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Pressure-Volume-Temperature Relations and Isotropic-nematic Phase Transitions for 4-(*trans*-4-Pentylcyclohexyl)benzonitrile

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Pressure-volume isotherms of 4-(*trans*-4-pentylcyclohexyl)benzonitrile were directly measured by means of piston-cylinder method at various temperatures. From the relation of the molar volume and the transition temperature which was determined by its clearing point, the parameter $\partial \ln T_c / \partial \ln V_c$, was found to assume a value of -5.24, which should be closely related with the intermolecular potential energy. The value of this parameter increased correlatively with the alkyl chain length in the homologous series of 4-(*trans*-4-alkylcyclohexyl)benzonitriles.

The liquid crystal molecules generally have a long and thin rod-like structure. The straight-chain hydrocarbon molecule also has a similar linear structure, however, it never shows liquid crystalline behavior. The characteristic difference between them lies in the flexibility of the linear structure. The flexibility of the straight-chain hydrocarbon molecule is dustributed uniformly over an entire molecule, while an ordinary liquid crystal molecule is roughly regarded to consist of two characteristic parts. One is a flexible part such as chain structure and the other is a rigid core part such as aromatic ring group. Such morphological classification of liquid crystal molecule is well known in the practical application field, whereas it has still been unsuccessful in phase transition theory to take the characteristic chemical structure into account.

Several phase transition theories have hitherto been proposed to explicate the nematic-isotropic phase transition. The intermolecular potential function assumed in those theories is roughly divided into the contributions of two parts, one is the orientation dependent part and the other is the volume dependent part. The volume dependent part determines the type of interaction which is dominant in the nematic-isotropic phase transition. From the intermolecular potential function thus derived, the clearing temperature is expressed as a function of the volume at clearing point:

$$T_c \propto V_c^{-\gamma}. \tag{1}$$

The exponent γ in Eq. 1 differs by the type of interaction assumed in the theory. Equation 1 may be transformed into the following expression:

$$\gamma = -\frac{\partial \ln T_c}{\partial \ln V_c}. \tag{2}$$

In Maier-Saupe theory,[1] dispersion force is assumed as the intermolecular force, in which the value γ is calculated to be 2, while in Pople-Karasz theory,[2] γ become 4 where they assumed repulsive force. It is clear in Eq. 2 that the value γ can be determined from a series of *P-V-T* measurements for liquid crystalline substances from which the actual interaction operating among the liquid crystal molecules may be analyzed.

In this study, *P-V-T* relations were measured for 4-(*trans*-4-pentylcyclohexyl)benzonitrile, hereafter refered as 5PCH. The volume dependent part of the intermolecular potential energy was also discussed.

Experimental

5PCH of 99% purity (Merck and Co., Inc.) was used as obtained without further purification. Density of this sample was measured by Lipkin-Devison type pycnometer. *P-V-T* relations were measured by using a piston-cylinder apparatus shown in Fig. 1. Variation of the pressure was detected by a manganin pressure gauge mounted in the cylinder. The degree of compression of the sample was estimated by a differential transformer attached to one end of a piston. Both the analog output of the differential transformer and that of the manganin pressure gage were acquisited to a microcomputer after the proper amplification and digital conversion. The microcomputer also served to control an oil pressurizing pump to compress the sample at a predetermined sequence by monitoring these signals. The volume of the cylinder was about 10 cm^3. The details of the present computer-controlled apparatus for *P-V-T* measurement will appear elsewhere.[3] The error of measurements of pressures and volumes were with ±0.03 MPa and ±0.002%, respectively. The piston-cylinder apparatus was kept in air bath which was thermocontrolled within ±0.01 K.

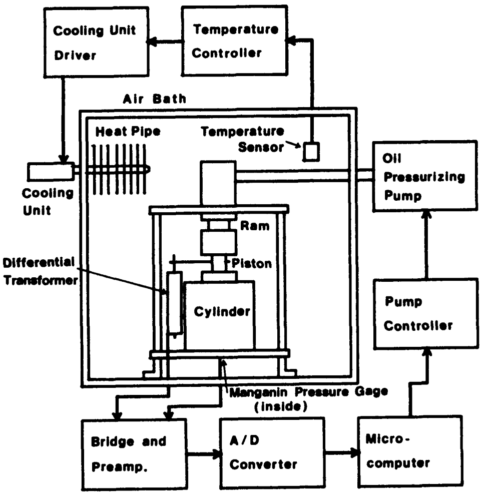


Fig. 1. The schematic diagram for the *P-V-T* measurement apparatus.

Results and Discussion

In Fig. 2, the density of 5PCH at atmospheric pressure is plotted as a function of temperature. The clearing temperature is read to be 327.59±0.08 K from the

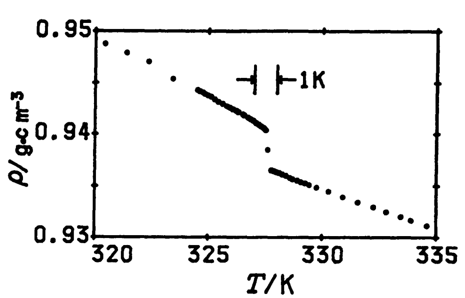


Fig. 2. The density *vs.* temperature for 5PCH.

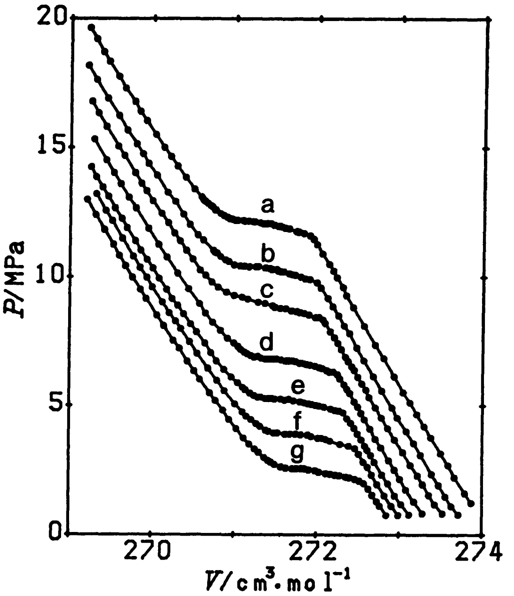


Fig. 3. The pressure-volume isotherms for 5PCH near the clearing transition. a: 333.19, b: 332.24, c: 331.40, d: 330.49, e: 329.79, f: 329.20, g: 328.60 K.

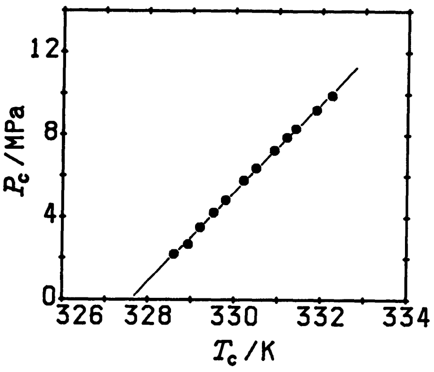


Fig. 4. The transition pressure *vs.* temperature for 5PCH.

figure. Transition occurs sharply within the temperature range of about 0.2 K. Figure 3 shows the series of pressure-volume isotherms for 5PCH in the vicinity of a clearing point at various temperatures. The plots are approximately linear in the isotropic side, and slightly curved in the nematic side. Drastic volume change at the transition is clearly observed. The molar volume at a clearing point decreased as temperature increased. From these isotherms, the pressure at a clearing point is obtained and plotted in Fig. 4 as a function of temperature. The plots show almost linear relation with a slope of 2.09±0.02 MPa/K. The clearing temperature at atmospheric pressure is estimated by extrapolation to be 327.55±0.03 K. This value agrees well with that obtained by the density measurement shown in Fig. 2. Figure 5 shows a full logarithmic plot of the temperature and the molar volume relation at a clearing point. The slope of this curve, $\partial \ln T_c / \partial \ln V_c$, is estimated to be -5.24 ± 0.09.

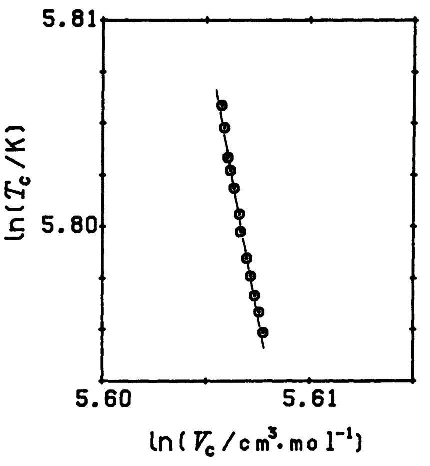


Fig. 5. The transition temperature *vs.* molar volume for 5PCH.

According to Maier-Saupe theory,[1] the intermolecular potential energy is expressed as follows:

$$U = -\frac{A}{2V^2}\cdot S\cdot(3\cos^2\theta-1), \qquad (3)$$

where V is the molar volume, A is the constant which is independent of pressure, volume and temperature, θ is the angle the long axis of molecule forms with the uniaxial direction of medium, and S is an order parameter. At the transition point, following well-known equation is obtained:

$$T_c = \frac{A}{4.541\,kV_c^2}. \qquad (4)$$

Equation 4 indicates that the transition temperature is inversely proportional to the square of molar volume at the transition point. The value of γ as calculated from Eqs. 2 and 4 is found to be 2. This value does not agree with our experimentally observed value.

Pople and Karasz have also proposed a theory[2] which is an extension of Lennard-Jones and Devonshire model of melting. They assumed the anisotropic intermolecular potential energy to be expressed by

$$W = W_0\left(\frac{V_0}{V}\right)^4, \qquad (5)$$

where W_0 and V_0 are constants. The transition temperature is expressed in their theory as follows:

$$T_c = \frac{zW(2S-1)}{2k\ln\frac{S}{1-S}}, \qquad (6)$$

where z is the coordination number of a given molecule and S is the order parameter at the transition. The substitution of Eq. 5 in Eq. 6 leads to the relation in

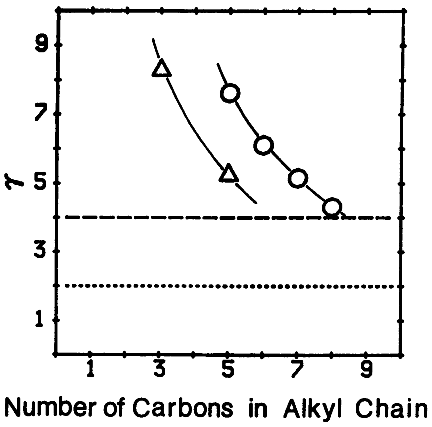


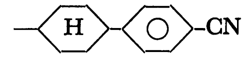
Fig. 6. The value γ *vs.* carbon number in alkyl chain. —○—: Data for CB series, —△—: data for PCH series, ······: Maier-Saupe model, ------: Pople-Karasz model.

which the transition temperature is inversely proportional to the fourth power of the molar volume at the transition point, which means that γ assumes the value 4. This value is much closer to ours than that calculated after Maier-Saupe theory. Hence, our observation seems to indicate that the repulsive interaction should have a dominant contribution to the nematic-isotropic transition. Some liquid crystals, however, show rather big γ value,[5,6] which do not agree with Pople-Karasz theory.

It was also found in the recent study[5] that the value γ decreases with increasing alkyl chain length for homologous series of 4′-alkyl-4-cyanobiphenyls (abbreviated as CB series). The value γ is plotted against the carbon number of alkyl chain for CB series and PCH series in Fig. 6,[4–6] and compared to above-mentioned values theoretically predicted. The dotted and the dashed horizontal lines each represents the expected relation by the Maier-Saupe and the Pople-Karasz theories, respectively. These lines show constant γ values which are independent of carbon number. The value γ for PCH series varies in a similar manner as that for CB series.

There have been several attempts in the theories to take into account the molecular shape factor to interpret the properties of the nematic-isotropic phase transition. The typical one may be represented by scaled particle theory.[7] Savithramma and Madhusudana have extended the Andrews method of deriving thermodynamic properties of an assembled particles, and compared their results with those obtained on the basis of scaled particle theory.[8] The common feature of both theories is the assumption that molecules are good regarded as rigid spherocylinders. Their calculations showed that the value γ assumes the value close to 4 for a spherocylinders having particular length to breadth ratio. This value seems to be in reasonably good agreement with the experimental data for 4,4′-azoxydianisole.[9] Their results, however, contrary to ours show that the value γ becomes exceedingly greater as the length to breadth ratio of molecule increases. Our experimental data indicates that the value γ becomes smaller as the molecule lengthens. They assumed the shape of molecule to be the spherocylinder. This is the obvious reason why their theoretical calculation showed inverse tendency against the experimental data, because it will not be favorable to assume rigid rod for the actual liquid crystal molecule.

As mentioned earlier, a liquid crystal molecule generally considered to be made up of a core part and a chain part. In homologous series of a compound PCH we have chosen, the core part of molecule is the same: For example, each molecule has a cyclohexylbenzonitrile core shown below. For the core parts are the same, the



variation of γ in a homologous series may be attributed to the difference in the alkyl chain parts. An alkyl chain has a conformational freedom, because it is made of linear framework of C–C single bonds. As the length of a chain increases, the conformational freedom increases. Therefore, decrease of γ in Fig. 6 may be caused by the increased flexibility of alkyl chain part. It should be noted next that the difference in the values γ between 5CB and 5PCH may be rendered to the structural difference of their core parts. The core part of CB series is made of a biphenyl structure. The core part of PCH series includes cyclohexane ring. The conformational freedom for the core of CB series should be lower than that of PCH. The value γ for 5CB is 7.62,[5] while that for 5PCH is 5.24, the difference is comparable to that between 5CB and 6CB, and is attributed to the change of flexibility between benzene ring and cyclohexane ring. Perrin and Bergès reported lately that the flexibility of the core is comparable to that of the alkyl chain.[10]

Though the evaluation of the effect of flexibility on liquid crystal formation still needs further analysis, it is clear that the value γ is closely related to the conformational character of liquid crystal molecule: Especially, the flexibility of alkyl chain part and that of core part where it plays an important role in the nematic-isotropic phase transition.

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