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# Liquid Crystals of Binary Mixtures. Induction of Nematic Phase by Intermolecular Charge-transfer Interaction and Application of Solid-solution Model

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**Synopsis.** Nematic phase induced by binary mixture consisting of electron donor and acceptor was examined by using modified solid-solution model. The experimental results of Araya and Matsunaga were explained by this approach, and the charge-transfer interaction energy between donor and acceptor in the nematic phase was estimated by analyzing their phase diagrams.

Much attention has been paid to a great number of liquid crystals, which show intermediate state between crystalline solid and isotropic liquid.[1)] Binary systems have been often used to achieve extended liquid crystalline temperature ranges. In binary mixtures consisting of electron donors and acceptors, parallel molecular arrangement required by liquid crystal formation becomes observable if an electron donor-acceptor charge-transfer interaction acts as the orientational forces.[2–5)] Park *et al.* examined nematic phase→isotropic liquid transition temperature ($T_{NI}$) in the binary system of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) and 4-cyano-4′-pentylbiphenyl (CPB), because there was a weak charge-transfer interaction between a donor of MBBA and an acceptor of CPB.[2)] In this case, although both components of MBBA and CPB exhibit nematic phase→isotropic liquid phase transition, the relation of $T_{NI}$ to the composition of MBBA–CPB mixture shows a broad curve whose maximum is located near 1 : 1 mole ratio, and $T_{NI}$ of mixture is higher than the straight line joining $T_{NI}$ of the two components. In order to understand the thermodynamic properties of the nematic phase, we applied a modified solid-solution model to the binary mixture of electron donor and acceptor, and explained well the relation of $T_{NI}$ to composition.[5)]

In binary mixture of donor and acceptor, even if the components show no liquid crystalline state, they may be considered to be potentially mesomorphic. Then, there is a possibility of induction of mesophase if those components are mixed. This was achieved by Araya and Matsunaga,[3)] who observed nematic phase in the binary mixtures of potentially-mesomorphic electron donors and acceptors of the type *N*-(*p*-X-benzylidene)-*p*-Y-aniline. It acts as a donor if X or Y is dimethylamino group, and as an acceptor if X or Y is nitro group. The remaining substituents are methoxy, ethoxy or propoxy groups. For the binary systems of ethoxy derivatives, the experimental relations of $T_{NI}$ to composition are given in Fig. 2 of Ref. 3, where nematic liquid crystals are stable in the hatched areas. In the present paper, for purposes of comparison with theoretical results, the $T_{NI}$ *versus* composition curves of those combinations are reproduced in Fig. 1, where curves (a) show the experimental relation. It is to be noted that the relationship also shows a broad curve whose maximum is located near 1 : 1 mole ratio.

Let us consider these experimental results on the basis of our previous theoretical approach of binary solid-

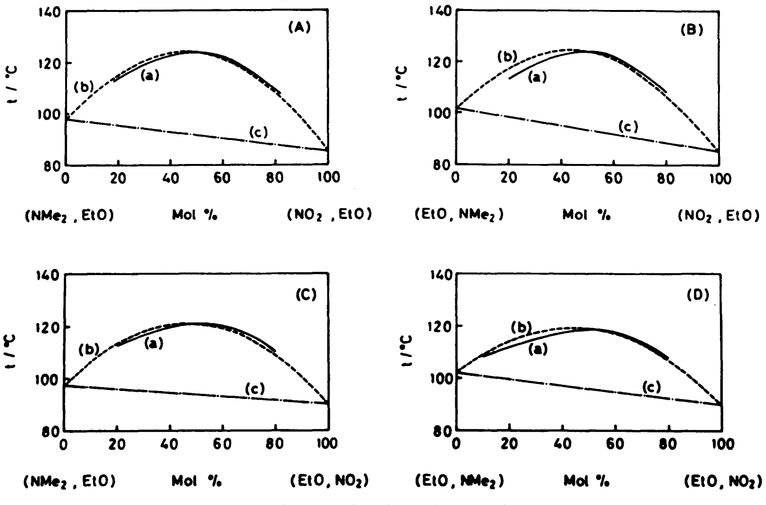

Fig. 1. Nematic phase→isotropic liquid transition temperature ($T_{NI}$) in the binary mixtures of *N*-(*p*-X-benzylidene)-*p*-Y-anilines, where the compounds are indicated by (X, Y). Curves (a) show experimental relation of $T_{NI}$ to composition as reported by Araya and Matsunaga;[3)] curves (b), theoretical relation of transition temperature ($T_c$) of order-disorder phase transition to composition as given by our modified solid-solution model; curves (c), straight lines joining $T_{NI}$ of the two components. For further details, see text.

solution model. We examine binary mixtures of electron donor and acceptor, where donor is (X, Y) = ($NMe_2$, EtO) or (EtO, $NMe_2$), and where acceptor is ($NO_2$, EtO) or (EtO, $NO_2$). The mole fractions of donor and acceptor are $x_D$ and $x_A$, respectively, where $x_D+x_A=1$. The model assumes that each of the components has nematic phase→isotropic liquid phase transition. In our compounds, however, each of the donor and acceptor shows no apparent nematic phase, but is considered to be potentially nematic. Araya and Matsunaga estimated the latent $T_{NI}$ of the components as 97.5 °C for ($NMe_2$, EtO), 102 °C for (EtO, $NMe_2$), 85 °C for ($NO_2$, EtO) and 90 °C for (EtO, $NO_2$).[3] Let us denote the latent $T_{NI}$ of pure donor or acceptor as $T_D$ or $T_A$, respectively. Our model also assumes that the nematic phase of binary mixture is taken as three dimensional lattice, which is divided into two sublattices D and A, and the effect of mixing of donor and acceptor was only discussed.[5] For mixture with composition ($x_D \geq x_A$), when all acceptor molecules occupy sites of A sublattice, the system is called in order state. When donor and acceptor molecules occupy sites of D and A sublattices randomly, it is in disorder state. The situation is similar in the case of the composition ($x_D \leq x_A$). Then, if the charge-transfer interaction between donor and acceptor is essential for parallel molecular arrangement to induce nematic phase, the order→disorder phase transition with respect to mixing of donors and acceptors should correspond to nematic→isotropic phase transition. In other words, if the order of molecular arrangement of donors and acceptors remains, the system is supposed to be in nematic phase, while if the order is lost, it goes to isotropic liquid.

According to our previous study,[5] the temperature at which the order→disorder phase transition of such a binary system occurs is given by $T_C=x_DT_D+x_AT_A+4x_Dx_AT_C°$, where $T_C°=zv/2k$. Here, it is assumed that one site of D or A sublattice is surrounded by $z$ equivalent nearest neighbor sites of A or D sublattice, respectively, and $v$ is given by $v=(1/2)(v_{DD}+v_{AA})-v_{DA}$. The terms $v_{DD}$, $v_{AA}$, and $v_{DA}$ indicate the energies between a pair of donor-donor, acceptor-acceptor and donor-acceptor molecules in nearest neighbor sites, respectively. Note that $v_{DD}$ and $v_{AA}$ arise from weakly attractive van der Waals forces between the same kind of molecules, while $v_{DA}$ comes from rather strongly attractive forces due to the charge-transfer interaction between donor and acceptor. When the charge-transfer interaction is strong enough, we have $|v_{DA}| \gg (1/2)(|v_{DD}|+|v_{AA}|)$ and $v \approx -v_{DA} > 0$. In this case, $T_C°=zv/2k(>0)$ increases considerably, and the relation of $T_C$ to composition shows a broad curve whose maximum is located near 1 : 1 mole ratio. If the order→disorder phase transition corresponds to the nematic phase→isotropic liquid transition, we can observe considerable induction of the nematic phase upon mixing donors and acceptors. On the other hand, when the charge-transfer interaction is so small as $v_{DA} \approx (1/2)(v_{DD}+v_{AA})$, we have $v \approx 0$, $T_C° \approx 0$ and $T_C=x_DT_D+x_AT_A$. Then, $T_C$ *versus* composition is simply a straight line joining $T_D$ at $x_D=1$ and $T_A$ at $x_A=1$, and no stability enhancement of the nematic phase occurs.

In the following, we discuss how the relation of $T_C$ to composition agrees with the observed $T_{NI}$ *versus* composition curve. For example, we take the binary system of ($NMe_2$, EtO) donor and ($NO_2$, EtO) acceptor. The experimental relation between $T_{NI}$ and composition is given by curve (a) of Fig. 1 (A). Here, curve (c) shows $x_DT_D+x_AT_A$, a straight line connecting $T_D$=97.5 °C and $T_A$=85 °C. Curve (b) represents $T_C=x_DT_D+x_AT_A+4x_Dx_AT_C°$ with parameter value of $T_C°$=32 °C, which was chosen so as to obtain best fit between $T_{NI}$ and $T_C$. Agreement between the curvatures of (a) and (b) is fairly good. The maximum value of $T_{NI}$ occurs at $x_D$=0.50, while that of $T_C$, at $x_D$=0.45. This agreement is also satisfactory. In view of these results, the relation of $T_C$ to composition corresponds well to that of $T_{NI}$ to composition, and we can conclude that the charge-transfer interaction is essential for parallel molecular arrangement to induce nematic phase. From the estimated value of $T_C°$, $zv$ is calculated as 0.53 kJ mol$^{-1}$.

In a similar way, the combination of the donor (EtO, $NMe_2$) with the acceptor ($NO_2$, EtO) gave values of $T_C°$=31 °C and $zv$=0.52 kJ mol$^{-1}$; the combination of ($NMe_2$, EtO) with (EtO, $NO_2$), $T_C°$=27 °C and $zv$=0.45 kJ mol$^{-1}$; the combination of (EtO, $NMe_2$) with (EtO, $NO_2$), $T_C°$=23 °C and $zv$=0.38 kJ mol$^{-1}$. For these systems, the relations of $T_C$ to composition are compared with the experimental relations of $T_{NI}$ to composition in Figs. 1 (B)—(D). In each case, the agreement between the two relations is satisfactory. Since the charge-transfer interaction is considerably strong, it appears that $|v_{DA}| \gg (1/2)(|v_{DD}|+|v_{AA}|)$ and that $zv_{DA} \approx -zv$ in each case. In order to estimate the $v_{DA}$ value, it is necessary to determine the $z$ value, but no further information has yet been obtained in the nematic phase of such binary mixtures.

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