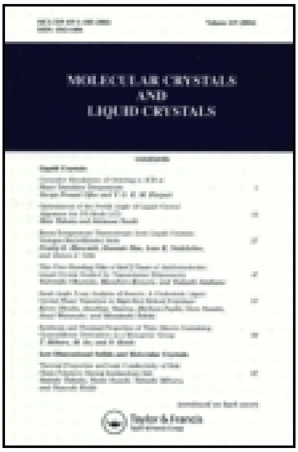

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Effects of Electrostatic Interactions on Orientational Order of Solutes in Nematic Solvents: NMR Experiments and Theoretical Predictions

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Effects of Electrostatic Interactions on Orientational Order of Solutes in Nematic Solvents: NMR Experiments and Theoretical Predictions

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Abstract The orientational order parameters of four aromatic solutes in nematic solvents, derived from proton dipolar couplings in NMR spectra, show a correlation with the dielectric anisotropy of the solvents. Explanation of the experimental behaviour is provided by a molecular theory based on the reaction field approximation.

Keywords: Electrostatic Interactions, Reaction Field, Orientational Order.

INTRODUCTION

Orientational order in liquid crystals is mainly due to the anisotropy of short-range interactions, which are modulated by the molecular shape. Thus, an elongated shape is the essential requirement for a molecule to be able to form a calamitic phase. On the contrary, no clear evidence exists about the relevance and the effects of electrostatic interactions. These are expected to affect molecular order and transition temperatures and might have a crucial role in stabilising some mesophases, *e.g.* smectics C. However, to disentangle electrostatic from short-range contributions is not an easy task, both from the experimental and the theoretical point of view. Information about interactions in liquid crystal phases can be derived by using simple solutes as probes: in this way it is possible to introduce selected changes in the structure of solute and solvent and to analyse how such changes affect the molecular order. The NMR technique has been widely used for this purpose; the anisotropic interactions characterising a given nematic are reflected by the orientational order parameters of solutes, which can be derived with high accuracy from dipolar or quadrupolar splittings [1]. From the experimental results a correlation between orientational order of the solute and dielectric anisotropy of the solvent has been suggested [2,3]. However, in the absence of any simple relation between electrostatic properties of the solutes and their orientational behaviour allowing the rationalization of the experimental findings, this is only a hypothesis which needs to be confirmed by a proper theoretical analysis.

The main features of the orientational behaviour of simple solutes, *i.e.* the different degree of alignment of the molecular axes, can be predicted by the *surface* tensor approach, a phenomenological model accounting for short-range interactions [4]. Within this approach, the mean field potential experienced by a molecule in the liquid crystal phase is defined on the basis of the anisometry of its surface, which is derived in a realistic way from the geometric structure. On the contrary, no account is taken of the structure of the solvent, which enters only through its orienting strength, essentially determined by the reduced temperature. Thus, if this model can provide reasonable predictions of the order behaviour of different solutes in a given solvent, it cannot explain the difference in order parameters observed when a given solute is dissolved in various solvents, at the same reduced temperature. Recently a theoretical method based on the *reaction field* approximation [5] has been developed for a molecular description of electrostatic interactions in liquid crystals [6-8]. These are represented in terms of the coupling between the charge distribution contained within the surface of the probe molecule and the polarization of the solvent, which is viewed as a continuum characterised by its dielectric permittivity. Both short-range and electrostatic interactions can be accounted for by a mean field potential consisting of a surface tensor and a reaction field term.

Application of this approach has enabled the assessment of the electrostatic contribution to ordering for a number of solutes in nematic solvents [7].

In the present work, the order parameters derived from proton dipolar couplings of naphthalene (NPT), 1,4-difluorobenzene (DFB), 1,4-dichlorobenzene (DCB) and 1,4-dibromobenzene (DBB) dissolved in six nematic solvents: EBBA, ZLI1132, a 55wt% ZLI1132+EBBA nematic mixture, PCH-7, I52 and I35 [3,9] are compared with the theoretical predictions obtained by the mean field approach mentioned above. The solutes are shown in Figure 1 together with their molecular frame.

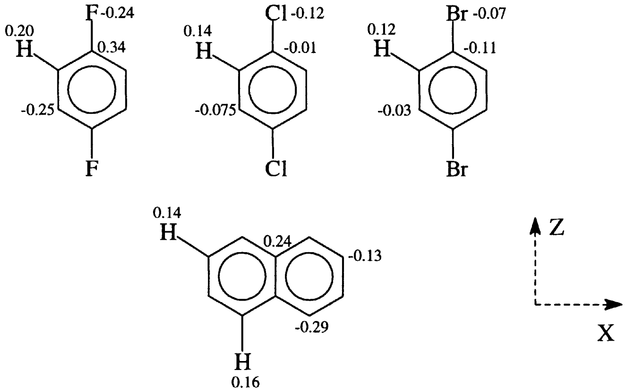

FIGURE 1. Structure of the solutes and atomic charges calculated as explained in the text. The molecular frame is also shown.

The structures, Nematic-Isotropic transition temperatures and dielectric anisotropies of the solvents are listed in Figure 2. As it appears from the reported values, the used nematics cover a wide range of dielectric anisotropies, so they represent a very useful set to investigate the dependence of the solutes orientational order on this property. It needs to be pointed out that the T^{NI} of EBBA, synthesised as reported in ref. 3, is lower than the value reported in literature [10]: this is because its degree of purity is not very high; in any case, for the aims of this work, this fact results to be insignificant because further tests, carried out on the same molecules in highly pure EBBA at the same reduced temperatures, demonstrated that the solutes order is in practice the same [11].

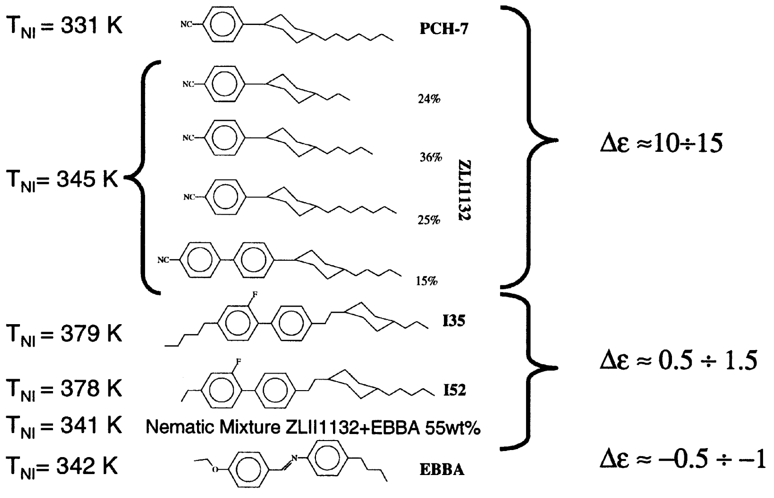

FIGURE 2 Solvents used in the NMR experiments. For T^{NI} and $\Delta\varepsilon$ values see ref. 3 and references therein.

THEORETICAL MODEL

The method used for the prediction of orientational order of solutes in the nematic phase has been presented elsewhere [7,8] and the reader is referred to the original papers for the theory. In the following only a summary of the main physical ingredients and of the computational procedure will be reported.

The orienting potential experienced by a molecule in the nematic phase is approximated as the sum of a surface tensor contribution, U_{st}, accounting for short-range interactions modulated by the molecular shape, and a reaction field term, U_{rf}, describing electrostatic interactions

$$U(\omega)=U_{st}(\omega)+U_{rf}(\omega)\,, \qquad (1)$$

where $\omega=(\beta,\gamma)$ are the angles defining the orientation of the mesophase director in the molecular (x,y,z) frame.

In the surface tensor model it is assumed that the orienting potential acting on a given element dS of the molecular surface depends on its orientation with respect to the mesophase director according to the expression $dU_{st} = \xi P_2(\hat{n}\cdot\hat{s})dS$, where $\hat{n}$ and $\hat{s}$ are unit vectors parallel to the director and to the outwards pointing normal to dS, respectively, and ξ is a parameter giving the strength of the orienting interaction. The overall potential acting on the probe molecule is obtained by integrating the elementary contributions over the whole molecular surface. The orientation dependence of the surface tensor contribution to the mean field potential can be made explicit by exploiting the properties of spherical harmonics; the following expression is obtained:

$$U_{st}(\omega) = -\xi \sum_m T^{2,m*} C_{2m}(\omega), \qquad (2)$$

where $C_{Lm}(\omega) = \sqrt{4\pi/(2L+1)}Y_{L,m}(\omega)$ are modified spherical harmonics [12] and $T^{2,m*}$ are irreducible spherical components of the so called surface tensor. The latter are defined as

$$T^{2,m} = -\int_S C_{2,m}(\theta_s, \varphi_s)\, dS \ , \qquad (3)$$

where the integral is over the molecular surface and the polar angles (θ_s, φ_s) specify the orientation of the vector $\hat{s}$ in the molecular frame. In this way the short-range contribution to the mean field potential, $U_{st}(\omega)$, can be calculated on the basis of the surface of the probe molecule.

The reaction field term accounts for the interaction between the molecular charges and the polarisation induced by them in the surrounding dielectric. Due to the anisotropy of the dielectric permittivity, in the nematic phase the strength of such a coupling depends on the molecular orientation. The contribution $U_{rf}(\omega)$ can be calculated by solving the Laplace equation for the electrostatic potential in a dielectric medium with a cavity containing a charge distribution with appropriate boundary conditions. The cavity is identified with the molecular volume and the boundary is defined as the molecular surface. For boundaries of arbitrary shape the problem is conveniently reformulated in terms of integral equations over the molecular surface. By following a procedure developed in the quantum mechanical description of solvation [6], the reaction field energy can be calculated as

$$U_{rf}(\omega) = \frac{1}{2}\int_S \phi^0(\vec{r})\sigma(\vec{r})d\vec{r} \ , \qquad (4)$$

where $\sigma(\vec{r})$ is the apparent charge density and and $\phi^0(\vec{r})$ is the electrostatic potential generated in vacuum by the permanent charges embedded in the cavity, both evaluated on the molecular surface. The surface charge density is the solution of the linear integral equation

$$\mathcal{A}\ \sigma = -g^0 - g^{ind}, \tag{5}$$

where $\mathcal{A}$ is an integral operator, depending on the permittivity of the dielectric, while g^0 and g^{ind} are functions of the electrostatic potential and of the normal component of the electric field at the surface points. They represent contributions deriving from the permanent and induced charge distribution, respectively. In our model the former are described as point charges located at the atomic centres, while a set of interacting dipoles in the same positions account for induction effects. The induced field is a linear function of the surface density σ , and can be written as [8]

$$g^{ind} = \mathcal{A}^{ind}\sigma\,; \tag{6}$$

therefore Equation (5) can be rewritten as

$$(\mathcal{A} + \mathcal{A}^{ind})\sigma = -g^0. \tag{7}$$

After partitioning the molecular surface into a grid of elements (tesserae) Equation (6) reduces to a system of algebraic equations

$$(\boldsymbol{A} + \boldsymbol{A}^{ind})\boldsymbol{\sigma} = -\boldsymbol{g}^0, \tag{8}$$

with the elements of the vectors $\boldsymbol{\sigma}$, $\mathbf{g}^0$, and of the matrices $\boldsymbol{A}$ and $\boldsymbol{A}^{ind}$ corresponding to surface tesserae. It should be reminded that in the nematic phase the charge density σ depends on the molecular orientation with respect to the director, as a consequence of the dielectric anisotropy. It is convenient to make explicit the angular dependence of the reaction field contribution to the mean field potential, Equation (4), by using its expansion on a basis of modified spherical harmonics

$$U_{rf}(\omega) = \sum_{L,m} F^{L,m*}\ C_{Lm}(\omega) \tag{9}$$

with

$$F^{L,m} = \frac{2L+1}{4\pi}\int U_{rf}(\omega)C^*_{Lm}(\omega)d\omega. \tag{10}$$

If Equations (2) and (9) are substituted into Equation (1), the overall orienting potential experienced by a probe molecule in the nematic phase can be expressed as

$$U(\omega) = -\xi \sum_{m} T^{2,m*} C_{2m}(\omega) + \sum_{L,m} F^{L,m*} C_{Lm}(\omega) . \tag{11}$$

From the mean field potential the orientational distribution function can be derived

$$f(\omega) = \frac{\exp[-U(\omega)/k_B T]}{\int \exp[-U(\omega)/k_B T] d\omega} ; \tag{12}$$

this allows the calculation of the elements of the Saupe ordering matrix [13]

$$S_{ij} = \frac{1}{2} \int (3n_i n_j - \delta_{ij}) f(\omega) d\omega , \tag{13}$$

where n_i is the component of the mesophase director along the ith molecular axis. This is a symmetric traceless tensor; therefore only two principal values are required to fully specify the orientational order.

NUMERICAL PROCEDURE

Prediction of the order parameters for a given solute is performed according to the following scheme.

A) The molecular geometry is optimised and the atomic charges are evaluated. In the present case *ab-initio* calculations were performed using the Gaussian-98 package [14]. Point charges were calculated according to the Merz-Singh-Kollman procedure [15].

B) The molecular surface is calculated for the optimised structure. According to the *rolling sphere* algorithm, it is defined as the surface drawn by a sphere rolling over the envelope of an array of overlapping beads centred at the nuclear positions [16,17]. In the calculations presented here standard van der Waals radii were used [18], together with a rolling sphere of radius R=3Å. The same surface, with a number of tesserae which is of about 1100 in the case of fluorobenzene, was used for calculation of the surface tensor and for the solution of the electrostatic problem.

C) The components of the surface tensor, $T^{2,m}$, are evaluated according to Equation (3).

D) The reaction field energy is calculated for a grid of orientations according to Equation (4), where the apparent charge density σ is the solution of the algebraic linear system Equation (8). Then the expansion coefficients $F^{L,m}$ are determined, see Equations (9) and (10). In addition to the molecular surface, the ingredients of the calculations are the atomic charges and polarizabilities and the dielectric permittivity of the nematic solvent. The Thole model [19] was used for the molecular polarization, with the parameterization recently proposed by Swart and van Duijnen [20]. The following atomic polarizabilities were assumed: α_C=1.508 Å^3, α_H=0.519 Å^3, α_F=0.436 Å^3, α_{Cl}=2.387 Å^3, α_{Br}=3.360 Å^3. The molecular polarizabilities obtained in this way are reported in Table 1. Note that anisotropic molecular polarizabilities are recovered, even though isotropic atomic polarizabilities have been employed, as a consequence of the geometric arrangement of the interacting dipoles.

TABLE 1 Calculated polarizabilities (Å^3).

	DFB	**DCB**	**DBB**	**NPT**
α_{xx}	61.70	11.72	13.21	14.03
α_{yy}	35.54	8.07	9.67	7.77
α_{zz}	67.86	17.08	20.64	16.24

E) Orientational order parameters are calculated according to Equation (13). No free parameter enters the model; the weight of the two contributions to the mean field potential is determined on the basis of the solvent properties [7]. In particular the parameter ξ, which gives the strength of the short-range orienting interactions, is determined by assuming for the solvent the Maier-Saupe approximation [13]. Its temperature dependence is described by the expression $\xi = \xi_0 \overline{P}_2^s T^{NI} / T_s^{20}$, where ξ_0 is a universal constant, while $\overline{P}_2^s$, T^{NI} and T_s^{20} are order parameter, nematic-isotropic transition temperature and uniaxial surface tensor component for the solvent [4]. For the temperature dependence of the dielectric anisotropy the following equation was used: $\Delta\varepsilon = \Delta\varepsilon^{NI} \overline{P}_2^s / \overline{P}_2^{s,NI}$, with the apex *NI* denoting values at the Nematic-Isotropic transition.

RESULTS AND DISCUSSION

Orientational order parameters derived from dipolar couplings for the four aromatic solutes in the various solvents are displayed in Figure 3. The plots show the difference $S_{zz}-S_{xx}$, measuring the biaxiality of order in the molecular plane, as a function of S_{yy}, the order parameter for the axis perpendicular to such a plane. The temperature dependence is implicit in such diagrams, since higher order parameters correspond to lower temperatures. For all molecules under examination the biaxiality of order decreases with increasing the dielectric anisotropy of the solvent. Dramatic effects are observed for DFB, whose behaviour changes from rod-like (the largest order parameter corresponds to the long molecular axis, *i.e.* the *z* axis) to disc-like (the axis with the largest absolute value of order parameter is the one perpendicular to the molecular plane, that is the *y* axis).

With the aim of analysing the effects of electrostatic interactions, we have calculated the orientational order parameters for the four molecules with the reaction field contribution corresponding to different values of the dielectric permittivity. The results, shown in Figure 4, refer to the following choices: $\bar{\varepsilon}=10.17$, $\Delta\varepsilon^{NI}=8$ (open circles) and $\bar{\varepsilon}=5.17$, $\Delta\varepsilon^{NI}=-0.52$ (open triangles). Such values are appropriate for solvents like 5CB and MBBA [13]. In addition, the results obtained in the absence of electrostatic interactions are also shown in the Figure ($\Delta\varepsilon=0$, solid squares). In this case the orienting potential contains only the surface tensor term. Calculations were performed for reduced temperatures ranging from 0.77 to 0.91 and a Nematic-Isotropic transition temperature $T^{NI}=350$ K was assumed.

Considering the results obtained with $\Delta\varepsilon=0$ we can see that order parameters and biaxiality of order are predicted to increase along the sequence: DFB, NPT, DCB and DBB. These results are not very far from the values derived from experiments in a solvent with low dielectric anisotropy such as, for example, I35. The introduction of the reaction field contribution produces a decrease of the biaxiality of ordering for positive dielectric anisotropy of the nematic solvent, viceversa when the dielectric anisotropy is negative. The observed and predicted effects are smaller in the latter case because of the smallness of the $\Delta\varepsilon$ values. So, the theoretical predictions provide a qualitative explanation of the experimental observations.

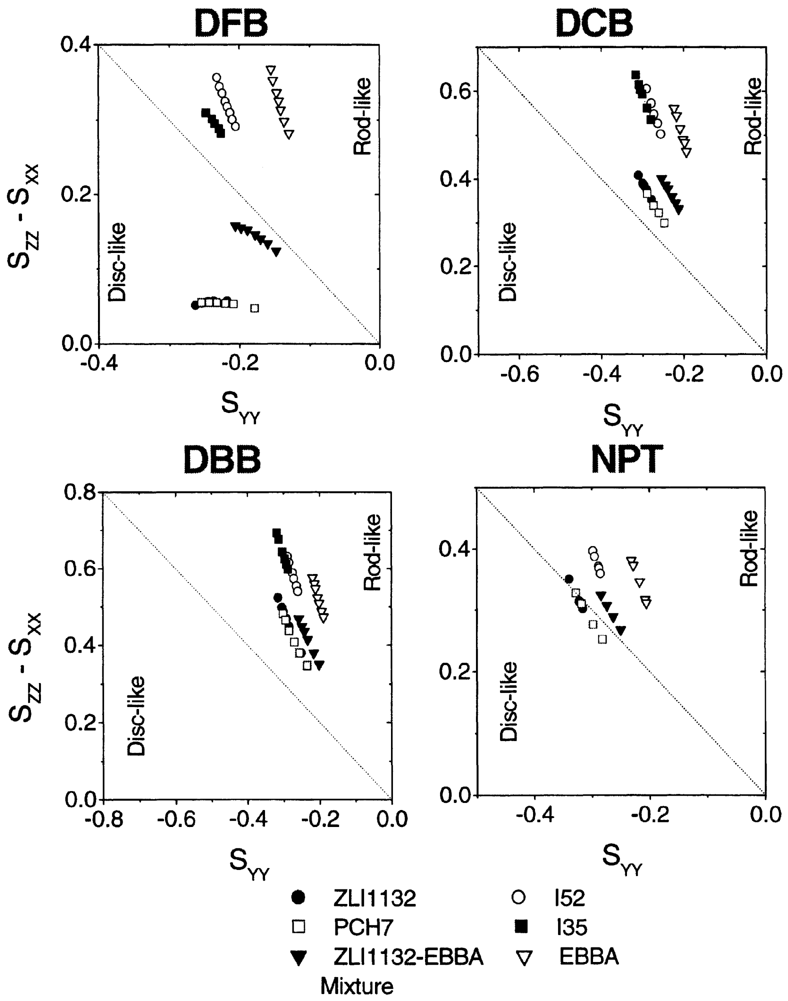

FIGURE 3. Experimental order parameters.

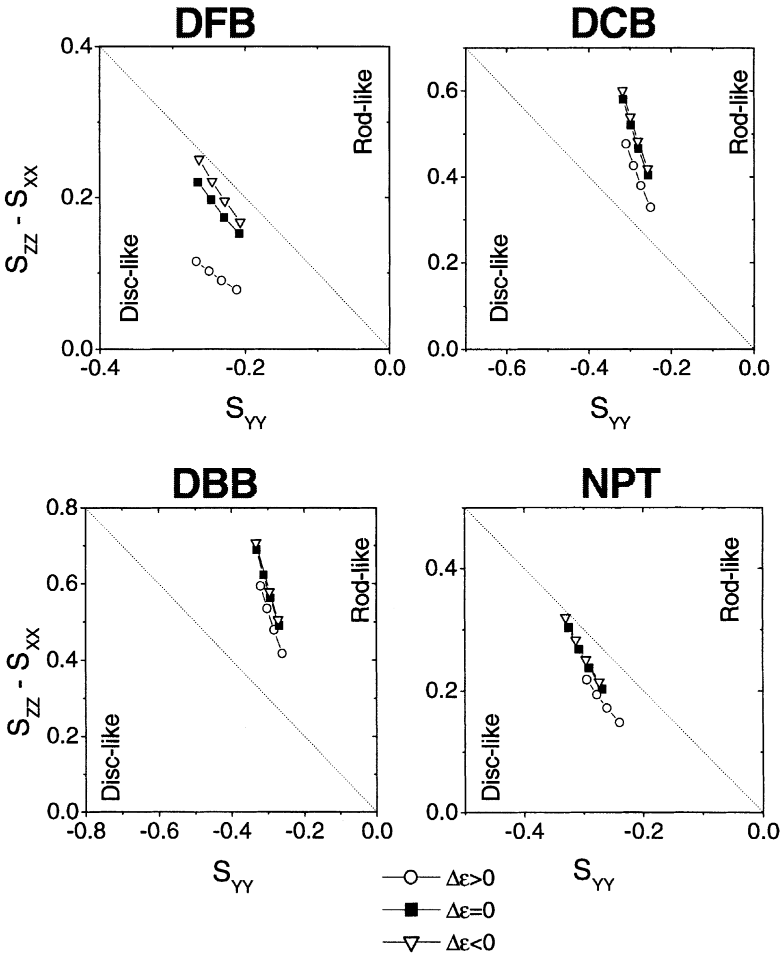

FIGURE 4. Predicted order parameters.

In all cases considered here the electrostatic contribution to the mean field potential results to be much smaller than the surface tensor term. Indeed, the effect of electrostatic interactions is extremely small, with the only exception of DFB, for which a significant contribution is predicted. This peculiar behavior has a twofold origin. First, the anisotropy of short-range interactions in the molecular plane, predicted on the basis of the surface anisometry, is rather weak. Second, electrostatic interactions are larger than for the other molecules under investigation due to the magnitude of atomic charges and polarizabilities and to the small dimension of the fluorine atom. The definitely stronger solvent dependence predicted for DFB is also in keeping with the experimental findings.

The similarity of behaviour shown by the the *p*-dihalobenzenes and naphthalene, in spite of their different electrostatic properties, deserves some comments. Also for other aromatic nonpolar molecules, such as anthracene and *p*-xylene, the measured and calculated biaxiality of order in the molecular plane increases in solvents with positive dielectric anisotropy (see [7] and references therein). On the other hand, the opposite trend is observed and predicted for anthraquinone and *p*-dinitrobenzene [7]. All this points out the difficulty in rationalising in simple ways how electrostatic interactions affect ordering in liquid crystals and the need of sophisticated models, based on a realistic account of the molecular structure. In this regard it can be reminded that no electrostatic effects at all would be predicted for these nonpolar solutes if reaction field were simply treated with the Onsager model [5].

Concluding, the qualitative agreement between theoretical predictions and experimental results supports the hypothesis that an explanation for the change of order observed when a solute is dissolved in different nematics can be found in the change in the anisotropy of electrostatic interactions, which can be related with the dielectric anisotropy of the solvent. The ability of our reaction field method to account for the anisotropy of electrostatic interactions in liquid crystals is confirmed by the present results. However, it appears that in general the predicted solvent effects are smaller than those experimentally observed. This issue, together with the fact that a given solute shows differences in the biaxiality of order even when it is dissolved in nematics with negligible dielectric anisotropy, points out the need of a more accurate description of the short range solute-solvent interactions by going beyond the surface tensor model, which completely neglects the structure of the solvent.

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