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# Pressure–volume–temperature relations and phase transition for 4-*n*-nonyl-4′-cyanobiphenyl

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## Abstract

We measured the pressure–volume–temperature relationships near the nematic to isotropic, smectic A to nematic and solid to smectic A phase transition points for 4-*n*-nonyl-4′-cyanobiphenyl (9CB). The values of the exponent of the inverse power potential (gamma) for each transition, which was defined as $-\mathrm{d}(\ln T_{\mathrm{tr}})/\mathrm{d}(\ln V_{\mathrm{tr}})$, were observed as 4.26, 2.67 and 2.66 for the isotropic to nematic, nematic to smectic A, and smectic A to solid transition respectively. The gamma value for the nematic to isotropic transition of 9CB was smaller than that of the *n*-octyl analogue 8CB or other, smaller, carbon groups of the cyanobiphenyl homologous series. The gamma value for the smectic A to nematic or the smectic to solid transition was smaller than that for the nematic to isotropic transition. This difference is interpreted by postulating that the mechanism of phase transition of smectic A to solid or smectic to nematic involves displacement along the long molecular axis, whereas the nematic to isotropic transition occurs with rotation of the molecule on its axis perpendicular to the direction of the long molecular axis.

## INTRODUCTION

Liquid crystal molecules have a long rod-like structure which consists of a core portion such as a benzene ring and a flexible part such as an alkyl chain. In the original nematic–isotropic transition theory, the main classes were the hard rod theory of Onsager [1], the order–disorder theory of Pople and Karasz [2] and the induced dipole theory of Maier and Saupe [3]. In the theories intermolecular interaction was defined as follows. In the hard rod theory the interaction was an effect of the excluded volume between the molecules, which are long, slender and hard rods; in the order–disorder theory it was a repulsive force which introduced a degree of orientational order into the term of repulsive force in the Lennard-Jones

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potential; and in the induced dipole theory it was the attractive force due to dispersion.

One of the parameters representing the intermolecular interaction ($U$) in the transition is the value of $\gamma$, which relates $U$ to the transition molar volume ($V_{tr}$) as follows

$$U_{tr} \propto T_{tr} \propto V_{tr}^{-n} \tag{1}$$

$$\gamma \equiv -\frac{d(\log T_{tr})}{d(\log V_{tr})} \tag{2}$$

where $T_{tr}$ is the transition temperature. The values of $\gamma$ have been calculated as 4, 2 and $\infty$ from the order–disorder theory, the induced dipole theory and the hard rod theory, respectively. These values of $\gamma$ were constants independent of the structure of a molecule in these theories. If the intermolecular potential is mainly attractive, $\gamma$ is equal to 2. If it is mainly repulsive, the value is larger than 4.

Earlier, we calculated the values of $\gamma$ from the measurements of pressure–volume–temperature ($P$–$V$–$T$) relationships for the homologous series of alkylcyanobiphenyls (RCB), alkylcyanophenylcyclohexanes (RPCH) and so on [4–8]. As a result we found that the values of $\gamma$ for these samples were not constant and that they were related to structure, in particular to the flexibility of the molecule. In the homologous series, the value of $\gamma$ became smaller as the length of the alkyl chain increased. On the other hand, regarding the core of substances having the same alkyl chains, the value of $\gamma$ for a substance including a cyclohexane ring was smaller than that for one including a benzene ring. We knew that a cyclohexane ring was more flexible than a benzene ring, and thus we concluded that the value of $\gamma$ became smaller as the molecule became more flexible. We estimated that the intermolecular potential was depressed in line with the effect of molecular shrinking due to such flexibility, so that the value of $\gamma$ became smaller.

In this paper, we report the $P$–$V$–$T$ relationships and the value of $\gamma$ for the nematic to smectic phase transition for 4-*n*-decyl-4′-cyanobiphenyl (9CB), which has two phenyl rings and a flexible alkyl chain. Furthermore, 9CB exhibits a smectic A phase, and we therefore estimated the values of $\gamma$ for the transitions from nematic to smectic A and from smectic A to solid. We then compared those values in relation to the phase transition mechanism.

## EXPERIMENTAL

The sample of 9CB was obtained from Merck Japan Co. Ltd. and was used without further purification.

The density of 9CB was measured with an oscillating type densimeter in the temperature range 316.15–332.15 K. Measurements were made every 0.1 K within the range 320.65–322.65 K, and otherwise every 0.3 K, after keeping the sample at each temperature for 1 h. The precision of the temperature and the density was better than ±0.0025 K and ±0.0001 g $ml^{-1}$, respectively.

The pressure–volume–temperature relationship was measured every 0.3 K within the range 322.45–329.65 K with an apparatus consisting of a cylinder and a piston. The volume of the cylinder, as measured by a volumetric method, was 9.987 $cm^3$. The cylinder was placed within a thermostated box in which the temperature was controlled to better than ±0.002 K by PID control, and compression was applied by an oil pressurizing pump. The pressure was calculated from the output voltage of a bridge with a manganin resistor within the cylinder, and the molar volume was measured from the output voltage of a differential transformer attached alongside the cylinder. The precision of the pressure and of the change of molar volume was better than ±0.03 MPa and ±0.002%, respectively.

Data acquisition of measurements of the density and the pressure–volume–temperature relationship was performed automatically by means of a microcomputer.

## RESULTS AND DISCUSSION

Fig. 1 shows the density vs. temperature relationship for 9CB. The density decreased with increasing temperature, and the transition from the nematic to the isotropic phase occurred with a discontinuity of the density. This transition was observed in a very narrow temperature range (ca. 0.1 K) and the sample was thus found to be very pure. The transition temperature

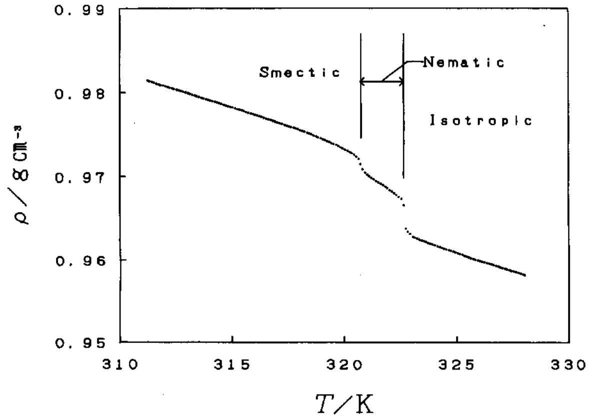

Fig. 1. Density vs. temperature for 4-*n*-nonyl-4′-cyanobiphenyl at atmospheric pressure.

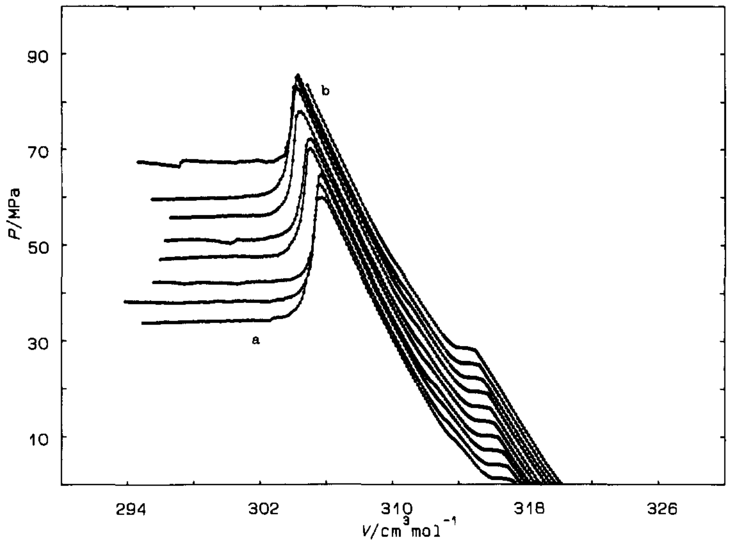

Fig. 2. Pressure–volume isotherms for 4-*n*-nonyl-4′-cyanobiphenyl from 322.45 K (a) to 329.65 K (b) for each 1 K.

from nematic to isotropic was found to be 321.30 ± 0.05 K. The change of density in this transition was 0.16%, which was similar to that for other members of the CB series. We also found a discontinuity of density for the transition from the nematic phase to the smectic A phase. The phase transition temperature from nematic to smectic A was 319.3 ± 0.05 K. We assumed that this phenomenon was near to a second order phase transition because of the smaller volume change than for the nematic–isotropic phase transition. We could not detect solidification aobve 316 K with a cooling rate of 1 K $h^{-1}$ for supercooling.

We show the pressure–volume isotherms for 9CB in Fig. 2. With compression of the isotropic phase at a certain temperature, a pressure plateau indicating a region of coexistence of the two phases appeared and there was a subsequent change to nematic. The transition points were determined on the intersection of the lines of the pressure plateau and the isotropic $P$–$V$ line. With increased compression, the transition to the smectic A phase occurred with a small region of level pressure. We found that, near the transition point from nematic to smectic A, the compressibility before and after the transition point was different. With further compression, the pressure reached a maximum value, then began to decrease and levelled out to a plateau. This plateau corresponded to the region of solid–smectic A coexistence. We found that the transition from smectic A to solid occurred via the metastable state. We regarded the transition points as the intersection of the lines of the pressure plateau and the smectic A $P$–$V$ curve.

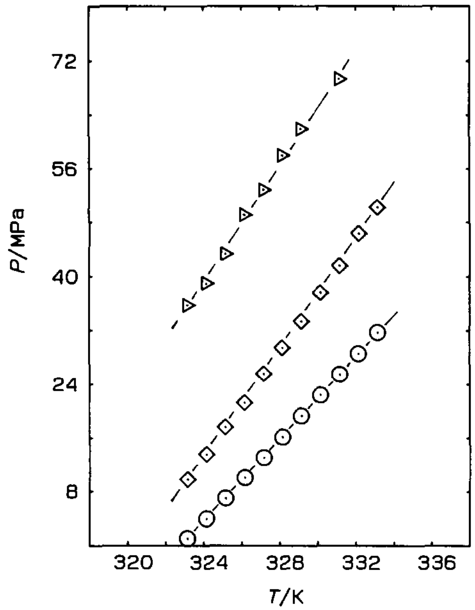

Fig. 3. Relationship between temperature and pressure at nematic–isotropic (○), smectic A–nematic (□) and solid–smectic A (△) transition points for 4-*n*-nonyl-4′-cyanobiphenyl.

The molar volumes at the three phase transition points decreased with increasing temperature. At the nematic to isotropic transition point, volume discontinuities decreased with increasing temperature.

Figure 3 shows the phase diagram of 9CB. All phase lines showed linear relationships and the slopes were 2.24, 2.60 and 2.95 MPa $K^{-1}$ for the nematic–isotropic, smectic A–nematic and solid–smectic A phase transitions, respectively. These slopes increased in the sequence nematic–isotropic, smectic A–nematic, and solid–smectic A. The transition temperatures at atmospheric pressure were calculated to be 321.42, 319.21 and 318.71 K for the nematic–isotropic, smectic A–nematic and solid–smectic A phase transition, respectively. These values agreed with the values from density measurement.

Figure 4 shows the log–log plots of the molar volume ($V_{tr}$) and temperature ($T_{tr}$) for the nematic–isotropic transition points. These plots showed good linear relationship and the slope $\gamma_{N-I}$ was calculated as 4.26. The log–log plots of $V_{tr}$ vs. $T_{tr}$ for the smectic A–nematic and solid–smectic A transitions also showed linear relationships. The values of $\gamma_{N-Sm}$ and $\gamma_{Sm-Sol}$ calculated from these slopes were 2.67 and 2.66, respectively.

The value of $\gamma_{N-I}$ was almost equal to that for the *n*-octyl analogue 8CB. The value is nearly equal to the power of the repulsive part of the Lennard-Jones potential. On the other hand, $\gamma_{N-Sm}$ is smaller than $\gamma_{N-I}$. The value coincides with the separation dependence of the Van der Waals attractive force. The value $\gamma_{Sm-Sol}$ corresponds with that of 4 calculated

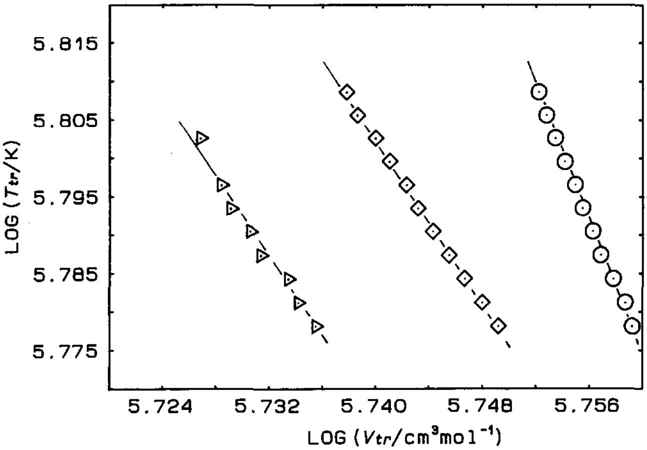

Fig. 4. Log–log plots of molar volume and temperature at the transition points from isotropic to nematic (○), nematic to smectic (□) and smectic to solid (△) for 4-*n*-nonyl-4′-cyanobiphenyl.

from the melting theory [9] by Lennard-Jones and Devonshire. The result for $\gamma_{N-Sm}$ is larger than the $\gamma_{N-Sm}$ values observed by Johnson and Collings for heptyloxyazoxybenzene (7OAB) and octyloxycyanobiphenyl (8OCB) at the smectic A to nematic transition point [10]. The values were 1.46 and 1.20 for 7OAB and 8OCB, respectively; these results indicate that 7OAB and 8OAB are more flexible molecules than the 9CB molecule.

The differences between $\gamma_{N-I}$ and $\gamma_{N-Sm}$ may relate to the modes of phase transition. Since the molecules in the nematic to isotropic phase transition undergo a rotation around the long molecular axis, the flexibility of the long molecular axis in the molecule has an effect on the phase transition. On the other hand, in the case of the nematic to smectic phase transition, the molecules slide toward an axis of orientation of the molecules. Therefore the flexibility in a direction perpendicular to the molecular axis has an influence on the nematic to smectic phase transition. The solid to smectic phase transition occurs in the same manner as the nematic to smectic phase transition. Therefore the value of $\gamma$ for the nematic to smectic transition is nearly identical with that for smectic to solid.

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