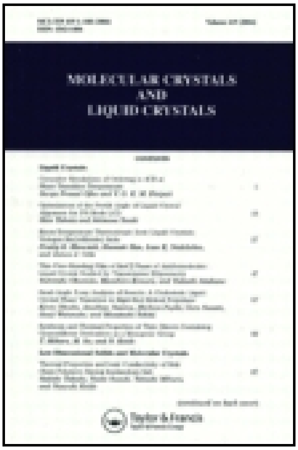

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Orientations of 1, 2-Dibromoethylene in Various Nematic Liquid Crystals

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ORIENTATIONS OF 1,2-DIBROMOETHYLENE IN VARIOUS NEMATIC LIQUID CRYSTALS

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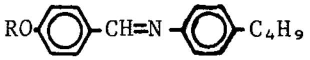
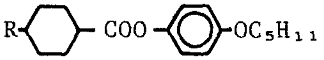
The liquid crystals give generally wide-line NMR spectra, showing little or no fine detail. This is due to the large number of protons in the molecule, resulting in a very large number of overlapping of peaks, and thus unresolved peaks. Both ^{1}H-NMR and ESR method for small amounts of a probe molecule added to a liquid crystal have been used to study orderings and phase transitions in liquid crystals.[1-6] In the case of the probe molecule is chosen to contain very few protons, its ^{1}H-NMR spectrum will consist of only a few narrow peaks. One of the most useful aspects of the probe spectra is that they provide a sensitive measure of the relative degree of orientation of liquid crystal.

This work consists essentially of a study on the behaviour of the ^{1}H-NMR(100MHz) spectra of 1,2-dibromoethylene in a number of liquid crystals, as a function of temperature. The formulae and the phase transition temperatures of all liquid crystals studied are shown in Table 1. A mixture of *cis* and *trans* forms of 1,2-dibromoethylene(DBE) was used. The ratio of *cis*- and *trans*-DBE was found to be 60:40 by gas chromatography through measured temperature range. In all samples, the total mole fraction of the solute(X) was held constant at 0.08.

Figure 1 shows ^{1}H-NMR spectra in each phase of CH3/DBE system at several temperatures. The spectra in solid/isotrop-

TABLE 1. List of the liquid crystalline compounds used.

Name and Formula	R	Nematic Range/°C	Abbreviation
 N-(*p*-alkoxybenzylidene)-*p*-butylaniline	C_2H_5	37-80	EBBA
	C_3H_7	41.1-55.7	PBBA
	C_4H_9	45.7-74.7	BBBA
 4'-pentyloxyphenyl *trans*-4-alkylcyclohexanecarboxylate	C_3H_7	37.3-66.2	CH3
	C_4H_9	29.5-66.5	CH4
	C_5H_{11}	34.1-75.9	CH5

ic(S/I) phase of the CH3/DBE system showed progressive increase in molecular mobility with increasing temperature. In the nematic(N) and solid/nematic(S/N) phases, the four signals due to oriented *cis*- and *trans*-DBE were observed on the broad background of CH3. Two doublet signals in inside and outside have been assigned to the protons of *trans*- and *cis*-DBE, respectively, by considering the chemical shifts and the strength of each signal. In the S/N phase, the four signals due to oriented probe molecule are broader than those in nematic phase. At 55°C, this mixture system changes to the nematic/isotropic(N/I) coexisting phase, and the spectrum becomes complex due to the appearance of signals from the isotropic part of the solvent. Figure 1(e) shows the relatively highly resolved spectrum above the clearing point of solution. Similar changes in the spectrum on warming have been also observed in all other systems.

We will discuss the temperature dependence of the order parameter for *cis*- and *trans*-DBE in these systems. The direct coupling D_{HH} was estimated from the splitting($\Delta\nu$) of each doublet signal for *cis*- and *trans*-DBE. Thus, the values

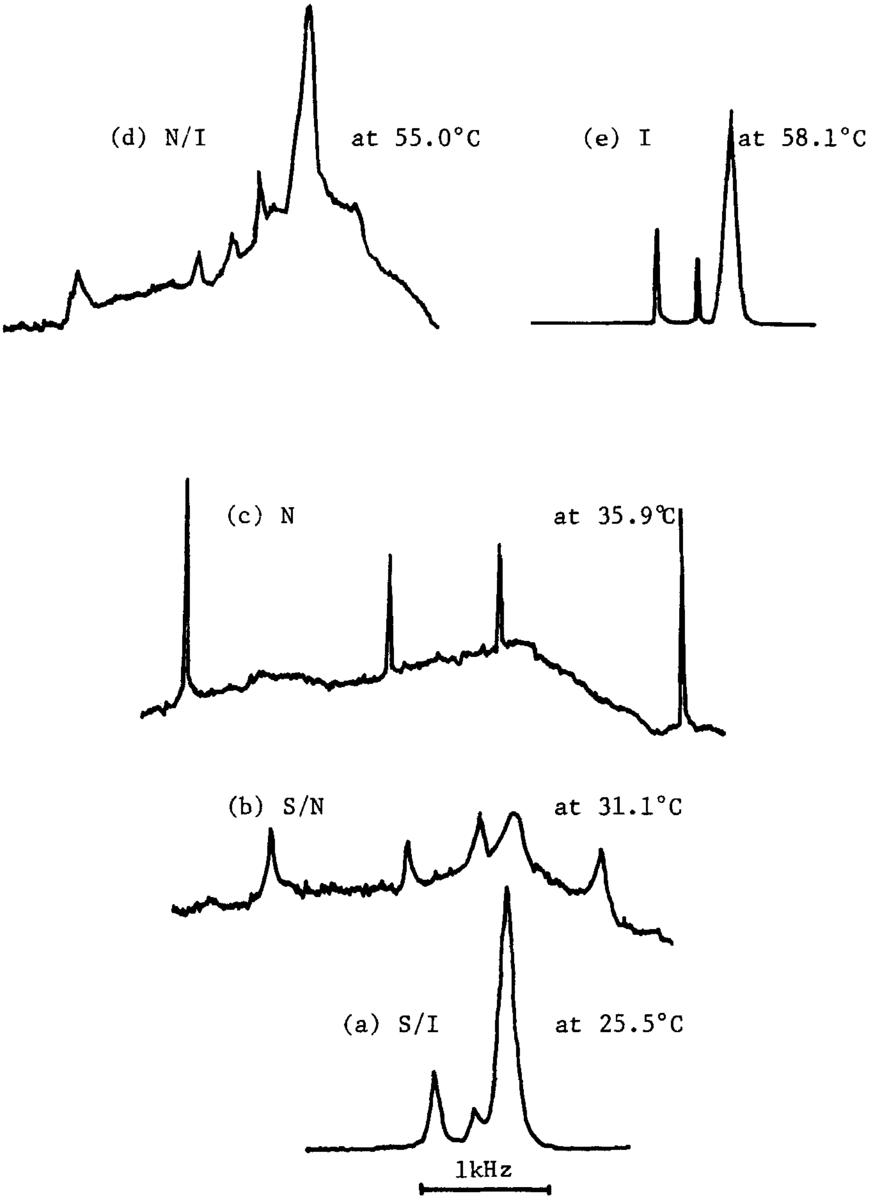


FIGURE 1. ^{1}H-NMR spectra in each phase of CH3/DBE system.

of the order parameter for *cis* and *trans* forms were determined separately. The order parameter is derived from the following equations.

$$\Delta\nu = 3|D_{HH}|$$

$$S = \frac{h\gamma^2}{4\pi^2 r^3} D_{HH}$$

where γ is the gyromagnetic ratio of proton, r is the interproton distance(*cis*-DBE; r=2.44A, *trans*-DBE; r=2.98A), and h is the Planck's constant. The sign of the S value can be determined from spectral analysis of a ^{13}C-enriched sample of the solute, but only the absolute value of the order parameter, $|S|$, is discussed in this paper. Figure 2(a) shows the temperature dependence of the $|S|$ values for *cis*- and *trans*-DBE in CH3. In the S/N phase, the $|S|$ values increase with increasing temperature. At around S/N-N transition temperature, the order parameter has the maximum value. We have previously reported the complete phase diagram of EBBA/DBE system.[6] As shown in the phase diagram, the mole fraction of added solute in the nematic part of S/N phase decreases rapidly with increasing temperature. Consequently, the extent of alignment of a liquid crystal would increase with decreasing the mole fraction of solute.

The decrease in the $|S|$ value on warming of the nematic phase is typical for this phase. The $|S|$ value for *cis*-DBE decreases more rapidly with increasing temperature as compared with those for *trans*-DBE. However, it can be seen from Figure 3 that although the magnitudes of the $|S|$ values for those solutes are quite different, the relative $|S|$ values decrease more or less in the same manner. This indicates that the relative temperature dependence of the order parameter of the solute depends only upon the solvent liquid crys-

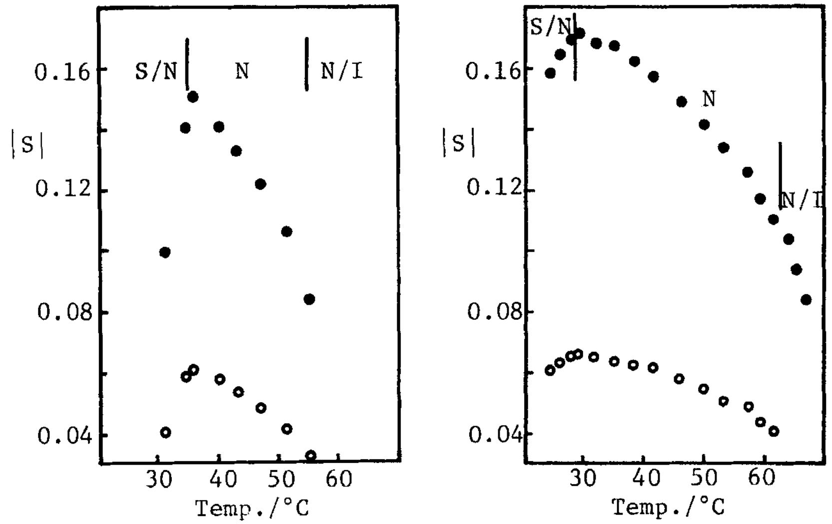


FIGURE 2. Temperature dependence of the |S| values for *cis*-DBE and *trans*-DBE in liquid crystal. (a) CH3/DBE, (b) CH5/DBE; ● *cis*-DBE, ○ *trans*-DBE

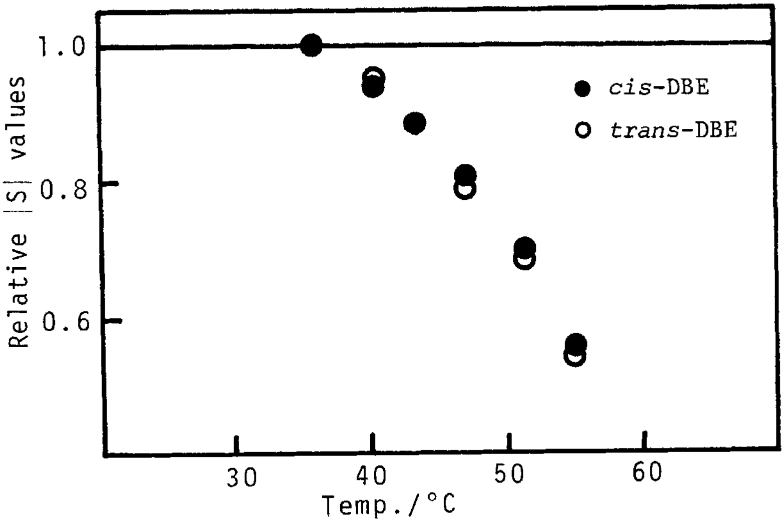


FIGURE 3. Temperature dependence of the relative |S| values for *cis*-DBE and *trans*-DBE in CH3.

tal. The relative |S| value here is the ratio of a |S| value to the one measured at the lowest temperature in the nematic region. Similar temperature dependences of the relative |S| values are also obtained for the other compounds studied.

We have previously reported that the |S| value of *cis*-DBE in EBBA/DBE systems at X=0.15 and 0.27 did not change with temperature in N/I phase.[6] However, as shown in Figure 2, the temperature dependences of the |S| value for CH5/DBE and BBBA/DBE systems are different from the previous results. The order parameter of these two systems changed continuously on going from the nematic to N/I phase.

Chen and Luckhurst using the ESR method have studied the degree of alignment of a paramagnetic probe, vanadyl acetylacetonate, in mixtures of n-azoxyanisole with various non-mesomorphic solutes, and reported that a plot of the degree of alignment θ_{33} against the reduced temperature T* produces a common curve for a wide range of solutes and concentrations.[3] They have suggested that the single curve in the reduced temeprature plot supports the notion that the alignment of the solute is a property of the mixture, and not of the solute alone. Based on their results, the differences of the orientation among liquid crystals used are discussed by the reduced temperature dependences of the order parameter for *cis*- and *trans*-DBE in each system. Plots of the |S| value against the reduced temperature are given in Figures 4 and 5, where $T^*=T/T_{N-N/I}$, T* being the reduced temperature and $T_{N-N/I}$ the nematic to nematic/isotropic transition temperature of the mixture. As shown in Figures 4 and 5, the reduced temperature dependences of the |S| values of *cis*- and *trans*-DBE are quite different. The reduced temperature plots of *trans*-DBE in each system exhibit clearly two curves which approach each other gradually with increasing T*.

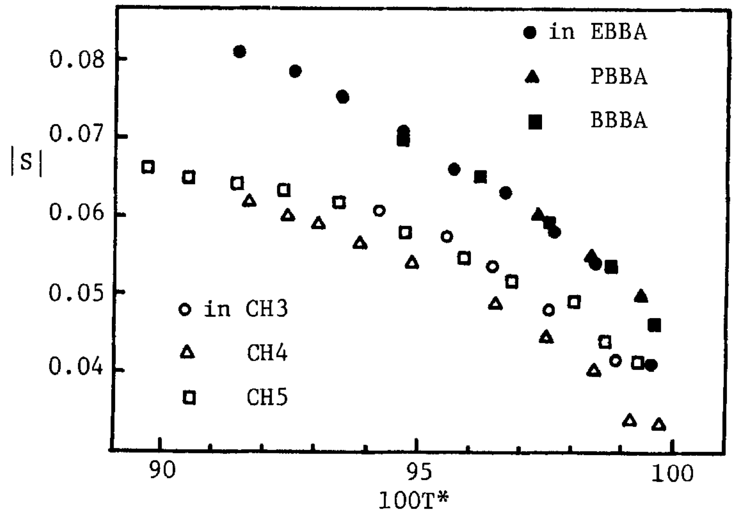


FIGURE 4. Plots of the |S| value for *trans*-DBE against the reduced temperature.

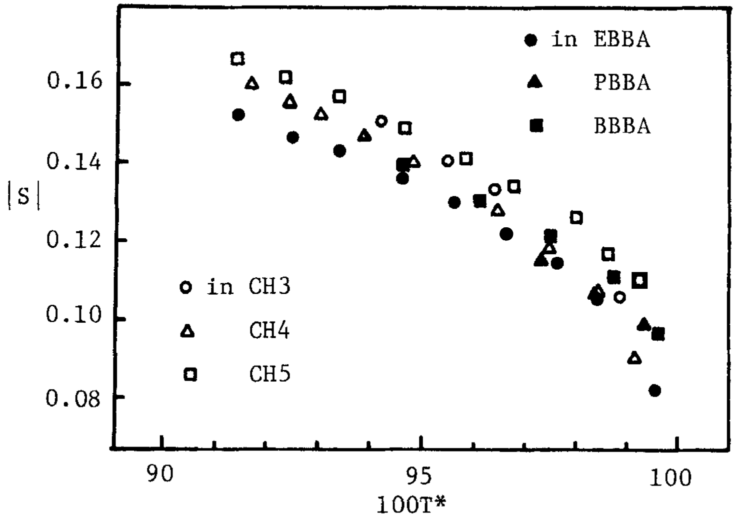


FIGURE 5. Plots of the |S| value for *cis*-DBE against the reduced temperature.

In the figure, the lower and upper lines result from CH3, CH4, CH5/DBE systems and EBBA, PBBA, BBBA/DBE systems, respectively. The $|S|$ value of *trans*-DBE in each homologous series increases in the same manner with decreasing the reduced temperature.

Two curves in the reduced temperature plots of the $|S|$ value of *trans*-DBE are very interesting result. On the other hand, plots of the $|S|$ value of *cis*-DBE in each system against T^* seem to lie on a common curve although the plots show some scatter from system to system. In such mixture systems, the liquid crystal-liquid crystal and the liquid crystal-solute interactions play an important role for the phase transition behaviour; therefore, these interactions may be correlated to the above reduced temperature dependence.

References

1. P.Diehl and C.L.Khetrapal, Mol. Phys.,14,283(1967)
2. G.Englert, A.Saupe, and J.P.Weber, Z. Naturforsch.,23a, 152(1968)
3. D.H.Chen and G.R.Luckhurst, Trans. Faraday Soc.,65,656 (1969)
4. Z.Luz and S.Meiboom, J. Chem. Phys.,59,275(1973)
5. D.F.Hillenbrand and H.Yu, J. Chem. Phys.,67,957(1977)
6. K.Fujimura, S.Mita, S.Kondo, and M.Takeda, Mol. Cryst. Liq. Cryst.,54,191(1979)