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Kazunori Asaba<sup>a</sup>, Akira S. T. Kubota<sup>a</sup>, Hideki F. Tanaka<sup>a</sup>, Atsuko Igarashi<sup>a</sup> & Shunsuke Kobinata<sup>a</sup>

<sup>a</sup> Department of Materials Science, Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama, 225, Japan

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## **Phase Behavior of Nematic-Nonnematic Binary Systems II**

### **- The Effect of Hydrogen Bonding -**

KAZUNORI ASABA, AKIRA S. T. KUBOTA, HIDEKI F. TANAKA,  
ATSUKO IGARASHI and SHUNSUKE KOBINATA

Department of Materials Science, Toin University of Yokohama  
1614 Kurogane-cho, Aoba-ku, Yokohama 225 Japan

Binary mixtures of nematic 4-pentyl-4'-cyanobiphenyl (5CB) with some kinds of non-nematic solutes were found to show the increase in nematic-isotropic transition temperature, contrary to usually observed decrease. All these 'unusual' solutes found in this work have active hydrogen atoms which can act as hydrogen bond donor. 'Unusual' increase in the clearing temperature was attributed to the hydrogen bonding interaction between 5CB and solutes. The effect of hydrogen bonding interaction between 5CB and various non-nematic solutes on thermal and spectroscopic properties were studied in detail.

Keywords: nematic liquid crystal; 5CB; binary system; hydrogen bond; phase transition; IR

### **Introduction**

The study of binary systems, consisting of non-nematic solute and nematic liquid crystal solvent, has been attracting much attention both theoretically and experimentally [1,2,3,4]. When a nonnematic solute is admixed to nematic liquid crystal, nematic-isotropic phase transition temperature ( $T_{NI}$ ) usually decreases. Therefore the highness of  $T_{NI}$  of a liquid crystal has been often regarded as a measure of the purity of the nematic liquid crystal. The addition of nonnematics to the liquid crystals also causes

the appearance of nematic-isotropic two-phase regions in which the nematic and the isotropic phases coexist. But some solutes causing 'unusual' increase in  $T_{NI}$  was reported [5,6,7,8].

In the previous paper [8], we reported that the addition of several carboxylic acid and phenol derivatives of biphenyl to nematic 4-pentyl-4'-cyanobiphenyl (5CB) resulted in the increase in  $T_{NI}$ . This 'unusual' behavior have been ascribed to the hydrogen bonding interaction between the solutes and 5CB.

To study the origin of this 'unusual' behavior in more detail, we examined various p-substituted benzoic acid and phenol derivatives as solutes to 5CB. We found the addition of benzoic acid derivatives to 5CB resulted in 'unusual' increase in  $T_{NI}$ . The addition of phenol derivatives to 5CB causes the decrease in  $T_{NI}$ , but the rate of decrease is very low compared with that of 'normal' solutes. The rates of decrease in  $T_{NI}$  with respect to solute concentration were found to follow the sequence of acidities of solutes as a whole. These observations indicated that this 'unusual' increase in  $T_{NI}$  is caused by the formation of hydrogen bond between 5CB and solutes.

The formation of hydrogen bond between cyano group and OH of benzoic acids and phenols was confirmed by the observation of IR spectrum.

### Experimental

Commercial 5CB (Merck Japan) was used without further purification. All non-nematic solutes were also purchased, and used without further purification.

The nematic-isotropic transition temperature of pure 5CB and all binary systems were measured under polarizing microscope using a hot stage. Infrared spectra were measured by HITACHI 270-30 IR spectrometer.

### Results and Discussion

Fig. 1 shows the phase diagram for the addition of benzoic acid derivatives to 5CB. In this and following diagrams,  $\Delta T_{NI}$  means the difference of clearing temperature between pure 5CB and binary systems,  $T_N$  denotes the temperature at which the isotropic phase begins to appear in the nematic phase on heating, and  $T_I$  means the temperature at which the nematic phase disappears completely.  $\Delta T_N$  and  $\Delta T_I$  means the difference of  $T_N$  and  $T_I$  of binary systems from the clearing temperature of pure 5CB. We observed the 'unusual' increase in  $\Delta T_{NI}$  for all of these binary systems. Fig. 2 shows the phase diagrams for the addition of phenol derivatives to 5CB. In this case, we observed slightly decrease in  $\Delta T_{NI}$ , but the rate of decrease in  $\Delta T_{NI}$  is very low compared with that for 'usual' solute, such as biphenyl as shown Fig. 2.

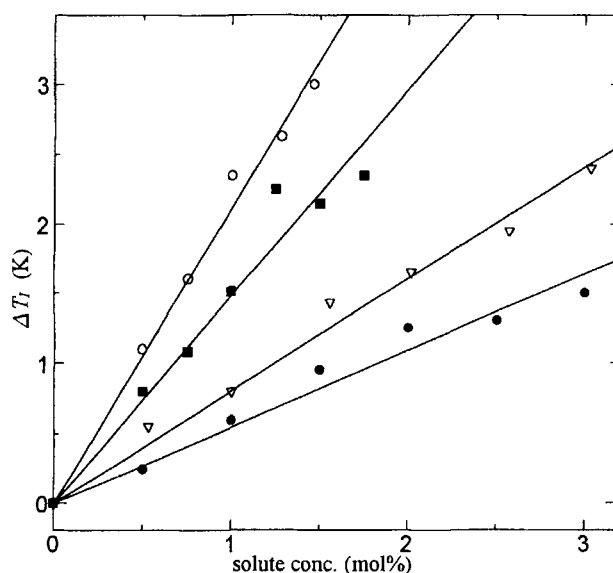


FIGURE 1 Phase diagram of p-substituted benzoic acid/5CB

benzoic acid : ●  
 p-F benzoic acid : ▽  
 p-CN benzoic acid : ■  
 p-NO<sub>2</sub> benzoic acid : ○

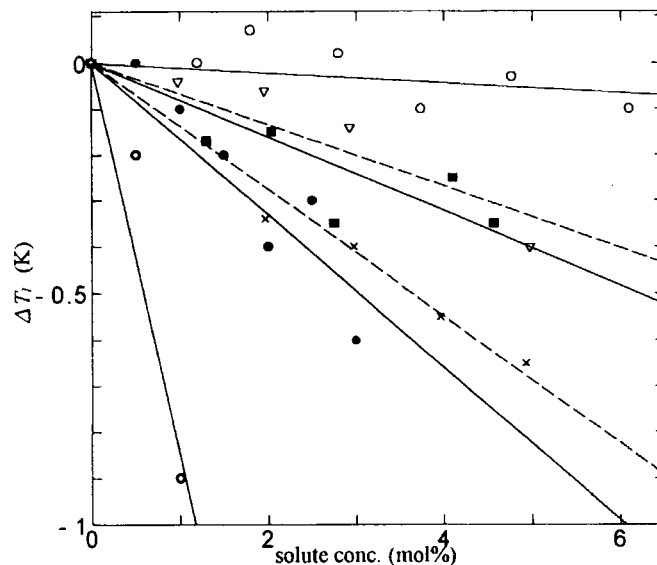


FIGURE 2 Phase diagram of p-substituted phenol/5CB

phenol : ●  
 p-F phenol : ×  
 p-Cl phenol : ▽  
 p-CN phenol : ■  
 p-NO<sub>2</sub> phenol : ○  
 biphenyl : ⊙

The marked difference for benzoic acid and phenol shows the importance of solidity of hydrogen bonded complex; benzoic acid and phenol both have active hydrogen atoms, which can act as hydrogen bonding donor, but donating power is considerably different. Carboxylic OH of benzoic acid is stronger hydrogen bonding donor than hydroxyl OH of phenol as can be seen in the values of gas-phase acidity and pKa [9]. Because benzoic acid and phenol give hydrogen bonded complexes of similar size and shape as shown in Fig. 3, the difference of thermal behavior stated above between these two binary systems may be attributed to the difference of stiffness of these complexes. Measurement for various n-alkyl carboxylic acids/5CB binary

systems show that the addition of these solutes decrease  $T_{NI}$ , contrary to the admixing of p-substituted benzoic acid. The difference between n-alkyl carboxylic acid and aromatic carboxylic acid may be attributed to the flexibility of n-alkyl chain. These preliminary results also show the importance of rigidity of hydrogen bonded complex in rising  $T_{NI}$ .

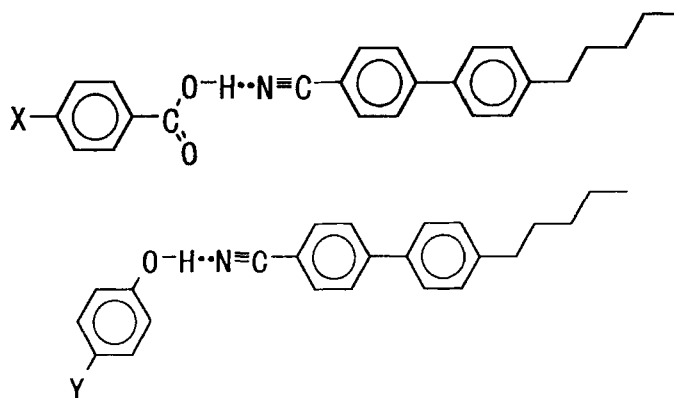


FIGURE 3  
The structure of hydrogen bonded complex

In Table 1, the results of Fig. 1 and Fig. 2 are summarized. The 3rd column shows the rate of increase in  $\Delta T_i$  with respect to solute concentration in mol% (c);  $d\Delta T_i/dc$ . Next column shows the difference of gas phase acidity between benzoic acid or phenol and these derivatives;  $H_{sub} - H_o$ , and 5th column shows the difference of pKa;  $pKa_{sub} - pKa_o$ . These two quantities are considered as the measure of hydrogen donating power in gas phase and in water solution, respectively. For the solutes cited in Table 1, gas phase acidity and pKa follow the same sequence. The order of Hammett's substitution constant for p-substituted group  $\sigma_p$  follows also this sequence [9]. These facts suggest that hydrogen donating power of these derivatives will take the same sequence even in nematic 5CB. It is noted that the rate of  $\Delta T_i$  increase follows this sequence as a whole, although some small

irregularity from this sequence are present.

TABLE 1 The correlation between  $\Delta T_i$  and acidities

| solute                   | plot | $d\Delta T_i/dc$<br>(K/mol%) | $H_{sub} - H_o$<br>(kJ/mol) | $pK_{a_{sub}} - pK_{a_o}$ | Hammett's<br>$\sigma_p$ |
|--------------------------|------|------------------------------|-----------------------------|---------------------------|-------------------------|
| benzoic acid             | ●    | +0.50                        | 0.0<br>(1423.0)             | 0.0<br>(4.20)             | 0.0                     |
| p-F                      | ▽    | +0.80                        | -50.6                       | -0.06                     | +0.07                   |
| p-NO <sub>2</sub>        | ■    | +1.47                        | -                           | -0.65                     | +0.75                   |
| p-CN                     | ○    | +2.11                        | -190.8                      | -0.78                     | +0.64                   |
| phenol                   | ●    | -0.16                        | 0.0<br>(1464.0)             | 0.0<br>(9.82)             | 0.0                     |
| p-F                      | ×    | -0.14                        | -9.6                        | -0.36                     | +0.07                   |
| p-Cl                     | ▽    | -0.07                        | -24.7                       | -0.68                     | +0.20                   |
| p-CN                     | ■    | -0.08                        | -69.5                       | -1.85                     | +0.64                   |
| p-NO <sub>2</sub>        | ○    | -0.01                        | -87.4                       | -2.92                     | +0.75                   |
| biphenyl                 | ⊙    | -0.85                        |                             |                           |                         |
| p-carboxylic<br>biphenyl |      | +2.65                        |                             |                           |                         |
| p-hydroxyl<br>biphenyl   |      | +0.39                        |                             |                           |                         |

These observations strongly indicate that this increase in  $T_{NI}$  is ascribed to the hydrogen bond formation between cyano group of 5CB and OH of carboxylic group of benzoic acid derivatives or hydroxyl group of phenol derivatives. The comparison of results for benzene derivatives obtained in this work with those for corresponding p-substituted biphenyl (p-carboxylic

biphenyl and p-hydroxyl biphenyl) reported previously [8] shows that the rate of increase in  $T_{NI}$  ( $d\Delta T_i/dc$ ) is considerably larger for the latter solutes, indicating the size and shape of hydrogen bonded complex are important factor in rising  $T_{NI}$ .

Thus, the thermal behavior of nematic-nonnematic binary systems are reasonably ascribed to the hydrogen bond formation between CN of 5CB and OH group of solutes. Although cyano group is known as a rather weak hydrogen bond acceptor, this conclusion was confirmed by IR measurement of binary systems. First, we used benzonitrile as a model of 5CB, and next, we used 5CB as a solvent.

Fig. 4 shows IR spectrum of phenol in the region of OH stretching vibration. The solvents are benzonitrile (a) and benzene (b). In benzene solution, phenol shows free (unbonded, monomer) OH vibration at  $3,560\text{cm}^{-1}$ , and another OH vibration at  $3,456\text{cm}^{-1}$  which is assigned to phenol's dimer [10]. But in benzonitrile, these OH absorption bands are disappeared, and new OH absorption band appears at  $3,428\text{cm}^{-1}$ . This new band suggests the formation of intermolecular hydrogen bond between OH of phenol and CN of benzonitrile. It is noted that the strength of this hydrogen bond for this complex is considered to be stronger than that of phenol dimer, because the red shift of OH is larger than that of dimer.

Fig. 5 shows IR spectrum of benzoic acid in the region of CO stretching vibrational mode. The solvents are benzonitrile (a) and benzene (b). In benzene solution, benzoic acid shows two CO absorption bands, one is at  $1,694\text{cm}^{-1}$  which is assigned to benzoic acid ring dimer, and another at  $1,740\text{cm}^{-1}$  which is assigned to benzoic acid monomer [10]. But in benzonitrile, a new band appears at  $1,728\text{cm}^{-1}$  as shown in Fig. 5(a). This new band suggests the presence of another kind of hydrogen bond, and is assigned



to the hydrogen bond between cyano group of solvent and carboxylic group of solute. This assignment is assured by the observation of IR spectrum of OH stretching region. In benzonitrile solution, a new broad absorption appears with some structure in the region from 3,300 to 3,100 $\text{cm}^{-1}$ , indicating that a weak hydrogen bond complex was formed in this solution besides benzoic acid dimers.

From these observations, we confirmed the formation of hydrogen bond between cyano group and aromatic OH groups. We obtained similar results in 5CB binary system (see Fig. 4(c) and Fig. 5(c)). In phenol/5CB binary system, (5mol%), we observe one OH absorption band of phenol-5CB hydrogen bonded complex. All phenol molecules seem to make hydrogen bond with solvent 5CB. On the other hand, in benzoic acid/5CB system, (5mol%), besides benzoic acid-5CB hydrogen bonded complex, ring dimer of benzoic acid exists in some extent as revealed from Fig. 5(a) and Fig. 5(b), indicating that the concentration of hydrogen bonded complex is low for this system compared with phenol/5CB system, but increase in  $T_{NI}$  is considerably large for the former solute. The ring dimer of benzoic acid may be affect increase in  $T_{NI}$ . The effect of ring dimer of benzoic acid on  $T_{NI}$  is now under investigation.

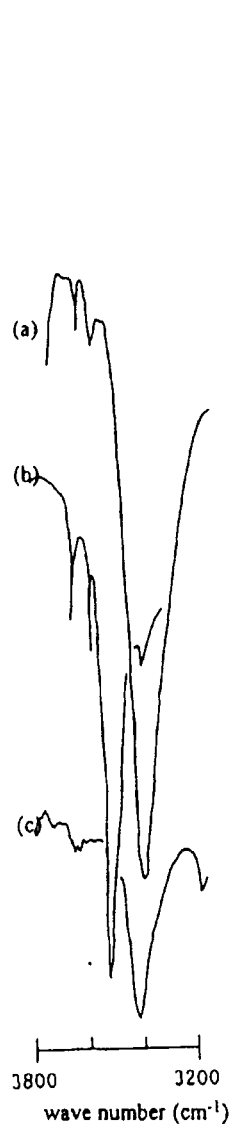


FIGURE 4 IR spectra of phenol

- (a) benzonitrile solution
- (b) benzene solution
- (c) 5CB solution

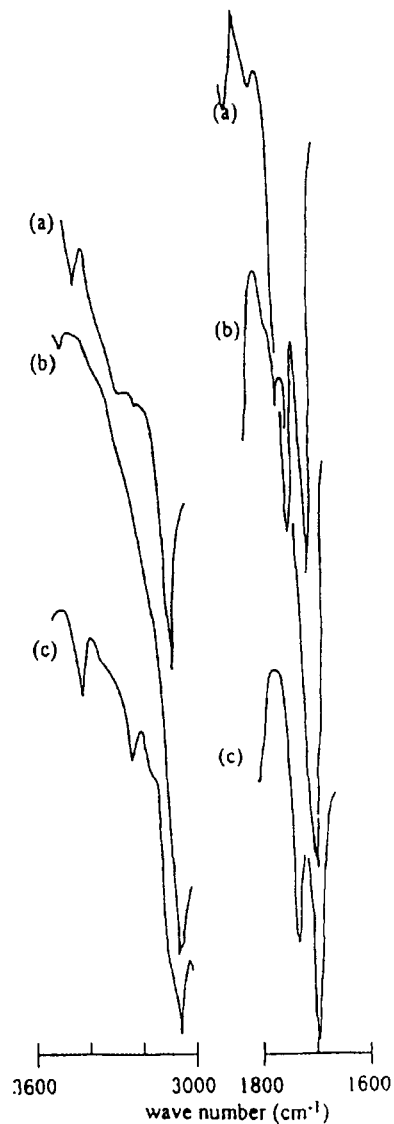


FIGURE 5 IR spectra of benzoic acid

- (a) benzonitrile solution
- (b) benzene solution
- (c) 5CB solution

### References

- [1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystal 2nd ed.*, (Clarendon press, Oxford, 1993) chap. 2.4, pp. 91-94 and references cited herein
- [2] B. Kronberg, D. F. R. Gillson and D. Patterson, *J. Chem. Soc. FaradayII*, **72**, 1673 (1976)
- [3] B. Kronberg and D. Patterson, *J. Chem. Soc. FaradayII*, **72**, 1686 (1976)
- [4] D. E. Martine in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray, (Academic Press, 1977), Chap. 10-11, pp. 221-261 and references cited herein
- [5] J. W. Park and M. M. Labes, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 147 (1977)
- [6] S. Sigaud, M. F. Achard, F. Hardouin and H. Gasparoux, *J. Physique Lett.*, **46**, L321 (1985)
- [7] K. Sunohara, A. Fujimaru, A. Shinya and S. Kobinata, *Mol. Cryst. Liq. Cryst.*, **265**, 181 (1995)
- [8] S. Yoshida, T. Narui, K. Asaba, J. Kawata and S. Kobinata, *Mol. Cryst. Liq. Cryst.*, **301**, 425 (1997)
- [9] N. S. Isaacs, *Physical Organic Chemistry*, (Longman Scientific & Technical, 1987), Chap. 4, pp. 129-170, Chap. 6, pp. 210-254 and references cited herein
- [10] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, (Chapman and Hall, London, 1975) Chap. 6, pp. 107-128, Chap. 10, pp. 183-202 and references cited herein