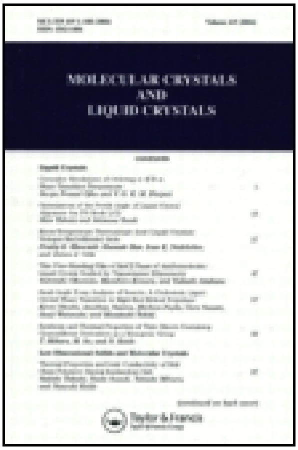

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Dielectric Measurements of Guest-Host Systems

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Dielectric Measurements of Guest-Host Systems

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Dielectric investigations on azo dye–5CB mixtures in the nematic and isotropic phases were carried out. The addition of the dye to the liquid crystal changes the values of the dielectric constants as well as the dielectric anisotropy, however the variations of the permittivity versus temperature and frequency are of the same type for both of the dye–5CB mixtures and the pure nematic host. It was found that the dyes having $-NO_2$ as the end group particularly influence the dielectric properties of the liquid crystal. The height of the potential barrier which hinders the rotation of the liquid crystal molecules in the nematic state and the order parameter of the host in the presence of a dye were estimated from the relaxation times in the nematic and isotropic phases.

Keywords: guest-host mixtures, azo-dyes, dielectric permittivity, order parameter

INTRODUCTION

Dielectric studies of nematic liquid crystals have been proved to be a valuable source of information on molecular arrangement and molecular motion as well as on specific intermolecular interactions in the nematic and isotropic phases. Therefore the dielectric properties of a number of nematic liquid crystals have been investigated both experimentally[1] and theoretically.[2–5] However, despite the fairly extensive literature available on the permittivity of pure liquid crystals, there is a little information relating the dielectric measurements of the dye–liquid crystal mixtures (guest-host systems).[6]

It is well known that the presence of a guest dye in a nematic liquid crystal changes the range of the nematic phase, causing either a decrease or an increase of the nematic–isotropic transition temperature t_{NI}[7–12] as well as a decrease of the melting point t_{CN}.[11,12] The influence of a dye on the host order parameter has also been observed.[10,12] It was recently[11,12] found that the order parameter of a guest dissolved in a liquid crystalline matrix depends strongly on the guest concentration

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too. Moreover the investigations of the "guest-host" effect are at present very extensive, especially about the nature of the intermolecular interaction.[7,12,13]

In this paper we studied the influence of the azo dyes on the dielectric properties of the nematic liquid crystal in order to obtain more information about specific intermolecular interactions between liquid crystal and guest molecules. Because the electro-optical parameters of the display depend considerably on the values of the dielectric constants and the anisotropy of the permittivity, the knowledge of the dielectric properties of the dye–liquid crystal mixtures has technical significance in guest-host display devices.

EXPERIMENTAL

The commercial liquid crystal 5CB-4-pentyl-4′-cyanobiphenyl (K15, according to BDH) was used without further purification as a host. This liquid crystal was chosen because its relatively high dielectric anisotropy in the oriented state makes it particularly suitable for dielectric studies. Moreover, 5CB possesses a high degree of chemical stability by exposure to air or static electric fields.

In order to study the influence of a guest on the dielectric properties of liquid crystal, several azo dyes with various molecular sizes and shapes were used. Table I presents the molecular structure of the investigated dyes (numeration of the dyes is according to Reference 12). The dye I (D2) was obtained from BDH, all the other dyes were synthesized and chromatographically purified in the Institute of Dyes of Łódź Technical University (Poland). The measurements were done at the concentration of the guest as high as possible considering solubility ($7 \cdot 10^{-3}$ mol/l – $1.5 \cdot 10^{-1}$ mol/l which corresponds to 0.25–5% wt).

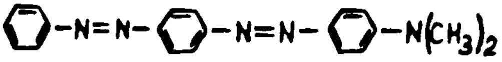
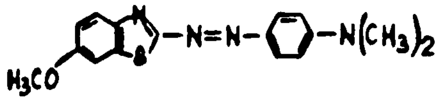
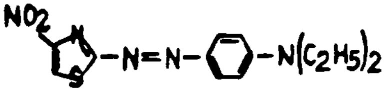
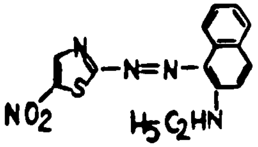
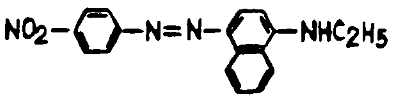
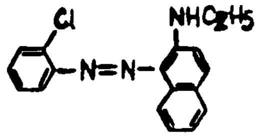
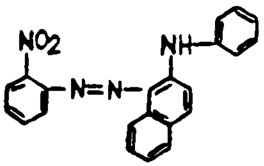
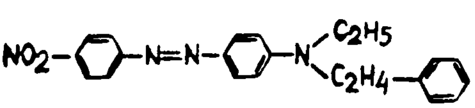
The order parameter of the nematic host $\langle P_2 \rangle_H$ was extracted from the refractive indices measured as a function of temperature using a Leitz-Jelley microrefractometer. The measurements were made at sodium D light. In order to extract the $\langle P_2 \rangle_H$ from refractive index data the Vuks approximation[14,15] and a method proposed by Haller *et al.*[16] were applied. The error of the n values was assigned to ± 0.004.

The order parameter of the guest dissolved in 5CB, $\langle P_2 \rangle_G$ was determined on the basis of the polarized absorption spectra, recorded by means of a Cary-17 spectrophotometer equipped with polarizers. The measurements were made in oriented "sandwich" cells of 7.5 μm thickness. The planar orientation of the liquid crystal phase was achieved by using a polyimide coated glass plate and by an additional rubbing process.

Two components of the dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ in the range of 1 kHz to 10 MHz were measured by means of a Hewlett-Packard 4192 A automatic balance bridge. The measurement cell was a shielded parallel plate condensor with 75 μm captor spacer, which was calibrated by measuring the capacitance of toluene. In order to obtain the values of the permittivity components of the aligned liquid crystals, the cell was placed in an electromagnet first in a position where the magnetic field **H** was parallel to the electric field **E** ($\varepsilon_\parallel$) and then rotated so that **E** and **H** were orthogonal ($\varepsilon_\perp$). It was estimated that the overall uncertainty in ε' was 1% and lower than 5% in ε''. The data were corrected for the static conductivity

TABLE I

Molecular structure of the dyes used

No[a]	Molecular structure
I	
III	
V	
VI	
VII	
IX	
X	
XI	

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[a] According to [12].

and for the high-frequency deviations caused by the inductance and resistance of the cables and connectors. The sample temperature was stable within ±0.25°.

RESULTS AND DISCUSSION

I. Dielectric permittivity in static fields.

Table II presents the dielectric constants and the anisotropy of the permittivity for pure 5CB and all the guest-host mixtures investigated at the frequency $\nu = 1.5$ kHz and at the reduced temperature $T^* = 0.977$. The dielectric constants, measured versus temperature for the nematic ($\varepsilon_\parallel$, $\varepsilon_\perp$) and isotropic (ε_{iso}) phases of pure 5CB and 5CB admixed with dyes I and IX, are presented as an example in Figure 1. The reduced temperature is defined as follows:

$$T^* = \frac{T}{T_{NI}} \tag{1}$$

where T_{NI} is the clearing point either for the pure liquid crystal or for the dye–liquid crystal mixture and T is the given temperature (in K).

Similar results as in Figure 1 for the temperature dependence of the dielectric constants of pure 5CB were previously obtained by other authors.[17-19] However, as it follows from Figure 1 and Table II the addition of the dye to the liquid crystal matrix changes the values of the dielectric permittivity and the dielectric anisotropy as well. Dye I as an example shows that the differences, especially in the vicinity of the nematic–isotropic transition can be distinct. Similar effects were previously obtained under the investigation of the temperature dependence of the order parameter.[12,20]

In order to compare the dielectric data with the molecular orientational order in the dye–liquid crystal mixtures the values of the host $\langle P_2 \rangle_H$ and guest $\langle P_2 \rangle_G$ order parameters are gathered in Table III. In this table the nematic–isotropic transition temperature t_{NI} from Reference 12 are also listed. The host order parameter $\langle P_2 \rangle_H$

TABLE II

Dielectric permittivity and dielectric anisotropy of the investigated dye–5CB mixtures ($T^* = 0.977$, $\nu = 1.5$ kHz)

No. of dye, concentration [mol/l]	$\varepsilon_\parallel$	$\varepsilon_\perp$	$\Delta\varepsilon$	ε_{iso}
Pure 5CB	17.35	6.94	10.41	11.12
I, $4.5 \cdot 10^{-2}$	17.92	6.62	11.30	11.10
III, $9.2 \cdot 10^{-2}$	17.60	6.95	10.65	11.22
V , $9.9 \cdot 10^{-2}$	18.05	7.03	11.02	11.46
VI , $4.8 \cdot 10^{-2}$	18.16	7.08	11.08	11.50
VII, $9.3 \cdot 10^{-2}$	18.37	7.67	10.70	11.71
IX, $16.5 \cdot 10^{-2}$	16.80	7.25	9.55	11.08
X, $13.6 \cdot 10^{-2}$	17.23	7.54	9.69	11.18
XI , $5.4 \cdot 10^{-2}$	18.20	7.30	10.90	11.56

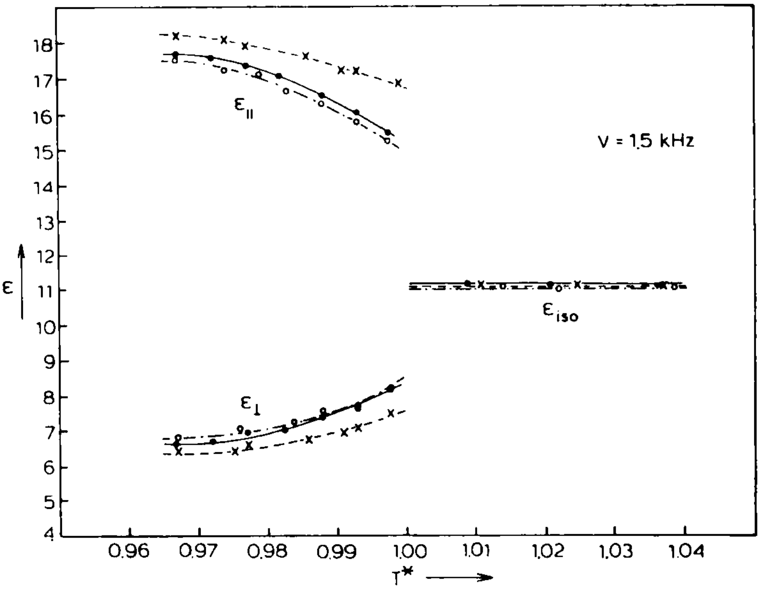

FIGURE 1 Temperature dependence of dielectric permittivity for: 5CB (———), dye I in 5CB, $c = 4.5\ 10^{-2}$ mol/l (– – – – –) and dye IX in 5CB, $c = 16.5\ 10^{-2}$ mol/l (– · – · – ·).

could be obtain only for some dye–liquid crystal mixtures. In other cases absorbing the sodium light by the dye made the measurements impossible.

The results presented in Tables II and III can be interpreted as showing that there is some weak correlation between the dielectric anisotropy constants, $\Delta\varepsilon$ and the order parameters: those dyes which increase the degree of the ordering cause also the rise of the $\varepsilon_\parallel$ and $\Delta\varepsilon$ (for example dyes I and III). However, in the case of the dyes which show lower orientational order in the guest-host mixtures than pure 5CB itself the dielectric values are much different: some of the dyes decrease the $\varepsilon_\parallel$ and $\Delta\varepsilon$, as for example dyes IX and X, whereas others increase both these

TABLE III

Clearing temperature t_{NI} and the host $\langle P_2\rangle_H$ and guest $\langle P_2\rangle_G$ order parameters of dye–5CB mixtures studied (concentration of dyes in 5CB as in Table II)

No.	t_{NI} [°C]	T* = 0.977 $\langle P_2\rangle_H$	$\langle P_2\rangle_G$
Pure 5CB	35.1	0.559	—
I	37.6	0.585	0.67
III	39.0	0.566	0.57
V	34.2	—	0.45
VI	34.3	—	0.17
VII	32.9	—	0.14
IX	31.4	0.541	0.09
X	30.2	—	0.04
XI	31.7	0.525	0.33

values (dyes V, VI, VII and XI). Looking at the values of the permittivity in the isotropic state ε_{iso} (Table II) one can see that those dye–5CB mixtures, for which occur the correlation between $\Delta\varepsilon$ and $\langle P_2\rangle$, have the dielectric constant ε_{iso} similar to pure 5CB. However, in the other cases the ε_{iso} of the mixtures is always significantly greater than that of the nematic host itself. We have calculated that such large changes cannot result from the increase of the effective dipole moment of the dye–5CB mixture with respect to pure 5CB which is caused by the own dipole moment of the dye only.

II. Dimer fraction in the dye–liquid crystal mixtures.

The most general theory of the dielectric constant of polar liquids is that due to Kirkwood[21] and Fröhlich.[22] Brodewijk[23] extended this theory of anisotropic liquids. However, the interpretation of the dipole correlation in the nematic phase is very complicated, in particular in relation to the internal field. Therefore, we confine our attention to considering the isotropic case only.

It is well known that in the p-cyano substituted compounds strong anti-parallel dipole association occur. Evidence for this behavior stems from X-ray diffraction measurements,[24] NMR[25] and dielectric studies.[26–31] For the compounds with a p-cyano group the dielectric permittivity does not show the usual behavior $\varepsilon \sim \mu^2/kT$. Instead of that μ must be interpreted as an effective dipole moment μ_{eff} which can be calculated from the dielectric data using the Kirkwood-Fröhlich equation:

$$\mu_{eff}^2 = \frac{gkT\varepsilon_o}{4\pi N}\,\frac{(\varepsilon_{iso} - \varepsilon_\infty^{iso})\,(2\varepsilon_{iso} + \varepsilon_\infty^{iso})}{\varepsilon_{iso}\,(\varepsilon_\infty^{iso} + 2)^2}. \tag{2}$$

k is the Boltzmann constant, T–the absolute temperature, N–the number of molecules per unit volume, ε_o–the dielectric constant of vacuum and $\varepsilon_\infty^{iso} = 1.05 \cdot n_{iso}^2$, as many authors assume for polar systems.[29,31,32] n_{iso} is the index of refraction.

The effective dipole moment μ_{eff} may be correlated with the dipole moment of the isolated molecule μ through the correlation factor g:

$$g = (\mu_{eff}/\mu)^2. \tag{3}$$

The g factor, first introduced by Kirkwood,[21] is a measure of the short range intermolecular forces that lead to the specific dipole–dipole correlation. In the absence of such forces, g is equal to 1. According to the Kirkwood-Fröhlich theory $g > 1$ are explained due to a predominantly parallel alignment, and $g < 1$ due to an antiparallel alignment of the dipole components.

The simplest model for dipole correlation considers only pairs of the associated molecules. Therefore, the liquid phase of the 5CB may be regarded as a binary mixture of dimers and monomers. Assuming that the monomer dipole moment $\mu_M = \mu$ and the dimer dipole moment $\mu_D = 0$, one obtains[30]:

$$\mu_{eff}^2 = \mu^2 g = \frac{u^2 n_M}{N} \tag{4}$$

where N = $n_M + 2n_D$, n_M is the number of monomers and n_D the number of dimers, $n_M + n_D = n$ is the total number of particles. Let $x_M = n_M/n$ and $x_D = n_D/n$ are the monomer and dimer fractions, respectively. Then:

$$g = \frac{n_M}{n_M + 2n_D} = \frac{x_M}{x_M + 2x_D} = \frac{1 - x_D}{1 + x_D}. \tag{5}$$

Hence one finds for dimer fraction:

$$x_D = (1 - g)/(1 + g). \tag{6}$$

Table IV summarizes the correlation factors g and the values of the dimer fractions for all the investigated dye–5CB systems. The measurements were done at the temperature 3–6 degrees above the clearing point and at frequency $\nu = 1.5$ kHz. The values of the refractive index n_{iso} and dipole moment μ were assumed as 1.596 and $(15.9 \pm 0.2) \cdot 10^{-30}$ C · m,[19] respectively. The n_{iso} remains constant in all the dye–5CB solutions within experimental uncertainties.

The accuracy in the estimation of x_D was ± 0.005. Therefore, it is evident from Table IV that some dyes cause the diminishing of the dimer fraction in the investigated samples. These are the very same dyes, which do not show any correlation between $\Delta\varepsilon$ and $\langle P_2 \rangle$ (dyes V, VI, VII and XI). Looking at the molecular structure of the investigated dyes (Table I) one can assume that no steric properties of the dye molecule are responsible for the observed effects, because any changes of the dimer fraction do not occur for the dyes IX and X. However, we observed the change of the dielectric constant ε_{iso} for those dyes, which have $-NO_2$ group either in para position or 1- or 2-position to the heterocyclic sulphur atom. For one of such dyes the measurements of the concentration dependence of the dielectric constant in the isotropic phase were made. The results are shown in Figure 2. In Figure 2A the dielectric permittivity ε_{iso} as well as the dimer fraction x_D versus concentration are given, whereas Figure 2B presents the concentration variation of the correlation factor g. As it is seen from this figure the largest changes of the dielectric properties occur at the low dye concentration. A similar effect was pre-

TABLE IV

Dimer fractions of the dye–5CB mixtures

No.	ε_{iso}	g	x_D
Pure 5CB	11.12	0.475	0.356
I	11.10	0.477	0.354
III	11.22	0.481	0.350
V	11.61	0.500	0.333
VI	11.50	0.495	0.338
VII	11.71	0.507	0.337
IX	11.08	0.476	0.355
X	11.18	0.478	0.353
XI	11.56	0.499	0.335

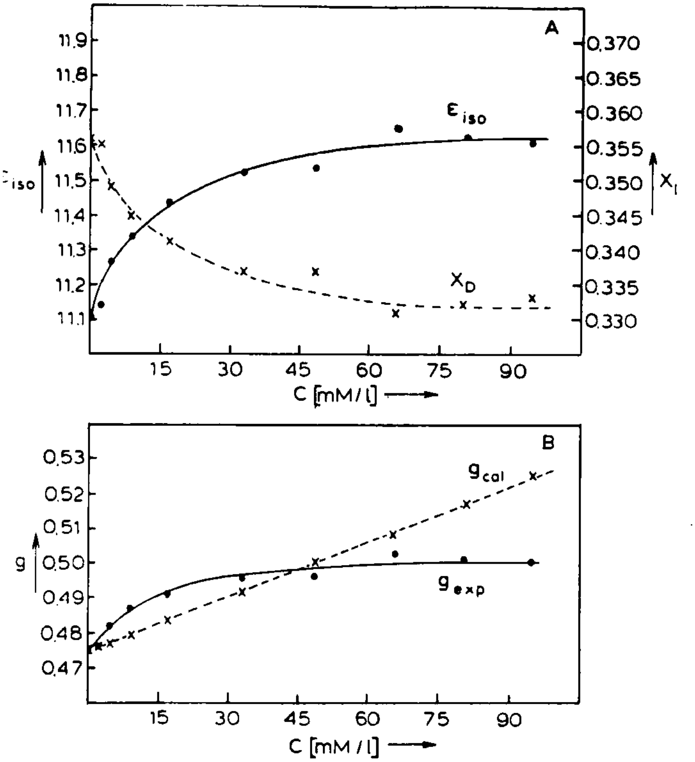

FIGURE 2 Concentration variation of: A. dielectric permittivity ε_{iso} and dimer fraction x_D. B. correlation factor g in isotropic phase for dye V in 5CB (ν = 1.5 kHz, t = 38°C).

viously observed for the concentration dependence of the order parameter measured by means of the absorption[11,12] and Raman[10] spectroscopy.

The dashed line in Figure 2B presents the calculated values of the correlation factor g assuming that each dye molecule causes the dissociation of one 5CB-5CB dimer (the concentration of 10^{-1} mol/l means 1 molecule of the dye per 40 molecules of the 5CB). It is evident from the comparison of the experimental and calculated data the behavior of the dye dissolved in nematic liquid crystal is much more complicated than that it would follow from assuming the occurrence of the dissociation process caused by dye molecules only. It seems that in our case the polar end group $-NO_2$ of the dye, which strongly interacts with the polar group $-CN$ of 5CB is considerably responsible for observed changes of the dielectric properties of the liquid crystal after dye addition. This effect needs to be further investigated.

III. Dielectric relaxation.

The frequency dependence of the real and imaginary permittivity components ε' and ε'' was measured at different temperatures for all the investigated dye-5CB mixtures. Our results of ε' for the pure 5CB as well as 5CB with dyes I and IX at reduced temperature $T^* = 0.977$ are presented in Figure 3. Similar results for the pure 5CB were previously obtained by other authors.[17,33] As it follows from Figure 3 addition of the dyes does not influence the character of the frequency variation of the dielectric constants, solely the point of the dielectric isotropy (ν_o) shifts somewhat towards lower frequencies.

The dispersion which occur in the parallel component is due to the strongly hindered rotation of the permanent electric dipole μ around the short molecular axis in the presence of the nematic potential. According to the Maier-Saupe mean field theory[34] the nematic potential have the form:

$$W = -q \cos^2\Theta, \tag{7}$$

where q is the height of the potential barrier.

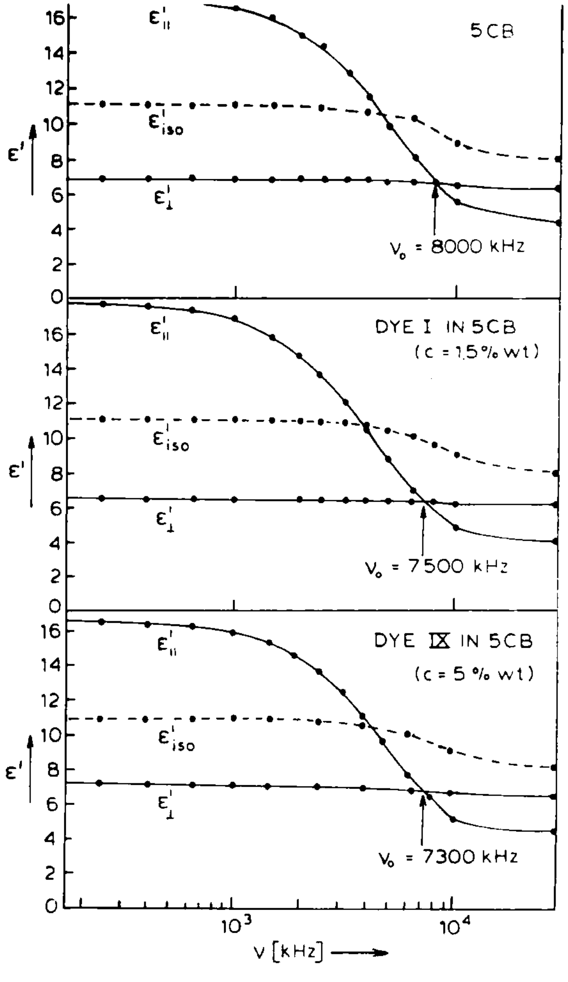

FIGURE 3 Real components of dielectric permittivity versus frequency at reduced temperature $T^* = 0.977$. ν_o is the frequency of dielectric isotropy.

The intermolecular forces, leading to the potential barrier, are cause for the orientation of the liquid crystal molecules, thus it is clear, that there is a relationship between q and order parameter $\langle P_2 \rangle_H$. This order parameter is defined by[35]:

$$\langle P_2 \rangle_H = \frac{1}{2}(\langle 3\cos^2\Theta \rangle - 1), \tag{8}$$

where

$$\langle \cos^2\Theta \rangle = \frac{\int_o^\pi \cos^2\Theta\, f(\Theta)\sin\Theta d\Theta}{\int_o^\pi f(\Theta)\,\sin\Theta d\Theta} \tag{9}$$

Here $f(\Theta)$ is the undisturbed distribution function of the nematic order. Its simplest form is following[4]:

$$f(\Theta) = f(0)\exp\left[-\frac{q}{kT}\sin^2\Theta\right]. \tag{10}$$

It is clear that when the degree of order increases the rotation of the molecule around its short axis becomes more and more difficult, which means that the relaxation frequency associated with $\varepsilon_\parallel$ shifts to lower frequencies. This effect is shown in Figure 4. In this figure the frequency dependences of the imaginary part of the permittivity for the pure 5CB, 5CB with dye I and dye IX at two reduced temperatures are presented. Looking into Table III one can see that dye I causes the increase of the $\langle P_2 \rangle_H$ with respect to the pure 5CB, whereas dye IX lowers the order parameter. These changes are reflected in the shift of the relaxation frequency given by the maximum of $\varepsilon''_\parallel$. Similarly, at the increasing temperature, when the $\langle P_2 \rangle_H$ decreases, the maximum of $\varepsilon''_\parallel$ shifts to higher values and vice versa.

Considering the plots of ε' and ε'' versus frequency for all the investigated samples, we noticed that all diagrams obtained were of the same type. Plotting ε'' versus ε' (Cole-Cole diagram), we obtained in all cases a semicircle with a center lying below the ε' axis. Thus, we were able to calculate the relaxation time using method described in Reference 1b. The relaxation times $\tau_\parallel$ for all the investigated samples are listed in Table V (the relaxation time $\tau_\perp$ could not be estimated in our experiment).

Maier and Saupe[3] and Martin *et al.*[4] have extended the Debye theory[36] of the dielectric relaxation in liquids to nematic liquid crystal and showed that the relaxation time τ is larger than the relaxation time τ_o for $q = 0$ (no nematic potential) by a factor:

$$\gamma = \frac{\tau}{\tau_o}, \tag{11}$$

called the retardation factor.

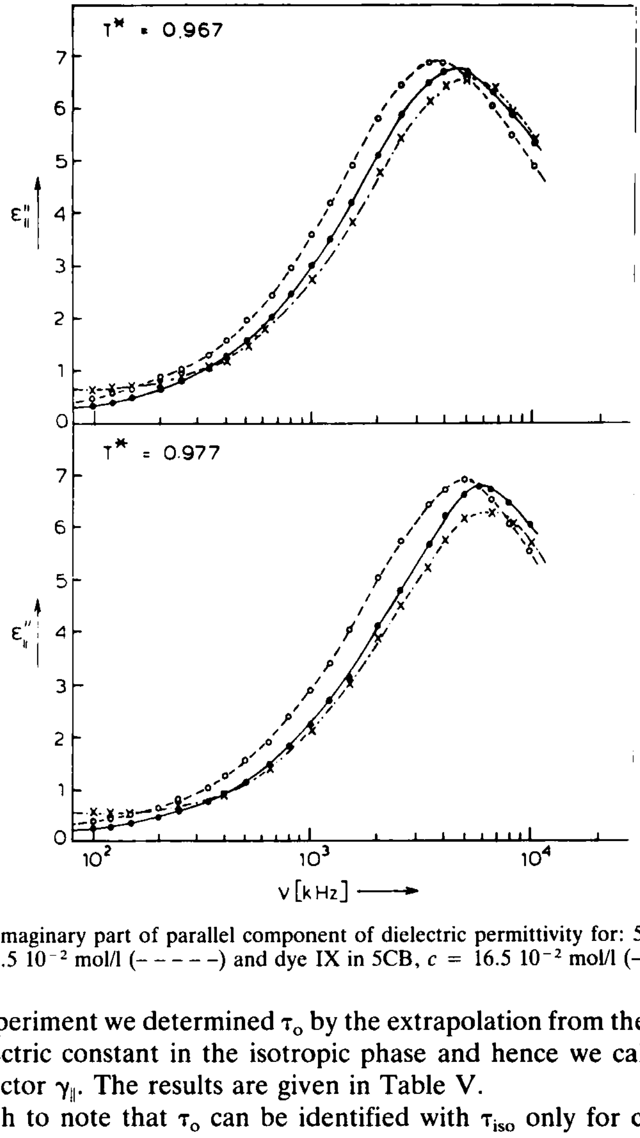

FIGURE 4 Imaginary part of parallel component of dielectric permittivity for: 5CB (———), dye I in 5CB, $c = 4.5\ 10^{-2}$ mol/l (– – – – –) and dye IX in 5CB, $c = 16.5\ 10^{-2}$ mol/l (– · – · – · –).

In our experiment we determined τ_0 by the extrapolation from the measurements of the dielectric constant in the isotropic phase and hence we calculated the retardation factor $\gamma_\parallel$. The results are given in Table V.

It is worth to note that τ_0 can be identified with τ_{iso} only for compounds that have the dipole moment oriented strictly along the long axis of the molecule and their relaxation spectrum in the isotropic phase is of a Debye-type. 5CB satisfies these requirements in the first approximation. The Cole-Cole diagram for 5CB in the isotropic state shows pure Debye relaxation mechanism on the low frequency side, whereas in the high-frequency region the small deviation is observed.[37] However, if the molecule possesses the contribution of the transverse component of the dipole moment the interpretation of the relaxation is much more complicated and τ_{iso} cannot be used to calculate $\gamma_\parallel$. For instance the value $\gamma_\parallel = 100$ obtained for PAA seems to be incorrect, because the dielectric spectrum of this liquid crystal is complex and strongly dominated by the reorientation of the molecule around its long axis.[38]

TABLE V

Relaxation times $\tau_{\parallel}$, retardation factor $\gamma_{\parallel}$ and height of the barrier q for rotation around the short axis of 5CB molecule (concentration of dyes as in Table II, $\Delta\tau = \pm 0.1 \cdot 10^{-8}$ s)

A. $T^* = 0.977$

No.	$\tau_{\parallel} \cdot 10^8$ [s]	$\gamma_{\parallel}$	q [eV]	q [kJ/mol]
Pure 5CB	2.9	5.0	0.085	8.22
I	3.8	6.5	0.095	9.14
III	3.1	5.3	0.087	8.39
V	4.3	6.5	0.094	9.09
VI	3.9	6.5	0.094	9.11
VII	3.7	6.2	0.093	8.94
IX	3.0	4.9	0.084	8.07
X	2.8	4.8	0.083	7.98
XI	4.1	6.7	0.096	9.27

B. T^* – various

No.	T^*	$\tau_{\parallel} \cdot 10^8$ [s]	$\gamma_{\parallel}$	q [eV]	q [kJ/mol]
	0.967	3.9	6.8	0.097	9.36
5CB	0.977	2.9	5.0	0.085	8.22
	0.993	2.2	3.8	0.072	6.93
	0.967	4.8	8.2	0.104	10.05
I	0.977	3.8	6.5	0.095	9.14
	0.993	2.6	4.5	0.082	7.87
	0.967	3.9	6.3	0.092	8.84
II	0.977	3.0	4.9	0.084	8.07
	0.993	2.3	3.7	0.070	6.76

Knowing $\gamma_{\parallel}$, we are able to estimate the height of the potential barrier q, using the plots given by Martin *et al.*[4] The obtained values are presented in Table V. For easier comparison of the obtained results with literature the q data are given in two various units. Although the method applied here gives only roughly estimated q values, our results are in good agreement with q values obtained by other workers[3,39,40] for other nematic materials. In principle, we are interested on the changing of the strength of the nematic potential after guest adding rather than on the absolute values of q.

Table VI presents the host order parameters $\langle P_2 \rangle_H$ obtained from the dielectric measurements using Equations (8)–(10). Comparing the results from Table VI with those from Table III one can see, that values of $\langle P_2 \rangle_H$ obtained from the optical measurements differ significantly from those determined on the basis of the relaxation process. Such differences were also previously observed by other authors[19,41] for cyano-substituted liquid crystals and seem to be understandable, because in the determination of the order parameter from the optical data the long range interactions are taken into account, whereas with respect to the dielectric relaxation

TABLE VI

Host order parameter $\langle P_2 \rangle_H$ obtained from the dielectric study ($T^* = 0.977$)

No.	$\langle P_2 \rangle_H$
Pure 5CB	0.48
I	0.52
III	0.49
V	0.52
VI	0.52
VII	0.51
IX	0.47
X	0.46
XI	0.53

the important quantity is the short range order. Madhusudana and Chandrasekhar[42] proposed the existence of the antiferroelectric short range orientation of strongly polar molecules and found that short range order parameter is lower than long range one.

From Table III and VI it can be seen that the order parameter of the nematic host rises after dyes I and III addition and diminishes in the presence of dyes IX and X, both in the optical and dielectric measurements. In the case of dyes V, VI, VII and XI the behaviour is different. Adding these dyes to 5CB we obtained a decrease of the order parameter determined from the optical measurements, whereas $\langle P_2 \rangle_H$ obtained from the dielectric studies increased. The results from Table VI are in good correlation with the change of $\Delta\varepsilon$ after dye addition (Table II). It seems, that specific intermolecular interactions between 5CB and the dyes with the strong polar $-NO_2$ end group causes the rise of the short range orientation, while the long range order is more affected by other factors (mainly by molecular geometry of dyes).[12,20,43]

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