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Elevations of Nematic-Isotropic Transition Temperature and Dichroic Ratio of Nonmesomorphic Guest-Nematic Host System with Increasing Guest Concentration

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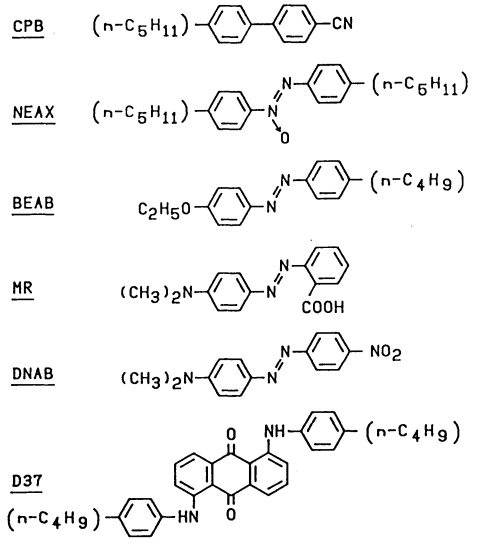
The nematic-isotropic transition temperature of 4-cyano-4'-pentylbiphenyl (host) has been elevated by admixture of 1,5-di-(p-n-butylanilino)-anthraquinone (guest), the elevation being as much as 2.1 °C for 1 mol% guest concentration (β=-0.689). This phenomenon has been considered to be attributable to the guest-host interaction which must be at least attractive and, in addition, of "many-body" type.

The high nematic-isotropic transition temperature (Tni) of nematic host and the large dichroic ratio, i.e., the high contrast of guest are practically needed for the guest-host display. Apart from these practical points of view, the phase transition behavior of guest-host or binary systems has been investigated from academic viewpoints.[1-8] Especially, theoretical studies on the phase transition of liquid crystal mixtures of rod-like and plate-like molecules have been performed, yielding an interesting result that the introduction of a plate-like guest increases Tni of the rod-like nematic host.[3-5] The purpose of the present letter is to report on the elevation of Tni of 4-cyano-4'-pentylbiphenyl (CPB, host) and increase in dichroic ratio with increasing concentration of 1,5-di-(p-n-butylanilino)-anthraquinone (D37, guest).



The samples used are CPB, NEAX (4,4'-dipentylazoxybenzene) and BEAB (4-ethoxy-4'-butylazobenzene) for nematic hosts and D37, MR (4-dimethylamino-2'-carboxylazobenzene) and DNAB (4-dimethylamino-4'-nitroazobenzene) for nonmesomorphic guests, and they are all obtained commercially. The sandwich cell was made by two borosilicate glass plates coated with PVA

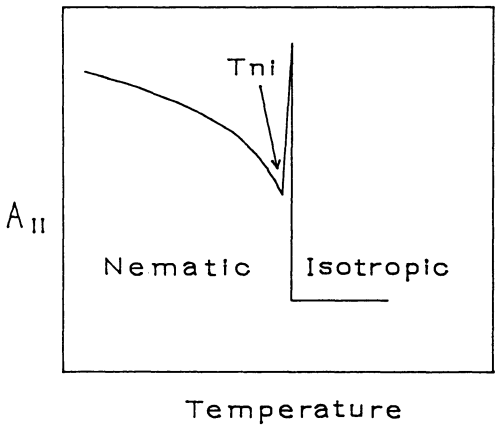


Fig. 1. Temperature dependence of $A_{\parallel}$ in the neighborhood of Tni.

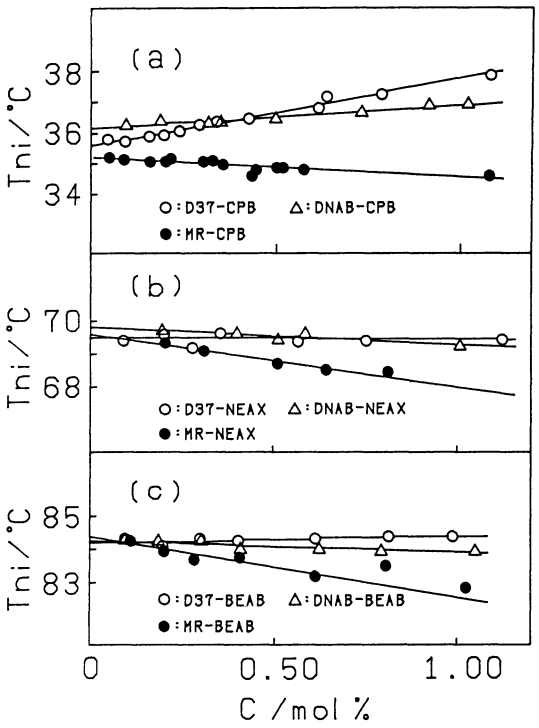


Fig.2. The dependences of Tni on guest concentrations, the host being CPB(a), NEAX(b), and BEAB(c).

which were rubbed to attain the homogeneous alignment of the host. The dichroic ratio (Rd) is defined as $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are absorbances for the light beams polarized parallel to and perpendicular to the rubbing direction, respectively. We have determined Tni availing of the light-scattering phenomenon which causes a sudden increase of $A_{\parallel}$ at Tni in the course of raising the temperature, as illustrated in Fig. 1.

In Fig. 2, Tni values were plotted against the guest concentrations when CPB(a), NEAX(b), and BEAB(c) were used as hosts. Our main interest is concerned with the result for the D37-CPB system, in which Tni of CPB is elevated with an increase in concentration of D37, the elevation being as much as 2.1 °C for 1 mol% D37 concentration. As quantitative measures of degrees of changes in Tni, β values[9] (=-dTni*/dx, where Tni* and x are the reduced temperature and the mole fraction of guest, respectively) are evaluated and listed in Table 1. A negative (positive) value of β means a rise (fall) in Tni and the magnitude of the absolute value of β is in proportion to that of the change in Tni. Elevations of Tni of the nematic liquid crystal (host) on being mixed with the guest were also observed in the DNAB-CPB and D37-BEAB guest-host systems, but their magnitudes are far smaller than that observed in the D37-CPB system (Table 1). Table 1 shows that most guest-host systems have exhibited, as usual, depressions of Tni when hosts are mixed with guests. Usually, an addition of the perturbing nonmesomorphic solutes to the nematogenic solvents leads to the depression of Tni.[10,11] The elevation of Tni in binary mixtures of nonmesomorphic guests and nematogenic hosts will be observed only when the nematic phase is stabilized by an increased orientation-order of nematic molecules which is induced by guest molecules. The orientation-order of nematic host molecules may be increased when one guest molecule interacts attractively with two or more host molecules simultaneously.

In Fig. 3, the Rd values for all guests measured at the peak of the first

Table 1. The values of β for various guest-host systems

Host	CPB			NEAX			BEAB		
Guest	MR	DNAB	D37	MR	DNAB	D37	MR	DNAB	D37
β	0.232	-0.276	-0.689	0.385	0.114	0.030	0.390	0.135	-0.033

band were plotted against temperature when NEAX and CPB were used as hosts, respectively. As seen from these two figures, in case of NEAX the Rd values for the three guests increase in the order of DNAB>D37>MR (Fig. 3a), while in CPB, D37>DNAB>MR (Fig. 3b). The reverse in the order of DNAB and D37 on changing the host may be due to the following reason: Rd values for D37 decrease only slightly on going from the host NEAX to CPB while Rd values for DNAB and MR decrease largely. The orientation of guest molecules is induced by that of nematic host and the optical anisotropy such as Rd value of the guest indicates the degree of the induced orientation. The differences of the Rd values of different guests incorporated in the same host are considered to represent the differences in orientational response of the guests to the orientation of the host. Thus, we have interpreted the above observation as that D37 responds efficiently to the orientation of CPB, although CPB is inferior to NEAX in an ability of inducing the orientation of the guest presumably due to that the orientation-order of CPB is lower than that of NEAX. The efficient orientational response of D37 to the orientation of CPB implies that there is some special attraction between D37 and CPB, as is also demonstrated below.

Figure 4 shows the Rd vs. temperature curves for various guest concentrations in the D37-CPB and DNAB-CPB systems, the guests (D37 and DNAB) raising Tni of the guest-host systems. It is worth noting that the D37-CPB system shows an increase in Rd value with an increase in the guest (D37) concentration in contrast to that the DNAB-CPB system shows no such an increase. It will be rather natural to

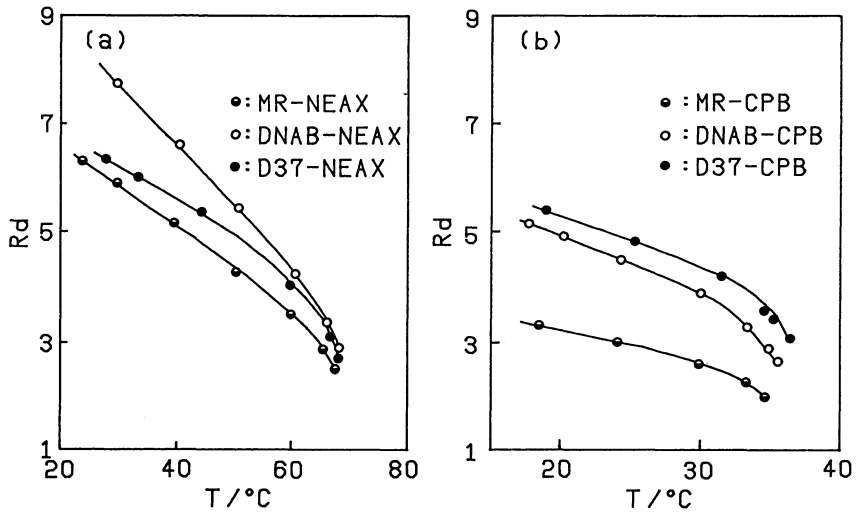


Fig.3. Rd vs. temperature curves for guest-host systems, the host being NEAX(a) and CPB(b).

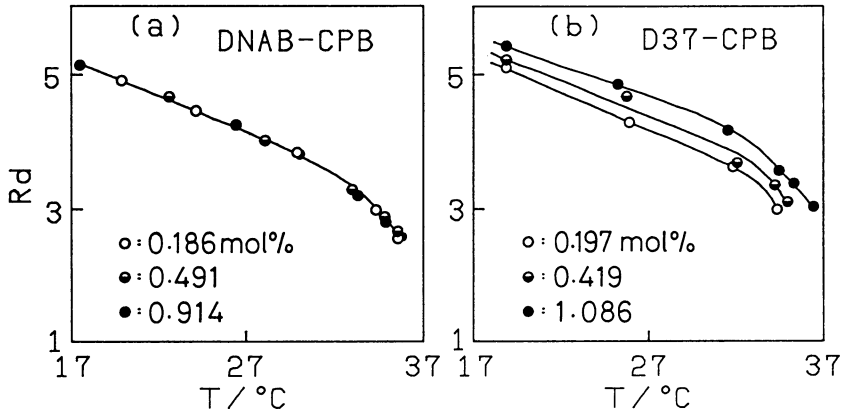


Fig.4. Rd vs. temperature curves for various guest concentrations, (a):DNAB-CPB system, (b):D37-CPB system.

expect that the Rd value is, as in the DNAB-CPB system, constant irrespective of guest concentration if the attractive interaction between guest and host is of "two-body" type and only operates within single guest-host pair. If the attractive interaction concerned is of "many-body" type, i.e., if one guest molecule interact attractively with two or more host molecules simultaneously, the "many-body" attractive interactions just mentioned can be "cooperative" in inducing an increase in the orientation-order of the guest molecule. This "cooperative" effect may become more effective on increasing guest concentration, resulting the increase in Rd value with the increase in guest concentration as observed in Fig. 4b. In the next full paper, we will report on Tni of the guest-host systems in which the host is CPB and the guests are several anthraquinone derivatives having simple substituents and analyze the nature of the attractive guest-host interactions in those systems.

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