

Orientational Mechanisms in Liquid Crystalline Systems. 2. The Contribution to Solute Ordering from the Reaction Field Interaction between the Solute Electric Quadrupole Moment and the Solvent Electric Field Gradient

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In the previous paper of this issue, [Celebre, G.; Ionescu, A. *J. Phys. Chem. B* doi: 10.1021/jp907310g], following a generalized reaction field approach in the linear response approximation, we were successful in obtaining an analytical compact expression for the mean-field anisotropic orientational potential U_{Q-EFG} theoretically experienced by a highly idealized nonionic and apolar solute, considered as a point quadrupole immersed in a uniaxial polarizable continuum medium (model of a nematic solvent comprised of dipolar mesogenic molecules). The term U_{Q-EFG} describes the electrostatic interaction between the electric quadrupole of the solute and the electric field gradient induced at the solute by the surrounding medium polarized by the distribution of electric charges representing the quadrupolar solute itself. In the present paper, the obtained potential has been considered as an additional orientational interaction contributing to the solute ordering, besides the well-recognized and very effective “short-range” (size-and-shape-dictated) mechanisms. Since in our theory the solvent is characterized by its dielectric tensor, the model has been widely tested by taking as references the experimental order parameters of several uniaxial and biaxial different small rigid probe molecules (H_2 , N_2 , acetylene, allene, propyne, benzene, hexafluorobenzene, 1,4-difluorobenzene, and norbornadiene) dissolved in the nematic solvents ZLI1132 ($\Delta\epsilon \gg 0$) and EBBA ($\Delta\epsilon < 0$); moreover, the order parameters of the same solutes in the so-called nematic “magic mixture” (45 wt % EBBA + 55 wt % ZLI1132), where the short-range orientational effects are commonly believed to be very dominant, have been conventionally assumed as reference of the absence of electrostatic orientational effects. The experimental order parameters of the treated solutes, obtained in the past by liquid crystal NMR and available from literature, have been then compared with those theoretically predicted by our theoretical approach in order to obtain useful hints about two basic points, (a) the real physical nature of the interactions (other than the “size-and-shape”) involved in the orientational mechanisms and (b) the conceptual effectiveness of the suggested mean-field approach in describing this kind of phenomena. Successes and failures of the approach in the predictions are discussed at length, along with their possible reasons and implications.

1. Introduction

The liquid crystal NMR spectroscopy (LXNMR) of small solutes dissolved in liquid crystalline solvents¹ is widely recognized to be an extremely important technique for providing the solute order parameters. These invaluable orientational information (constituting the elements of the symmetric, real, and traceless Saupe ordering matrix S^1) are “the material” by means of which it is possible to test theoretical hypotheses about the nature of ordering in liquid crystals (making this particular state of matter so interesting from fundamental and technological points of view). However, the explanation of the mechanisms underlying the molecular order in mesophases is not an easy task; many models and theories have been formulated to give answers to this question (see, for example, ref 1c and references therein, where a comprehensive survey about the problem is given), but a general and fully satisfying description of orientational phenomena is still lacking. Very recently, following a phenomenological mean-field approach to the orientational problem, it has been formulated the ansatz that just two independent mechanisms are sufficient to rationalize the ordering phenomena.² This, in some way, conceptually supports the very

usual approximated description of the anisotropic orientational potential $U(\beta, \gamma)$ as a sum of two contributions³

$$U(\beta, \gamma) = U_{sr}(\beta, \gamma) + U_{lr}(\beta, \gamma) \quad (1)$$

In eq 1, $U_{sr}(\beta, \gamma)$ represents a short-range size-and-shape-dependent term, commonly recognized as dominant,⁴ whereas $U_{lr}(\beta, \gamma)$ is a longer-range potential (the angles β and γ give the orientation of the mesophase director, Z_{LAB} , aligned in the solute molecular frame). Various (basically phenomenological) models proved to be effective in describing the short-range term $U_{sr}(\Omega)$ (see, for example, refs 5–8); on the contrary, the nature and the role of $U_{lr}(\Omega)$ is still not completely understood. As widely discussed in the previous paper of this issue⁹ (henceforth referred to as Paper I), several mechanisms (based on electrostatic, induction, and dispersion effects^{10–14}) have been suggested for this second contribution to the orientational ordering. From a mean-field point of view, the most known hypothesis is that based on the Buckingham multipole expansion,⁴ whose third term, describing the interaction between the electric quadrupole moment of the solute (expressed by the molecular tensor Q) and the electric field gradient (EFG) of the solvent, has been recognized for a long time¹⁵ to be effectively involved in this kind of phenomena. This approach has been quite successful because it is very simple and manageable, and the value of the

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parameter called EFG (or F'_{ZZ}) can be freely optimized in order to reproduce as well as possible the available experimental data. On the other hand, this description is only phenomenological; there is no guarantee, in principle, that F'_{ZZ} represents the real (if any) electric field gradient present in the solvent and experienced by the solute. As a matter of fact, F'_{ZZ} could be considered just as an ad hoc parameter (not necessarily related to some physical property of the solvent) needed to reproduce the data. Therefore, this description lend itself to be considered too naïf and conceptually weak, and a number of criticisms have been indeed raised to it^{14,16,17} (the reader is referred to the Paper I⁹ for a detailed discussion of this point). However, pragmatically speaking, it allowed for the very useful creation of the so-called “zero-EFG” nematic mixtures nicknamed magic mixtures,⁴ the most famous of which (henceforth called MM) is made by mixing, at room temperature, 45 wt % of EBBA (*N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline) and 55 wt % of ZLI1132 (an eutectic mixture of three different *trans*-4-alkyl-(4-cyanophenyl)cyclohexanes and of *trans*-4-*n*-pentyl-(4'-cyanobiphenyl-4)cyclohexane). Apart from the theoretical implications, the practical experience shows that the ordering of very small probe molecules dissolved in MM can be predicted (within a 10% error) by considering only short-range interactions.^{4,18,19} At least some of the inadequacies of the model could depend on the strategic choice of adopting the appealing and convenient mean-field approximation (where the solvent is described as a continuum and any specification concerning the molecular features of the single molecules of the solvent as well as the orientational correlations between the probe and the solvent molecules are lacking¹⁴). In an effort to obviate the possible flaws inherent in the mean-field nature of the description, Monte Carlo (MC) simulations have been carried out by using particles with embedded central-point quadrupoles^{20–22} in order to study the relationship between the solute's quadrupole moment and the field gradient caused by the quadrupoles of solvent liquid crystal molecules. These simulations failed to reproduce the observed trends in order parameters of small solutes in liquid crystals and, in particular, the negative order parameter experimentally found for acetylene dissolved in the EBBA nematic mesophase.²¹ This fact suggested the idea of using distributed quadrupoles for the solute particles involved in the MC simulations;²³ in this case, the negative sign of the order parameter of acetylene in EBBA was at last reproduced,^{23a} and also, very recent results about D_{3h} solutes in nematic liquid crystals (where electric quadrupole moments of both solute and solvent molecules are represented by point quadrupoles distributed among molecular bonds) seem to be quite encouraging.^{23b,c} In light of these promising qualitative results from computer simulations, which would seem to indicate that the conceptual key for understanding this additional orientational mechanism has to be searched for in a detailed microscopic description of specific (site–site) electrostatic interactions rather than in a continuum mean-field (MF) approach to the problem, two interdependent basic questions still remain standing, (1) is, in principle, the MF approach “physiologically” inadequate to provide a meaningful, physically reliable, realistic, and satisfactory general description of possible orientational effects due to the Q–EFG interaction? and (as a consequence of this or as a side effect) (2) is F'_{ZZ} just an ad hoc parameter, or it can be in some way (a posteriori) related to some real physical property of the solvent? Intrigued by these questions and looking for a theoretically reliable and “firm” point of reference, following a generalized reaction field approach in the linear response approximation (LRA-RF), we derived in Paper I⁹ an analytical

compact expression for the mean-field anisotropic orientational potential U_{Q-EFG} experienced by a highly idealized nonionic and apolar solute, considered as a spherical point quadrupole in a uniaxial polarizable continuum medium (model of a nematic solvent comprised of dipolar mesogenic molecules). The obtained potential has been considered as an additional orientational interaction, besides the so-called “short range” (size- and shape-dependent) mechanisms, nowadays quite universally recognized as very effective and, probably, dominant. Since in our theory the solvent is characterized by its dielectric tensor, the model has been widely tested by taking as references the experimental order parameters (available from literature) of several nonpolar uniaxial and biaxial different small rigid probe molecules (H_2 , N_2 , acetylene, allene, propyne, benzene, hexafluorobenzene, 1,4-difluorobenzene, and norbornadiene) dissolved in the nematic solvents ZLI1132 ($\Delta\epsilon \gg 0$) and EBBA ($\Delta\epsilon < 0$); moreover, the order parameters of the same solutes in MM (where, as said above, the short-range orientational effects are commonly believed to be very dominant) have been conventionally assumed as reference of the absence of electrostatic orientational effects. The experimental order parameters of the solutes have been compared with those theoretically predicted by our theoretical model in order to grasp, if possible, useful hints about the conceptual effectiveness of the suggested mean-field approach in describing this kind of phenomena and the real physical nature of the interactions (other than the “size- and shape”) involved in the orientational mechanisms.

2. Theoretical Background

The solute order parameters S_{ab} can be given by exploiting the equilibrium statistical mechanics²⁴

$$S_{ab} = \langle 3 \cos \theta_a^Z \cos \theta_b^Z - \delta_{ab} \rangle / 2 = \frac{\int (3 \cos \theta_a^Z \cos \theta_b^Z - \delta_{ab}) \exp(-U(\beta, \gamma)/kT) \sin \beta d\beta d\gamma}{2 \int \exp(-U(\beta, \gamma)/kT) \sin \beta d\beta d\gamma} \quad (2)$$

where θ_a^Z is the angle between the a axis of the solute molecular frame and the Z_{LAB} direction (fixed along the mesophase director) and δ_{ab} is the Kronecker delta function. The heart of eq 2 is, of course, the anisotropic potential $U(\beta, \gamma)$ of eq 1, describing, as said above, the orientational solute–solvent interactions. Following the aims of the present study (widely expounded in the Introduction), eq 1 is rewritten as

$$U(\beta, \gamma) = U_{sr}(\beta, \gamma) + U_{Q-EFG}(\beta, \gamma) \quad (3)$$

2.1. $U_{sr}(\beta, \gamma)$. In this work, the needed term $U_{sr}(\beta, \gamma)$ of eq 1 has been used to “calibrate” the short-range orientational effects in order to reproduce the order parameters of the test solutes in MM (conventionally assumed as reference of the absence of orientational effects other than those size- and shape-dependent). Therefore, for the sake of convenience, we chose to simply give $U_{sr}(\beta, \gamma)$ in a phenomenological way as a spherical harmonics expansion

$$U_{sr}(\beta, \gamma) = sr_1 P_2(\cos \beta) + sr_2 \text{Re}[C_{22}(\beta, \gamma)] \quad (4)$$

where $P_2(\cos \beta)$ is the second-order Legendre polynomial,²⁵ $C_{22}(\beta, \gamma)$ represents a modified spherical harmonic²⁶ (whose real part is $\text{Re}[C_{22}(\beta, \gamma)] = (3/8)^{1/2} \sin^2 \beta \cos(2\gamma)$) and sr_1 and sr_2 (in kT units) are just two suitable parameters adjusted from time to time in order to reproduce the order parameters of the studied solute in MM.

2.2. $U_{Q-EFG}(\beta, \gamma)$. This part represents the central topic of the paper. The form of $U_{Q-EFG}(\beta, \gamma)$ to be introduced in eq 1 is

that LRA-RF derived in Paper I,⁹ where the nonionic and nonpolar solute is considered as a spherical point quadrupole in a uniaxial polarizable continuum medium. The general form of the interaction can be written as (see eq 3 of Paper I)

$$U_{Q-EFG}(\beta, \gamma) = -\frac{1}{2}F'_{ZZ}\left[Q_{zz}P_2(\cos \beta) + \sqrt{\frac{2}{3}}\Delta Q \operatorname{Re}[C_{22}(\beta, \gamma)]\right] \quad (5)$$

where the capital subscripts indicate the coordinates in the LABoratory frame; the small subscripts are those in the solute molecular PAS (principal axis system) of the \mathbf{Q} tensor, and $\Delta Q = Q_{xx} - Q_{yy}$. The LRA-RF formula for F'_{ZZ} obtained in Paper I is the following⁹

$$F'_{ZZ}(\beta, \gamma) = \pm \frac{6\pi}{R^5\epsilon_0}\left(\frac{\Delta\epsilon}{\epsilon_{||}(1 - \epsilon_{\perp} + (\epsilon_{||} - 1)\Psi)} - \frac{3}{1 + 2\epsilon_s}\right)\left[Q_{zz}P_2(\cos \beta) + \sqrt{\frac{2}{3}}\Delta Q \operatorname{Re}[C_{22}(\beta, \gamma)]\right] \quad (6)$$

where ϵ_0 is the vacuum permittivity, $\epsilon_{||}$ and ϵ_{\perp} are the parallel and perpendicular components (with respect to the nematic director aligned along Z_{LAB}) of the axially symmetric dielectric constant of the medium, $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$, $\epsilon_s = (\epsilon_{||} + 2\epsilon_{\perp})/3$ (in the isotropic limit, $\epsilon_{||} = \epsilon_{\perp} = \epsilon_s \equiv \epsilon_{\text{iso}}$), R is the radius of the virtual spherical cavity containing the solute, and Ψ is given by²⁷

$$\Psi = \int_0^1 \frac{dz}{1 + (\epsilon_{||}/\epsilon_{\perp} - 1)z^2} = \begin{cases} \arctan \sqrt{\epsilon_{||}/\epsilon_{\perp} - 1} / \sqrt{\epsilon_{||}/\epsilon_{\perp} - 1} & \epsilon_{||} > \epsilon_{\perp} \\ 1 & \epsilon_{||} = \epsilon_{\perp} \\ \ln \left(\frac{1 + \sqrt{1 - \epsilon_{||}/\epsilon_{\perp}}}{1 - \sqrt{1 - \epsilon_{||}/\epsilon_{\perp}}} \right) / (2\sqrt{1 - \epsilon_{||}/\epsilon_{\perp}}) & \epsilon_{||} < \epsilon_{\perp} \end{cases} \quad (7)$$

As explained in detail in Paper I, the sign \pm in eq 6 means that it is impossible, in principle, to discriminate a priori between two possible mathematical solutions for $F'_{ZZ}(\beta, \gamma)$. Moreover, it is worthwhile emphasizing that the obtained EFG (eq 6) depends on the orientation (β, γ) of the solute. This is perfectly reasonable and expected as a consequence of using a RF approach to describe the orientational dependences, where the reaction field (and its derivatives) induced along the director by the solute will depend on the orientation of the solute itself. By introducing eq 6 into eq 5, the following expression for the mean-field anisotropic orientational potential U_{Q-EFG} will be obtained

$$U_{Q-EFG}(\beta, \gamma) = \mp \frac{3\pi}{R^5\epsilon_0}\left(\frac{\Delta\epsilon}{\epsilon_{||}(1 - \epsilon_{\perp} + (\epsilon_{||} - 1)\Psi)} - \frac{3}{1 + 2\epsilon_{\text{iso}}}\right)\left[Q_{zz}P_2(\cos \beta) + \sqrt{\frac{2}{3}}\Delta Q \operatorname{Re}[C_{22}(\beta, \gamma)]\right]^2 \quad (8)$$

As stated in Paper I,⁹ we are unable to conclude, at the moment, if the found sign independence is a consequence of the “spherical cavity” assumption and/or if it is intrinsic to the used RF methodology; anyway, this leaves us free to determine the proper sign according to the physical consistency of the results predicted by using eq 8. We will try to rationalize the right sign a posteriori and, if possible, to relate this to the original sign of the solute’s quadrupole (so that, in practice, a sort of “memory” of the sign is kept).

3. Results and Discussion

In order to test our model, we considered the order parameters of nine nonpolar probe molecules, seven of which are uniaxial (five rod-like, H_2 , N_2 , acetylene, allene, and propyne; and two disk-like, benzene and hexafluorobenzene) and the other two of which are biaxial (1,4-difluorobenzene and norbornadiene). The \mathbf{Q} tensors and the order parameters of the solutes in ZLI1132, EBBA, and MM are available from the literature (refs 14, 18a, 19, and 23, and references therein). The general procedure that we used to carry out the tests was as follows: we proceeded first by adjusting the sr_1 and sr_2 parameters of $U_{\text{sr}}(\beta, \gamma)$ (eq 4) in order to reproduce the order parameters in MM; then, we fixed the obtained values of sr_1 and sr_2 , and we simulated the solute order parameters in ZLI1132 ($\epsilon_{||} = 17.69$; $\epsilon_{\perp} = 4.56$) and EBBA ($\epsilon_{||} = 4.58$; $\epsilon_{\perp} = 4.87$) by taking into account the total anisotropic orientational potential $U(\beta, \gamma)$ (eq 3) this time, with the additional term U_{Q-EFG} (eq 8) besides the fixed term $U_{\text{sr}}(\beta, \gamma)$ (for the source of dielectric data, see ref 28 and references therein). A very important ingredient of eq 8 (and of eq 6, of course) is R , that is, the radius of the cavity containing the solute. In order to avoid to treat this as one more adjustable parameter in the model (finding the “best” R value for each solute–solvent pair), we proceeded in the following way: (1) Starting from bond lengths and angles, available from classical organic chemistry textbooks,²⁹ and standard van der Waals radii (taken from ref 14 and, as usual, from ref 30), we roughly estimated the volume of the smallest sphere able to contain entirely a molecule of the solute. For acetylene, allene, propyne, benzene, hexafluorobenzene, difluorobenzene, and norbornadiene, we obtained quite similar results (spheres of about 3 Å radius, more or less), whereas, as obvious, smaller radii were obtained for H_2 and N_2 (~ 1.2 and ~ 2.5 Å, respectively). These values resulted in being properly chosen

TABLE 1: Ingredients of Equation 8 for Different Uniaxial Solutes^a

uniaxial solutes	Q_{zz}	sr_1	ZLI1132			EBBA		
			R	S_{zz} (exp)	S_{zz} (calc)	R	S_{zz} (exp)	S_{zz} (calc)
H_2	0.2	0	3.0	0.011	0.012	2.0	−0.014	−0.014
N_2	−0.6	−0.21	4.5	0.039	0.029	2.5	0.051	0.107
acetylene	1.8	−0.42	5.0	0.19	0.21	3.0	−0.040	−0.029
allene	0.7	−0.61	5.0	0.20	0.15	3.0	0.090	0.095
propyne	1.45	−0.74	5.0	0.28	0.25	3.0	0.060	0.043
benzene	−2.5	2.2	4.8	−0.25	−0.26	3.0	−0.12	−0.12
HFB	3.1	2.4	4.8	−0.21	−0.21	3.5	−0.30	−0.27

^a Rod-like solutes: z molecular axis along the figure axis; disk-like solutes: z molecular axis perpendicular to the rings. The quadrupole moments are given in 10^{-39} C m² units; sr_1 values are in kT units, and cavity radii are in Å. Moreover, the calculated S_{zz} values of the molecules dissolved in ZLI1132 ($\epsilon_{||} = 17.69$; $\epsilon_{\perp} = 4.56$) and EBBA ($\epsilon_{||} = 4.58$; $\epsilon_{\perp} = 4.87$) are reported and compared with the experimental order parameters^{14,23a} obtained by LXNMR at room temperature.

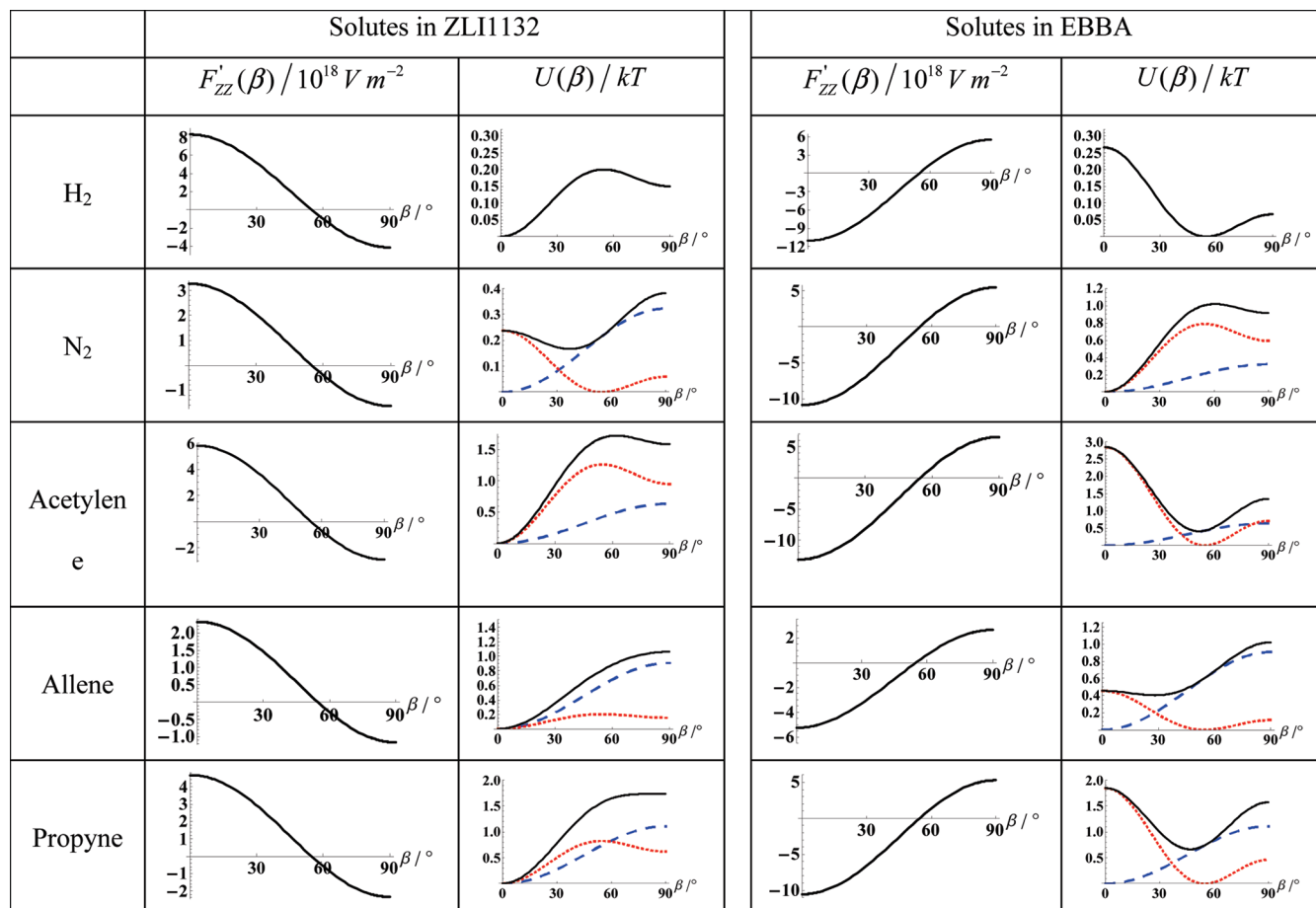


Figure 1. Plots of F'_{zz} and U (U_{sr} : blue dashed line; U_{Q-EFG} : red dotted line; U_{TOT} : black solid line) versus the orientation β of the solute along axis z with respect to the Z_{LAB} , along the nematic director (attention should be paid to the different scales of the insets).

TABLE 2: Ingredients of Equation 8 for the Two Different Biaxial Solutes Norbornadiene (NBD) and 1,4-Difluorobenzene (DFB)^a

biaxial solutes	Q_{zz}	ΔQ	sr_1	sr_2	R	ZLI1132		EBBA		
						calc.	exp.	R	calc.	exp.
NBD	-0.6	-1.65	0.15	0.0	6.0	$S_{zz} = -0.035$ $S_{xx} - S_{yy} = -0.02$	$S_{zz} = -0.04$ $S_{xx} - S_{yy} = -0.02$	5.0	$S_{zz} = -0.03$ $S_{xx} - S_{yy} = 0.01$	$S_{zz} = -0.03$ $S_{xx} - S_{yy} = 0.03$
DFB	-3.5	5.0	-0.75	-0.75	6.5	$S_{yy} = -0.24$ $S_{zz} - S_{xx} = 0.075$	$S_{yy} = -0.20$ $S_{zz} - S_{xx} = 0.05$	5.0	$S_{yy} = -0.1$ $S_{zz} - S_{xx} = 0.16$	$S_{yy} = -0.1$ $S_{zz} - S_{xx} = 0.3$

^a Quadrupole moments are given in 10^{-39} C m² units; sr_1 and sr_2 values are in kT units, and cavity radii are in Å. The calculated S_{aa} and $S_{bb} - S_{cc}$ values of the solutes dissolved in ZLI1132 and EBBA are reported and compared with the experimental order parameters obtained at room temperature by LXNMR.^{18a,19} (The solute frames are shown in Figure 4).

for the uniaxial solutes in EBBA (only $R(H_2)$ needed to be increased to 2 Å; see next sections), but they revealed to be too small for the biaxial probemolecules in EBBA and, in general, for the solutes in ZLI1132. Therefore, (2) we decided to proceed by increasing the scarce radii by a fixed amount, to take into account a sort of “solvent effect” virtually experienced by the solutes. Unfortunately, we verified that this amount changes not only by changing the solvent but also the uniaxial and biaxial solutes. The amounts for ZLI1132 (~ 2 Å for the uniaxial solutes; ~ 3 Å for the biaxial solutes) and for the biaxial solutes in EBBA (~ 2 Å) were roughly estimated starting from what was reported in ref 14, where the authors treated ZLI1132 and EBBA as consisting of spherocylinders of 2.6 Å radius. The R values determined in this way (reported in Tables 1 and 2) were finally used for the calculations, whose results are presented in the next sections. We are aware, of course, that the procedure described above is not flawless; however, also the “spirit” of

the whole work and, consequently, the significant basic assumptions affecting our model (the perfectly spherical cavity, the point quadrupole approximation, and so on) should be taken into account in evaluating the approach to the choice of the R values. Therefore, congruently with our purposes, we think that the obtained dimensions of the virtual cavities are quite reasonable; they have credible values within physically acceptable ranges. The fact that plausible values of R can be found for the model to satisfactorily reproduce the experimental results (see next sections) is, in our opinion, already an encouraging result.

3.1. Uniaxial Rod-Like Solutes in ZLI1132 and EBBA.

In Table 1, the ingredients of eq 8, the values of sr_1 and the calculated values of S_{zz} (the z coordinate being along the molecular figure axis) for H_2 , N_2 , acetylene, allene, and propyne dissolved in ZLI1132 and EBBA, are reported (sr_2 and ΔQ are of course 0, being the uniaxial solutes; moreover $sr_1 = 0$ for

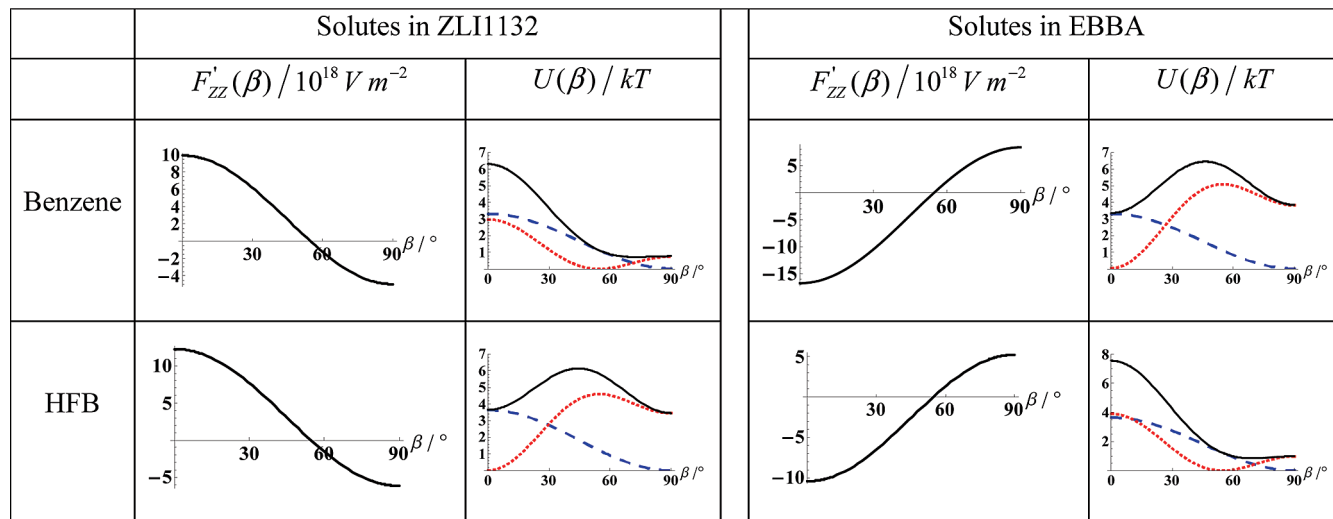


Figure 2. Plots of F'_{ZZ} and U (U_{sr} : blue dashed line; U_{Q-EFG} : red dotted line; U_{TOT} : black solid line) versus the orientation β of the molecular z axis (perpendicular to the rings) with respect to the Z_{LAB} (attention should be paid to the different scales of the insets).

H_2 , where only the term U_{Q-EFG} is taken into consideration¹⁵) and compared with the experimental order parameters obtained by LXNMR at room temperature (taken from refs 14 and 23a, and references therein). Moreover, the behaviors of the electric field gradient F'_{ZZ} and of the different terms of the anisotropic orientational potential as functions of β (representing the orientation of the solute long axis z with respect to the Z_{LAB} direction, fixed along the nematic director) for the different solutes are shown in Figure 1. From Table 1, it is possible to observe that the experimental order parameters in both of the solvents are quite well-reproduced (also, the controversial issue of the negative sign of the order parameter of H_2 and acetylene in EBBA^{15,23a} is accounted for by the model). Interesting considerations emerge also by the examination of Figure 1. About the sign of F'_{ZZ} in eq 6 (and, as a consequence, in eq 8), we realized (by trial and error) the validity of the following formula

$$\text{Sign}[F'_{ZZ}] = -\text{Sign}[Q_{zz}] \quad (9)$$

This revealed to be the right choice in order to obtain the good results reported in Table 1; all of the different choices, widely tested, give unphysical, unrealistic, or simply very bad results. Following this choice, the trends of F'_{ZZ} versus β in ZLI1132 (see Figure 1) resulted in being basically opposite with respect to those obtained in EBBA (therefore, probably related to the sign of the dielectric anisotropy of the solvent), whereas the behaviors of the different solutes along the single nematics ZLI1132 and EBBA were qualitatively quite similar (of course taking into account the different scales). The plots of the anisotropic potential are also reported in Figure 1; also in this case, the qualitative trends (in particular, for U_{Q-EFG} , represented in the figure by the red dotted lines) are quite similar for the different solutes along the single nematics, except for the N_2 solute, where the behavior is found to be about opposite; this should be expected because N_2 is the only rod-like solute having a negative Q_{zz} value.

3.2. Uniaxial Disk-Like Solutes in ZLI1132 and EBBA.

Two cases of this kind are of particular interest (for details, the reader is referred to the considerations presentes in refs 2 and 23a), benzene and hexafluorobenzene (HFB) in EBBA and ZLI1132. As a matter of fact, benzene and HFB are quite similar in size and shape, but they have quadrupole moments that, although comparable in magnitude, are opposite in sign (see

Table 1; for both solutes, the z axis is perpendicular to the ring). The order parameters of these solutes are negative and have opposite trends with the change of nematic solvent; for benzene, they decrease in magnitude when ZLI1132 is replaced by EBBA (with the S_{zz} in MM lying exactly in between),^{23a} on the contrary, for HFB, they increase in magnitude, and the S_{zz} in MM is very similar to that in ZLI1132.^{23a} As explained in the works of ref 23, these trends cannot be explained by simple phenomenological mean-field models nor by the reaction field model proposed in ref 28, where the sign of Q_{zz} is lost due to the dependence of the interaction potential on the Q_{zz} squared.² Therefore, in order to check the effectiveness of our method, we tested it also on benzene and HFB in ZLI1132 and EBBA. The procedure (proven to work so effectively for rod-like solutes) of calibrating $U_{sr}(\beta)$ on the MM order parameters and then adding the U_{Q-EFG} term to compare the calculated S_{zz} values in ZLI1132 and EBBA with the experimental ones failed for these disk-like solutes. The obtained bad results were the following, $S_{zz}(\text{benz/ZLI}) = -0.19$ (versus the reference experimental value $S_{zz} = -0.25$), $S_{zz}(\text{benz/EBBA}) = 0.28$ (versus the exp. $S_{zz} = -0.12$), $S_{zz}(\text{HFB/ZLI}) = 0.08$ (versus the exp. $S_{zz} = -0.21$), and $S_{zz}(\text{HFB/EBBA}) = -0.20$ (versus the exp. $S_{zz} = -0.30$). At this point (relying on the reliability of our form of $U_{lr}(\beta)$, supported by the good results previously obtained for rod-like solutes), we tried to reverse the procedure by fixing first U_{Q-EFG} and then changing sr_1 to find, if possible, a solution describing the right experimental trends of benzene and HFB order parameters in ZLI1132 and EBBA. By using this alternative approach, we were successful in reproducing the experimental S_{zz} values (see Table 1), and the resulting plots of F'_{ZZ} and U are shown in Figure 2. The sr_1 values, given in Table 1, resulted in being quite similar for benzene and HFB; this should be expected due to the solute similarity in size and shape, and it is, in our opinion, another signal of the reliability of the model. Very interesting remarks can be made by observing Figure 2 where, for the two disk-like solutes, the electric field gradient F'_{ZZ} and the anisotropic orientational potential versus β are shown (β is the orientation of the molecular z axis, perpendicular to the ring, with respect to the Z_{LAB} direction; moreover, the sign of F'_{ZZ} and, as a consequence, that of U_{Q-EFG} in eq 8 have been chosen by following eq 9). The trends of $F'_{ZZ}(\beta)$ for benzene and HFB in ZLI1132 and EBBA, respectively, are qualitatively similar (therefore, confirming what was already observed above for the

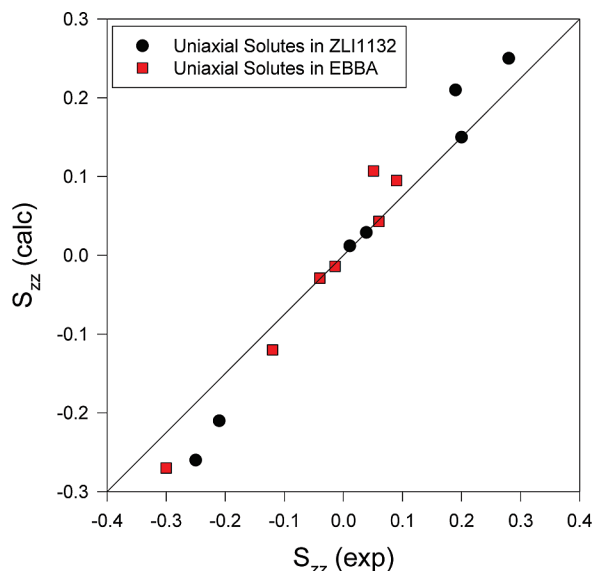


Figure 3. Calculated versus experimental order parameters of all of the studied uniaxial solutes in ZLI1132 (black circles) and in EBBA (red squares).

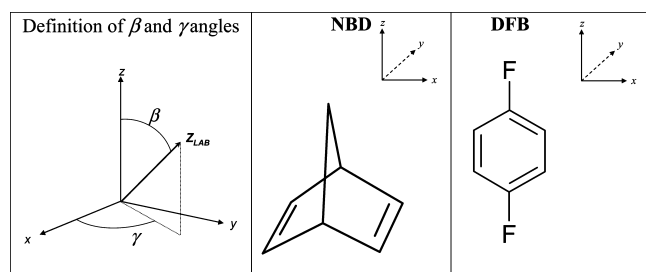


Figure 4. Graphical representations of β and γ angles, and structures of norbornadiene (NBD) and 1,4-difluorobenzene (DFB) with their molecular frames.

rod-like solutes and the probable relation of the behavior of $F'_{ZZ}(\beta)$ with the solvent $\Delta\epsilon$, whereas the $U(\beta)$ functions of

benzene in ZLI1132 are similar to those of HFB in EBBA and vice versa. Finally, in Figure 3, a graphical representation of the good quality of the whole agreement between experimental and calculated order parameters for all of the treated uniaxial solutes is shown.

3.3. Biaxial Solutes in ZLI1132 and EBBA. We tried to test our theoretical model also on the cases of 1,4-difluorobenzene (DFB) and norbornadiene (NBD) dissolved in ZLI1132 and EBBA (see Figure 4 for graphical definitions of angles β and γ and solute molecular frames). These cases are very important for two main reasons, (1) the solutes are biaxial, and therefore, this is a good way to test the general effectiveness of our mean-field model and (2) the experimental LXNMR orientational results for DFB^{18a} and NBD¹⁹ show very peculiar and intriguing behaviors. As a matter of fact, depending on the solvent, DFB exhibits a disk-like (in ZLI1132) or rod-like (in EBBA) orientational behavior. This effect has been shown to be basically due to the additional anisotropic orientational potential (describing the “non-size-and-shape” mechanisms), with the $U_{sr}(\beta, \gamma)$ term able, by itself, to explain the order parameters of DFB in MM.^{18a} The case of NBD in MM, ZLI1132, and EBBA is also very interesting; its ordering in MM is basically uniaxial (see Figure 5 of ref 19); on the contrary, when dissolved in EBBA, NBD shows a very small positive orientational biaxiality, opposite in sign to that exhibited in ZLI1132.¹⁹ For these two biaxial solutes, we proceeded as usual by adjusting first the sr_1 and sr_2 parameters of $U_{sr}(\beta, \gamma)$ (eq 4) to reproduce the order parameters in MM; then, we kept fixed their values, and we calculated the solute order parameters in ZLI1132 and EBBA by using eq 2, where eq 8 has been introduced by means of eq 3 (of course, besides the term $U_{sr}(\beta, \gamma)$ with the optimized sr_1 and sr_2 , as stated above). The right sign of $U_{Q-EFG}(\beta, \gamma)$ in eq 8 has been determined (by trial and error) to be negative. As reported in Table 2, the trends of order parameters of DFB and NBD in ZLI1132 and EBBA are excellently reproduced by the simulations, and the experimentally observed effect of the change of solvent on the solute order parameters are described very well. This is very clear from Figure 5, where, besides the plots of $F'_{ZZ}(\beta, \gamma)$, the contour plots

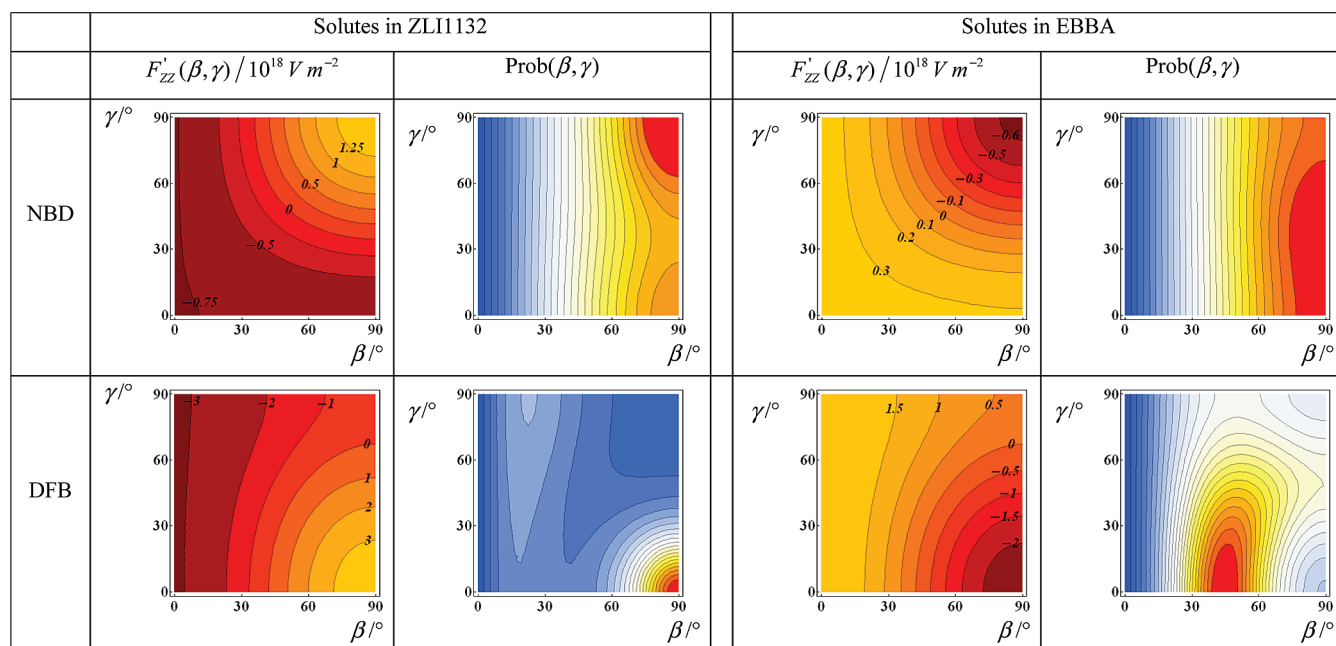


Figure 5. Contour plots of $F'_{ZZ}(\beta, \gamma)$ and $\text{Prob}(\beta, \gamma)$ versus the angles β and γ (see Figure 4 for their graphical definition). The red “hot” zones in the $\text{Prob}(\beta, \gamma)$ plots represent the high orientational probability zones.

of the orientational probabilities $\text{Prob}(\beta, \gamma)$ of DFB and NBD in ZLI1132 and EBBA are shown. For DFB in ZLI1132, the highest orientational probability (red “hot” zone in the plot) corresponds to the molecule about perpendicular to the director ($\beta \approx 90^\circ$); on the contrary, for DFB in EBBA, the statistically more populated situations are approximately those corresponding to the long molecular axis of DFB tilted within the range of $50^\circ \geq \beta \geq 40^\circ$ with respect to the nematic director and with the angle γ , involving the orientation of the short molecular axis, within the range of $30^\circ \geq \gamma \geq 0^\circ$. Also, in the case of NBD, the qualitative trends of the order parameters are very well accounted for, and the differences of $\text{Prob}(\beta, \gamma)$ in ZLI1132 and EBBA are evident (in particular, comparing the behavior of γ along the $\beta \approx 90^\circ$ coordinate, which is the most probable orientational tilt angle). It is worthwhile to recall that NBD is a quasi-spherical molecule¹⁹ and its ordering is very small; therefore, its description is quite a subtle question. The good results obtained by our model are therefore even more satisfactory.

4. Conclusions

In this work, the performances of an analytical, “exact” (i.e., nonphenomenological) mean-field model (derived in Paper I⁹) conceived for the description of the ordering effects acting on a probe molecule dissolved in a uniaxial solvent and due to the Q–EFG interaction (between the electric quadrupole of the solute and the electric field gradient of the nematic solvent) have been widely tested. Taking as references their real order parameters (taken from LXNMR experiments reported in the literature), several uniaxial and biaxial solutes have been studied in the nematic solvents ZLI1132 ($\Delta\epsilon \gg 0$) and EBBA ($\Delta\epsilon < 0$). Although the analytical formulation of the model (based on a generalized reaction field approach in the linear response approximation⁹) has been carried out, for convenience, by assuming that the solute is represented by a point quadrupole at the center of a virtual, perfectly spherical cavity and that the solvent is only characterized by its dielectric tensor, the obtained results are very encouraging. All of the experimental data have been satisfactorily reproduced; in particular, the model (for the first time by a nonphenomenological mean-field model) has been able to account for the intriguing and controversial negative order parameter of H₂ and acetylene in EBBA. Also, the order parameters of the disk-like solutes benzene and hexafluorobenzene in ZLI1132 and EBBA have been quite well predicted, even though, in this case, the approximation of assuming the order parameters in MM as a reference of the absence of electrostatic orientational effects revealed to be inadequate. Moreover, from a whole analysis of the outcomes concerning the uniaxial solutes, the relation between the EFG and the sign of the dielectric anisotropy of the nematic solvents (already suggested in ref 28) is here confirmed. Finally, other interesting results concern the studied biaxial solutes; the very peculiar orientational behaviors of the biaxial molecules 1,4-difluorobenzene and norbornadiene in ZLI1132 and EBBA have been very well described by our model. Of course, there are also limitations in the formulation; the main deficiency, in our opinion, is that the mathematical derivation is not able to solve the indeterminacy of the sign of the EFG (see eqs 6 and 8); therefore, the sign has been established from time to time in order to avoid unphysical, unrealistic, or simply very bad results. However, this produced a posteriori an intuitive formula (eq 9) that proved to be very effective in predicting the right sign. As a closing remark, a small comment is required; despite the significant theoretical and technological progresses of these last years in the physics of liquid crystals, many very well known and basic

aspects remain quite far from to be exhaustively and satisfactorily understood. Also, the basic question asked in the Introduction section about the adequacy of the mean-field approach to treat this kind of orientational interaction cannot be exhaustively answered and therefore is still open. However, we think (and we hope) that the proposed approach can be useful as a further contribution and, at the same time, as a stimulus in the right direction to better understand these really important and intriguing phenomena.

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