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Pressure-Volume-Ternperature Relation of Liquid Crystals and the Effect of Molecular Rigidity on the Nematic-Isotropic Phase Transition

T. Shirakawa [a] , M. Arai [a] & T. Tokuda [a]

[a] Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo, 158, Japan

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Pressure-Volume-Temperature Relation of Liquid Crystals and the Effect of Molecular Rigidity on the Nematic–Isotropic Phase Transition

T. SHIRAKAWA, M. ARAI and T. TOKUDA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158 Japan

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Pressure-Volume-Temperature relations and the slope of the log-log plot of the transition temperature vs. molar volume at the transition points $(-d\ln Tc/d\ln Vc)$ were measured in the vicinity of the isotropic to nematic phase transition point for 4′-mono-4-propyl cyanophenyl cyclohexane (3PCH). The value of $-d\ln Tc/d\ln Vc$ was found to be 8.29 for 3PCH, which is larger than that obtained for other nematogenic substances, but is smaller than the extrapolated value for the alkylcyanobiphenyl homologous series. The results are well explained by the hypothesis that the cyclohexyl ring behaves more softly than the benzene ring under pressure in the isotropic to nematic phase transition. This suggests that the effective potential is not only intermolecular, but also involves an intramolecular potential.

INTRODUCTION

Nematogenic substances generally have a long rod like structure which is made up of two parts, one rigid and the other flexible. In the theory of nematics, the way of estimation of the rigidity and flexibility of the molecules and how it should be taken into account in the theory are considered to be the key problems in interpreting the properties of actual nematic phases. However, very few studies have ever been presented on the nematics which take into account the rigidity or flexibility of the molecules.[1,2] This is probably because most of the thermodynamic properties of nematic compounds usually do not reflect sensitively the rigidity or flexibility of molecules. In previous papers[3,4] we have reported that the parameter $-d\ln Tc/d\ln Vc$ is more sensitive than any other properties tested, such as thermal expansion, order parameter, heat capacity and volume discontinuity of phase transition, where Tc is the transition temperature and Vc is the molar volume at the transition point. We have also reported that in the homologous series of alkylcyanobiphenyls (RCB), the value $-d\ln Tc/d\ln Vc$ decreased with the increase of alkyl chain length, which is inconsistent to the extension nematic theory of Onsager's hard rod model.[4]

Generally, the rigid portion of nematogenic molecule consists of benzene rings or saturated rings and those group with unsaturated linkage. The rigidity of RCB molecule was varied in the present studies by simply replacing the unsaturated ring group with the saturated cyclohexyl ring. Cutler *et al.* have pointed out that alkylcyclohexane is more compressible than alkylbenzene.[6] The aim of the present studies is to estimate the effect of ring saturation on the phase transition of nematogenic molecules, and to refine phase transition theories to include the information on the chemical structure of the molecules.

The effect of molecular rigidity in a phase transition is discussed in this paper from the measurement of pressure-volume-temperature (P-V-T) relations, and the transition properties of 3PCH are discussed.

EXPERIMENTAL

The material 4′-mono-4-propyl cyanophenyl cyclohexane (3PCH) was obtained from Merk Japan Co. Ltd. and was used without further purification. The clear points of 3PCH were measured with a differential scanning calorimeter (Rigaku Denki Co. Ltd. No. 8055). The density of the materials was measured with a Lipkin-Devison type picnometer. P-V-T relationships were measured with a piston cylinder apparatus. A differential transformer attached to one end of piston detects the degree of compression of the fluid which is indicated on a digital voltmeter. The volume of the cylinder was about 14 cm^3. The pressure was measured with a manganin pressure gauge. The pressure measured was corrected by using the melting points of benzene at high pressure and the compression measured was corrected by using pentadecane. The precision of the pressure measurements were better than ± 0.15 MPa and that of compression measurements were better than $\pm 0.1\%$. The temperature could be read with a precision of 0.02 K and the stability of the temperature controller was better than ±0.01 K in the range from 290 K to 340 K.

RESULTS AND DISCUSSIONS

Figure 1 shows the density vs. temperature curve for 3PCH. The nematic-isotropic transition temperature was found to be 319.72 K. The volume change at the nematic-isotropic transition temperature

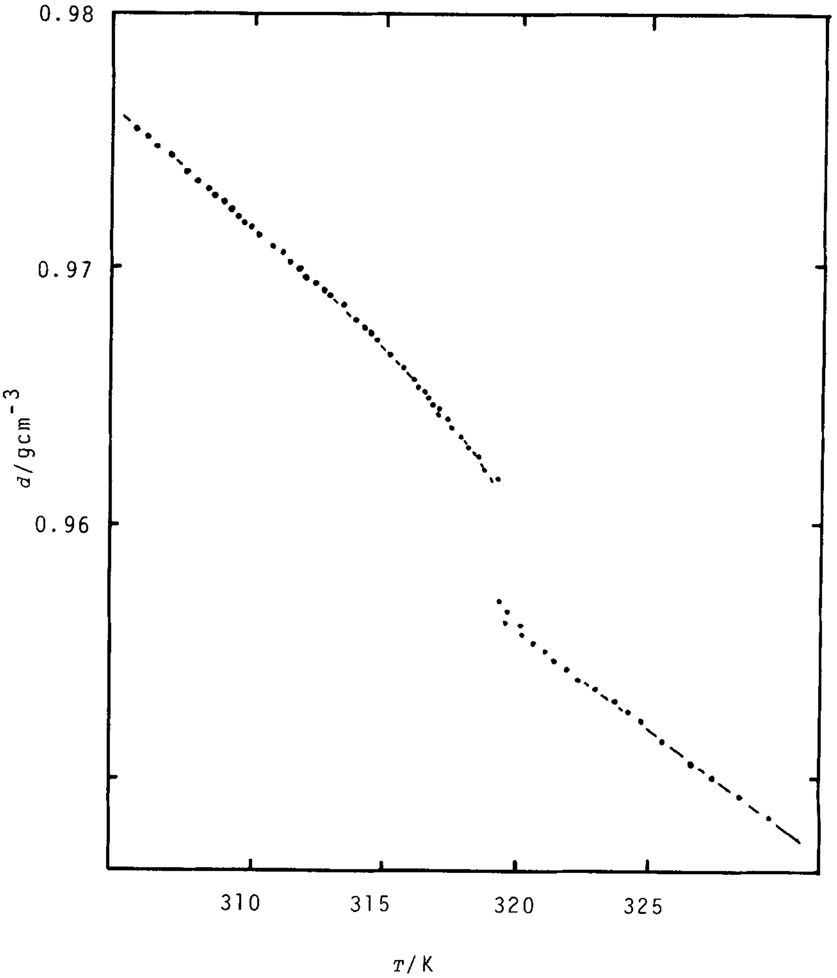

FIGURE 1 Density as a function of temperature for 3PCH.

was found to be 0.52%. This value was twice as much the volume change for the 4′-*n*-alkylcyanobiphenyl homologs.[4] The density curve changed with temperature convex upward in the nematic phase followed by a linear decrease in the isotropic region. The thermal expansion coefficients for both nematic and isotropic phases are expressed in the following two equations

$$\begin{aligned} d_n/(\mathrm{g\,cm^{-3}}) &= 0.98318 + 0.30031 \times 10^{-3}(T - 273.15) \\ &\quad -0.16388 \times 10^{-4}(T - 273.15)^2 \\ d_i/(\mathrm{g/cm^{-3}}) &= 1.01604 - 0.17114 \times 10^{-2}(T - 273.15) \\ &\quad +0.901348 \times 10^{-5}(T - 273.15)^2. \end{aligned}$$

where the subscript *n* and *i* each expresses nematic and isotropic phases respectively.

Figure 2 shows P-V isotherms for 3PCH from 316.90 K to 338.20 K. Plateaus in pressure are clearly observed at the isotropic to nematic phase transition. The molar volume at both the isotropic-nematic and the nematic-isotropic phase transitions decreased with increasing temperature.

The theories on liquid crystalline states have been devised by many authors.[1,2,8-15] The origin of the theories of the liquid crystal state may be classified into three basic theories; the first one is Onsager's proposed "hard rod theory",[8] the second is Pople and Karasz's proposed "order disorder theory with two lattice model",[9] and the last one is that of Maier and Saupe's "mean field theory".[10] These theories all assume a type of intermolecular potential different from each other. They have calculated the free energy and transition properties on the basis of the potential function they have chosen. In testing these theories, they have used thermodynamic quantities which are not sensitive to the chemical structure of nematogenic molecules.

McColl and Shih first measured $-d\ln T/d\ln V$ at constant order parameter for PAA.[16] We have also reported that the value of $-d\ln Tc/d\ln Vc$ at the clear point was more useful than other thermal properties to test the volume dependent part of the intermolecular potentials.[3,18]

Figure 3 shows a log-log plot of the molar volume Vc and temperature Tc at the isotropic to nematic phase transition initiated points. The curve shows a linear relation. The slope $-d\ln Tc/d\ln Vc$ is found to be -8.29. At the nematic to isotropic phase transition initiated points, the same tendency was observed and $-d\ln Tn/d\ln Vn$ was

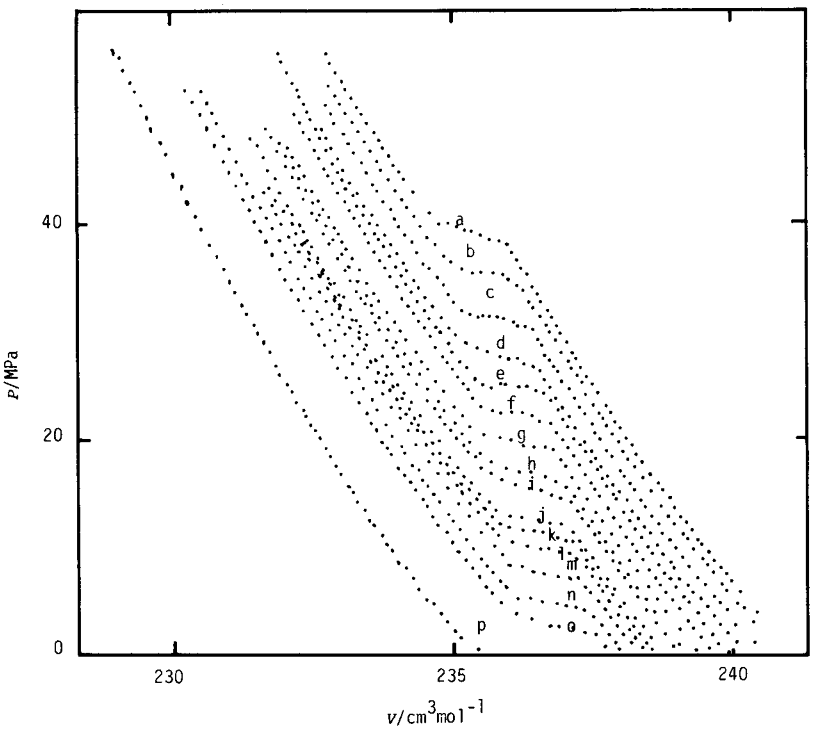

FIGURE 2 Pressure-volume isotherms for 3PCH. (a) 338.20, (b) 336.61, (c) 334.72, (d) 332.74, (e) 331.01, (f) 330.00, (g) 328.63, (h) 327.51, (i) 326.43, (j) 325.61, (k) 324.56, (l) 323.65, (m) 322.74, (n) 320.95, (o) 320.07, (p) 318.01 K.

found to be -8.33. Subscript c and n each expresses the disappearance point of the nematic phase and isotropic phase, respectively. Table I lists the $-d\ln Tc/d\ln Vc$ values calculated from the theories together with the experimentally observed values for 3PCH and a series of RCB. Our observed value $d\ln Tc/d\ln Vc$ for 3PCH is larger than those calculated by both the Pople–Karasz and Maier–Saupe theories. Marcelja is the one who has proposed the theory of nematics which takes into account the effect of molecular comformation, however, he did not calculate the $-d\ln Tc/d\ln Vc$ values.[1] The calculated value of $-d\ln Tc/d\ln Vc$ by the theory of Savithramma and Madhusudana which includes the length/radius of the molecule, also does not coincide with our experimental value. In a previous paper,[4] we have observed that $-d\ln Tc/d\ln Vc$ for alkylcyanobiphenyl homologs decreased with increasing number of carbon atoms in the alkylchain as shown Table I. On the contrary those theories based on

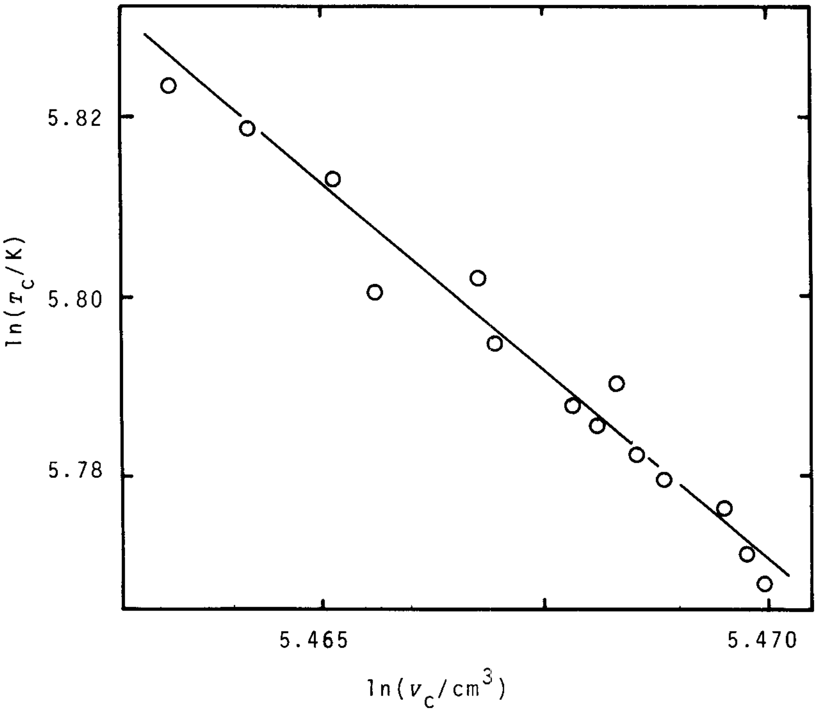

FIGURE 3 Log-log plots of the molar volume at the transition points and transition temperature for 3PCH.

extended hard rod model give $-d\ln Tc/d\ln Vc$ value which increase with alkyl chain length. This inclination appeared in the homologous series of RPCH.[7]

Figure 4 shows the plots of $-d\ln Tc/\ln Vc$ vs. number of carbons for RCB and 3PCH. The value of $-d\ln Tc/d\ln Vc$ for 3PCH is larger than that for 5CB, but smaller than the extrapolated value for 3CB (13.5). The structure difference between 3PCH and 3CB molecules exists in the hard rod part of the molecules in which 3CB has a biphenyl ring while 3PCH has a phenylcyclohexyl ring. The P-V-T relation measured for 3PCH suggests that the substituted cyclohexyl ring does not play similar function as the benzene ring for the nematic to isotropic phase transition. Cutler, McMickle, Webb and Schiessler[6] observed that the compression of a cyclohexyl ring is larger than that of a benzene ring. The aromatic ring is well regarded to be a planer disc which is rigid for external forces, however, the cyclohexyl ring is less resistant to external forces than the benzene ring. This result

TABLE I

Calculated and observed values of $-d\ln Tc/d\ln Vc$

Compound	3PCH[a]	5CB[b]	6CB[b]	7CB[b]	8CB[c]
(L/D)	(2.5)	(2.75)	(3.0)	(3.28)	(3.53)
experimental	8.29	7.62	6.10	5.15	4.3
Maier *et al.*[10]	2	2	2	2	2
Pople *et al.*[9]	4	4	4	4	4
Savithramma *et al.*	> 100	> 100	> 100	> 100	> 100

[a] Present studies.
[b,c] Cited from reference 3, 4.

means that the cyclohexyl ring has apparently a softer potential than the benzene ring.

The value $-d\ln Tc/d\ln Vc$ is correlated with the volume dependent part of the molecular potential. On the measuring of the value $-d\ln Tc/d\ln Vc$ 3 PCH and RCB, we observed a tendency of the compression order of the cyclohexane ring and the benzene ring similar to Cutler *et al.*

Keyes and Daniels reported the $-d\ln(d/d_0)/d\ln(T/T_0)$ (which is equivalent to $-d\ln Vc/d\ln Tc$) on three nematics and one cholesteric in the vicinity of their clearing transitions.[17] They observed that more flexible molecules start out with a more rapid change of density. These results coincided with our experimental results.

Tranfield and Collings also observed values for $-(V/T))(dT/dV)$ for alkoxyazoxybenzene homologs (ROAB) which decreased with increasing the alkoxyl group carbon number.[19] These results are also explained by the fact that a long alkoxyl chain is more flexible than a short alkoxyl chain. The value $-(V/T)(dT/dV)$ of ROAB was smaller than the 3PCH value; that is due to the difference in the rigid part of the molecules. There is a ON=N bond in the hard rod part of alkoxyazoxybenzene while 3PCH has no bond other than a C—C bond. Since the ON=N bond is more flexible than the cyclohexyl ring, $-d\ln Tc/d\ln Vc$ for ROAB is smaller than 3PCH.

These results mean that at the phase transition of the nematic to isotropic phase, the effective potential is not only the intermolecular potential, but also the intramolecular structure dependent part of the potential.

In the transition of the polyphenyls, Cailleau, Baudour, Meinnel, Dworkin and Moussa suggested that the comformation of non-rigid polyphenyl molecules results from a delicate balance between compet-

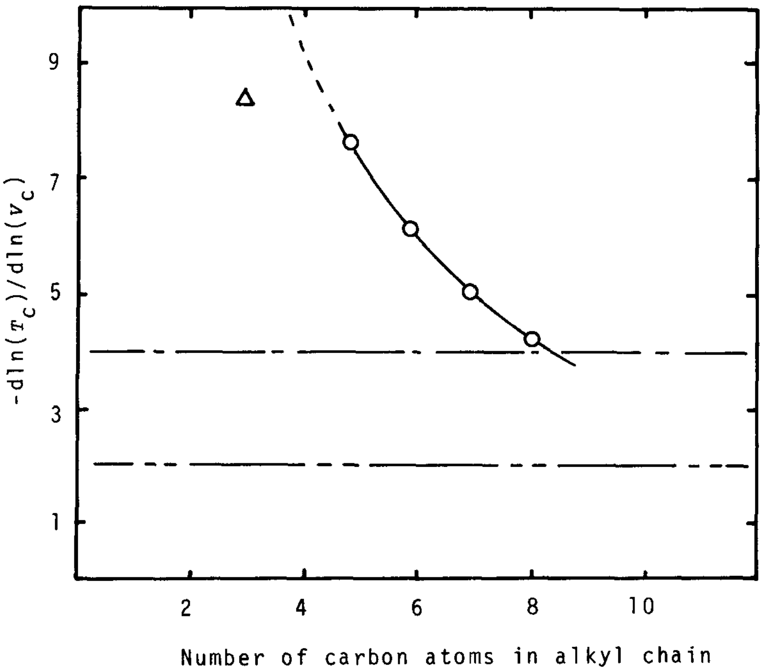

FIGURE 4 $-d\ln Tc/d\ln Vc$ plotted against the number of carbon atoms in alkyl chain for 4′-*n*-alkylcyanobiphenyl homologues and 3PCH. ——— is the value of calculated from the theory of Maier-Saupe. —·— is the value of calculated from the theory of Pople-Karasz.

ing intramolecular and intermolecular forces.[20] In the nematic to isotropic phase transition, to observe the effect of intramolecular force similar to plastic crystal phase transitions offers the key to solution of the transition process of complicated molecules.

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