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Two Kinds of State in the Smectic-Ad Phase of Octyloxycyanobiphenyl (8OCB) and Octylcyanobiphenyl (8CB)†

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From both ac calorimetry and picosecond time-resolved fluorescence experiments, new phases are observed such that on cooling 4-octyloxy-4′-cyanobiphenyl undergoes the phase transitions, I, N, SmAd and K in order and on the other hand, on heating, gives the phase transitions, K, new K′, new SmAd′, N and I in order. The SmAd′ phase is metastable, since the heat capacity of the SmAd′ phase changes to that of the SmAd phase just below the SmAd-to-N transition and hereafter the heat capacity has a large value corresponding to the SmAd phase. A clear difference between the K and the K′ phases appears in the fluorescence experiment and it takes more than 30 min to transform from the K phase to the K′ phase, unlike the other transitions. A similar behavior of the phase diagram is obtained from ac calorimetry of octylcyanobiphenyl.

1. INTRODUCTION

We propose a phase diagram for 4-octyloxy-4′-cyanobiphenyl (8OCB) as schematically illustrated in Figure 1*a*. So far, many studies of the

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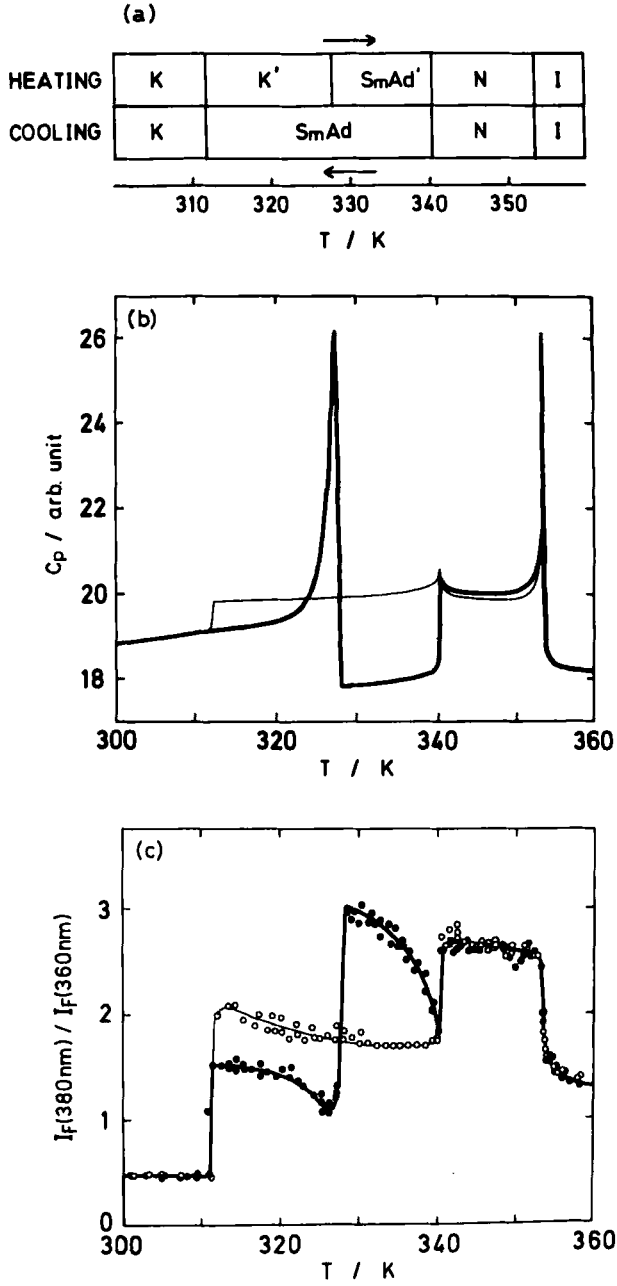

FIGURE 1 (a) The phase scheme of 8OCB on cooling and on heating. (b) The temperature dependence of the ac heat capacity drawn by a thin curve for cooling and by a thick curve for heating. (c) The temperature dependence of the fluorescence intensity ratio plotted by open circle for cooling and by closed circle for heating.

phase diagram have been carried out; however this presentation first reports the existence of the new phases SmAd′ and K′ denoted in Figure 1a for the heating run. The above facts will be confirmed from two kinds of results by ac calorimetry and picosecond time-resolved fluorescence experiments. A similar behavior of the phase diagram to that of 8OCB is obtained for 4-octyl-4′-cyanobiphenyl (8CB).

2. EXPERIMENTAL

For both of the experiments, 8OCB purchased from BDH Chemicals Ltd. was used without further purification. The heat capacity of 8CB was also measured for the material obtained from BDH Chemicals Ltd. In the ac calorimetry experiment, the liquid crystal material was held between a pair of phosphorbronze plates with a thickness of 100 μm. The thickness of the sample was kept at about 100 μm. Ac heat was applied to this sample cell through a surface of the phosphorbronze plate, on which alternately chopped light from a halogen lamp (Ushio Electric Inc., type JC-24V-150W) was radiated. According to this ac heat cycle, the temperature of the cell rose and fell alternately. The inverse of the amplitude of the ac temperature is proportional to the total heat capacity of the liquid crystal and the pair of metal plates under a proper set of experimental conditions. Details of the ac calorimetry for liquid crystals including liquid materials were described elsewhere.[1,2] The temperature of the cell for the ac heat capacity measurement of 8OCB was changed stepwise, and then the measurement of the ac temperature was carried out at *ca.* every 30 mK for both cooling and heating runs. The measurements were made in the temperature range 300–360 K. Each run took about seven hours.

For the picosecond time-resolved fluorescence experiments, the sample of 8OCB was placed in a quartz cell of $1 \times 10 \times 10$ mm and degassed by repeated freeze-pump-thaw cycles. The spectra were obtained by using a synchronously-pumped, cavity-damped dye laser and a time-correlated photon-counting system. Details of this system were mentioned elsewhere.[3] The temperature of the cell was controlled within an accuracy of ± 0.05 K. The measurements were performed when the sample reached thermal equilibrium, judged by the condition that the intensity of the fluorescence spectra no longer changed.

3. RESULTS AND DISCUSSION

In Figure 1*b*, the tempereture dependence of the ac heat capacity of 8OCB is drawn as a thin curve for the cooling run and as a thick

curve for the heating run. On cooling, the heat capacity behaves like a step in a stair at the SmAd-to-K transition. This is due to the fact that ac calorimetry can exclude the contribution of the latent heat from the total heat capacity. When cooled down from the I phase, the SmAd phase takes place in the temperature region 312–340.5 K; on the other hand, when heated up from the K phase, another smectic-Ad phase in which the heat capacity has a small value, denoted by SmAd′, appears in the temperature region 327.5–340.5 K. Furthermore, when the sample was slowly heated from the K phase to 340.24 K just below the N-to-SmAd transition temperature and successively cooled by about 1 K, the heat capacity changed to a larger value during this cooling process. If we approached much closer to the N-to-SmAd transition temperature, the heat capacity became larger and finally saturated at a maximum value. The state finally obtained from the above procedure corresponds to the SmAd phase, because the saturated value of the heat capacity is equal to that for the SmAd phase. Therefore we conclude that the SmAd′ phase may be classified as a metastable state.[1] When the sample was heated from the K phase rather quickly, as in the experiment shown in Figure 1*b*, the temperature of the transformation from the SmAd′ phase to the N phase was somewhat retarded and this effect was retained even in the N phase. Then such a heat capacity of the N phase in the heating run was obtained as drawn by the thick curve; the heat capacity was slightly larger than the heat capacity in the cooling run as seen in Figure 1*b*. It should be pointed out that, when we measured the ac heat capacity with a sample arrangement such that the liquid crystal was simply put on a metal plate at a thickness of about 100 μm, the same results as those shown in Figure 1*b* were obtained. Therefore, the former tightly closed sample cell does not affect the results for the ac heat capacity. For 8CB, a temperature hysteresis of the heat capacity was obtained similar to that in Figure 1*b*.

In the ac heat capacity measurements, when the sample was cooled to a temperature above the SmAd-to-K transition temperature and then heated up again, in this heating run, we could obtain the same result as in the cooling run as far as the I phase, as shown in Figure 2. Therefore, there exists no temperature hysteresis in this case.

No sign of the appearance of the K-to-K′ phase transition could be observed at 312 K in the ac heat capacity obtained in the heating run. However, the heat capacity increases abruptly toward the K′-to-SmAd′ transition temperature. This indicates that fluctuations become larger closer to this transition temperature. This behavior is quite unique in the heat capacity anomalies in 8OCB.

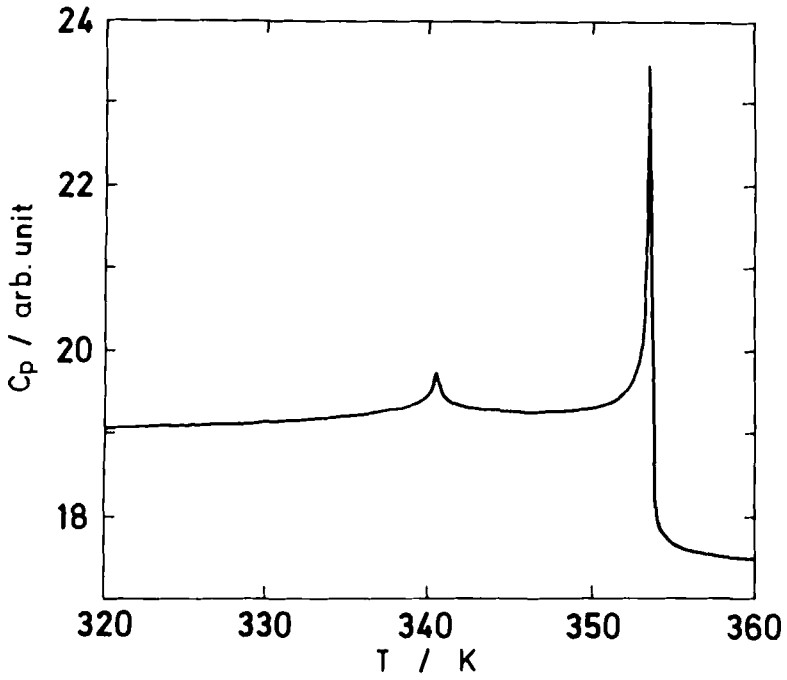

FIGURE 2 The temperature dependence of the ac heat capacity on heating in the case when 8OCB was cooled down to a temperature above the K-to-SmAd transition temperature and successively heated up.

In Figure 1*c*, the fluorescence intensity ratio $I_F(380\text{ nm})/I_F(360\text{ nm})$ of 8OCB is plotted as a function of temperature; the data denoted by open circles were taken on cooling and those by closed circles on heating. In the K phase, at about 360 nm, the fluorescence spectrum for a steady state has a maximum, and from time-resolved experiments the life time was estimated to be less than 1 ns. Therefore, the electronic state of the molecules stays in a monomer-like state. In the K phase, owing to the restraints on molecular motion, an excimer-like spectrum is not observed. On the other hand, in the other SmAd, SmAd', N, and I phases, in additon to the above fast decaying spectrum, after 200 ps another maximum appears around 380 nm; this is associated with excimer-like states. Strictly speaking, in each phase, the maximum takes place at a slightly different characteristic wavenumber and also the strength of the fluorescence intensity is different. Then, the above ratio indicates some evidence for the proportion of the occurrence of the excimer-like states. Furthermore, the differ-

ences in the intensity ratios among the phases suggest that the molecular state of 8OCB changes even in the ground state for each phase.

In agreement with the results from the ac calorimetry, as seen in Figure 1c, in the range 312–340.5 K, the SmAd phase appears on cooling, whilst on the other hand, in the range 327.5–340.5 K, the SmAd′ phase appears on heating.[4] In the latter case, the intensity ratio is larger than in the former. This fact tells us that the ground-

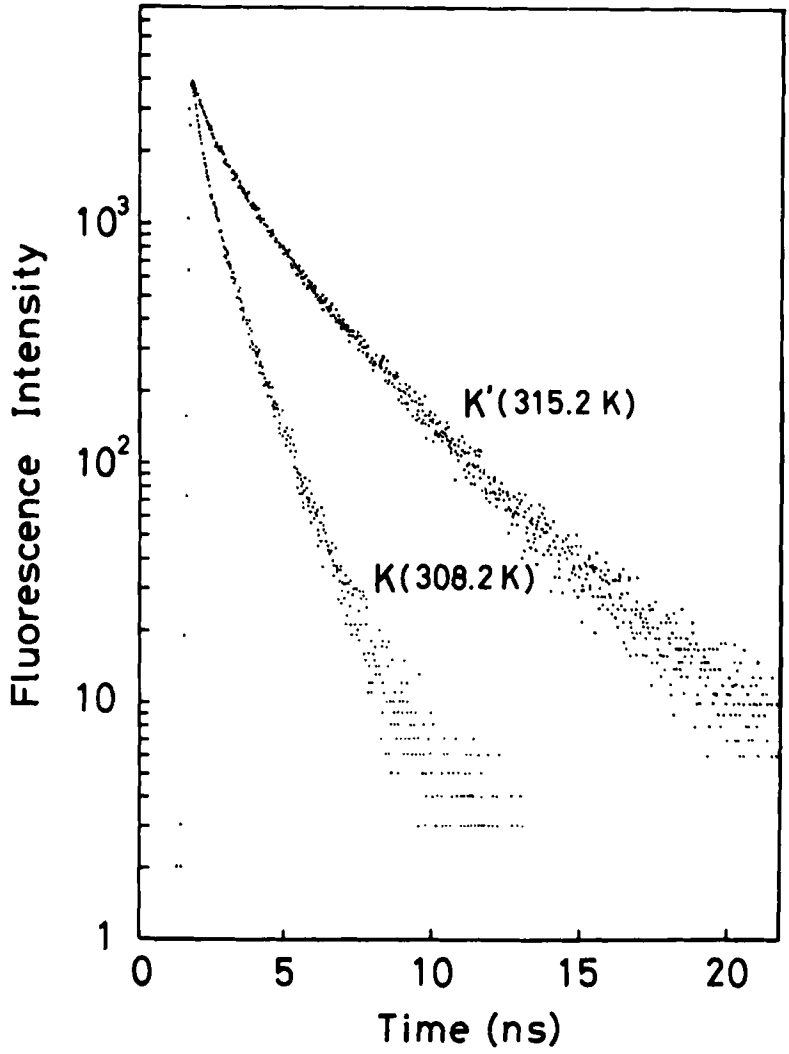

FIGURE 3 The fluorescence decay curves both in the K and K′ phases.

state molecular structure itself is different. In connection with this fact, in the fluorescence decay of both phases, the life times for the slow decaying part associated with the excimer-like fluorescence are also different at the same temperature.

It was found that 8OCB undergoes the K-to-K′ phase transition at 312 K on heating, the same temperature coincidentally at which the SmAd-to-K phase transition occurs on cooling. For the transformation from the K phase to the K′ phase, more than 30 min are required and then the anomaly at the transition smears out when the temperature scan rate increases. For this reason, the results of the present ac heat capacity experiments may not give clear evidence at this transition temperature. In Figure 3, the fluorescence decay curves both, in the K and K′ phases, are shown; in there, the tendencies of the decay are similar to each other. The decay results cannot be explained in terms of a single-exponential decay, but the characteristic time is longer for the K′ phase than for the K phase. Then, on both sides of the K-to-K′ transition temperature, a big discrepancy exists in the relaxation time.

Finally, attention should be paid to the size of the sample cell in the fluorescence experiments, i.e., $1 \times 10 \times 10$ mm. Therefore, all of the above mentioned phenomena take place independently of the sample dimensions of 8OCB.

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