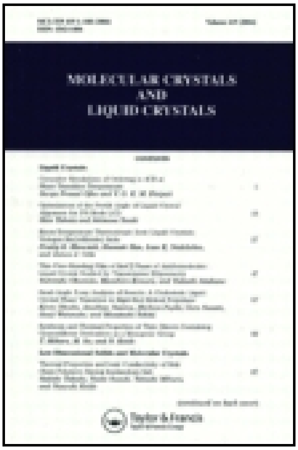

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Comparative Studies of the Degree of Order of the Guest and Host Molecules in 4-Cyano-4′-n-Heptyl-p-Phenylcyclohexane (PCH7) Mixtures

D. Bauman [a]

[a] Institute of Physics, Technical University, Piotrowo 3, 60-965, Poznań, Poland

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Comparative Studies of the Degree of Order of the Guest and Host Molecules in 4-Cyano-4′-*n*-Heptyl-*p*-Phenylcyclohexane (PCH7) Mixtures

D. BAUMAN
Institute of Physics, Technical University, Piotrowo 3, 60-965 Poznań, Poland

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The dielectric relaxation parameters and the refractive indices for the nematogen 4-cyano-4′-*n*-heptyl-*p*-phenylcyclohexane (PCH7) and for the azo dye-PCH7 mixtures are reported. The host order parameter, $\langle P_2 \rangle_H$ both from the temperature dependence of the refractive indices and from the dielectric relaxation time is estimated. Additionally, the guest order parameter, $\langle P_2 \rangle_G$ from the absorption dichroic ratio is determined. It is found, that the order parameter obtained from the optical study is changed differently than that derived from the dielectric relaxation measurements when the dyes with the polar —NO_2 end group are added. A comparison of $\langle P_2 \rangle_H$ for pure PCH7 with that for the nematogen 4-cyano-4′-*n*-pentyl-*p*-biphenyl (5CB) or for the azo dye-liquid crystal mixtures shows that the short range order in the nematic host depends on the degree of the aggregation of the liquid crystal molecules in the samples investigated.

Keywords: guest-host mixture, electric permittivity, refractive index, order parameter

INTRODUCTION

Dielectric, refractive index and absorption measurements of a dye with nematic mixtures (guest-host systems) have proved to be a valuable source of information on molecular arrangement and molecular motion as well as on specific anisotropic interactions between guest and nematic host molecules. Recently, some dielectric properties of the azo dyes dissolved in 4-cyano-4′-*n*-heptyl-*p*-phenylcyclohexane (PCH7) in the static electric field have been studied.[1] Investigation of the dielectric dispersion (up to 13 MHz) of the pure PCH7 and dye-PCH7 mixtures and an estimation of the host order parameter from the relaxation times in the nematic and isotropic phases is the subject of the present work. It was also intended to study the host and guest order parameters derived from the refractive indices and polarized absorption measurements, respectively. The results of this work are compared with an earlier study for the mixtures of the azo dyes with 4-cyano-4′-*n*-pentyl-*p*-biphenyl (5CB).[2,3]

EXPERIMENTAL

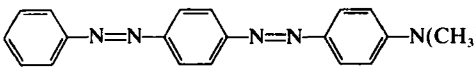
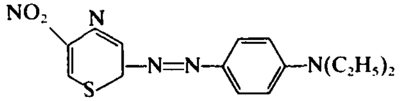
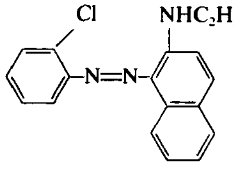
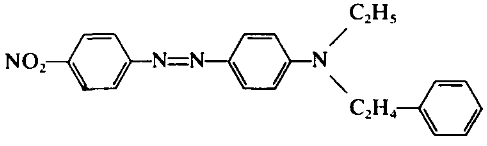
4-cyano-4′-*n*-heptyl-*p*-phenylcyclohexane (PCH7) was supplied by the Merck Company, FRG and was used without further purification. The solid-nematic transition temperature, t_{KN} was 30°C and nematic-isotropic transition temperature, t_{NI} was 54.7°C, what is in the substantial agreement with the literature.[4] The molecular structure of the azo dyes, used as the guests, is presented in Table I. Dye I (D2) was obtained from BDH, the other dyes were synthesized and chromatographically purified in Institute of Dyes, Łódź Technical University, Poland. Numeration of the dyes is according to the notation in Reference 2. The concentrations of the guests in PCH7 was as high as possible considering the solubility and they are listed in Table II, together with the nematic-isotropic transition temperature of the dye-PCH7 mixtures investigated.

The experimental apparatus used for the dielectric measurements has already been described.[3] Two components of the dielectric permittivity in the nematic state, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ as well as the dielectric constant in the isotropic phase, ϵ_{iso} were measured in the range of 1 kHz to 13 MHz. The magnetic field (~1T) was applied to orientate the samples. It was estimated that the overall uncertainty in ϵ' was 1% and lower than 5% in ϵ''.

The refractive indices, n_e, n_o and n_{iso} for the pure and dyed PCH7 in the nematic and isotropic phases were measured for sodium D light as a function of the tem-

TABLE I

Molecular structure of the dyes studied.

No. of dye[a]	Molecular structure
I	
V	
IX	
XI	

[a]According to Reference 2.

TABLE II

Molar concentration, c_M and nematic–isotropic transition temperature, t_{NI} of the dye–liquid crystal mixtures investigated.

Substance	c_M[M/dm^3]	t_{NI}[°C]
dye I in PCH7	$4.5 \cdot 10^{-2}$	58.4
dye V in PCH7	$3.3 \cdot 10^{-2}$	56.9
dye IX in PCH7	$16.5 \cdot 10^{-2}$	53.9
dye XI in PCH7	$5.4 \cdot 10^{-2}$	53.4

perature using a Leitz-Jelley microrefractometer. The liquid crystal and dye molecules were oriented homogenously by means of the rubbing procedure. On the basis of the refractive indices data, the host order parameters, $\langle P_2\rangle_H$ for the pure liquid crystals and the dye-liquid crystal mixtures were estimated using Vuks approximation.[5] The $\overline{\alpha}/\Delta\alpha$ values which are required to estimate the order parameter from the refractive index data were obtained by means of the procedure described by Haller *et al.*[6] $\overline{\alpha}$ is the mean polarizability and $\Delta\alpha$ is the anisotropy of the polarizability of a perfectly oriented medium with $\langle P_2\rangle_H = 1$. The uncertainty in n values measurements was assigned as ± 0.004, while the error in the determination of $\langle P\rangle_H$ from the Haller extrapolation was estimated to be ± 0.015.

The order parameter of the guest dissolved in the nematic host, $\langle P_2\rangle_G$ was determined on the basis of the polarized absorption spectra, recorded with using a Cary-17 spectrophotometer equipped with polarizers. Further experimental details have been reported elsewhere.[2]

RESULTS AND DISCUSSION

The frequency dependence of the electric permittivities was measured at the different temperatures both for the pure PCH7 and for the dye-PCH7 mixtures. The results of the real, $\epsilon_{\|}'$ and the imaginary, $\epsilon_{\|}''$ part of the complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ for the pure PCH7 in the nematic phase at the reduced temperature $T^* = 0.977$ are plotted in Figure 1. The reduced temperature is defined as follows:

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

where T_{NI} is the clearing temperature for the given sample and T is the temperature of interest (in K).

As it is seen from Figure 1 in the parallel component, $\epsilon_{\|}'$ of PCH7 in the measured frequency region only the low frequency dispersion region exists, what is characteristic for dipolar nematic materials having the dipol moment, μ oriented along the long molecular axis. This dispersion is ascribed to the restricted rotation of the molecules around the short molecular axis in the presence of the nematic potential.[7] It was observed that the addition of the small concentration of the dye to PCH7 does not influence the character of the variation of the dielectric constants with

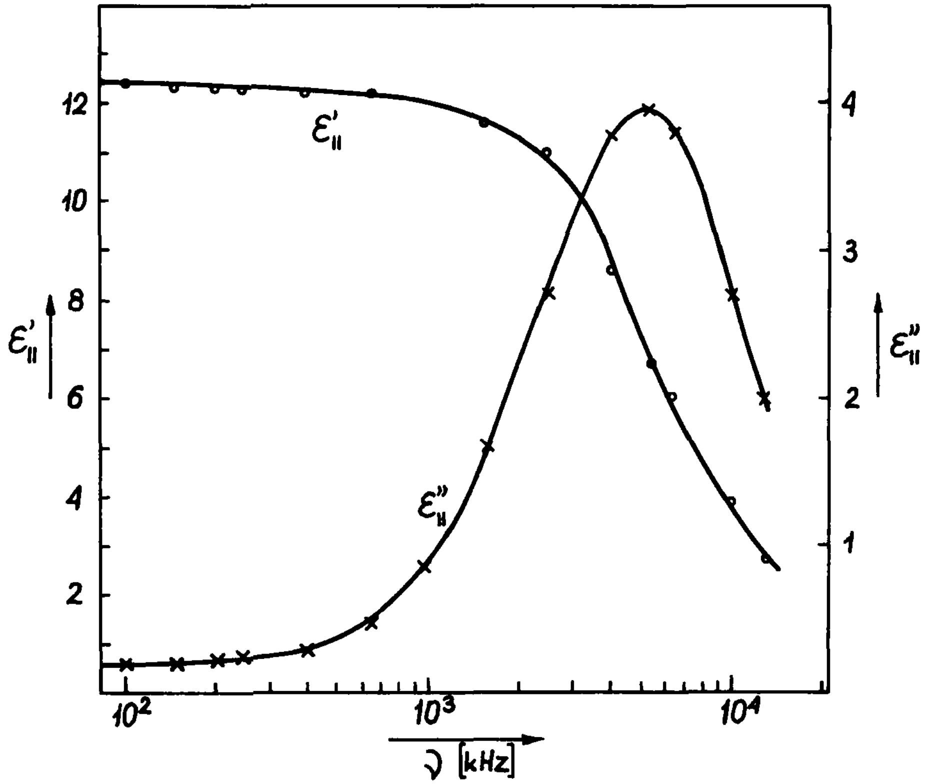


FIGURE 1 Dielectric permittivity ($\epsilon'_{\parallel}$) and dielectric loss factor ($\epsilon''_{\parallel}$) *versus* frequency for PCH7 at $T^* = 0.977$.

the frequency, solely the position maximum of the dielectric loss, $\epsilon''_{\parallel}$ either does not change (dye IX) or increases (the other dyes). From the frequency corresponding to this maximum the relaxation time could be estimated assuming that the dipolar orientation relaxes with a single rate coefficient (a simple Debye process). The relaxation times, $\tau_{\parallel}$ for all the samples investigated at $T^* = 0.977$ are listed in Table III (with some later data). For comparison, the data for 5CB are also presented in this table. The relaxation time, $\tau_{\perp}$ cannot be estimated in our experiment.

Meier and Saupe[8] and Martin *et al.*[9] have extended the Debye theory on the dielectric relaxation[10] and showed that in the nematic phase the relaxation time τ is larger than the relaxation time τ_0 in the absence of the nematic potential by a factor:

$$\gamma = -\frac{\tau}{\tau_0}, \tag{2}$$

called the retardation factor.

TABLE III

Parameters derived from dielectric relaxation study for dye with 5CB and PCH7 mixtures (concentration of dye as in Table II, $T^* = 0.977$).

Substance	$\tau \cdot 10^8$[s]	$\tau_0 \cdot 10^9$[s]	q[kJ/mol]	$\langle P_2 \rangle_H$
pure 5CB[a]	2.9	5.8	8.22	0.48
5CB + dye I[a]	3.8	5.9	9.14	0.52
5CB + dye V[a,b]	4.3	6.7	9.09	0.52
5CB + dye IX[a]	3.0	6.0	8.07	0.47
5CB + dye XI[a]	4.1	6.1	9.27	0.53
pure PCH7	2.5	3.4	10.21	0.54
PCH7 + dye I	2.7	3.4	10.51	0.55
PCH7 + dye V	2.9	3.7	10.45	0.55
PCH7 + dye IX	2.5	3.4	9.96	0.53
PCH7 + dye XI	3.4	3.7	10.89	0.57

[a] From Reference 3.

[b] Concentration of dye V in 5CB is equal $9.9 \cdot 10^{-2}$ M/dm^3.

It is worth noting that τ_0 can be identified with the relaxation time in the isotropic liquid phase, τ_{iso} (the Debye relaxation time) for compounds that have the longitudinal component of the dipole moment only ($\mu_l = \mu$, $\mu_t = 0$) and their relaxation spectrum in the isotropic phase is of a Debye-type. PCH7 satisfies this requirement in the first approximation. The Cole-Cole diagram for PCH7 in the isotropic state shows pure Debye relaxation mechanism on the low frequency side, whereas in the high-frequency region the deviation is observed.[11] In this study τ_{iso} both for pure PCH7 and PCH7-dye mixtures was determined on the basis of the dielectric constant using the equation[7]:

$$\epsilon'_{iso} = \epsilon(\infty)_{iso} + \frac{\epsilon(0)_{iso} - \epsilon(\infty)_{iso}}{1 + \omega^2 \tau^2_{iso}} \tag{3}$$

where $\omega = 2\Pi\nu$ ($\nu \leq 13$ MHz), $\epsilon(0)$ and $\epsilon(\infty)$ are the low and high frequency limit of electric permittivity, respectively, and $\epsilon(\infty) = 1.05\, n^2$, as many authors assumed for polar compounds.[12-14] The measurements were done at various temperatures in the isotropic phase and τ_0 was obtained through the extrapolation to the temperature of interest. Hence the retardation factor γ was calculated. Knowing γ one can estimate the barrier height of the nematic potential, q. The values of τ_0 and q are presented in Table III. Although the absolute values of q, obtained using the method applied here, are not very reliable, one can expect that some trends are reasonably well reproduced. From Table III it is seen that when the dye is added to the nematic host, the height of the potential barrier, q increases in the most cases. This suggests the increase of the orientation of the liquid crystal molecules in the nematic phase.

The host order parameter, $\langle P_2 \rangle_H$ can be determined on the basis of q value through the distribution function of the nematic order having the following form[3,8,9]:

$$f(\theta) = \mathrm{C} \exp\{(-q/kT) \cdot \sin^2\theta\}, \tag{4}$$

where θ is the angle between the director, **n** and the long axis of the liquid crystal molecule.

The obtained $\langle P_2\rangle_H$ values are listed in Table III. From these results the following indications can be seen: 1) the host order parameters of PCH7 and the dye-PCH7 mixtures are greater than $\langle P_2\rangle_H$ of 5CB and the dye-5CB mixtures at the same reduced temperature and 2) the dye added to the liquid crystal changes the values of $\langle P_2\rangle_H$ with respect to that for the pure nematic host.

From the optical study both the host, $\langle P_2\rangle_H$ and guest, $\langle P_2\rangle_G$ order parameters can be determined: $\langle P_2\rangle_H$ from the refractive index data and $\langle P_2\rangle_G$ from the polarized absorption measurements.

The refractive indices for the pure PCH7 and PCH7 with dyes I and IX *versus* reduced temperature are shown in Figure 2A. Similarly as in the case of 5CB[2] the change of the refractive index as well as birefringence values after the dye addition is observed. On the basis of the birefringence data the host order parameter, $\langle P_2\rangle_H$ was estimated. Figure 2B shows the temperature dependence of $\langle P_2\rangle_H$ for the pure PCH7 and for those dye-PCH7 mixtures like in Figure 2A, whereas Table IV presents the $\langle P_2\rangle_H$ values for all the samples investigated at $T^* = 0.977$, together with those of 5CB. Because of the absorbing sodium light by dye *V*, the measurements of the refractive indices and thus the estimation of $\langle P_2\rangle_H$ for this dye in PCH7 are not possible. The values of $\langle P_2\rangle_H$ determined for the pure PCH7 in this study are in the substantial agreement with those obtained by other authors from the optical measurements.[4,15]

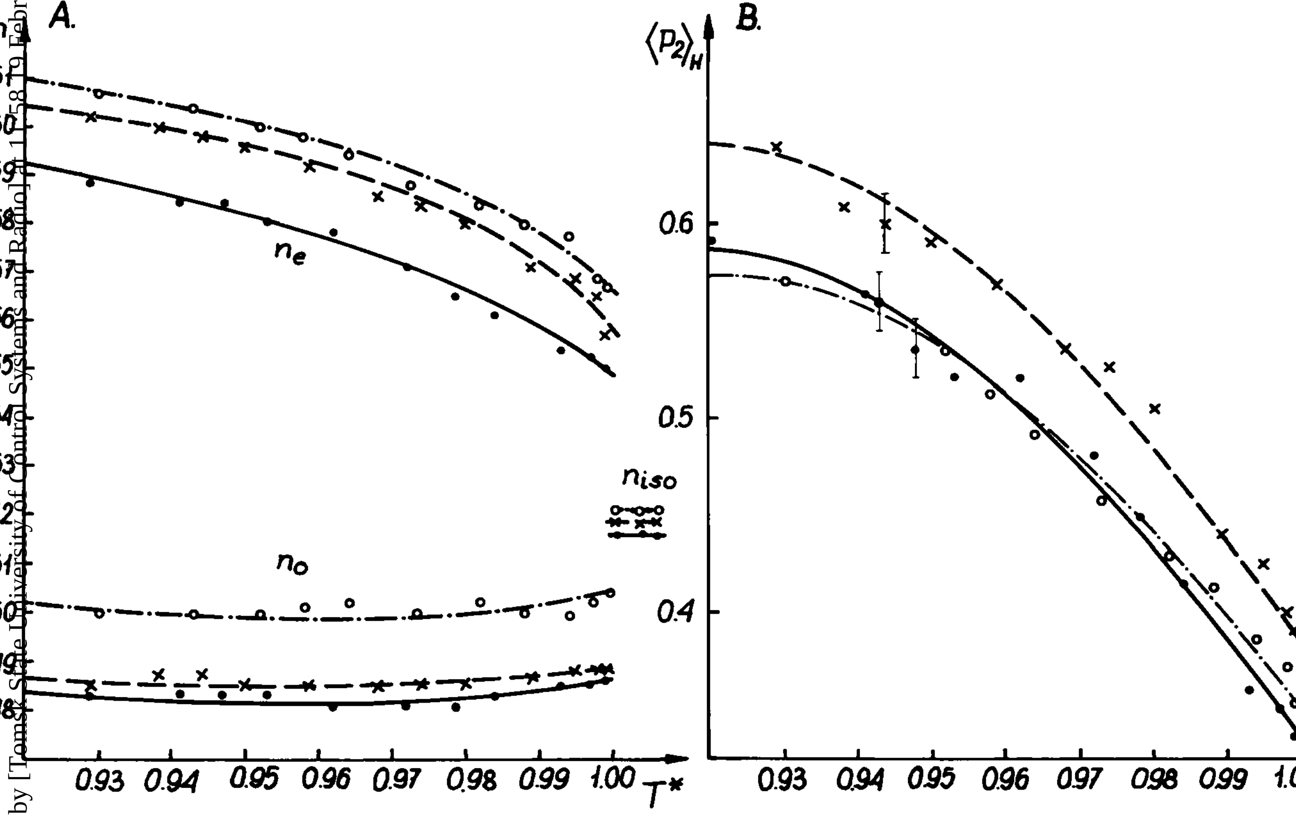
The guest order parameters, $\langle P_2\rangle_G$ were obtained on the basis of the absorption dichroic ratio $D = A_\parallel/A_\perp$ from the equation:

$$\langle P_2\rangle_G = \frac{D-1}{D+2}. \tag{5}$$

Here $A_\parallel$ and $A_\perp$ are the polarized absorption components measured, respectively, in parallel and perpendicularly to the long molecular axis of liquid crystal.

The results of $\langle P_2\rangle_G$ are presented in Table IV. The experimental uncertainty in this case is ±0.01. One can see, that $\langle P_2\rangle_G$ of dye I in PCH7 is larger than $\langle P_2\rangle_H$ of the pure PCH7 and that of dye I-PCH7 mixture. It happens often when the length of the guest exceeds that of the host[16,17] and can be explained in term of the tendency of the guest molecules to balance out the more extreme deviations of the smaller host molecules from **n**. The length of the dye I molecule, calculated from the known bond lengths and configuration in molecules[18] including the van der Waals radii of the terminal atoms[19] is equal about 22 Å, whereas the length of the monomer PCH7 is about 18 Å (considering the flexibility of the alkyl chain).

It should be noticed that on the basis of the dichroic ratio one can estimate the order parameter referring to the transition moment direction of the dye, which is often different from the direction of a long molecular axis.[20] From Table IV follows that $\langle P_2\rangle_G$ for dye IX both in 5CB and in PCH7 is indescribably small. It seems, however, that in this case such a small value is not due to the large angle between the long molecular axis and the moment transition direction (~24.6°[21]), but to the



GURE 2 Temperature dependence of refractive indices (A) and host order parameter (B) for: PCH7 (——), PCH7 with dye I (---) th dye IX (-·-·-).

TABLE IV

Host, $\langle P_2\rangle_H$ and guest, $\langle P_2\rangle_G$ order parameters for dye–liquid crystal mixtures determined from optical measurements ($T^* = 0.977$).

Substance	$\langle P_2\rangle_H$	$\langle P_2\rangle_G$
pure 5CB[a]	0.559	—
5CB + dye I[a]	0.585	0.67
5CB + dye V[a]	—	0.45
5CB + dye IX[a]	0.541	0.09
5CB + dye XI[a]	0.525	0.33
pure PCH7	0.456	—
PCH7 + dye I	0.518	0.68
PCH7 + dye V	—	0.54
PCH7 + dye IX	0.445	0.18
PCH7 + dye XI	0.438	0.47

[a]From Reference 3.

random arrangement of this dye molecules in the liquid crystal matrix resulting from theirs almost round shape (Table I).

Comparing $\langle P_2\rangle_G$ values for the dye-PCH7 mixtures with those for the dye-5CB mixtures one can see that the former are greater than the later inspite of the opposite relation observed for $\langle P_2\rangle_H$. Such a behaviour is connected with the specific interaction between the dye and the liquid crystal molecules, which is different in various guest-host mixtures. It was also previously observed for the homologous series of the alkylcyanobiphenyl.[22] Looking at the $\langle P_2\rangle_H$ values for the dye-liquid crystal mixtures presented in Table III, it is seen that the dye added to the liquid crystalline matrix more improves or less perturbs the orientation of the nematic host in the case, when the host is oriented in the lower degree. For example, $\langle P_2\rangle_H$ is increased about 4.7% and 13.6% for 5CB and PCH7, respectively, in the presence of dye I at the same concentration. The changes of $\langle P_2\rangle_H$ after the dye addition affect the changes of $\langle P_2\rangle_G$ and therefore the values of $\langle P_2\rangle_G$ for the dyes in PCH7 are greater than those for these same dyes in 5CB.

Now let us compare the host order parameters determined from the optical study (Table IV) with those obtained from the dielectric measurements (Table III) at the same reduced temperature. It can be seen that results listed in Table IV differ from those presented in Table III, what indicates the inadequacy of the both method used. Similarly, other authors studying the homologous series of alkylcyanobiphenyl[23] and phenylcyclohexane[4] have found that the order parameter, $\langle P_2\rangle_H$ obtained from the dielectric study differs from that determined by means of the other methods.[4,13,15,24] They have used the Maier-Meier theory[7] to estimate $\langle P_2\rangle_H$ from the polarizability and the dielectric constants. There are differences between results presented in References[4,23] and those obtained in this study. They can be due to the neglecting of the dipole association by the Maier-Meier theory. Such an association occurring in liquid crystals with polar end group —CN is well documented.[12,13,25,26] The method applied here seems to be better than that derived from the Maier-Meier theory because it takes into account the short-range order, which dominates the dielectric relaxation process. In the determination of the order parameter from the optical data, however, the long range interactions are the important quantity. Therefore, the differences between $\langle P_2\rangle_H$ derived from the optical study and that obtained on the basis of the relaxation time are not impossible. However, it is unexpected that optically determined $\langle P_2\rangle_H$'s for PCH7 are greater than those obtained from the relaxation time, and opposite relation is observed for 5CB. It seems that such a behaviour is connected with the different degree of the aggregation for the both liquid crystals. The aggregation of 5CB molecules is strong and the Kirkwood factor, g,[27] determined in the isotropic phase is equal 0.475[3], whereas the aggregation of PCH7 molecules is weaker and g factor is equal 0.637.[1] Similarly like in the case of PCH7, Martin *et al.*[9] have also obtained the higher order parameter from the dielectric study ($\langle P_2\rangle_H = 0.79$) for *p*-azoxyanisole (no molecular aggregation predicted) when compared with $\langle P_2\rangle_H = 0.53$ obtained from other experiments.[28]

It was recently found[1,3] that the addition of the dye to 5CB and PCH7 can change the degree of the aggregation of the liquid crystalline matrix. Especially, the dyes with the polar end group —NO_2 increase strongly the correlation factor, g in the samples investigated, what means that the degree of the aggregation decreases. From Table III and IV one can see that dye V and dye XI having such a group decrease $\langle P_2\rangle_H$ obtained from the refractive index measurements and increase $\langle P_2\rangle_H$ estimated from the dielectric relaxation. However, in the case of dye I and dye IX, which do not change the g factor of the pure host,[1,3] the trend of the changes in $\langle P_2\rangle_H$ are the same both in the optical and dielectric measurements. This confirms the suggestion that the aggregation influences the short range order of the nematic host, while the change of the long range order after the dye addition is affected mainly by the molecular geometry of the guest.[2,17,29]

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