Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Behaviour of Nematic and Non-Nematic Binary Systems IV-P-Terphenyl and its Analogues in 5CB

T. Ito [a], N. Kanzaki [a], R. Fukazawa [a], K. Asaba [a] & S. Kobinata [a]

[a] Toin University of Yokohama, 1614 Kurogane-cho, Aoba-Ku, Yokohama, 225-8502, JAPAN

Version of record first published: 24 Sep 2006

To cite this article: T. Ito, N. Kanzaki, R. Fukazawa, K. Asaba & S. Kobinata (2000): Phase Behaviour of Nematic and Non-Nematic Binary Systems IV-P-Terphenyl and its Analogues in 5CB, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 346:1, 145-154

To link to this article: http://dx.doi.org/10.1080/10587250008023874

Mol. Cryst. Liq. Cryst., 2000, Vol. 346, pp. 145-154
Reprints available directly from the publisher
Photocopying permitted by license only

Phase Behaviour of Nematic and Non-Nematic Binary Systems IV-P-Terphenyl and its Analogues in 5CB

T. ITO, N. KANZAKI, R. FUKAZAWA, K. ASABA and S. KOBINATA

Toin University of Yokohama, 1614 Kurogane-cho, Aoba-Ku, Yokohama 225–8502, JAPAN

If there are suitable molecular interactions between nematic and non-nematic molecules and the resulting complexes have suitable length-to-width ratio, nematic-isotropic phase transition temperature (T_{NI}) can rise contrary to usually observed fall. This types of rise in T_{NI} were observed in binary systems composed of 5CB and aromatic acids, and were ascribed to the formation of hydrogen bonded complexes between 5CB solvent and non-nematic solutes [1–3].

We newly found that the T_{NI} rose in the binary systems in which there can not be expected to exist any hydrogen-bonded complexes. We studied the possibility of the complex formation by molecular interactions other than intermolecular hydrogen bonding between 5CB and non-nematic solutes. Their consequences on thermal properties of binary systems were investigated.

Keywords: charge-transfer complex; continuous variation method; weak cluster-type complexes; electronic absorption spectrum; MOPAC

INTRODUCTION:

In general, when a non-nematic solute is added to a nematic, nematic-isotropic phase transition temperature (T_{NI}) decreases with increase in non-nematic concentration [4-6].

We have found that the formation of hydrogen bond complexes between the nematic 5CB

and suitable solutes, such as benzoic acid and phenol derivatives, caused the rising of T_{NI} or definite lowering of the rate of decreases in T_{NI} with respect to solute concentration [1-3]. It has been proved that considerable part of benzoic acid exist as ring dimer in 5CB and suggested that these ring dimer might contribute T_{NI} increase. In this paper, we studied the several solutes, which have similar molecular length and width with ring dimer of benzoic acid, such as p-terphenyl, anthracene and biphenylene. We observed; T_{NI} rose in the binary systems composed of p-terphenyl and anthracene solute in 5CB, in spite of the hydrogen bonding interactions were not expected to exist in them, while biphenylene/5CB system showed T_{NI} decrease. The presence of specific molecular interactions in these systems was studied by measuring electronic absorption spectrum of mixtures of these substance based on the continuous variation method. [7]

EXPRIMENTAL:

Commercial 5CB (Merck Japan) was used without furthers purification. p-terphenyl and anthracene (Tokyo Kasei), biphenylene (Aldrich Japan) were used without further purification.

Absorption spectra were measured with a Shimazu model UV-160A spectrophotometer, using cells having 5-, 0.1- and 0.02-cm thicknesses.

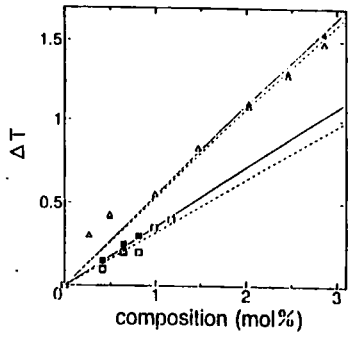
Nematic-isotropic transition temperature of p-terphenyl / 5CB, anthracene / 5CB and biphenylene / 5CB and tetracyanoethylene (TCNE) / 5CB dilute mixtures were measured by using a hot stage under polarizing microscope.

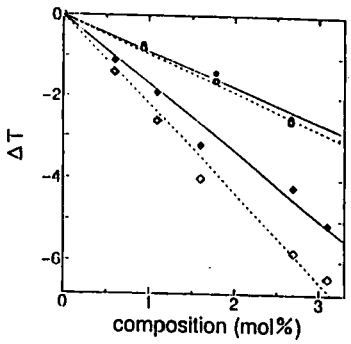
RESULTS AND DISCUSSION:

The addition of non-nematic solutes usually causes the decease in T_{NI}, along with the appearance of a narrow two-phase coexisting region [4] [5]. But we found the addition of p-terphenyl or anthracene to 5CB caused the distinct increase in T_{NI}, as shown in figure 1.

In this figure T_I is the temperature at which nematic phase disappear completely on heating.

T_N is the temperature at which an isotropic phase begins to appear on heating.





p-terphenyl/5CB		dT_{NI}/dC_B
△	T_N	0.53
▲	T_I	0.55

anthracene/5CB		dT_{NI}/dC_B
□	T_N	0.32
■	T_I	0.36

(a)

biphenylene/5CB		dT_{NI}/dC_B
○	T_N	-0.94
●	T_I	-0.88

TCNE/5CB		dT_{NI}/dC_B
◇	T_N	-2.17
◆	T_I	-1.67

(b)

FIGURE 1 The results of thermal measurement in the binary systems of 5CB mixed with several solutes.

The abscissa is the concentration of solutes in mol%. The vertical axis plots the temperature difference between T_N, T_I of binary systems and the clearing temperature of pure 5CB. The temperature increases in T_{NI} were reported for several solutes/5CB mixtures and these abnormal increases in T_{NI} were ascribed to the hydrogen-bond formation between the cyano group of host 5CB and the solutes which have the power of hydrogen bonding donor [1-3]. It is noted that although there can not be expected to exist any significant hydrogen bonding interaction between p-terphenyl, anthracene and 5CB, ΔT_N and ΔT_I increased definitely with the solute concentration. It is also noted that the rate of T_{NI} increase for p-terphenyl/5CB, dT_{NI}/dC_B, as shown in figure 1, is as large as in that of benzoic acid.[1] These extraordinary increases in T_{NI} suggest that there should be special interactions other than hydrogen bonding between 5CB and solutes. To confirm the above possibility, we relied on the continuous variation method, which is known to be quite useful to detect the complex formation by any specific interactions. [7]

In this method, the solutions of each substance are mixed at various ratios (0~100%) under the condition that the sum of concentration of two solutions is constant. From the plot of absorbance with respect to the composition of mixed solution, the existence of complex and its composition can be determined.

For the equilibrium reaction between a nematic (A) and a non-nematic (B) molecules; $mA + nB \rightleftarrows A_mB_n$, the equilibrium constant K of association is expressed as,

$$K = \frac{C_{AmBn}}{(C_{A0} - mC_{AmBn})^m (C_{B0} - nC_{AmBn})^n} \tag{1}$$

C_{A0} and C_{B0} are the initial concentration of A and B. Total initial concentration $C_0 = C_{A0} + C_{B0}$ is held constant. C_{AmBn} is the equilibrium molar concentration of the complex A_mB_n. According to Lambert-Beer's law, the absorbance per unit optical path-length d can be written;

$$d = d_0 + \bar{d} = [\varepsilon_B C_0 + (\varepsilon_A - \varepsilon_B) C_{A0}] + [(\varepsilon_{AmBn} - m\varepsilon_A - n\varepsilon_B) C_{AmBn}] \tag{2}$$

where ε_A, ε_B and ε_{AmBn} are the molar absorption coefficients of respective components at certain wave length.

The d_0, the first term of equation (2), stands for the absorbance per unit optical path length when there are no specific intermolecular interactions such as to lead complex formation, and give straight line in the plot of continuous variation method, figure 2-(a). The $\bar{d}$, the second term of equation (2), represents the contribution of complex formation to the absorbance, and leads to the deviation from the straight line in the plot of continuous variation methods, figure 2-(c).

TABLE 1. The conditions of the measurement in continuous variation method. The second column shows the concentration before mixing.

	Conc. (mol/l)	Wave length	Path length	Temperature
5CB / p – terphenyl	$\frac{1.85\times10^{-3}}{1.86\times10^{-3}}$	275nm	0.02 cm	19.0 ℃
5CB / anthracene	$\frac{3.91\times10^{-4}}{3.97\times10^{-4}}$	250nm	0.1 cm	19.5 ℃
5CB / biphemylene	$\frac{3.49\times10^{-4}}{3.49\times10^{-4}}$	250nm	0.1 cm	20.0 ℃

Schematic results of continuous variation method are shown in figure 2. The straight d-line in figure 2-(a) indicates that there are no complex formations. The curved solid line of d in figure 2-(b) shows the complex formation. In this case d is decomposed straight line (d_0) and curved $\bar{d}$-line of figure 2-(c).

In this figure, the $\bar{d}$ shows a peak at concentration $C_{A0} = \frac{m}{m+n}C_0$, indicating the formation of m:n complex between A and B; A_mB_n.

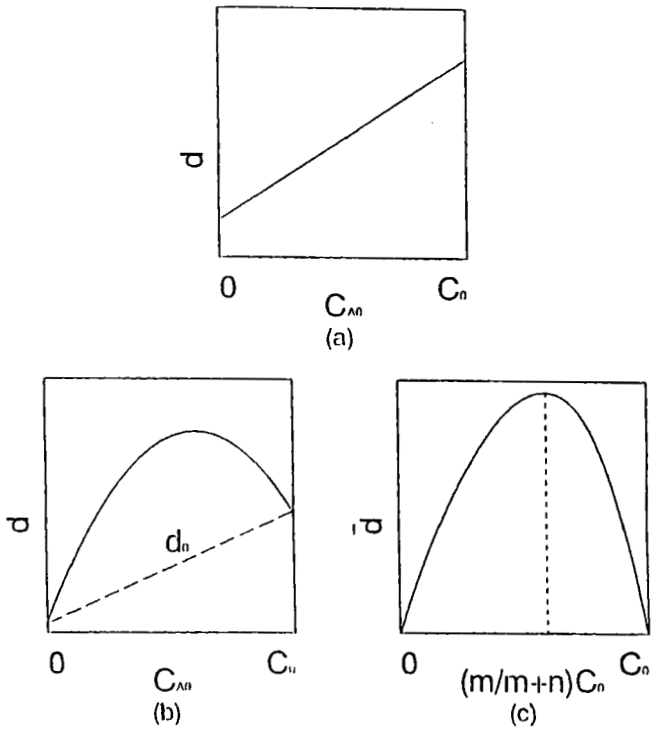


FIGURE 2. A plot of continuous variation method; In the case of (a), there are no specific interactions between A and B. (b), In the case of (b) and (c) there

Figure 3- (a) and figure 3- (b) show the results of continuous variation method on p-terphenyl, 5CB and anthracene, 5CB systems in cyclohexane solutions, respectively. The conditions of measurement were summarized in table 1. Because we could not observe any new absorption band, which can be ascribed to complex formation, the wavelengths in table 1 were chosen at the position, which gave the most sensitive result. In figure 3, upper curve is the plot of d of equation (2), and lower curve plot $\bar{d}$ of equation (2). There are distinct deviations from linear dependence with respect to the composition of solutions. In the case of p-terphemyl/5CB in cyclohexane, the deviation from linearity ($\bar{d}$) shows one peak nearly at the composition 5CB : p-terphenyl =1.5:1. In the case of anthracene/5CB in cyclohexane, we similarly observed one peak at about the composition 5CB:anthracene =1.5:1. These observations show that 5CB and anthracene or p-terphenyl form rather complicated aggregate with the composition 5CB:solute=3n:2n (n=1,2,$\cdots$) in cyclohexane solution. The molecular interactions which lead to the formation of these aggregate will naturally present also in the solute/5CB binary systems, and result in the rise of T_{NI} in these systems. It was reported that 5CB and TCNE form one-to-one charge transfer complex in dichroloethylene solution. [8] The formation of one-to-one complex in this system was reconfirmed in acetone solution by means of the continuos variation method as shown in figure 3-(3). In this case, the $\bar{d}$ curve shows one peak at the middle of the total concentration of C_0, indicating 1:1 composition of the CT complex. It was also reported that TCNE/5CB binary system showed an extraordinary decrease in T_{NI}. The formation of firm 1:1 complex may destroy orientational interaction of 5CB molecules and weaken the liquid crystallinity, causing T_{NI} decrease. In this respect, it is noted that biphenylene/5CB form 1:1 complex in cyclohexane solutions as shown in figure 3-(d). Then, the decrease of T_{NI} in biphenylene/5CB system may be ascribed to the formation fo 1:1 complex, similarly to TCNE/5CB case. While, the rising of T_{NI} observed in p-terphenyl/5CB and anthracene/5CB systems were ascribed to the formation of the weak cluster-type complexes.

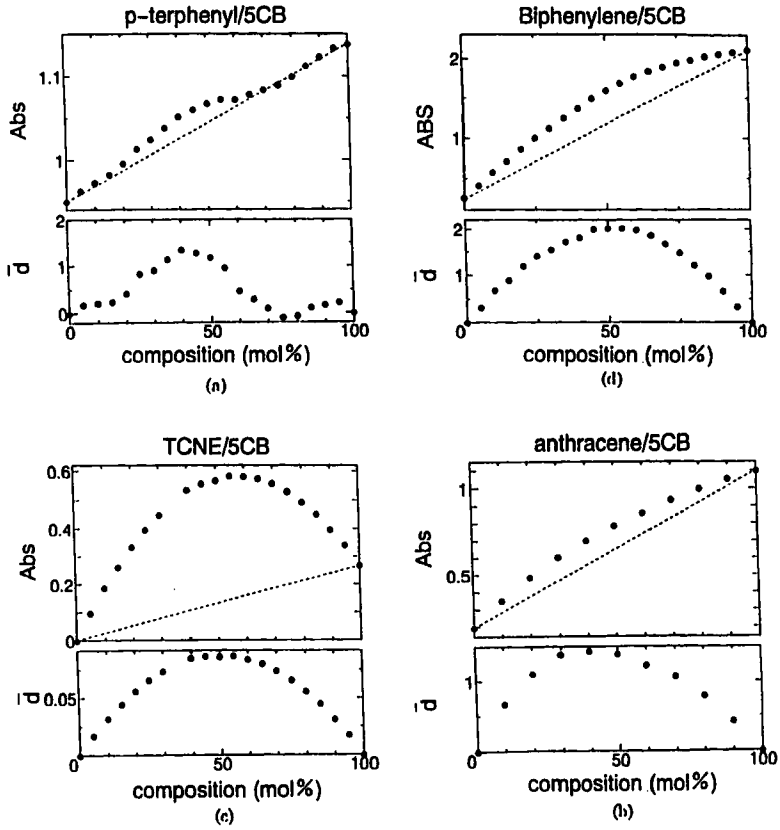


FIGURE 3. The result of continuous variation measurement on (a)p-terphenyl/5CB in cyclohexane (b)anthracene/5CB in cyclohexane (c) TCNE/5CB in acetone (d) biphenylene/5CB in cyclohexane solution.

As to intermolecular interactions, which lead to the complex formation, we think the charge transfer interactions are most probable.

To confirm above inference, we carried out the molecular orbital calculations on 5CB and solutes by using MOPAC. The results are shown in table Ⅱ.

It is noted that the sequence of the rate of T_{NI} change in figure 1 is well consistent with that of electronegativity of molecules calculated by the sum of ionization potential (Ip) and electron affinity (Ea) on the basis of Mulliken's definition of electronegativity.

TABLE Ⅱ. The results of the calculation by semiempirical molecular orbital method (MOPAC)

	5CB	p-terphenyl	Anthracene	Biphenylene
Ip (eV)	9.121	8.711	8.354	8.688
Ea (eV)	1.013	0.804	1.076	0.646
Ip+Ea (eV)	10.134	9.515	9.430	9.334

Table Ⅱ shows that 5CB acts as electron acceptor, and p-terphenyl, anthracene and biphenylene can act as donors, of which biphenylene is the strongest donor. In the case of TCNE/5CB, 5CB acts as an electron donor and TCNE act as acceptor. It is noted that the size of biphenylene and TCNE are rather smaller than those of anthracene and p-terphenyl , and very similar to the size of biphenyl and phenyl cores in 5CB molecule, which enable an efficient overlap of π molecular orbitals between 5CB and these solute. Owing to these, the rather distinct one-to-one complexes are formed between 5CB and TCNE or biphenylene, which results in the decrease in T_{NI}.

We are now investigating the equilibrium constants of complex formation to confirm the above inference.

References

[1] K. Asaba, A.Igarashi and S. Kobinata, *Jpan. J. Appl. Phys.*, **37**, 6482(1998).
[2] K. Asaba. A. S. T. Kubota, H. F. Tanaka, A. Igarashi and S. Kobinata, Mol. Cryst. Liq. Cryst., **318**, 243(1998).
[3] S. Yoshida, T. Narui, K. Asaba, J. Kawata and S, Kobinata, *Mol. Cryst. Liq. Cryst.*, **301,** 425(1997).
[4] D. E. Martin, The Molecular Physics of Liquid Crystal, eds. G. R. Luckhurst and G. W. Gray(Academic Press, New York, 1977), chap. 10 and 11, and references therein.
[5] P. G. de Gennes and J. Prost: The Physics of Liquid Crystals (Clarendon Press, Oxford, 1993) Chap. 2.4, and references cited therein.

[6] B. Kronberg, D. F. R. Gillson and D Patterson: *J. Chem. Soc. Faraday,* **II 72,** 1673(1976).
[7] R. Tsuchida, *Bull. Chem. Soc. Jpn.,* **10,** 27(1935).
[8] K. Kato, S. Kobinata, S. Maeda, *Liq. Cryst,* **5,** No2, 595(1989).