b(\mathbf{q})$ [Eqs. (8) and (9)], has a minimum at $q = q_0$ ($q = q_0$ maximizes $\langle |\rho_q|^2 \rangle$) and that $A(q_0)$ vanishes at the SmB_H-SmB_x supercooling limit (by Landau's symmetry arguments this transition must normally be discontinuous). This statement merely reflects the fact that $\langle |\rho(\mathbf{q}_0)|^2 \rangle$ has Bragg peaks in the SmB_x phase. Therefore, $b(q_0)$ will be large if the SmA-SmB_H transition is close, in the thermodynamic sense, to the SmB_H-SmB_x transition; leading to enhanced (negative) values of α_2 and the tendency toward tricriticality or, as observed here, first-order behavior. The prevalence of SmB_x phases and paucity of SmB_H phases suggests that the SmB_x (or SmE) phase is always lurking nearby in systems with SmA-SmB_H phase transitions, as does the observed strong enhancement of positional correlations.[2,9] Therefore, empirical evidence presented here and elsewhere[1,2,7,9] supports the BN model of the SmB_H phase, Aharony's phase diagram, Goodby's criteria, and our earlier discussion[7] of SmA-SmB_H phase phenomenology.

IV. CONCLUSIONS

High-resolution ac microcalorimetry experiments on the *n*4COOBC series have demonstrated that first-order SmA-SmB_H phase transitions exist. The relative strength of the thermal anomalies in the *n*4COOBC and *nm*OBC homologous series; i.e., the fact that the anomaly is first order in the materials with the weaker lateral dipole moment (*n*4COOBC) and continuous, or nearly so, in the others (*nm*OBC), gives mutual support to Goodby's criteria[3] and to our view that SRHPO drives the SmA-SmB_H transition toward tricriticality or beyond as illustrated on the generic phase diagram (Fig. 2) of Aharony *et al.*[5] and as modeled in the theory of Bruinsma and Nelson. By implication the materials studied thus far probe a very narrow range of intermolecular interactions.

The internal consistency of these ideas supports our suggestion[7] that SmA-SmB_H tricriticality (in contrast to the SmB_H phase) is ubiquitous in liquid crystals due to the pervasiveness of positional order fluctuations (SRHPO); which may in fact be prerequisite to the formation of the SmB_H phase in materials studied to date. That is, the SmB_H may be a fluctuation induced phase; arising in precisely the same way as the biaxial nematic in the Grinstein and Toner model[10] of the nematic-smectic-A-smectic-C multicritical point,[10] though without the complications of defect mediated melting. The Bruinsma-Nelson model[8] of the SmB_H is not only consistent with the picture we have given but, indeed, suggests it. We stress that we are not suggesting that all SmB_H phases need be fluctuation induced (anymore than all biaxial nematics), but only that known phenomenology strongly suggest it for materials studied thus far. The dearth of SmB_H phases generally [by comparison with SmB_X (or E) phase] suggests that the need for SRHPO may extend well beyond the two classes of compounds discussed here; apparently the SmB_x (or E) phases win the competition most often because their fluctuations, and hence close proximity, are prerequisite to SmB_H formation.

Although the above scenario is appealing it should only be used as a working hypothesis because there still exists somewhat puzzling empirical evidence; namely, the extensive heat capacity studies of Pitchford *et al.*[4] on the *nm*OBC series which yielded large positive values of α in materials where the crystal phase, SmE in this case, is known to be several tens of degrees below the SmA-SmB_H transition. X-ray experiments on those materials would tell us whether SRPHO is still playing an important role. X-ray measurements should also be performed on the 650BC/PP5CC mixtures studied previously in this laboratory;[7] which showed some evidence of being far removed from the effect of parasitic fluctuations. Mixture systems, however, are subject to the complication of Fisher renormalization of critical exponents.

The ideal approach is to make further modifications of the *nm*OBC molecular structure designed to expand the range of molecular interactions probed (see Fig. 2). At question is the existence of ideal SmA-SmB_H criticality in one extreme (small x, where x is the lateral dipole moment in Goodby's scheme) and SmA-SmB_x transitions in the other (large x). One of us (V.S.) is currently engaged in the synthesis of such materials.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Defense Advanced Research Projects Agency/Office of Naval Research (DARPA/ONR) Grant No. N00014-86-K-9772, and the National Science Foundation (NSF) Solid State Chemistry Program under Grant Nos. DMR87-03524 and DMR 85-15221.

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[1] V. Surrendranath, D. Fishel, A. de Vries, R. Mahmood, and D. L. Johnson, Mol. Cryst. Liq. Cryst. **131**, 1 (1985).

[2] R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981); R. J. Birgeneau and J. D. Litster, J. Phys. (Paris) **39**, 399 (1978).

[3] J. W. Goodby, *Liquid Crystals and Ordered Fluids,* edited by A. C. Griffin and J. F. Johnson (Plenum, New York, 1984), Vol. 4, p. 175.

[4] C. C. Huang, J. M. Viner, R. Pindak, and J. W. Goodby, Phys. Rev. Lett. **46**, 1289 (1981); T. Pitchford, G. Nounesis, S. Dumrongrattana, J. M. Viner, C. C. Huang, and J. W. Goodby, Phys. Rev. A **32**, 1938 (1985).

[5] A. Aharony, R. J. Birgeneau, J. D. Brock, and J. D. Litster, Phys. Rev. Lett. **57**, 1012 (1986).

[6] C. A. Schantz and D. L. Johnson, Phys. Rev. A **17**, 1504 (1978); D. L. Johnson, C. F. Hayes, R. J. DeHoff, and C. A. Schantz, Phys. Rev. B **18**, 4902 (1978).

[7] R. Mahmood, M. Lewis, R. Biggers, V. Surendranath, D. Johnson, and M. E. Neubert, Phys. Rev. A **33**, 519 (1986), and references therein.

[8] R. Bruinsma and D. R. Nelson, Phys. Rev. B **23**, 402 (1981).

[9] S. C. Davey, J. Budai, J. W. Goodby, R. Pindak, and D. E. Moncton, Phys. Rev. Lett. **53**, 2129 (1984).

[10] G. Grinstein and J. Toner, Phys. Rev. Lett. **51**, 238b (1983).