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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 15 Sep 2010.

To cite this article: P. E. Cladis & J. W. Goodby (1982): Pressure Study of a Hexatic B and Crystal B Phase, *Molecular Crystals and Liquid Crystals*, 72:9-10, 307-312

To link to this article: <http://dx.doi.org/10.1080/01406568208084725>

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PRESSURE STUDY OF A HEXATIC B AND CRYSTAL B PHASE

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(Submitted for Publication January 22, 1982)

ABSTRACT

Pressure temperature phase diagrams of two compounds exhibiting smectic B phases are presented. In one compound, the smectic B phase is liquid (no long range positional correlations) and is called a hexatic B phase, whereas in the other the smectic B phase is crystalline in nature. "Transition bars", which are often observed at a smectic A to crystal B transition are observed above 1.5 kbar (and not below) in the former compound and the smectic A phase appears quite piezo-resistant. In contrast, for the latter compound, the smectic A phase disappears above 1.94 kbars. These results suggest that the two smectic phases are stabilized by different forces and we suggest a model.

INTRODUCTION

Recently, x-ray measurements have demonstrated that some smectic B phases are actually crystalline in nature whereas others are more liquid-like and resemble older notions of the structure of the smectic B phase.^(1,2,3) For example, the smectic B phase of N-(4-n-butyloxybenzylidene)-4-n-octylaniline (4O.8) was found to have long-range positional correlations of the hexagonal in-plane packing of the molecules as well as as of the layer stacking. This kind of smectic B phase was called crystal B.⁽²⁾ On the other hand, in n-hexyl 4-n-pentyloxybiphenyl -4-carboxylate (65OBC) the structure of the smectic B phase was found⁽³⁾ to resemble the model proposed by Birgenau and Litster⁽⁴⁾ for a three-dimensional hexatic liquid in which there are no long-range positional correlations whatever, but there is long-range bond orientational order, i.e., the orientation of the hexagonal packing is the same within the layer and from layer to layer but not in exact register. This smectic B phase is called hexatic B.

Both 65OBC and 4O.8 also exhibit smectic A phases. A comparison of the two transitions: (smectic A-crystal B) and (smectic A- hexatic B), in thin samples (<25 microns) revealed⁽⁵⁾ that the two B phases could be distinguished by observing the transition textures in the polarizing microscope. The first order crystalline B - smectic A transition is usually marked by the appearance of transition bars. The hexatic B-smectic A transition for 65OBC was much more difficult to observe as there were no transition bars.⁽⁵⁾

Here we present the results of our measurements of the phase transitions of 4O.8 and 65OBC as a function of pressure using an optical pressure bomb⁽⁶⁾ in conjunction with a polarizing microscope.

EXPERIMENT

~100 micron thick samples, held between 1/4" thick c-cut sapphire windows, were loaded into the pressure bomb. The temperature of the bomb was controlled to less than $\pm 0.1^{\circ}\text{C}$ and the pressure determined by a manganin gauge with a precision of 10 bars.

In these samples, the crystal B-smectic A transition was clearly marked by transition bars. Conversely, however, the hexatic B to smectic A phase change was very difficult to observe at low pressures. The transition was marked by subtle changes in the radial spines of the focal conic domains producing a rippling effect across the fan banks. Surprisingly, however, above 1.5 kbar, transition bars began to appear at this transition also!

RESULTS

The resulting phase diagrams obtained by these techniques are shown in Fig. 1 for 4O.8 and Fig. 2 for 65OBC.

Table I and Table II show the slopes and zero pressure ($P=0$) transition temperature (T_c) of the phase boundaries assuming them to be straight lines.

TABLE I. Parameters of Fig. 1

4O.8

Transition	$T_c(P=0)$	$dT_c/dP (^{\circ}\text{C}/\text{kbar})$
B-N	(54.6)	20.53
B-A	48.8	24.57
A-N	62.7	17.18
N-I	77.74	23.36

TABLE II. Parameters of Fig. 2. $(AB)_1$, refers to the transition below 1.5 kbar and $(AB)_2$ above 1.5 kbar.

65OBC

Transition	$T_c(P=0)$	$dT_c/dP (^{\circ}\text{C}/\text{kbar})$
melting	63.7	29.56
E-B	63.3	25.25
$(AB)_1$	68.4	31.84
$(AB)_2$	(71.26)	27.73
A-I	85.4	27.88

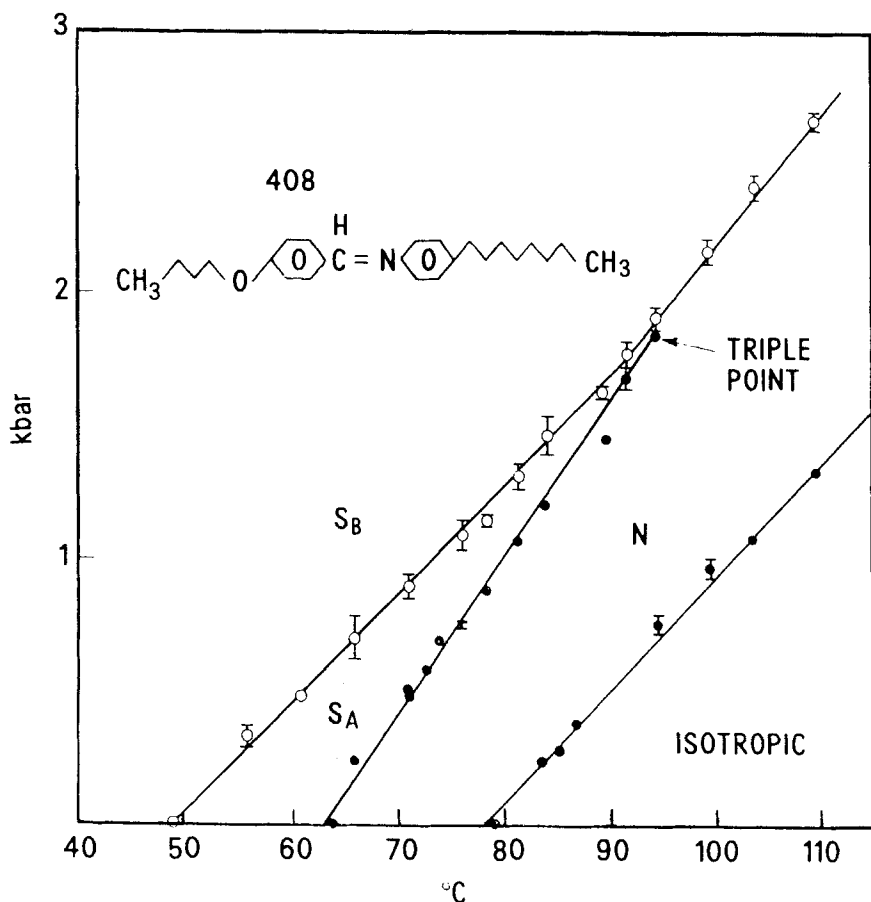


Fig. 1 The pressure-temperature phase diagram of 4O.8. The triple point is at 94°C and 1.94 kbar. N refers to the nematic phase. S_B is the crystal B phase.

Fig. 1 shows a triple point for 4O.8 at 94°C and 1.94 kbar. The length of a molecular model of the fully extended all *trans* conformation of 4O.8 is 30Å; its measured layer spacing was 28.4Å.⁽⁷⁾ Extrapolating the smectic B-nematic transition line to zero pressure, a "virtual" B-N transition occurs at 54.64°C.

In Fig. 2, 65OBC shows a monotropic smectic E phase below 2.2 kbars. Above 2.2 kbars, the sample only solidified (shown as X's on the figure).

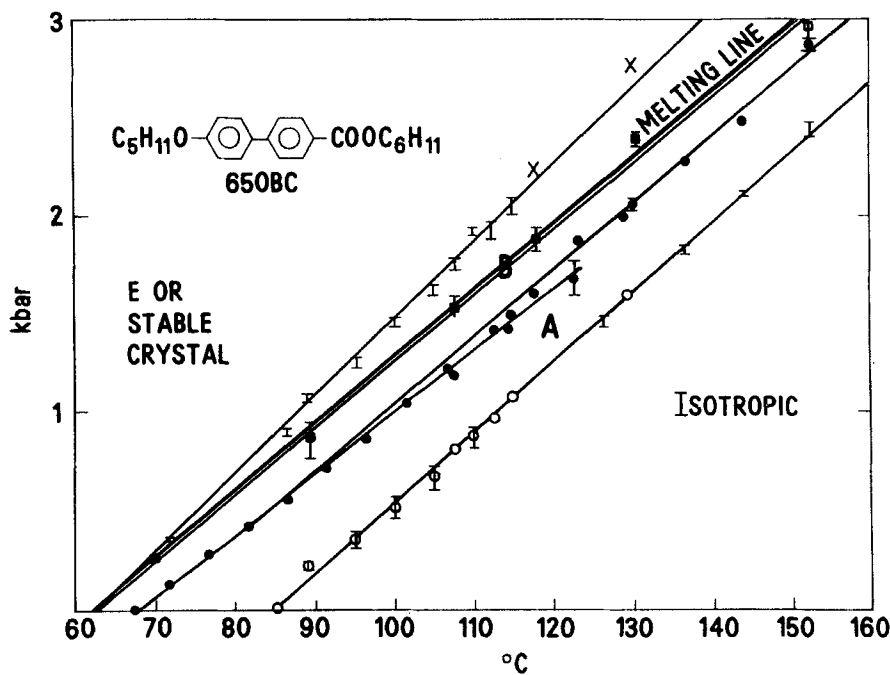


Fig. 2 Pressure-temperature phase diagram of 65OBC. Above 1.5 kbars, the A-B transition line becomes steeper and transition bars are observed.

Above 1.5 kbar, the A-B transition line changes slope and "transition bars" now mark the transition. We have referred to the transition line below 1.5 kbar as $(A-B)_1$ and the one above as $(A-B)_2$. The $(A-B)_1$ line extrapolates to a zero pressure transition temperature of 68.4°C. Since its slope is not as steep as the A-I line a B-A-I triple point could occur at around 4 kbars.

The $(A-B)_2$ transition diverges very slightly from the A- isotropic transition. In contrast to the piezo-phobic smectic A phase in 4O.8 (and many other compounds⁽⁸⁾), the smectic A phase is quite piezo-resistant.

Note that the melting line of 65OBC is also remarkably parallel to the A-I transition.

A molecular model estimates 65OBC to be 29Å long in its all *trans* conformation, but the A and B layer spacing of a disordered sample were found

to be 26.2\AA at one atmosphere. The second harmonic of this fundamental appeared in the B phase. In addition, the one atmosphere x-ray pattern of the E phase revealed lattice parameters of 24\AA and 21\AA with both E and B spacings co-existing at 58°C . Below 30°C , a solid phase was observed with characteristic spacing (and second harmonic) of 24\AA .

DISCUSSION

In 4O.8, the nematic phase broadens with increasing pressure, the A phase is eclipsed and the smectic B phase is of the crystal type. In 65OBC, there is no nematic phase, even though the molecular length is comparable to that of 4O.8. The A phase becomes more stable with pressure as the B phase becomes more crystal in nature and the E phase becomes unstable relative to a solid phase which looks like a continuation of the E-phase in the P-T plane. We look now at some molecular features which could account for these differences.

To date molecules showing piezo-resistant smectic A phases have an ester function somewhere in the molecular core structure and methylene chains extending from each end of the core. In the case of 8S5, there is an O in the C-S group,

for 65OBC and 90SI it is O in the C-O group.

In addition, one notices that these molecules display a relatively large discrepancy between the fully extended molecular length and the measured x-ray spacing. In the case of 8S5, the fully extended molecular length is of the order of 32\AA whereas the measured layer spacing is 28\AA . In the case of 65OBC, these lengths are 29\AA and 26\AA , respectively. In contrast, a molecular model of 4O.8 measured 30\AA and its layer spacing was found to be 28.4\AA . The discrepancy between these two lengths suggests that the pressure resistant smectic A phases are looser packed due possibly to the hard-core, short range repulsive interactions of the lone pairs of electrons associated with the ester and/or carbonyl oxygen atoms.

The ester function also seems to be implicated in the formation of hexatic B rather than crystal B phases also. However, for the B phase, only O in the C-O group

forms hexatic B phases whereas O in the C-S group forms crystal B phases, indicating that the combined effect of lone pairs from both oxygens is needed to stave off the collapse to a crystal phase. Applying pressure, however, could tip the balance in favor of a crystal B phase.

In all B phases, the molecules rotate rapidly ($\sim 10^{11}\text{S}^{-1}$)⁽¹⁰⁾ about their long axis in a fairly co-operative fashion. Such a co-operative rotation could lock in hexagonal ordering without introducing positional correlations. At higher pressures, positional correlations become stronger as the intermolecular distance is decreased and the hexatic B transforms to crystal B at higher pressures.

In order to put the speculation that transition bars are a signature of the first-order smectic A- crystal B transition on a firmer footing, both thermodynamic and x-ray measurements of 65OBC as a function of pressure would be useful. At one atmosphere, we know that the smectic A to hexatic B transition is second order⁽⁹⁾ and transition bars are not observed. If the observation of transition bars at this transition at higher pressures signals the onset of crystal B formation (as, in a sense, one observes along the smectic E-hexatic B line), the thermodynamic character as well as the x-ray line shapes should change as a function of pressure.

CONCLUSION

We have measured the pressure temperature phase diagram of 65OBC which has a hexatic B phase and 4O.8 which has a crystal B phase. We find the two phase diagrams to be rather different. In particular, the smectic A phase of 65OBC became more stable with increasing pressure whereas the smectic A phase of 4O.8 disappeared above 1.94 kbar.

We have proposed that this may be because the looser packing of the smectic A phase of 65OBC is stabilized by short range repulsive forces due to the lone pairs of electrons of the ester and/or carbonyl oxygen atoms. The stability of the hexatic B phase may be similar in origin. Above 1.5 kbar, pressure forces a closer packing and the hexatic B collapses to a crystal B.

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