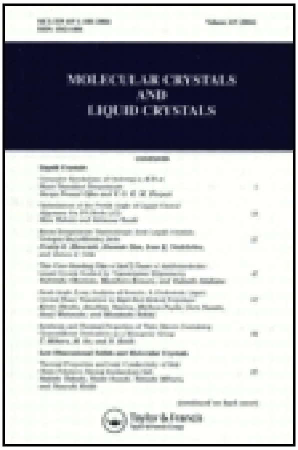

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On the Consistency and Applicability of Internal Field Models in Nematics

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ON THE CONSISTENCY AND APPLICABILITY OF INTERNAL FIELD MODELS IN NEMATICS

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Abstract Information on anisotropy of the local field of light wave in nematics is obtained mainly from refractivity measurements. Such investigations, supplemented by those concerning thermal dependence of density ρ(T), allow for determining optical polarizability anisotropy of nematogenic molecules, as well as their orientational order parameter.

This paper discusses, on the basis of extensive experimental data, the following problems:

- applicability of approximate relations between refractive indices of nematic liquid crystals (NLCs) and their molecular parameters for describing optical properties of nematic mesophase has been estimated;
- anisotropy of the local field factor F_k has been investigated, as well as its influence on calculated anisotropy of molecular polarizability.

Influence of various extrapolation procedures on calculated molecular parameters of the NLCs has been investigated.

INTRODUCTION

Nematic mesophase is, from the molecular point of view, distinguished by a characteristic feature of long-range orientational ordering of the molecules.[1] This ordering is quantitatively described by the nematic order parameter S, introduced by Tsvetkov.[2]

Direction of liquid crystal molecules alignment in normal conditions is not uniform over the whole bulk, which reveals a domain structure. It is possible, by means of certain measures, to extend the range of molecular orientation beyond domain limits this is referred to as a texture. Thin liquid crystal layer (up to about 100 μm) is usually contained between two transparent isotropic plates, with respective boundary conditions determining the actual texture type.[3] A NLC sample with planar or homeotropic alignment is an optically uniaxial medium; it possesses the features of a liquid monocrystal.

Relations between ordinary and extraordinary refractive indices (n_o and n_e, respectively) of a nematic and principal components of polarizability tensor of its molecules, i.e. longitudinal (parallel to molecular long axis) α_l and transverse (perpendicular to it) α_t ones, have been obtained by modifying respective relations for uniaxial solid crystals. In order to achieve this, principal polarizabilities of the molecules, α_l and α_t , have been replaced by effective polarizabilities α_e (parallel to the long axis of a nematic) and α_o (perpendicular to this axis), respectively. The latter have been in turn obtained by averaging polarizabilities of molecules over their orientations.[4] This averaging yields the following relations:

$$\alpha_o = \bar{\alpha} - \frac{1}{3} S \Delta\alpha \tag{1}$$

$$\alpha_e = \bar{\alpha} + \frac{2}{3} S \Delta\alpha \tag{2}$$

where

$$\bar{\alpha} = \frac{1}{3}(\alpha_l + 2\alpha_t) = \frac{1}{3}(\alpha_e + 2\alpha_o) = \alpha_N \tag{3}$$

is mean molecular polarizability, and

$$\Delta\alpha = \alpha_l - \alpha_t \tag{4}$$

denotes polarizability anisotropy. As the order parameter S is given by the relation

$$S = \frac{1}{2}\left(3\langle\cos^2\theta\rangle - 1\right) \tag{5}$$

then also α_e and α_o are temperature dependent. On the other hand, α_l, α_t and α_N, due to their physical sense, depend neither on temperature nor on the actual phase of the liquid crystal material.

In nematic liquid crystals, relations between macroscopic parameters n_o , n_e and ρ and molecular ones $\Delta\alpha$, α_l and α_t together with the parameter S may be schematically expressed in the following way:

$$\begin{Bmatrix} n_o \\ n_e \\ \rho \end{Bmatrix} \xrightarrow{\mathrm{I}} S\Delta\alpha \xrightarrow{\mathrm{II}} \begin{Bmatrix} S \\ \Delta\alpha \end{Bmatrix} \tag{6}$$

Relations that describe the transition denoted in the above by „I" may be written in the following generalized form (7):

$$\left(n_k^2 - 1\right) = 4\pi N F_k^j \alpha_k \qquad \begin{matrix} k = o,e,i \\ j = N,V,L \end{matrix} \tag{7}$$

where:

F_k^j is the local field factor, its actual form varying according to the model adopted;

α_k these are principal polarizabilities of a nematic medium (or effective molecular polarizabilities);

N number of molecules per unit volume.

As it has already been mentioned, expressions for local field factors in NLCs have been obtained by modifying corresponding formulae for uniaxial solid crystals.

Saupe and Maier[5] have modified Neugebauer's relations[6] for solid crystals, thus obtaining (8):

$$K_k^j\left(\text{for} \begin{matrix} k = o,e,i \\ j = N \end{matrix}\right) = K_k^N = \left(1 - N\gamma_k\alpha_k\right)^{-1} \tag{8}$$

where γ_e and γ_o are internal field constants that satisfy relation (9):

$$\gamma_e + 2\gamma_o = 4\pi \tag{9}$$

For isotropic phase, in which $n_e = n_o = n_i$ (n_i being the refractivity index of the isotropic phase) and $\gamma_e = \gamma_o = 4\pi/3$, relations (8) yield the well-known Lorentz-Lorenz formula (10):

$$\varepsilon_o\left(n_i^2 - 1\right) = N\left(\frac{3}{n_i^2 + 2}\right)^{-1} \alpha_i \tag{10}$$

from which mean polarizability of molecules in the isotropic phase α_i is calculated. The set of equations (8) and (9) will thereinafter be referred to as Neugebauer-Saupe-Maier equations and denoted by the NSM acronym. In order to determine α_e and α_o from these equations, it is assumed that the following condition, reasonable from the physical point of view, is satisfied:

$$\alpha_N(T) := \frac{1}{3}\left(\alpha_e(T) + 2\alpha_o(T)\right) = \left\langle \alpha_i \right\rangle = \text{const} \tag{11}$$

< > denotes averaging over all measurement data in the isotropic phase.

Equation (11) is equivalent to the statement that, in the nematic phase, mean molecule polarizability $\alpha_N(T)$ does not depend on temperature T and is equal to mean polarizability in the isotropic phase.

Chandrasekhar and Madhusudana[7] have modified, in the same manner, semi-empirical relations given by Vuks,[8] which has resulted in the following formulae (12):

$$K_k^j\left(\text{for}\ \begin{matrix} k = o,e,i \\ j = N \end{matrix}\right) = K_k^V = \left(1 - \frac{4}{3}\pi N\bar{\alpha}\right)^{-1} = \frac{\left\langle n^2 \right\rangle + 2}{3} \tag{12}$$

where

$$\langle n^2 \rangle = \overline{n^2} := \frac{1}{3}\left(n_e^2 + 2n_o^2\right) \tag{13}$$

Equations (12) and (13), known as Vuks-Chandrasekhar-Madhusudana (VCM) formulae, allow for determining α_e and α_o from n_e, n_o and N in the nematic phase.

Finally, Pelzl[9] has applied, in order to describe optical properties of the nematic phase, the Lorentz-Lorenz formulae, modified to give the following (14):

$$F_k^j\left(\text{for}\ \begin{matrix} k = o,e,i \\ j = L \end{matrix}\right) = K_k^L = \left(1 - \frac{4}{3}\pi N\alpha_k\right)^{-1} = \frac{n_k^2 + 2}{3} \tag{14}$$

These formulae will thereinafter be referred to by the LLC acronym.

The form of the VCM, MSN and LLC equations is a result of the model, adopted to describe local electric field of light wave in a nematic.[10-19] Applicability of these models may thus be decided only on the basis of experimental data.

EXPERIMENTAL

Temperature and dispersion characteristics of the refractive indices $n_o = f_1(t,\lambda)$, $n_e = f_2(t,\lambda)$ and $n_i = f_3(t,\lambda)$ have been measured with an Abbe refractometer. Birefringence $\Delta n = n_e - n_o$ has been measured by means of the interference wedge dynamic method,[20] which is a modified variant of the method described by Haller.[21] Systematic error of refractometric measurements in the isotropic phase is of the order of 0.0005. In the nematic phase this error increases to about 0.001. This increase by more than two times is due to broadening of limiting line, corresponding to limit angle more than two times is due to broadening of limiting line, corresponding to limit angle of total internal reflection. Systematic error of the dynamic method of birefringence measurements is about 2 %. This error is caused mainly by poor precision of wedge geometry determination. Error of temperature determination is from 0.2 C to 0.5 C. Density has been measured with a pycnometer, with a relative error $\Delta\rho/\rho \leq 3$ %.

In order to have broad experimental basis for an analysis of birefringence in nematics, own results have been supplemented with certain reference data. All nematogens, which optical characteristics have been employed for calculations, are listed in Table 1.

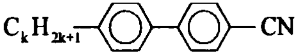
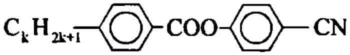
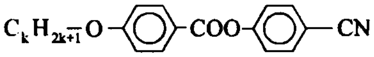
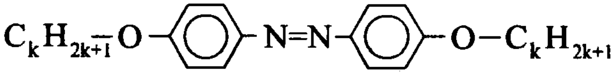
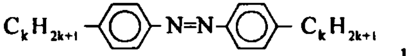
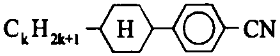
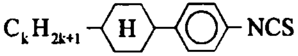
RESULTS AND DISCUSSION

As the estimation of the CMV, MSN and LLC equations for a description of mesophase optical properties is to be based on experimental data, we must employ a set of reasonably selected verification criteria, derived from these data. In order to provide such, the following has been calculated from the CMV, MSN and LLC equations:

1. effective polarizabilities α_o and α_e;
2. mean polarizabilities of NLC molecules in the isotropic (α_I) and nematic (α_N) phases;
3. mean polarizability α_{teor} of NLC molecules, calculated from bond polarizabilities on the basis of the tensor additivity model of these polarizabilities (the PTA model);
4. principal polarizabilities α_l and α_t of NLC molecules;
5. the S parameter of the NLC orientational ordering;
6. local field factor F_k;
7. influences of the Haller and Subramhaynam extrapolation procedures on the calculated values of α_l, α_t and S.

It should be noted that the α_o and α_e values based on the MSN model have been calculated with an assumption of $\alpha_N = <\alpha_I>$, where < > denotes averaging over all measurement data in the isotropic phase.

TABLE 1 Nematogens, which optical characteristics have been employed for local field investigations in nematics

CHEMICAL FORMULA		CHEMICAL NAME		λ[nm]	REFERENCES
	k=5,6,7,8	4-n-alkyl-4' cyanobiphenyls	ACB	546 589 633	own results[29] and[22]
	k=5,6,7,8,9,10	4-n-alkylobenzoate-4'-cyanophenyls	ABCP	546 589	own results[28] and[23]
	k=5,6,7,8,9,10	4-n-alkoxybenzoate-4'-cyanophenyls	AOBCP	546 589	own results and [23]
	k=3,4,5,6,7,8	p,p'-di-n-alkoxyazoxybenzenes	DAOAB	546 633	[16] and [24]
	k=3,4,5,6,7,8	p,p'-di-n-alkylazoxybenzenes	DAAB	546 633	[16] and [24]
	k=5,7,10	4-(trans-4'-n-alkylcyclohexyl)-cyanobenzenes	PCH	589	own results[30]
	k=6	4-(trans-4'-n-alkylcyclohexyl)-iso-thiocyanatobenzenes	CHBT	589	own results[30]

Effective polarizabilities α_o and α_e of the nematic medium

In order to trace reproduction regularity of the α_o and α_e polarizabilities and their anisotropy $S\Delta\alpha = \alpha_e - \alpha_o$ (where $\Delta\alpha = \alpha_l - \alpha_t$ is molecular polarizability anisotropy) for various models considered, the following functions have been plotted:

$\alpha_o = f(T-T_c)$, $\alpha_e = f(T-T_c)$, $S\Delta\alpha = f(T-T_c)$ for k = const

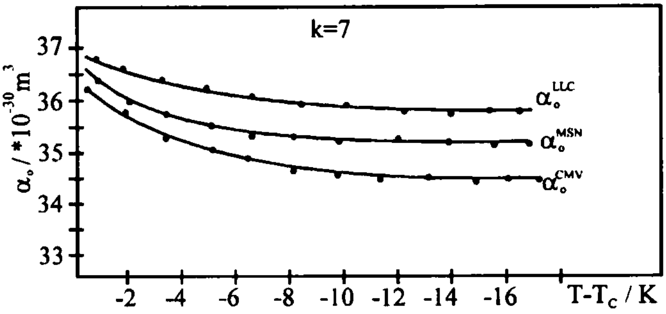


FIGURE 1 Temperature characteristics of the α_o polarizability of ABCP, k = 7.for various models (CMV, MSN and LLC)

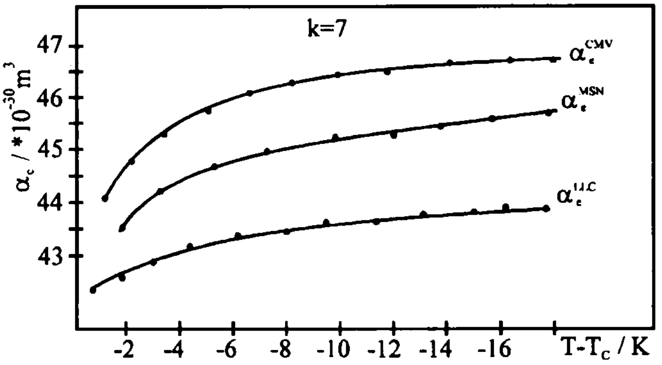


FIGURE 2 Temperature characteristics of the α_e polarizability of ABCP, k = 7 for various models (CMV, MSN and LLC)

Figs. 1, 2 and 3 show, as an example, temperature dependences of α_o, α_e and $S\Delta\alpha$ respectively, determined from the CMV, MSN and LLC models for ABCP, k = 7. The following relations are obvious from these:

$$\left(\alpha_e\right)^{LLC} < \left(\alpha_e\right)^{MSN} < \left(\alpha_e\right)^{CMV} \qquad (15)$$

$$(\alpha_o)^{CMV} < (\alpha_o)^{MSN} < (\alpha_o)^{LLC} \tag{16}$$

$$(S\Delta\alpha)^{LLC} < (S\Delta\alpha)^{MSN} < (S\Delta\alpha)^{CMV} \tag{17}$$

These relations are valid for all molecules from this series. It may be noted that temperature dependences of the $S\Delta\alpha = f(T\text{-}T_C)$ curves directly reveal temperature dependence of the S parameter, as it is physically reasonable to assume $\Delta\alpha$ to be constant. Fig.3 shows that influence of the model employed on the form of the orientational order parameter S dependence on temperature is within the limits of experimental error.

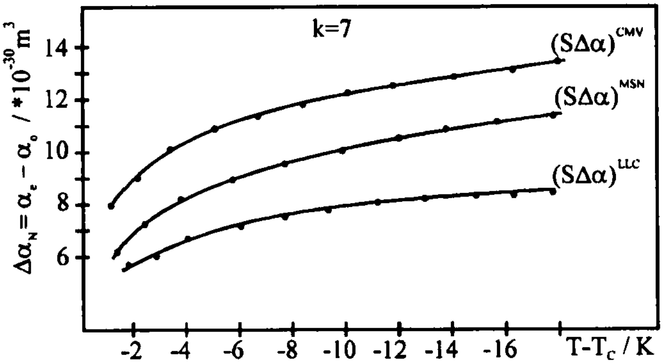


FIGURE 3 Temperature characteristics of the polarizability anisotropy $S\Delta\alpha = \alpha_e - \alpha_o$ of ABCP, k = 7 for various models (CMV, MSN and LLC)

Mean polarizability α_N in the nematic phase

Mean polarizability in the nematic phase α_N has been calculated from the CMV and LLC models (which is denoted as α_N^{CMV} and α_N^{LLC}, respectively). It is physically sound to expect α_N (α_N^{CMV}) or (α_N^{LLC}) not to depend on temperature, with its mean value equal to α. Haller et al. [25] have suggested that relations

$$\alpha_N = \langle\alpha_I\rangle \tag{18}$$

and

$$(S\Delta\alpha)_e / (S\Delta\alpha)_o \approx 1 \tag{19}$$

be treated as the applicability criterion for the CMV model. Relations (18) and (19) may also be treated as the applicability criterion for the LLC model. Values of $(S\Delta\alpha)_e$ and $(S\Delta\alpha)_o$ are calculated only from n_e and n_o , respectively, from the CMV (12) or LLC

(14) equations. For this purpose an assumption should be made that α_N, given by (6), satisfies for the CMV and LLC models the condition of $\alpha_N = <\alpha_I>$. In the MSN case, the model itself assumes that mean polarizability of NLC molecules in the nematic phase α_N is equal to $<\alpha_I>$, and thus $(S\Delta\alpha)_e$ and $(S\Delta\alpha)_o$ also become equal. This excludes application of the criteria (18) and (19) for this model.

Results are shown in Table 2, in the form of values averaged over all measurement data. Differences between α_N values (α_N^{CMV} or α_N^{LLC}) and average $<\alpha>$ values (α_N^{CMV} or α_N^{LLC}) are within the limits of experimental error. It may be noted that for the LLC model the differences $|\alpha_N^{LLC} - <\alpha_N^{LLC}>|$ are nearly twice as high as in the CMV model ($|\alpha_N^{CMV} - <\alpha_N^{CMV}>|$).

TABLE 2 Averaged values of mean polarizability $<\alpha_N>$ in the nematic phase and ratios $<\alpha_N>/<\alpha_I>$ and $(S\Delta\alpha)_e/(S\Delta\alpha)_o$ for molecules of the ABCP series

	k	5	6	7	8	9	10
CMV	$\langle\alpha_N\rangle$	34.87*	36.86	38.64	40.37	42.24	44.37
	$\frac{\langle\alpha_N\rangle}{\langle\alpha_I\rangle}$	0.998	0.999	0.998	0.999	0.999	1.000
	$\left\langle\frac{(S\Delta\alpha)_e}{(S\Delta\alpha)_o}\right\rangle$	0.970	0.990	0.980	0.980	1.000	0.990
LLC	$\langle\alpha_N\rangle$	34.77	36.72	38.47	40.24	42.08	44.25
	$\frac{\langle\alpha_N\rangle}{\langle\alpha_I\rangle}$	0.995	0.995	0.994	0.995	0.995	0.997
	$\left\langle\frac{(S\Delta\alpha)_e}{(S\Delta\alpha)_o}\right\rangle$	0.870	0.920	0.890	0.900	0.920	0.920

* Polarizability values in Tables 2, 3, 4 and 5 are given in A^3 ($1\ A^3 = 10^{-24}\ cm^3 = 1.113\ 10^{-40}\ C^2\ m^2\ J^{-1}$).

From the data in Table 2 we may deduce that the first Haller criterion (18), based on mean molecular polarizability of the NLC in the nematic phase, does not exclude applicability of these models (i.e. CMV and LLC) for describing optical properties of the mesophase. On the other hand, the second Haller criterion (19) (which is more sensitive) gives marked preference to the CMV model and questions applicability of the LLC model for description of the optical properties of the NLC mesophase.

Extrapolation procedures

The "II" transition in equation (6), or splitting of the $S\Delta\alpha$ product, calls for additional information and assumptions. Usually, experimentally proven fact is taken into account that $\log(\alpha_e - \alpha_o)$ and $\log \alpha_e/\alpha_o$ are, for $|\tau|$ large enough, linear functions of $\log(-\tau)$, where τ, known as reduced temperature, is given by the formula (20):

$$\tau = \frac{T - T_{NS}}{T_{NS}} \tag{20}$$

This allows for linear extrapolation of above-mentioned functions up to the values corresponding to $\tau = -1$ (i.e. $T = 0$ K), for which $S = 1$ is assumed.

Haller[25] has made use of the linearity of the $\log(S\Delta\alpha)$ function, and extrapolation procedure based on this function is thus referred to as Haller extrapolation procedure

Linearity of the $\log(\alpha_e/\alpha_o)$ function has, in turn, been utilized by Subramhanyam,[26] and thus extrapolation procedure based on the linearity of the $\log(\alpha_e/\alpha_o)$ function shall be referred to as the Subramhanyam extrapolation procedure.

To sum up, we may say that extrapolation procedures under consideration are based on the following assumptions:

1. Haller extrapolation procedure:
   a) $\log(S\Delta\alpha)$ linear function of $\log(-\tau)$ for large values of $|\tau|$
   b) $\lim\limits_{\tau \to -1} S(\tau) = 1 \Rightarrow \lim\limits_{\tau \to -1} \left[\log(S\Delta\alpha)\right] = \log \Delta\alpha$
2. Subramhanyam extrapolation procedure:
   a) $\log(\alpha_e/\alpha_o)$ linear function of $\log(-\tau)$ for large values of $|\tau|$
   b) $\lim\limits_{\tau \to -1} S(\tau) = 1 \Rightarrow \lim\limits_{\tau \to -1} \left(\alpha_e/\alpha_o\right) = \log\left(\alpha_e/\alpha_o\right)$

Let us note here that extrapolation procedures are not an integral part of the models hitherto discussed (CMV, MSN and LLC).

Molecular polarizabilities α_l and α_t

In order to determine longitudinal (α_l) and transverse (α_t) principal polarizabilities of NLC molecules from principal polarizabilities of the nematic medium α_e and α_o, with no measurement data on refractive indices for solid crystal phase, extrapolation procedures of Haller[25] or Subramhanyam[27] must be employed. Extrapolation procedures do not make an integral part of any of the models hitherto discussed (CMV, MSN and LLC). Reference shows, however, that it has been a common practice to link the Haller procedure with the CMV model, while the Subramhanyam procedure used to be linked with the MSN model.[25,26,27] Thus, a comparison of the α_l, α_t and S values determined from the MSN and CMV models has inevitably involved a comparison of different extrapolation procedures.[26,27] This problem has been addressed in.[28,29,30] In order to determine how extrapolation procedures may influence calculated values of α_l, α_t and S, these procedures have been replaced with one another. Influence of the model employed (CMV, MSN and LLC) and extrapolation procedure (Haller, Subramhanyam) on the α_l and α_t parameters is shown in Tables 3, 4 and 5. From this data we may see that, with the same extrapolation procedures employed, no appreciable difference between results obtained from the CMV and MSN models can be found for all molecules of the series under consideration. Considerable differences between the $(S\Delta\alpha)^{CMV}$ and $(S\Delta\alpha)^{MSN}$ values reveal themselves, however, in different values of the S parameter, calculated from both models.

It may be noted that results of the Subramhanyam procedure are less sensitive to experimental error than those of the Haller procedure.

Tests have shown that the values of polarization anisotropy $\Delta\alpha = \alpha_l - \alpha_t$ are very sensitive to type of procedure, and temperature range of extrapolation lines fitting.

From the above we may deduce that differences in the $\Delta\alpha$ values determined from the CMV and MSN models, quoted in earlier works,[26,27] have in fact been due to different extrapolation procedures employed. This leads to the conclusion that local field factor in the MSN model should be nearly isotropic. In order to provide a better analysis of this problem, behaviour of this factor in all models under consideration has been investigated.

TABLE 3 Comparison of longitudinal polarizability α_l values, calculated from various models (CMV, MSN, LLC, PTA[28]) with various extrapolation procedures (Haller or Subramhanyam) employed; values in $A^3 = 10^{-24}$ cm^3

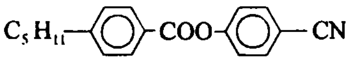
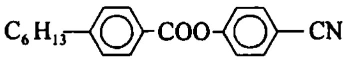
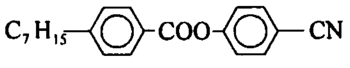
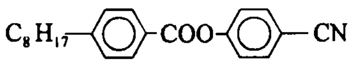
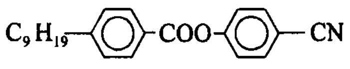
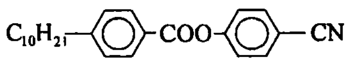
MOLECULE	$\alpha_{l\,(H)}^{CMV}$	$\alpha_{l\,(S)}^{CMV}$	$\alpha_{l\,(H)}^{NMS}$	$\alpha_{l\,(S)}^{NMS}$	$\alpha_{l\,(H)}^{LLC}$	$\alpha_{l\,(S)}^{LLC}$	α_{l}^{PTA}
	48.2	46.0	48.6	45.7	43.4	42.2	40.3
	50.2	48.8	49.0	47.5	45.2	44.6	42.0
	53.2	51.9	53.1	51.2	47.7	47.3	44.2
	54.1	52.7	54.5	52.3	49.1	48.5	46.0
	56.4	55.3	56.4	54.6	51.3	50.9	48.1
	58.9	57.1	58.3	56.0	53.8	52.9	49.9

TABLE 4 Comparison of transverse polarizability α_t values, calculated from various models (CMV, MSN, LLC, PTA[28]) with various extrapolation procedures (Haller or Subramhanyam) employed

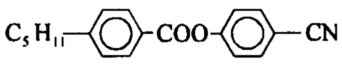
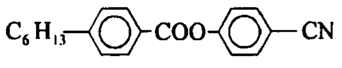
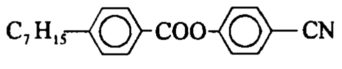
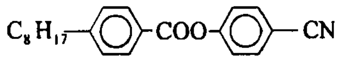
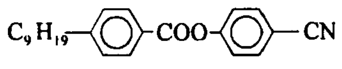
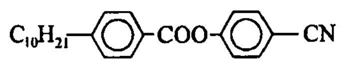
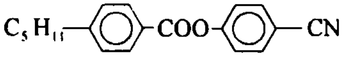
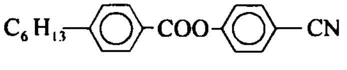
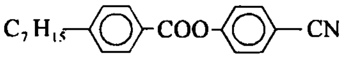
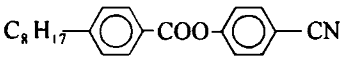
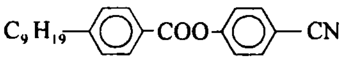
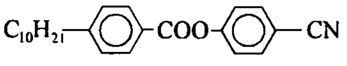
MOLECULE	$\alpha_{t\,(H)}^{CMV}$	$\alpha_{t\,(S)}^{CMV}$	$\alpha_{t\,(H)}^{NMS}$	$\alpha_{t\,(S)}^{NMS}$	$\alpha_{t\,(H)}^{LLC}$	$\alpha_{t\,(S)}^{LLC}$	α_{t}^{PTA}
	28.2	29.4	28.0	29.6	30.5	31.3	29.9
	30.2	30.9	30.8	31.6	32.5	33.0	31.7
	31.4	32.1	31.5	32.5	33.8	34.4	33.4
	33.5	34.3	33.4	34.5	35.8	36.4	35.3
	35.1	35.7	35.2	36.1	37.5	38.0	37.0
	37.1	37.8	37.4	38.5	39.5	40.1	38.9

TABLE 5 Comparison of polarizability anisotropy $\Delta\alpha = \alpha_l - \alpha_t$ values, calculated from various models (CMV, MSN, LLC, PTA[28]) with various extrapolation procedures (Haller or Subramhanyam) employed

MOLECULE	$\Delta\alpha_H^V$	$\Delta\alpha_S^V$	$\Delta\alpha_H^N$	$\Delta\alpha_S^N$	$\Delta\alpha_H^L$	$\Delta\alpha_S^L$	$\Delta\alpha^{PTA}$
	20.0	16.6	20.6	16.1	12.9	10.9	10.4
	20.0	17.9	18.3	16.0	12.8	11.6	10.3
	21.8	19.8	21.6	18.7	13.9	12.9	10.8
	20.6	18.4	21.0	17.8	13.4	12.1	10.7
	21.3	19.6	21.3	18.5	13.8	12.9	11.1
	21.8	19.1	20.9	17.5	14.3	12.7	11.0

Local field anisotropy

Fig.4 shows the local field factor F_k as a function of T_c - T for a molecule of ABCP, k = 7. For other molecules temperature characteristics of their corresponding factors are the same.

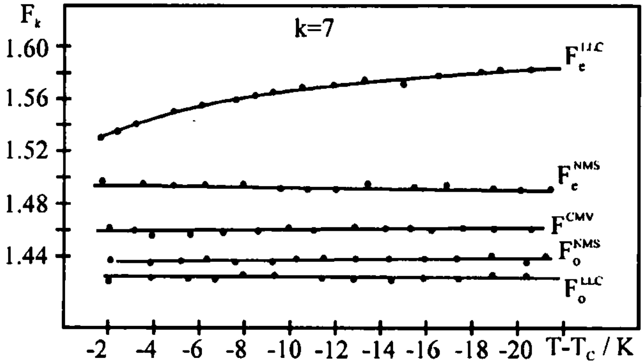


FIGURE 4 Temperature dependence of the internal field factor F_k for ABCP, k = 7

Table 6 shows, for the entire ABCP series, with $T - T_c = 5$ K, ratios of the local field factor values for the MSN and LLC models and ratios α_o/α_e (MSN and LLC) and γ_e/γ_o (MSN).

These ratios may be considered a measure of anisotropy of these quantities. We may see that anisotropy of the local field factor in the MSN model is small, compared to anisotropies of the α_e and α_o, as well as γ_e and γ_o, parameters that determine it. On the other hand, anisotropy of the local field factor F^{LLC} in the LLC model is comparable to this of the effective polarizability.

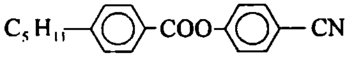
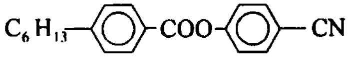
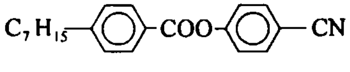
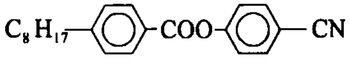
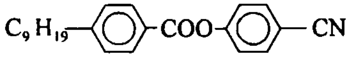
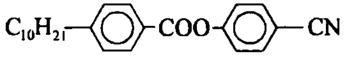
It has already been mentioned that the Lorentz model of nematic local field (LLC) takes into account only one physical factor contributing to anisotropy of this field, namely polarizability anisotropy of the medium. Formally, the expression for F^{LLC} includes only one parameter α_e^{LLC} or α_o^{LLC}. The MSN model accounts for two local field anisotropy factors; apart from polarizability anisotropy of the medium, also anisotropy of spatial distribution of polarization centres has been included in the form of adjustable γ_e and γ_o parameters. Investigations have shown that low local field anisotropy in the MSN model is obtained due to the fact that polarizability of the γ factor and effective polarizability are of opposite sign. Moreover, temperature changes of the g factors and of corresponding polarizabilities are also of opposite sign. As a result, in spite of large anisotropies and marked temperature dependence of both α_e and α_o (as well as of γ_e and γ_o), anisotropy of the local field factor is small. This means that with enough freedom left (two adjustable parameters) the local field factor shows small anisotropy, as it is the case with the MSN model.

In the case of the LLC model, tendency to reduce local field anisotropy leads to considerable reduction of effective polarizabilities and thus to better agreement with results obtained from the PTA model (see tables 3, 4 and 5).

As it has already been mentiond, this model leads to physically unreasonable change of molecular polarizability value at the transition from isotropic to nematic phase.

It thus seems reasonable to argue that, if local field in a nematic is anisotropic, then its anisotropy is of a little significance. This explains consistency of results obtained from the CMV model, which assumes isotropic local field, as well as small differences between results obtained from the CMV and MSN models.

TABLE 6 Ratios of local field constants F_e/F_o, effective polarizabilities α_e/α_o and Neugebauer factors for the ABCP series, with $T - T_c = -5$ K

MOLECULE	$\frac{F_e^{NMS}}{F_o^{NMS}}$	$\frac{\alpha_e^{NMS}}{\alpha_o^{NMS}}$	$\frac{\gamma_e}{\gamma_o}$	$\frac{F_e^{LLC}}{F_o^{LLC}}$	$\frac{\alpha_e^{LLC}}{\alpha_o^{LLC}}$
	1.02	1.30	0.80	1.09	1.20
	1.03	1.25	0.85	1.09	1.20
	1.04	1.25	0.87	1.09	1.20
	1.03	1.24	0.86	1.08	1.18
	1.04	1.25	0.87	1.09	1.19
	1.03	1.26	0.85	1.09	1.20
Average value for series	1.03± 0.01	1.26± 0.02	0.85± 0.03	1.09± 0.01	1.20± 0.01

Physical meaning of the Neugebauer parameters γ

Parameters γ_o and γ_e in the Neugebauer model deserve special attention, as investigation of agreement between their behaviour and physical meaning should allow for evaluation of correctness of this model.

It has been found that the anisotropy $\Delta\gamma = \gamma_e - \gamma_o$ is, within good accuracy, linearly correlated with the effective polarizability anisotropy $S\Delta\alpha = \alpha_e - \alpha_o$, calculated from the MSN model. This correlation is shown in the Fig.5. Linear correlation between $\Delta\gamma$ and $(S\Delta\alpha)$ imples that $\Delta\gamma$ is a linear function of the order parameter S.

This allows for the statement that, if in a nematic, spatial ordering of polarization centres exists, then its anisotropy is a linear function of the parameter S of orientational molecular ordering.

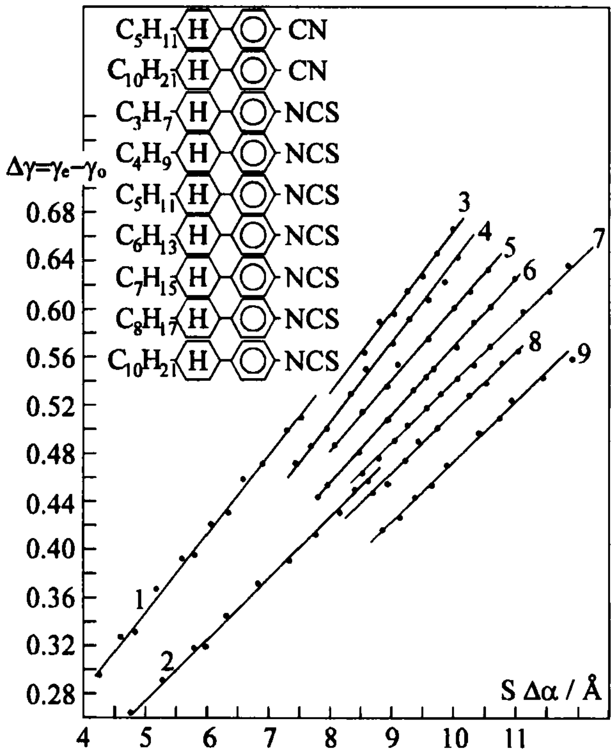


FIGURE 5 Correlation between the $\Delta\gamma$ and $(S\Delta\alpha)_N$ anisotropies for nematics in the PCH and CHBT series

Order parameter

Assuming that $\Delta\alpha$ does not depend on temperature, the $S\Delta\alpha$ = f(T) curve determines order parameter temperature characteristics S(T). From these, through extrapolation procedures, we may determine absolute values of S(T). Both order parameter value and its temperature dependence are, in general, different for different compounds it the homologous series. The form of these curves in practice shows no dependence on the local field model applied.

Influence of atomic composition of the nematogens, as well as of their chain shape and length, on the order parameter (in fixed reduced temperature) does not exceed 4 % of the mean value for nematics under consideration. This is shown in Tables 7 and 8.

TABLE 7. Mean values and standard deviations of the order parameter S of homologous series, for $\tau^* = 0.97$

SERIES	ACB	ABCP	AOBCP	DAAB	MS
S	0.58±0.01	0.59±0.02	0.57±0.03	0.57±0.02	0.517

TABLE 8. Ratios of the order parameter values determined from refractometric (S_{ref}) and NMR (S_{NMR}) measurements for the DAAB series

k	3	4	5	6	7	8
S_{ref} / S_{NMR}	1.17±0.01	1.25±0.01	1.11±0.01	1.12±0.01	1.10±0.01	0.84±0.01

CONCLUSIONS

To summarize, we may state that:

1. Presence of adjustable parameters γ_o and γ_e in expressions for the local field factors, derived from the MSN model, provides these expressions with flexibility and makes them suitable for reliable estimation of the local field anisotropy.
2. If the local field in a NLC is anisotropic, this anisotropy is comparatively small, and thus relations based on the CMV model give consistent results.
3. In order to conclude whether values of the γ_o and γ_e parameters, determined from refractometric measurements, give any physical information or are of purely formal nature, further investigations are necessary.
4. Physically unsound behaviour of results of the LLC equations puts their applicability in doubt.
5. Haller procedure, as compared to Subramhanyam procedure, yields higher molecular anisotropy for the same local field model applied.
6. Influence of extrapolation procedure on the value of molecular anisotropy is comparable to that of the local field model.
7. From the practical point of view it seems reasonable to employ the simplest CMV model, together with the Subramhanyam extrapolation procedure.
8. Relation between $\Delta\alpha$ and molecular structure shows nearly no dependence on the extrapolation procedure employed.

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