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Kazuhiro Tsuji <sup>a</sup>, Michio Soral <sup>a</sup>, Hiroshi Suga <sup>a</sup> & Syuzō Seki <sup>a</sup>

<sup>a</sup> Faculty of Science, Osaka University Toyonaka 560, Osaka, Japan  
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A NEW PHASE IN *p-n*-HEXYLOXYBENZYLIDENE-AMINO-*p'*-CHLOROBENZENE

KAZUHIRO TSUJI, MICHIO SORAL,  
 HIROSHI SUGA, and SYUZÔ SEKI  
 Faculty of Science, Osaka University  
 Toyonaka 560, Osaka, Japan

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ABSTRACT: The heat capacity of *p-n*-hexyloxybenzylideneamino-*p'*-chlorobenzene (abbreviated as HBAC) was measured in the temperature range 15 to 385 K by an adiabatic calorimeter. A new phase was discovered between the crystal and the smectic B phase. Transition temperatures, enthalpies and entropies of the transitions are as follows:  $T_{tr}=327.70\text{ K}$ ,  $\Delta H_{tr}=10.88\text{ kJ mol}^{-1}$ , and  $\Delta S_{tr}=33.2\text{ J K}^{-1}\text{ mol}^{-1}$  for the crystal-the new phase transition and  $T_{tr}=333.90\text{ K}$ ,  $\Delta H_{tr}=12.35\text{ kJ mol}^{-1}$ , and  $\Delta S_{tr}=37.0\text{ J K}^{-1}\text{ mol}^{-1}$  for the new phase-the smectic B phase transition, respectively.

The liquid crystalline state of HBAC had been reported by Arora,<sup>2</sup> and Ferguson,<sup>1</sup> and Billard, Dubois, and Zann.<sup>2</sup> The mesogenic states and the transition temperatures are described in the linear representation after Verbit:<sup>3</sup>  
 $\text{K } 59.0 \text{ S}_B \text{ } 91.0 \text{ S}_A \text{ } 98.0 \text{ I}^1 \text{ and K } 59.3 \text{ S}_B \text{ } 89.4 \text{ S}_A \text{ } 97 \text{ I}^2$   
 Both of them reported that HBAC exhibited only two smectic phases and the crystal transformed directly to the smectic B phase. Our DSC experiments<sup>4</sup> reconfirmed the presence of the reported three phase transitions. However, the shape of the peak due to the transition from the crystal to the smectic B was broad and rather unusual. This observation motivated us to investigate the transition by use of a precise heat capacity calorimeter.

The sample was synthesized by the azeotropic dehydration reaction of *p-n*-hexyloxybenzaldehyde

and *p*-chloroaniline in benzene solution. The crystals obtained were purified by recrystallization from ethanol solution and further by the molecular distillation. Both processes were repeated twice. The calorimeter used was of the adiabatic type and the details of the experimental study will be reported elsewhere.

To make clear the existence of the newly found phase, the primary enthalpy diagram around 330 K is shown in Fig. 1, in which the results of two series of experiments are shown. Data of these two series are normalized so as to give the same value of enthalpy at 340 K. No anomalous temperature drift was observed in the first series up to point 3 (330 K). Then, the sample temperature started to show a decrease below the initial temperature in spite of the energy supply (points 4 and 5). In these temperature regions, the phase transition took place so sluggishly that a long period of time was required to reach thermal equilibration. Up to point 6 (331 K) the drift was found to be an endothermic one, whereas at point 7 (332 K) the drift turned out to be an exothermic one. From the 8th point (333 K) the drift turned out to be a normal endothermic one usually observed in the melting process.

In order to understand such an unusual behavior the sample was then well annealed at around 330 K prior to the second series of measurements. In this case special attention was paid to confirm the equilibration. The results are shown in Fig. 1 by the open circles. The solid line represents the equilibrium enthalpy curve of HBAC based on the results of the second series which verified the existence of a new phase.

These results explain also why endothermic or exothermic temperature drift was observed in the first series. In the literature,<sup>1,2</sup> it is mentioned that the crystal of HBAC directly transforms into the smectic B phase. Actually, however, the process from the crystal to the smectic B takes place in two steps.

Figure 2 shows schematically the enthalpy and the Gibbs energy curves of HBAC based on our results

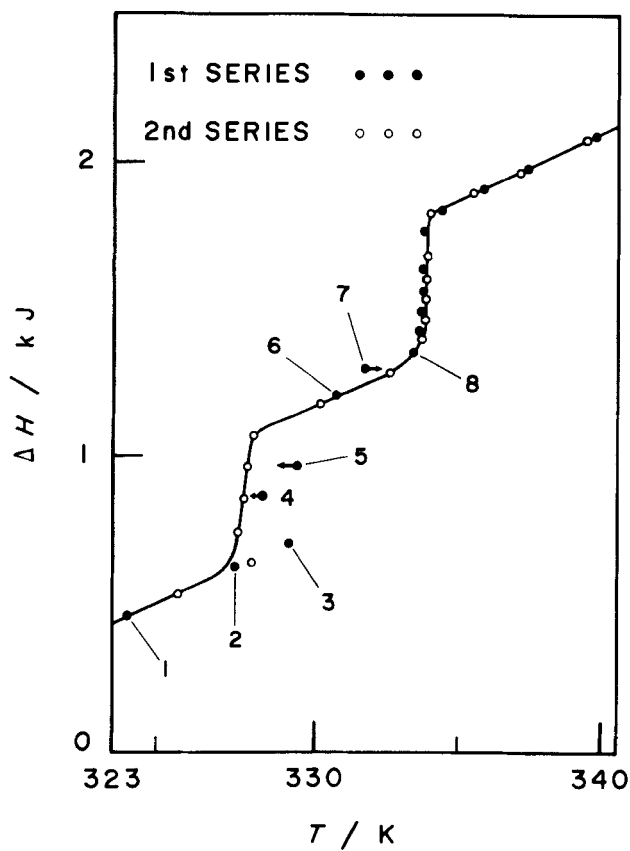


FIGURE 1. The enthalpy curves of HBAC. The weight of the container including sample is 97.27 g. The arrows indicate the direction of the spontaneous change in sample temperature.

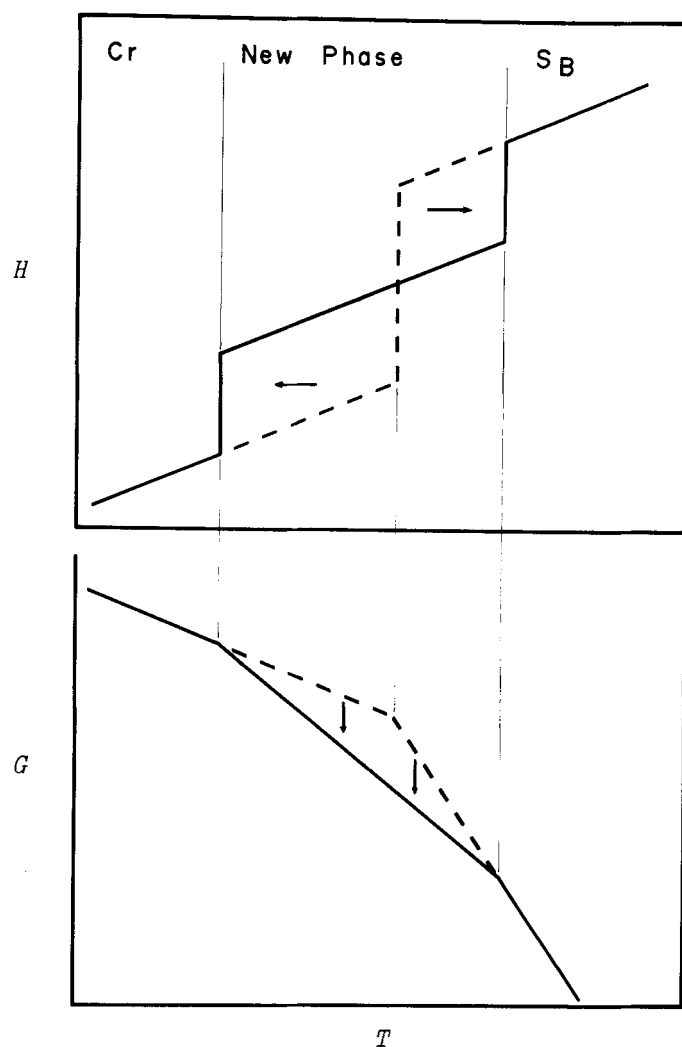


FIGURE 2. Schematic enthalpy and Gibbs energy curves of HBAC. The solid line is estimated from our heat-capacity measurements and means the equilibrium state. Dotted line is drawn based on the DSC measurements. Rapid heating process corresponds to this dotted path in a non-equilibrium state.

TABLE 1. Transition temperatures, enthalpies and entropies of transitions of HBAC.

	Cryst.-New Phase	New Phase-S <sub>B</sub>
$T_{\text{tr}} / \text{K}$	327.70	333.90
$\Delta H_{\text{tr}} / \text{kJ mol}^{-1}$	10.88	12.35
$\Delta S_{\text{tr}} / \text{J K}^{-1} \text{mol}^{-1}$	33.2	37.0

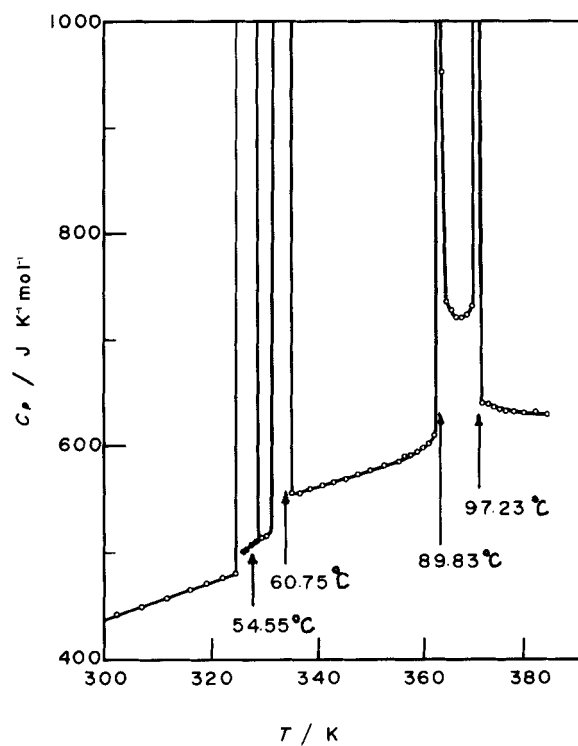


FIGURE 3. Heat capacity curves of HBAC between 300 and 385 K. Solid circles represent the heat capacity of the supercooled new phase.

and those reported elsewhere.<sup>1,2</sup> If the heating rate is rather rapid, the sample is superheated because of the slowness of the rate of the phase transition and is liable to pass along the single step path represented by the dotted line in the figure. Around 330 K the difference of the Gibbs energy between the crystal and the new phase becomes sufficiently large to change the irreversibly into the stable new phase. This change corresponds to the temperature descent in the enthalpy curve. Since the phase change is associated with the enthalpy increment, the temperature of the sample decreases under the adiabatic conditions. The same situation is possible at rather higher temperatures where the process becomes exothermic.

Although the rate of transition was very sluggish, the rate of thermal equilibration of the new phase itself was normal and the heat capacity of the new phase was measured by the standard procedure. All of the heat capacity data in phase transition regions are reproduced in Fig. 3. The transition temperatures, the enthalpies and the entropies of transitions are summarized in Table 1.

The existence of the new phase between the crystal and the smectic B is established. The state of aggregation of this new phase has not been examined yet. However, the magnitude of the transition entropy may disprove the possibility that this new phase is a crystalline state. Thus, this new phase is supposed to be either smectic H or smectic E.<sup>5</sup>

## REFERENCES

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4. We employed Du Pont 990 Thermal Analyzer and set the adjustable heating rate to be about  $0.1^{\circ}\text{C}/\text{min}$ .
5. Concerning the temperature variation of the smectic phase, see for example, A. de Vries, Pramāna, Suppl. 1, 93 (1975).