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Prediction from Molecular Shape of Solute Orientational Order in Liquid Crystals

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I. Introduction

Liquid crystals represent a very interesting state of matter because they show anisotropic properties normally found in solids, in combination with a degree of fluidity characteristic of liquids.[1−4] Liquid-crystal molecules show, on average, a significant preferred orientational order due to anisotropic intermolecular forces acting on every single molecule. The study of intermolecular forces arising from an anisotropic intermolecular potential is both important and complex.

To study the anisotropic intermolecular potential in a liquid crystal, the use of liquid-crystal molecules as probes presents itself as a logical choice. However, this approach has serious problems associated with it. First, not many experimental methods are available to address isolated liquid-crystal molecules directly. Nuclear magnetic resonance (NMR) has been an important method. However, because most liquid-crystal molecules possess a large number of spins, NMR spectra of liquid-crystalline phases often show only a poorly resolved structure.[5,6] This problem can be solved to some extent by appropriate methods of isotope substitution, but the problems of chemical synthesis involved should not be underestimated. Second, liquid-crystal molecules tend to be very flexible and are rapidly interconverting among an appreciable number of different conformations. In principle, every conformer samples the anisotropic potential in its own specific fashion, quickly leading to an unwieldy number of parameters required to describe the interaction between a liquid-crystal molecule and its environment.[7] Simplifying assumptions, in which the flexibility of the molecules is completely neglected and in which axial or biaxial symmetry is postulated, are usually not sufficiently realistic and have met with a limited degree of success.[8]

The complicated nature of intermolecular interactions has greatly hampered progress in achieving a detailed understanding of the physical nature of the orientation process. Since experiments performed on liquid crystals provide only the overall degree of orientational order, questions such as whether one or several factors contribute to this order, and whether such contributions can be described in terms of well-defined physical interactions, are not easily answered. Despite the difficulties in sorting out different contributions to molecular ordering, electrostatic long-range interactions, dispersion and induction forces, and repulsive short-range interactions have been considered in a qualitative fashion. However, a more quantitative description, preferably with some predictive power, has not resulted from these studies.

An alternative way of probing the intermolecular potential is through the use of relatively small probe molecules dissolved in the liquid-crystal solvent. To keep the discussion simple we shall focus on the

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simplest possible liquid crystals, viz. nematic phases which, in an external field, form a highly aligned anisotropic phase with uniaxial, cylindrical symmetry and with the opposing directions along this axis, commonly called the director, indistinguishable. Solutes dissolved in such partially oriented liquid crystals also acquire a degree of orientational order, the sign and magnitude of which depends on many factors. Since the number of spins in the solute molecules is relatively small, well-resolved NMR spectra can usually be observed. NMR thus provides a powerful means of studying the orientational behavior of solute molecules which experience the orienting potential present in the anisotropic mesophase. The study of an abundance of solutes in a large variety of liquid crystals, nematic and otherwise, has resulted in a large body of information about molecular properties, notably relative geometries derived from direct dipolar coupling tensors, quadrupolar coupling tensors, indirect coupling tensors, absolute signs of indirect couplings, nuclear shielding tensors, and about potential energy barriers in molecules rapidly interconverting among several conformations. In principle, this information can be extracted without having to acquire detailed insight into the orientation mechanisms at play in the solute−solvent system.[9−11]

The determination of solute physical properties in the liquid phase has proved to be a rewarding activity for many years. In addition, solute orientational order is a strong manifestation of the intermolecular forces present in anisotropic phases. The detailed study of orientational order shows great promise for obtaining a deeper understanding of the various factors which govern orientational behavior in anisotropic environments, and is therefore an important topic in its own right.

To make any headway, simplifying approximations are necessary. One of the most successful assumptions in describing the orientational ordering in nematics and which, despite its apparent crudeness, has not lost its appeal today, is the "mean field" theory of Maier and Saupe.[12,13] Suffice it to say at this point that a central feature of the Maier−Saupe approach is the particular $P_2(\cos\theta)$ dependence of the mean field on the degree of molecular orientation. This dependence leads to the long-range order characteristic of nematic liquid crystalline phases. Note that Maier−Saupe theory does not specify the physical nature of the intermolecular potential; its success demonstrates that second-rank interactions dominate.

In a fairly elementary picture of intermolecular forces an important role is reserved for long-range electrostatic forces which arise in a straightforward fashion from the interaction between the charge distributions of the molecule considered and the molecules surrounding it. When the charge distribution of one molecule perturbs the charge distribution of another, induction and dispersion forces come into play. When the electron clouds of neighboring molecules start to overlap, short-range repulsive foces become dominant.

Both the long- and short-range interactions will turn out to be crucial in the description to follow. A practical way of dealing with long-range interactions is to expand the potential $\phi^B(A)$ which the charge distribution of molecule B causes at the center of molecule A in a Taylor series around the center of A. This so-called multipole expansion[14,15] results in an interaction:

$$U = q^{A}\phi^{B}(A) - \sum_{\alpha}\mu_{\alpha}^{A}\,E_{\alpha}^{B}(A) - {}^{1}/_{3}\sum_{\alpha,\beta}Q_{\alpha\beta}^{A}\,F_{\alpha\beta}^{B}(A) + ... \tag{1}$$

with $\phi^{B}(A)$, $E^{B}(A)$, and $F^{B}(A)$ the potential, electric field, and electric field gradient (efg) caused by B at the position of A, and q^{A}, μ^{A}, and Q^{A} the charge, the electric dipole moment, and the electric quadrupole moment of A. The electrostatic energy resulting from this interaction involves both molecules A and B in their ground states. When the perturbing effect of the charge distribution of molecule A on molecule B is taken into account, long-range induction and dispersion energies, whose calculation involves excited states of A and B, and which depend on first and higher molecular polarizabilities, arise. The multipole expansion converges rapidly as long as molecules A and B are far apart, but breaks down before the charge distributions start to overlap. Thus a description in terms of molecular point multipoles constitutes a major approximation. At short range the multipole expansion must be abandoned completely, and repulsive short-range interactions take over. The calculation of short-range interactions from first principles is notoriously difficult.

From the first observation of NMR spectra of molecules partially oriented in nematic phases there has been speculation about the precise mechanisms underlying the observed degree of order. It was concluded at an early stage that there exists no correlation whatsoever between the degree of solute orientation and molecular electric dipole moments.[16] In view of the symmetry of the mean field in the nematic phase, in which opposite directions along the director are indistinguishable, this lack of correlation has been rationalized using the argument that the average electric field experienced by the solute, together with all its other odd powers, is expected to be zero. However, the neglect of molecular dipole moments as a mechanism of orientational ordering has been criticized recently,[17−19] and their importance remains a matter of some debate.[20] Early observations also led to the notion that the observed degree of orientation showed some tendency to increase with the size and shape anisotropy of the solute. Attempts at obtaining clear correlations, however, met with limited success. This was partly because the intuitive idea of orientational order due to repulsive short-range interactions arising from size and shape anisotropy could not be expressed rigorously as a term in the overall Hamiltonian leading to this order. Despite, or maybe because of the failure to obtain satisfactory correlations with solute physical properties, it soon became accepted among workers in the field that both electrostatic and short-range repulsive interactions had to play a role. For several decades, however, such ideas were only expressed in a qualitative manner.

The situation took a turn for the better when a conscious effort was made to probe the anisotropic liquid-crystal environment employing small, well-characterized probe molecules as solutes. In particular, experiments in which isotopomers of hydrogen and methane were used have led to significant advances.[21−41] These experiments have shown convincingly that an important contribution to the orientational order of molecular hydrogen and its deuterated and tritiated analogues arises from the fact that, in nematic solvents, these solutes experience an appreciable average nonzero electric field gradient which can couple with their electric quadrupole moment. Maybe unexpectedly, for the hydrogens this electrostatic contribution provides the dominant orientation mechanism. Moreover, the sign of the orientation parameter was found to depend on the sign of the electric field gradient experienced by the solute in the nematic solvent used.[26,28,36,40,41] In the case of the partly deuterated methanes, only when the contribution to the quadrupolar splitting arising from the external solvent electric field gradient, as estimated from the D_2 experiments, was subtracted from the observed values did the remaining quadrupolar splittings agree with those predicted using electronic structure calculations.[27,28,42] This is strong evidence that methane and hydrogen experience essentially the same positional distribution within the liquid-crystal solvent.

A real breakthrough in experimental methods which can be used to obtain information about orientational mechanisms has been achieved by mixing liquid crystals for which the isotopomers of molecular hydrogen experience opposite average electric field gradients. This novel approach involving nematic mixtures provides an important key; the long-range contributions to the overall orientational order of the isotopomers of molecular hydrogen can now be controlled and removed at will by the experimentalist.[29,43] It has been tempting to assume that other, larger solutes dissolved in these mixtures experience the same average long-range interactions as do molecular hydrogen and methane. This is obviously a severe and controversial assumption. However, as we shall show below, a large body of data on solutes of varying sizes and shapes in mixtures where the electric field gradient experienced by molecular hydrogen is removed (zero efg mixtures) can be understood in terms of a single orientation mechanism.[43−46] The most likely candidate for such a mechanism is a short-range repulsive potential; this approach is consistent with the notion of the zero efg experienced by molecular hydrogen. The use of zero efg mixtures is quite general and not restricted to certain classes of solutes. It is interesting to note that a similar situation prevails in ordinary liquid crystals for saturated aliphatic and cyclic hydrocarbon solutes whose long-range electrostatic interactions with the solvent are relatively unimportant. Several phenomenological schemes for modeling short-range interactions have been proposed.[19,34,35,43,44,47−80]

In recent years the above experimental and theoretical ideas have been applied to a plethora of solutes in different nematic phases as well as several zero efg mixtures. From these studies a wealth of information and understanding about the mechanisms which cause partial orientational order in anisotropic potentials has materialized. At present the state of the art is such that, under conditions for which only short-range contributions to the orientational potential are important, elements of the order tensor can be predicted to approximately the 10% level. The story behind this exciting new development is the topic of the present review article.

II. NMR of Oriented Molecules

Solute molecules dissolved in a solvent which provides an anisotropic environment show complicated NMR spectra which are usually dominated by direct dipolar couplings D and quadrupolar couplings B. The molecular orientation also modifies the chemical shifts σ and indirect coupling constants J from the values observed in an isotropic environment; these changes will not be the subject of the present paper.[9−11]

The dipolar coupling observed in NMR studies of oriented molecules can be expressed as the temperature and quantum average of a traceless symmetric second-rank tensor operator $\hat{D}_{\mathrm{pq}}$ where p and q represent the nuclei which are coupled:

$$\hat{D}_{\mathrm{pq}}(Q_{\mathrm{m}},\Omega) = -\frac{h}{4\pi^2}\frac{\gamma_{\mathrm{p}}\gamma_{\mathrm{q}}}{r_{\mathrm{pq}}^{\;3}(Q_{\mathrm{m}})}\sum_{\alpha,\beta}\hat{\Phi}_{\mathrm{pq},\alpha}(Q_{\mathrm{m}})\hat{\Phi}_{\mathrm{pq},\beta}(Q_{\mathrm{m}})\hat{S}_{\alpha\beta}(\Omega) \tag{2}$$

The quantities γ_{p} and γ_{q} are the gyromagnetic ratios of nuclei p and q, r_{pq} their internuclear distance, and $\hat{\Phi}_{\mathrm{pq},\alpha}$ the cosine of the angle between the internuclear direction and the molecule-fixed α-axis. The dependence on Q_{m} signifies that the dipolar coupling changes as the molecule undergoes internal motions, indicated by normal modes Q_{m}.

$\hat{S}_{\alpha\beta}$ is the second-rank tensorial orientation operator, also traceless and symmetric, which depends on the Euler angles Ω defining the orientation of the molecule with respect to space-fixed axes. The orientation operator is given by

$$\hat{S}_{\alpha\beta}(\Omega) = {}^{3}/_{2}\cos\theta_{\alpha}\cos\theta_{\beta} - {}^{1}/_{2}\delta_{\alpha\beta} \tag{3}$$

where θ_{α} is the angle between the molecule-fixed α-axis and the space-fixed Z-axis taken along the director which is here taken to be the magnetic field direction.

Temperature and quantum averages of a general operator $\hat{A}$ are expressed as:

$$A = \sum_{n} P_n(T)\langle n|\hat{A}(Q_{\mathrm{m}},\Omega)|n\rangle \tag{4}$$

$$P_n(T) = \frac{\mathrm{e}^{-E_n/k_{\mathrm{B}}T}}{\sum_{j}\mathrm{e}^{-E_j/k_{\mathrm{B}}T}} \tag{5}$$

where n labels the rotational−vibrational quantum states and P_n is the familiar Boltzmann factor.

Since the orientation operator is represented by a symmetric, traceless second-rank tensor, its expectation value $S_{\alpha\beta} = \langle\hat{S}_{\alpha\beta}(\Omega)\rangle$ has a maximum number of five independent nonzero components. The following limiting values hold for the various components:

$$-{}^{1}/_{2} \le S_{xx}, S_{yy}, S_{zz} \le 1 \tag{6}$$

$$-{}^{3}/_{4} \le S_{xy}, S_{xz}, S_{yz} \le {}^{3}/_{4} \tag{7}$$

The number of five independent S-components is reduced if the solute molecule possesses symmetry, and only those tensor elements which transform according to the totally symmetric representation of the solute point group survive.[9] The solutes considered in this work belong predominantly to the following categories:

(i) The solute has a 3-fold or higher axis of symmetry. If this axis is chosen along the molecular z-axis then $S_{xy} = S_{xz} = S_{yz} = 0$ and $S_{xx} = S_{yy} = -{}^{1}/_{2}S_{zz}$. Thus, there is only one independent order parameter.

(ii) The solute has two perpendicular planes of symmetry. If the x-axis is parallel to both planes and the y- and z-axes are in the planes, then $S_{xy} = S_{xz} = S_{yz} = 0$ and $S_{xx} \neq S_{yy} \neq S_{zz} \neq 0$. Thus, there are two independent order parameters.

(iii) The solute has only a plane of symmetry. If the z-axis is taken perpendicular to the plane and the x- and y-axes in the plane, then $S_{xz} = S_{yz} = 0$ and $S_{xx} \neq S_{yy} \neq S_{zz} \neq S_{xy} \neq 0$. Thus, there are three independent order parameters.

The quadrupolar couplings observed in NMR studies of oriented molecules which contain nuclei with $I \ge 1$ can be expressed as the temperature and quantum averages of an operator $\hat{B}_{\mu}$ where μ labels the quadrupolar nuclei in the molecule:

$$\hat{B}_{\mu}(Q_{\mathrm{m}},\Omega) = \frac{1}{2}\frac{eQ_{\mu}}{h}\sum_{\alpha,\beta}\hat{V}^{\mu}_{\alpha\beta}(Q_{\mathrm{m}})\hat{S}_{\alpha\beta}(\Omega) \tag{8}$$

Here, eQ_{μ} stands for the nuclear quadrupole moment of nucleus μ and $\hat{V}^{\mu}_{\alpha\beta}(Q_{\mathrm{m}})$ for the negative of the electric field gradient tensor at the position of nucleus μ. Again, $\hat{V}^{\mu}_{\alpha\beta}(Q_{\mathrm{m}})$ represents a second-rank traceless tensor.

When the quantum averages of the dipolar and quadrupolar tensor operators are calculated under conditions of rapid isotropic tumbling where all angles Ω are equally probable, both averages are zero. When the orientational averaging is performed over a molecular motion which is anisotropic, dipolar and quadrupolar couplings can be observed in the NMR spectrum.

From the above it is clear that the direct dipolar and quadrupolar couplings depend on the geometric and electronic structure of the solute molecule, respectively. Moreover, the observed quantities are averages over all molecular motions, both intramolecular and reorientational. The magnitude of the observed D and B couplings is determined by the values of the tensor elements of the orientational S-tensor. The degree of orientational order of the solute is an immediate result of the mechanisms which describe the interaction between hitherto unspecified physical properties of the solute on one hand, and details of the anisotropic environment, or “field”, on the other.[28] In this sense the study of orientation parameters is a study of intermolecular interactions, and any theory with some hope of success in predicting orientation parameters has to address the question of which interaction mechanisms between solute and solvent molecules prevail under certain conditions. It is obvious that a notoriously complicated problem such as intermolecular interactions can only be treated pragmatically on the basis of well-chosen approximations. In the following we shall develop an effective way of modeling intermolecular interactions for the simplest possible anisotropic environment, viz. uniaxial nematic liquid crystalline phases, which will be capable of predicting elements of the orientation tensor at approximately the 10% level.

It has been stated above that the observed direct dipolar and quadrupolar couplings are temperature and quantum averages of the associated operators. Since molecules are nonrigid structures which undergo extensive reorientational motion, averaging over all these motions is a crucial part of the quantum mechanical process. Assuming that the solute molecule is rigid in first approximation, the dependence of D and B on the vibrational normal modes Q_m can be neglected, leaving only the averaging of $\hat{S}_{\alpha\beta}(\Omega)$ over the reorientational motion. If real molecules with internal motion are considered, averaging over vibrational motions becomes important. However, it is not obvious that the averaging over vibrational and reorientational motions can be carried out independently. In reality, coupling between vibrational and reorientational motions is present, a phenomenon often called correlation.[28] This coupling severely complicates the averaging process, leading to interesting effects which have indeed been observed. Fortunately, vibration−rotation interaction is usually rather small and its effect on the values of orientation parameters and D and B couplings is limited. One notable exception is the case of methane and its deuterated analogues. Due to their tetrahedral symmetry, these molecules would be expected to show no anisotropic dipolar or quadrupolar couplings in their NMR spectra when dissolved in an anisotropic phase. The experimental fact that they still do can be explained completely in terms of vibration−rotation interaction.[25,27,28] Even though the contributions to dipolar and quadrupolar splittings arising from correlation are not enormous in magnitude, extensive experimental and theoretical studies on methane and its isotopomers dissolved in nematic phases have contributed significantly to a more detailed understanding of intermolecular interactions. For a detailed discussion on vibration−rotation interaction the reader is referred to the literature.[28,32,81,82]

III. A Benchmark Example—H_2, D_2, T_2, HD, HT, and DT

The use of small, well-characterized solutes as a means of probing the orienting potential in liquid crystalline phases has been a very rewarding strategy. For this purpose, no solutes are better suited than molecular hydrogen and its isotopomers. In the following, research carried out on these species in various nematic phases and the implications for orientation mechanisms will be reviewed in some detail.

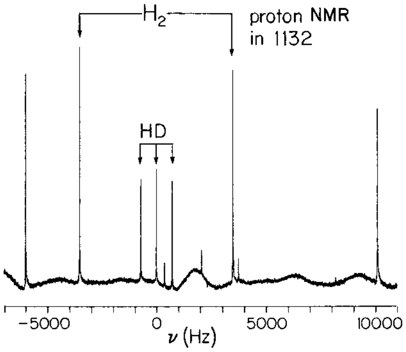

Figure 1. ^{1}H NMR spectrum of a mixture of H_2, HD, and D_2 in 1132 at 298 K. The extra lines are from an impurity. (Reproduced with permission from ref 24. Copyright 1982 American Physical Society.)

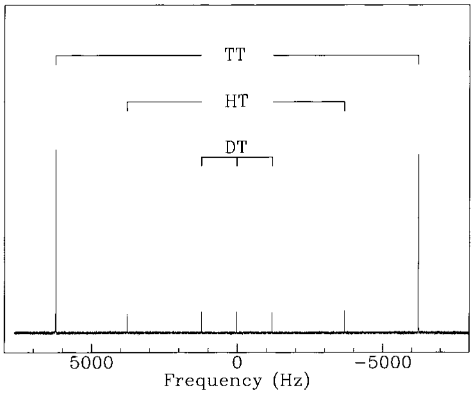

Figure 2. Tritium NMR spectrum of a mixture of T_2, H_2, and D_2 in EBBA at 300 K after irradiation of the sample tube to achieve isotope scrambling. (Reproduced with permission from ref 41. Copyright 1997 American Physical Society.)

NMR spectra of these molecules dissolved in various nematic phases have been obtained.[21,24,29,35,36,39,41,43] The ^{1}H NMR spectrum of oriented *ortho*-H_2 (Figure 1) consists of a doublet separated by $|3D_{HH}|$. The ^{3}H NMR spectrum of oriented *ortho*-T_2 (Figure 2) is also a doublet with splitting $|3D_{TT}|$. The ^{2}H NMR spectrum of D_2 (Figure 3) contains transitions arising from both the *ortho* and *para* species and can be analyzed analytically. An interesting observation is that the scalar coupling J between two equivalent deuterons leads to a splitting between two lines of unequal intensity. The order in which these lines occur in the spectrum enables the experimentalist to obtain the sign of the orientation parameter S_{zz}; this is because of the one-to-one correspondence with the sign of the indirect coupling (known to be positive). Surprisingly, in some nematic phases the sign of the orientation parameter is positive, in others negative.[24] In addition, over a temperature range between 220 and 320 K, no differences between the degrees of orientational order of *ortho*- and *para*-D_2 have been observed.[28] Both ^{1}H and ^{3}H spectra of HT (Figure 2) are doublets with splitting $|2D_{HT} + J_{HT}|$. Finally, the ^{1}H spectrum of HD (Figure 1) and the ^{3}H spectrum of DT (Figure 2) consist of three equally spaced lines with splittings $|2D_{HD} + J_{HD}|$ and $|2D_{DT}$

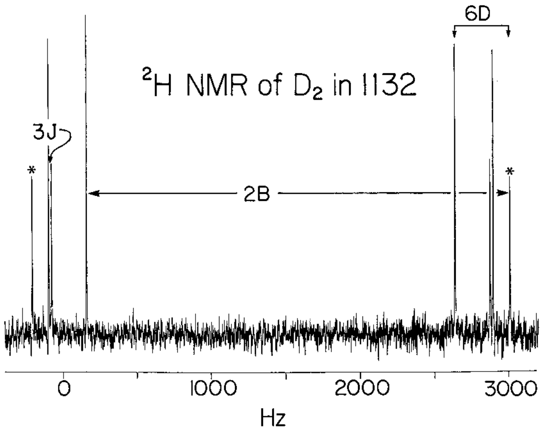

Figure 3. A 61.4 MHz deuteron NMR spectrum of D_2 partially oriented in the liquid crystal 1132 at 298 K. The asterisks label the lines from *para*-D_2. (Reproduced with permission from ref 34. Copyright 1987 International Society of Magnetic Resonance.)

$+ J_{DT}|$. The ^2H spectrum of HD is a doublet of doublets with splittings $|2B_D|$ and $|2D_{HD} + J_{HD}|$.

A striking observation when studying the hydrogens as probe molecules is that in all nematic phases employed there is a significant isotope effect on the degree of orientational order of the different isotopomers.[24,41] Invariably it was found that $|S_{H_2}| < |S_{HD}| < |S_{D_2}| < |S_{DT}| < |S_{T_2}|$. In addition, in many liquid crystals the value of $|S_{HT}|$ for the most asymmetrical isotopomer lies between the order parameters observed for D_2 and HD. An exception to this trend arises in the special mixtures which are the subject of this review. Obviously, the above state of affairs demands a sensible explanation.

To address the problem of how a small solute molecule obtains a degree of orientional order in a liquid crystal environment, a model describing the interaction between solute and solvent is required. The interaction to be modeled contains both long-range electrostatic and short-range repulsive contributions. As will become apparent, in the case of the hydrogens the orientational order is dominated by a particular long-range contribution. However, there is no need to specify the interaction from the start. The simple model that we consider involves an average second-order mean-field tensor $F_{\alpha\beta}$ which interacts with some second-order tensorial property $\beta_{\alpha\beta}$ of the solute molecule. The interaction between higher-order tensor fields and molecular properties is taken to be unimportant. The tensor $\beta_{\alpha\beta}$ is assumed to be determined by the electronic structure, and hence by the geometry, of the solute, and will therefore depend on its vibrational (normal) coordinates. In a uniaxial nematic phase with the magnetic field and the director along the laboratory Z-direction, the "field" $F_{\alpha\beta}$ should reflect the cylindrical symmetry of the phase. The interaction Hamiltonian (ignoring its isotropic part) is[28]

$$H' = -{}^1/_2\sum_{\alpha,\beta}\hat{F}_{\alpha\beta}\hat{\beta}_{\alpha\beta}(Q_m) = -{}^1/_3\hat{G}\sum_{\alpha,\beta}\hat{\beta}_{\alpha\beta}(Q_m)\hat{S}_{\alpha\beta}(\Omega) \qquad (9)$$

with

$$\hat{G} = \hat{F}_{\|} - \hat{F}_{\perp} \qquad (10)$$

Assuming that the above interaction is solely responsible for the orientational order of the solute molecules, for the cylindrically symmetric hydrogens this expression reduces to

$$H' = -{}^1/_3\hat{G}(\hat{\beta}_{\|}(Q_m) - \hat{\beta}_{\perp}(Q_m))\hat{S}_{zz}(\Omega) \qquad (11)$$

This term in the overall Hamiltonian of the rotating and vibrating solute molecule constitutes the perturbation induced by the liquid crystal "field". If we want to calculate S_{zz}, the temperature and quantum average of the orientation operator, we can either perform a complete quantum mechanical calculation including the above perturbation, or we can apply perturbation theory. In any case, one should realize at this point that in homonuclear diatomics restrictions due to the Pauli principle apply. H_2 and T_2 occur in two different modifications, one with total nuclear spin $I = 1$ which can only combine with odd-numbered rotational states (*ortho*-H_2 and *ortho*-T_2), the other with total spin $I = 0$ (and hence not observable in NMR) in combination with even-numbered J-states (*para*-H_2 and *para*-T_2). A similar distinction can be made between *ortho*-D_2 (total nuclear spin $I = 0$ or 2, with even J) and *para*-D_2 (total nuclear spin $I = 1$, with odd J). For HD, HT, and DT these Pauli restrictions do not apply, thus allowing both even and odd J-values. As a consequence, the values of S_{zz} have to be calculated using the appropriate J-states for the various isotopomers, and isotope effects on the solute orientational order may be expected.[24,28,40,41] In a classical description of the rotational degree of freedom such an isotope effect would not occur.

At this point we shall have to be more specific about which of the possible long-range contributions to the overall orientational order should be considered. Although there is no a priori knowledge about which contributions play a role, we shall for the moment assume that the only relevant mechanism at play involves the interaction between an average electric field gradient $F_{\alpha\beta}$ felt by the solute particle (efg) in the liquid-crystal solvent and the overall molecular quadrupole moment $Q_{\alpha\beta}$ of the solute molecule.[26] The justification of this seemingly arbitrary approach will have to be in the predicted results. Both the efg and the molecular quadrupole moment are described by traceless second-rank tensors. Their interaction contributes a term

$$H' = -{}^1/_3\sum_{\alpha,\beta}\hat{F}_{\alpha\beta}\hat{Q}_{\alpha\beta} \qquad (12)$$

to the Hamiltonian. Realizing that for a nematic phase the F-tensor has to possess cylindrical symmetry, and that the same holds for the Q-tensor in the axially symmetric solute molecules, eq 12 reduces to

$$H' = -{}^1/_2\hat{F}_{ZZ}\hat{Q}_{zz}\hat{S}_{zz} \qquad (13)$$

with the molecular quadrupole tensor operator defined as

$$\hat{Q}_{\alpha\beta} = {}^{1}/_{2}\sum_{k} e_k(3\hat{r}_{\alpha k}\hat{r}_{\beta k} - \hat{r}_k{}^2\delta_{\alpha\beta}) \tag{14}$$

Here the summation is over all charged particles, both nuclei and electrons, in the molecule. For molecular hydrogen and its isotopomers the molecular quadrupole moment is known experimentally and theoretically.

Another important consequence of the notion of an external average electric field gradient experienced by the solute is that the nuclei in the solute do not just experience an intramolecular electric field gradient caused by all the charged particles inside the molecule, but that an external contribution F_{ZZ} is also expected. In the case of the deuterons in HD, DT, and D_2 this results in extra contributions to the quadrupolar splittings in their NMR spectra. It was precisely these extra contributions which indicated the presence of the average efg, F_{ZZ}, in the first place.[26,28]

In a recent ab initio quantum mechanical approach the problem of the vibrating and rotating hydrogens, perturbed by the interaction between the efg and solute quadrupole moment, has been solved numerically with F_{ZZ} as the only adjustable parameter. In this calculation high-quality wave functions describing the nuclear motion and available data for highly correlated electronic wave functions at many different geometries have been used. Vibrational anharmonicity, centrifugal distortion, the changes of the nuclear quadrupole moment with internuclear distance, and the dependence of the molecular quadrupole moment on the rotational quantum number have been included.[40]

The results of the above complete ab initio calculations show very strong support for the notion that the predominant contribution to the orientational order of hydrogen and its isotopomers is the interaction between the efg and the solute molecular quadrupole moment. By adjusting F_{ZZ} for a given liquid crystal sample, the observed trend in orientation parameters for the different isotopomers is nicely reproduced, while the direct dipolar and quadrupolar couplings observed in the NMR spectra are calculated to a good degree of accuracy. In return, these calculations provide an estimate for F_{ZZ}.[40]

Results on the asymmetrical isotopomers HD, DT, and HT did not completely fit the trend predicted by the above ab initio calculations. These results have been interpreted as arising from a small liquid-crystal-independent contribution to the solute orientational order. A model based on a Lennard-Jones interaction between solute and surrounding liquid-crystal solvent provides evidence that the unusual behavior of the asymmetrical isotopomers could be due to the fact that the center of mass around which the molecule rotates and the geometrical center do not coincide for the asymmetrical species.[36,41]

Additional support for the idea that an average electric field gradient F_{ZZ} is experienced by solutes other than molecular hydrogen in nematic solvents was obtained at a relatively early stage from the experiments on methane and its isotopomers referred to above. The theory of correlation between vibrational and reorientational motion was capable of explaining the observed direct dipolar couplings in the NMR spectra quite well, but failed in reproducing the quadrupolar splittings. When it was assumed that the methanes and hydrogens dissolved in the same nematic phase experienced an *identical* mean electric field gradient, transferring the values obtained for the hydrogen case to the methane case led to excellent agreement with the observed quadrupolar splittings.[27,28]

Further evidence that solute particles experience a nonzero average electric field gradient in liquid-crystal solvents comes from work on atomic noble gas solutes. Atomic solutes which have *nuclear* quadrupole moments would experience this external efg, leading to quadrupolar splittings in their NMR spectra. Noble gas atoms which can be employed for such studies are ^{21}Ne, ^{83}Kr, ^{129}Xe, and ^{131}Xe. The first ^{131}Xe NMR spectrum of xenon in an anisotropic liquid used poly-γ -benzyl-L-glutamate (PBLG).[83] A triplet with a sizable quadrupole splitting was observed. Later studies of ^{129}Xe in binary mixtures of nematic phases,[84] of ^{21}Ne,[85] of ^{83}Kr and ^{131}Xe,[86] and of ^{21}Ne, ^{83}Kr, and ^{131}Xe,[87] in various nematic liquid crystals were carried out. Recently a study of ^{129}Xe and ^{131}Xe in a lyotropic liquid crystal has been reported.[88] These studies demonstrated not only that the atoms experience an external efg in liquid crystals, but also indicated that another contribution to the quadrupolar splittings is present. This second contribution is thought to arise from deformation of the electronic cloud of the noble atoms by the anisotropic environment, leading to a nonspherical electron distribution around the quadrupolar nucleus, and hence to splittings in the NMR spectrum. Since these Sternheimer antishielding effects are not easy to calculate, a reliable separation of the various contributions is difficult. However, the results obtained with the noble gas atoms support the notion that solute particles experience a nonzero average efg in nematic liquid crystals.

The results on dihydrogen, methane, and the noble gases, together with a large body of additional circumstantial evidence to become evident when liquid-crystal mixtures are discussed below, indicate the important role played by the electric field gradients experienced by solutes and the coupling of these gradients with solute molecular quadrupole moments.

IV. Solute–Solvent Systems Dominated by Short-Range Interactions

From the preceding section it is clear that interactions involving electrostatic molecular moments (especially the quadrupole) contribute to orientational ordering of solutes in liquid crystals. In addition, for solute molecules larger than dihydrogen and methane, it will be argued below that short-range repulsive interactions are important. To facilitate the investigation of the anisotropic short-range potential, it seems desirable to use samples for which interactions involving the solute quadrupole (and hopefully other electrostatic) moments have been removed. Two approaches to this problem have been pursued.

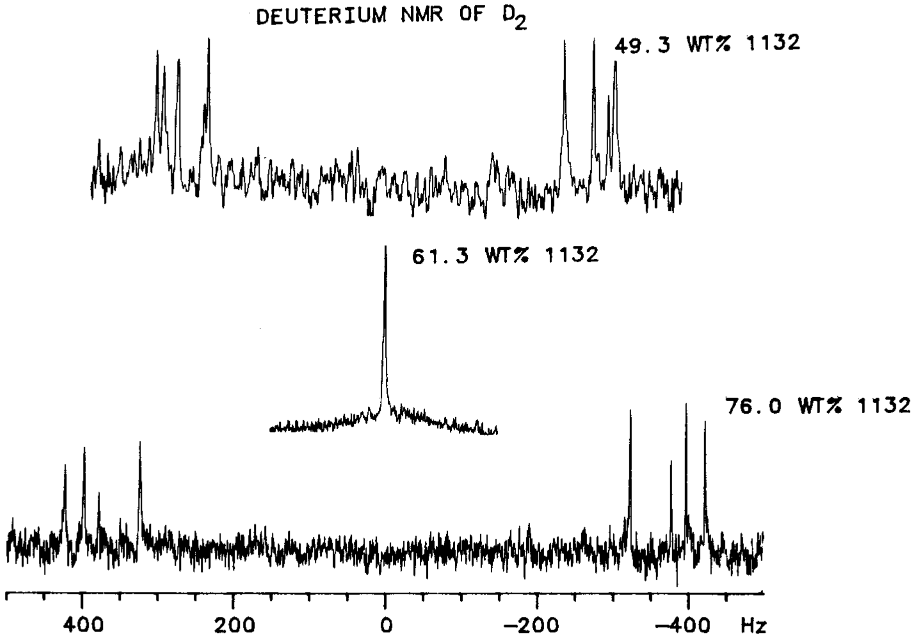

Figure 4. A 61.4 MHz deuteron NMR spectrum of D_2 dissolved in nematic mixtures of EBBA and 1132 at 310 K. (Reproduced with permission from ref 29. Copyright 1984 Elsevier Science Publishers B.V.)

In one approach, the solutes chosen for investigation are those that have a rather homogeneous charge distribution, have almost zero electric multipole moments, and possess small polarizabilities. Thus, for such solutes there is effectively no interaction with the long-range fields associated with the liquid-crystal environment. The compounds that until now have been chosen for such studies are saturated straight-chain[57,64,65,71,75,89,90] and cyclic[78] hydrocarbons. In section VIII we shall see that this approach has had a great deal of success for the limited range of solutes represented by such saturated hydrocarbons. We shall refer to such solutes as "magic solutes" because their electronic structure precludes the presence of significant anisotropic long-range electrostatic interactions.

The alternative approach, which we outline in some detail below, is to design liquid-crystal solvents for which all solutes experience essentially zero long-range electrostatic interactions. This possibility allows for investigation of solutes of any type, including those with quite large electrostatic moments. The idea is based on the fact that the orientation parameters of hydrogen and its isotopomers are of different sign in different liquid crystals. This has led to an interesting idea with profound implications: by making mixtures of liquid crystals in which the orientational order of hydrogen is of opposite sign, it should be possible to control the degree of orientation of this solute. All degrees of orientational order between the limits set by the component liquid crystals should be obtainable, provided that the mixtures behave as nematic phases. In particular, if the composition of the mixture and the temperature are carefully chosen, the degree of orientational order could be zero. Indeed, by making up appropriate mixtures of the component liquid crystals Merck ZLI-1132 (which is a eutectic mixture of alkylcyclohexylcyanobenzene and alkylcyclohexylcyanobiphenyls) and *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline (EBBA),[29] or alternatively (4-*n*-pentyl)-4′-cyanobiphenyl (5CB) and EBBA,[43] essentially zero orientational order of hydrogen and its isotopomers can be achieved. Since for these particular solutes we have reasoned before that the predominant orientation mechanism involves the interaction between the mean electric field gradient experienced by the solute and the solute molecular quadrupole moment, the implication is that certain mixtures can be made up in which the mean electric field gradient experienced by the solute is equal to zero. Such mixtures have been made, and the orientational order of dissolved dihydrogen is an order of magnitude less than in the component liquid crystals. For these situations, where the average electric field gradient as experienced by dideuterium appears to be zero, the phrase "magic mixtures" has been coined. Figure 4 shows a set of representative experiments indicating the change of D_2 orientational order with solvent mixture composition. The orientational order is almost zero for the spectrum from 61.3 wt % 1132 at 310 K, while the zero efg "magic mixture" composition is 55 wt % 1132 at 301.4 K.

The interesting question now arises whether the observation of zero orientational order for the hydrogens in appropriate mixtures is also exhibited by other, larger solute molecules. The experimental answer is that by employing suitable mixtures of liquid crystals the degree of orientation can be influenced appreciably in many cases, but that zero orientational order usually cannot be achieved. This result is not surprising; as indicated earlier, additional interactions are expected to play an important role in the orientational order of these larger solutes. Let us assume for the moment that in a certain liquid crystal mixture the solute "sees" the same mean electric field gradient as the hydrogens do. In that case "magic mixtures" provide a universal means of removing one mechanism that contributes significantly to solute orientational order. The problem of solute orientational order in these mixtures is therefore of a simpler nature than that in the component liquid crystals. However, how simple the remaining problem is going to be depends crucially on our ability to model the remaining orientation mechanism(s). In the following it will be argued that all anisotropic long-range electrostatic interactions (including those involving the solute dipole, quadrupole, and polarizability anisotropy) are unimportant in these mixtures. Thus the orientational order of solutes in "magic mixtures", and of "magic solutes" in other liquid crystal solvents, can in general be described by a *single*, short-range mechanism which is determined by the detailed size and shape of the solute molecule. Moreover, it will be shown how this short-range mechanism can be very effectively modeled in a phenomenological fashion. As a consequence of the ideas expressed in this paragraph it is tempting to investigate a description of the orientational order of an arbitrary solute in an arbitrary nematic phase in terms of two mechanisms only: (i) the interaction between the mean electric field gradient experienced by the solute and the molecular quadrupole moment; and (ii) a short-range mechanism related to the solute size and shape. As will be shown below, these ideas will indeed be supported by experiment to a very satisfactory degree. With hindsight it can therefore be stated that the notion of "magic mixtures" in conjunction with the study of small, well-characterized probe molecules has provided a veritable breakthrough in the unraveling of the possible mechanisms contributing to solute orientational order, essentially resulting in the ability to predict orientation parameters to quite an acceptable degree of accuracy.

Convincing evidence that the orientational order of a solute is determined by two orientation mechanisms, that can either compete or cooperate, is given by the observation that both acetylene[91,92] and methyl fluoride[93] exhibit positive order parameters in some liquid crystals, and negative in others. These observations are explained in a logical manner by the interaction between solute molecular quadrupole moment and average efg on one hand, and the size and shape effect on the other.

The approach outlined above, although broadly applicable, is based on rather crude assumptions and therefore has limitations. To appreciate the current state of affairs a summary of the central assumptions will be given. First, the problem of solute orientational order will be discussed within the framework of the mean field approximation. In this context, the mean field is taken to be the average liquid-crystal contribution to the single-particle potential felt by the solute.[94,95] Often the simplifying assumption that all solutes, regardless of type or size, experience the same mean field is made. This assumption would certainly not be valid if specific solute−solvent interactions were important. Although the validity of this approximation for e.g. the electric field gradient has been questioned,[19,68,96−98] a precise treatment of the problem in which this approximation is avoided is not currently available. Secondly, the fact that the total interaction can be broken down into the sum of long-range and short-range contributions presupposes a separability that in a more detailed picture might not be upheld. Thirdly, of the terms which occur in the multipole expansion describing the long-range electrostatic interactions between solvent and solute the coupling between the mean electric field gradient experienced by the solute and the molecular quadrupole moment of the solute is taken as the dominant contribution, assuming that the neglect of all other contributions is warranted. Note that the possible importance of the solute dipole is the subject of current debate.[19,20] Fourthly, it is assumed that the solvent mean field has only a negligible influence on the electronic structure of the solute and that it mainly affects the solute rotational and vibrational degrees of freedom. This assumption implies that the external mean electric field gradient can be added on directly to the internal electric field gradients present in the isolated molecule, hence neglecting Sternheimer type effects. The influence of Sternheimer effects on the quadrupolar couplings of molecular deuterium has been discussed.[37] However, such effects are irrelevant in the zero electric field gradient mixtures which are central to this review. Fifthly, the "magic mixtures" have zero efg at only one temperature, thus in principle limiting the scope of the use of these mixtures for temperature studies. However, in practice the small efg's that arise because of temperature changes in these mixtures contribute negligibly to the orientation potential, and temperature dependence studies have in fact been reported.[44,46] Despite this list of rather severe conditions that have to be met, the success of the current models in predicting orientational order of solutes in the specially designed liquid crystal "magic mixtures" discussed in the next section is unmistakable (vide infra). Of course it should be realized that the degree of predictability is not perfect and at present is limited to approximately the 10% level. However, a higher degree of predictability would require a description of orientational order at a more sophisticated level than is currently available for a general solute−solvent system.

V. Orientational Order in Zero Electric Field Gradient Mixtures

In the previous section the importance of "magic mixtures" has been emphasized. It has also been stressed that for solute molecules other than hydrogen and its isotopomers, removal of the orientation mechanism caused by the interaction between an average electric field gradient and the solute quadrupole moment does not result in near-zero orientational order. The remaining orientation mechanism(s) probably depend(s) on the size and shape of the solute. In this section arguments based on extensive experimental evidence will be presented which show that introduction of a *single* short-range mechanism appears to be sufficient.

The initial work on zero electric field gradient nematic liquid crystals utilized the mixture 55 wt % 1132 and 45 wt % EBBA at 301.4 K. Studies were carried out on a collection of solutes of varying sizes, shapes, and symmetries, including solutes that exist in more than a single conforma-

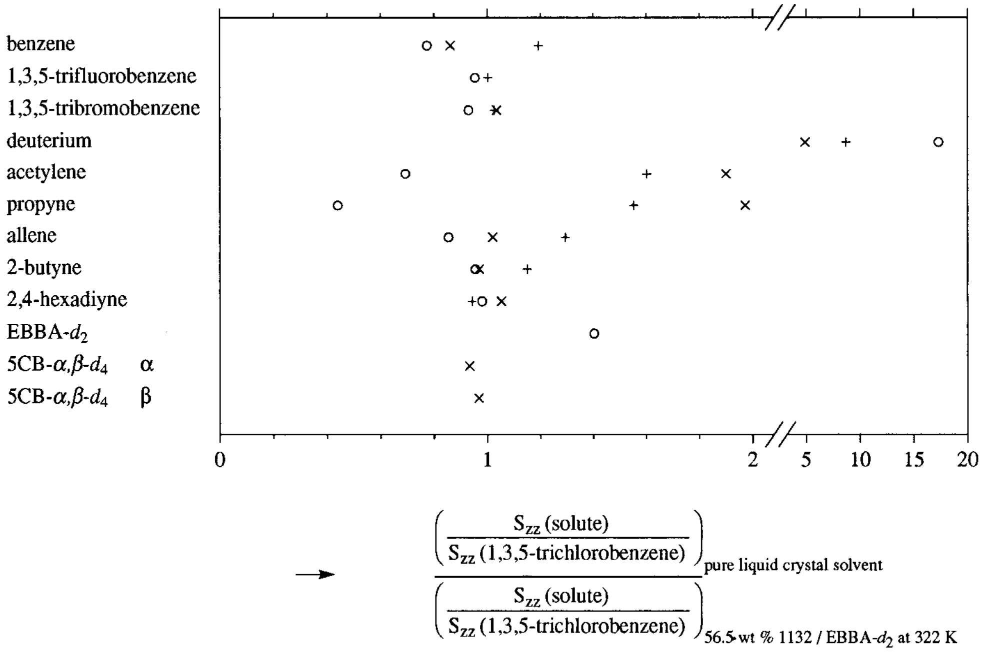

Figure 5. Ratio of the experimental molecular order parameter S_{zz} for sets of solutes in pure liquid-crystal solvents: EBBA-d_2 (○, at 301.4 K, data taken from ref 55), 1132 (+, at 301.4 K, data taken from ref 55), and 5CB-α,β-d_4 (×, at 294 K—benzene at 296 K, data taken from ref 35) and in 56.5 wt % 1132 in EBBA-d_2 at 322 K both scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene in these solvents. If available, the ratio using the experimental quadrupolar line splittings $\Delta\nu$ (instead of S_{zz} of the solute) for deuterons of the deuterated liquid crystals, scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene in these solvents, is also shown. For deuterium in both pure 1132 and 5CB-α,β-d_4 and acetylene in EBBA-d_2 the absolute ratios are shown as these solutes possess an order parameter S_{zz} of opposite sign in those solvents compared to the 56.5 wt % 1132/EBBA-d_2 mixture. (Reproduced with permission from ref 43. Copyright 1993 Taylor & Francis Ltd.)

tion.[29,31,34,36,39,43−46,55,58,60,62,67,70,76,79,87,92,99−111] It was found that phenomenological models for the anisotropic short-range interactions provided the best rationalization of the experimental results, which will be summarized in section VIII.

In a recent ^{1}H and ^{2}H NMR study different zero electric field gradient mixtures, viz. 55 wt % 1132/EBBA at 301.4 K, 56.5 wt % 1132/EBBA at 322 K, and 70 wt % 5CB/EBBA at 316 K were used. The orientational order of a variety of solutes, predominantly of high symmetry and hence characterized by one independent orientation parameter but largely differing in shape, size, and flexibility, was studied. Data available for the same series of solutes dissolved in the component liquid crystals EBBA, 1132, and 5CB were used for comparison.[43]

An important point to realize is that data on orientational order of solutes in liquid crystals taken from the literature are often obtained under poorly specified conditions. Differences in solute concentration, temperature and liquid crystal purity can result in huge changes in solute orientational order. When comparing results for a series of solutes dissolved in the same liquid crystal, the obvious choice is to use a sample that contains all the solutes at once. This may not always be possible because of the inherent complexity of the NMR spectrum and the high overall combined solute concentration that may result. Thus it is normally necessary to compare results obtained in different sample tubes, and hence some way must be found to compare reliably all measurements through some appropriate scaling procedure. In the following we shall only consider data for which proper scaling procedures can be or have been applied. One possibility is to compare samples at the same reduced temperature. Perhaps a better approach is to add some compound as an orientational reference. The solute 1,3,5-trichlorobenzene is often added to samples for this reason. By linearly scaling solute order parameters using values of S_{zz} (trichlorobenzene) obtained from the different samples, scatter in the solute orientation parameters between different sample tubes could be reduced appreciably, to a level of < 3%. However, since in the calculation of order parameters the mean intermolecular potential is in the exponential, the dependence of orientation parameters on this intermolecular potential is not linear. A better way of scaling would therefore involve the calculation of how much a certain change in potential would affect the orientation parameter. Such a calculation depends to some extent on the potential chosen. By selecting a reasonable $P_2(\cos\,\theta)$ potential the scatter could be reduced somewhat more, maybe to the 1% level.[43]

Having applied such scaling corrections, the question of whether the average solute orientational order can be described in the same way in unrelated liquid crystals can be addressed experimentally. To this end it is instructive to compare the ratio of S_{zz}(solute)/S_{zz}(trichlorobenzene) in one liquid-crystal solvent to the same ratio in a different liquid-crystal solvent. In the presence of *equivalent* orientation mechanisms both ratios should be essentially identical; in the presence of different mechanisms deviations are expected. Such comparisons are presented in Figure 5 for the "pure" liquid crystal solvents EBBA, 1132,

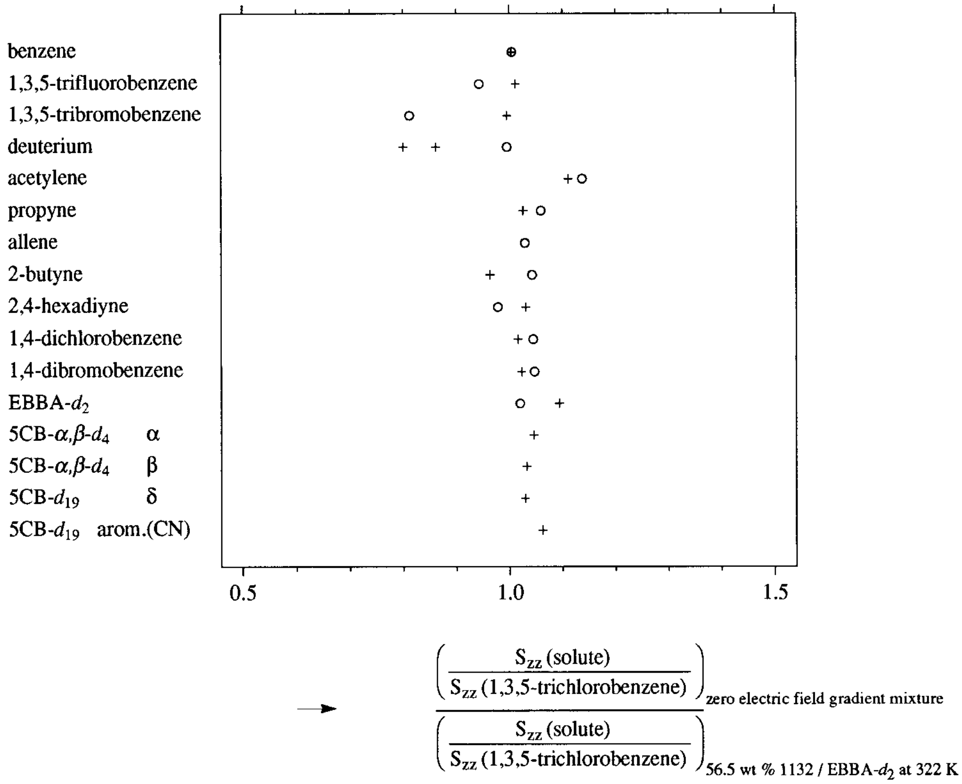

Figure 6. Ratio of the experimental molecular order parameter S_{zz} for sets of solutes in zero mean electric field gradient mixtures: 55 wt % 1132 in EBBA-d_2 (○, at 301.4 K, data taken from ref 55), 70.0 wt % 5CB-α,β-d_4 in EBBA-d_2 (+, at 316 K), and in 56.5 wt % 1132 in EBBA-d_2 at 322 K both scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene in these solvents. If available, the ratio using the experimental quadrupolar line splittings $\Delta\nu$ (instead of S_{zz} of the solute) for deuterons of the deuterated liquid crystals, scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene in these solvents, is also shown. (Reproduced with permission from ref 43. Copyright 1993 Taylor & Francis Ltd.)

5CB, and the zero efg mixture 56.5 wt % 1132/EBBA at 322 K. The large deviations of the ratios from unity show convincingly that the orientational behavior in the pure liquid crystals differs significantly from that in the zero efg mixture. In contrast, in Figure 6 results for various zero efg mixtures are compared to those in the zero efg mixture 56.5 wt % 1132/EBBA at 322 K. Strikingly, all points are close to unity, demonstrating that the orientational behavior in *all* zero efg mixtures is virtually identical. As a consequence, all the solute orientation parameters measured in one zero electric field gradient mixture can be used to predict those in another mixture by simply using one reference compound. Moreover, when a phenomenological short-range description (vide infra) is used to model the solute orientational behavior, the agreement between experimental and calculated orientation parameters for the entire series is striking and approximately at the 10% level. These considerations provide strong evidence for the notion that solute orientational order is governed by a single mechanism in the special mixtures.[43]

A subsequent ^{1}H NMR study involved experiments on *m*-dichlorobenzene, *o*-dichlorobenzene, *p*-dichlorobenzene, *o*-dicyanobenzene, furan, tetrathiofulvalene, and fluorobenzene in the zero electric field gradient mixtures 56.5 wt % 1132/EBBA and 70 wt % 5CB/EBBA. These solutes are all characterized by two independent orientation parameters, thus probing the mean-field potential in more detail. Again 1,3,5-trichlorobenzene was used as a reference molecule, and as before proper attention was paid to the scaling procedure. When the various solute orientation parameters S_{zz} and $S_{yy}-S_{xx}$ are scaled according to the observed S_{zz} parameters of the reference molecule, very satisfactory agreement for the results in both mixtures is obtained, again indicating that "scaled" order parameters can be transferred from one zero electric field gradient mixture to another. Assuming a single orientation mechanism and employing three different models to describe the interaction, it was concluded that, irrespective of the method of analysis, the same orientation mechanism is operative in both mixtures. As before, this provides strong support for the presence of a *single* mechanism in these mixtures.[45]

Recently a ^{1}H NMR study of the solutes *o*-dichlorobenzene, *m*-dichlorobenzene, 1,3-bromochlorobenzene, benzene, and 2-butyne with 1,3,5-trichlorobenzene as a reference compound has been carried out in the zero electric field gradient mixtures 55 wt % 1132/EBBA and 70 wt % 5CB/EBBA as a function of temperature. Through the range of temperatures studied, an analysis of the orientation parameters S_{zz} and, where applicable, $S_{yy}-S_{xx}$, again indicated that the solutes experience a very similar anisotropic potential in both mixtures. The results analyzed in terms of a phenomenological model for the orientation parameters show that the short-range potentials at the same reduced temperature are the same in both mixtures. Experimental values of $S_{yy}-S_{xx}$ for a given value of S_{zz} agree to about 5%, indicating the extent to which the potentials, as monitored by one molecule in both mixtures, agree.[46]

In other work the quadrupolar splittings observed in the ^{2}H NMR spectra of the liquid crystalline molecule 5CB-d_{19} have been studied in three zero electric field gradient mixtures. This solute is flexible and can be thought of as existing in 27 different conformer states, each with their own probability. For each of the three mixtures a temperature study was performed over a sufficiently narrow temperature range that the extent to which the electric field gradients present differed from zero did not significantly affect the solute orientational order. The quadrupolar splittings of 5CB-d_{19} in the 55 wt % 1132/EBBA and 56.5 wt % 1132/EBBA mixtures turned out to be almost equal at any given temperature, but the quadrupolar splittings in the 70 wt % 5CB/EBBA mixture are quite different. In all cases a single mechanism for the short-range potential was assumed and a number of phenomenological descriptions were used to model this mechanism. It was found that, at the same reduced temperature, the short-range potential parameters are the same for all three "magic mixtures", regardless of the precise details of the models used. However, none of the NMR spectra of the solute 5CB-d_{19} in the 5CB/EBBA mixture overlap with any of those from the 1132/EBBA mixtures; the difference is fully explained from the temperature dependence of the internal energy contribution to the conformer probabilities.[44]

In summary, all the evidence collected in recent years about the way in which solute molecules orient in nematic mixtures which possess zero or near-zero electric field gradients indicates that a single mechanism dominates the orientational order and that a simple scaling procedure suffices to transfer the orientation parameters from one mixture to the other. Moreover, there are strong indications that the mechanism is short-range and that a phenomenological treatment is capable of modeling this solute−solvent interaction. A discussion of such models will follow in section VII.

VI. The Anisotropic Intermolecular Potential

The exact description of the anisotropic part of the single-particle pseudopotential, which determines orientational order, is a formidable task. As discussed in the previous section, interactions contributing to this pseudopotential can be thought of as being long- and short-range in character. The short-range part depends in detail on the precise nature of the electronic structure of the two interacting species, and thus presents particular difficulty; exact solutions are impossible. To make any progress some gross approximation of the truth is essential, especially for systems as complicated as liquid crystals. To this end researchers have developed a "mean field" approximation[12,13] that has met with great success. In this approximation one completely ignores the details of the liquid crystal molecule, and approximates its presence as an average or mean field. Some electronic property of a single molecule then interacts with the mean liquid-crystal "field". If this interaction is anisotropic, the molecule is predicted to have orientational order which can be calculated from the anisotropic part of this mean-field potential. The precise nature of the intermolecular potential is usually not specified. However, it is possible to use the mean field framework and often to interpret the mean field parameters in terms of long- and short-range contributions. The main problem lies in the description of the short-range interactions (see section VII).

The original mean field calculation for liquid crystals was that by Maier and Saupe.[12,13] The intermolecular forces acting on a single molecule are essentially approximated by a single-molecule potential. Thus, each molecule is viewed as moving in a field generated via its interactions with all the surrounding molecules, and it is assumed that this field is independent of the degrees of freedom of every molecule except the one being considered. In their description the liquid crystal molecules are axially symmetric rods which require a single order parameter to describe second-rank tensorial properties. The physical basis of the anisotropic mean field does not have to be specified. It is only assumed that the pair potential between two rod molecules A and B has the form

$$U_{\mathrm{A,B}} = U_{\mathrm{A,B}}(\vec{r}_{\mathrm{AB}},\theta_{\mathrm{A}},\phi_{\mathrm{A}},\theta_{\mathrm{B}},\phi_{\mathrm{B}}) \qquad (15)$$

where θ and ϕ are the polar and azimuthal angles that the rods make with the vector $\vec{r}_{\mathrm{AB}}$ joining their centers. To obtain such a single-molecule potential representing the interaction of a molecule with its environment, the potential for the intermolecular forces is averaged over all degrees of freedom of the other molecules in the nematic phase, as well as over the translational degrees of freedom of the given molecule, neglecting short-range orientational effects. The most salient feature of the Maier−Saupe "mean field" approximation is the particular dependence of the mean field on the molecular orientational order leading to the long-range order characteristic of nematic liquid crystalline phases. Maier and Saupe calculated the mean field seen by one particle in the presence of many other particles, and showed that for an interaction potential that varies with angle as $P_2(\cos\theta)$ it can be written as

$$U(\theta) = -\epsilon' S P_2(\cos\theta) \qquad (16)$$

where θ is now the angle between the long molecular direction and the average direction, or director, of all the molecules in the sample considered, and S is the order parameter for this direction. The parameter ϵ' scales the intermolecular interaction and is taken as proportional to the inverse molecular volume squared, with the idea that the anisotropic interactions arise from dispersion forces. Any interaction potential can of course be written as a series expansion in an appropriate basis. In the Maier−Saupe description the potential is restricted to the first term (of rank two) of such an expansion which transforms according to the uniaxial symmetry of the nematic phase. Unquestionably, the success of assuming a $P_2(\cos\theta)$ dependence has been appreciable.

Magnetic resonance experiments are not capable of probing the complete orientational distribution function; however, scattering experiments are.[112] Neutron scattering experiments on a nematic liquid crystal comprised of a mixture of normal and perdeuterated *p*-azoxyanisole indicate the presence of a small $P_4(\cos\theta)$ contribution to the orientational distribution function, while the dominant term by far is the $P_2(\cos\theta)$ term. These observations are consistent with the Maier−Saupe model.[113]

Most mean field treatments of liquid crystals involve extensions of the Maier−Saupe theory. The reader is referred to the excellent book by R. Y. Dong for a detailed discussion of some of these theories.[8] Most of these approaches attempt to include the entire anisotropic intermolecular pseudopotential as arising from a single mechanism which often incorporates both long- and short-range interactions. In most of these theories the precise nature of the intermolecular interactions is not specified.

A description which is often used is the so-called potential of mean torque.[8,52,94,95,114−116] The pair potential between two rigid rodlike molecules can be expanded in terms of spherical harmonics in which the distance and orientation dependences of the pair potential are completely separated. To obtain a single-molecule potential, averaging over all orientations and intermolecular distances is carried out. This single-molecule potential is now expressed as a sum of terms which contain Legendre polynomials of increasing order. Because of the apolar nature of nematics only terms containing even Legendre polynomials are retained. The Maier−Saupe theory results when only the first term containing the Legendre polynomial of order 2 in this expansion is kept.

For nematogens that have less than cylindrical symmetry, additional terms are required in the description of the potential.[95] If terms of rank two only are kept, and if the solute−solvent interactions are assumed to be anisotropic dispersion forces which depend on the molecular polarizability tensor, the potential can be written as[117]

$$\frac{U(\Omega)}{k_{\mathrm{B}}T} = \epsilon[D_{00}{}^{2}(\Omega) + \lambda\mathrm{Re}D_{02}{}^{2}(\Omega)] \qquad (17)$$

where the D are Wigner rotation matrixes. The biaxiality parameter λ is calculated from the polarizability tensor components α_{ab} as

$$\lambda = \sqrt{\frac{3}{2}}\,\frac{\alpha_{xx} - \alpha_{yy}}{2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}} \qquad (18)$$

The success of this polarizability model as a mechanism for orientational ordering may be related to the fact that the polarizability tensor scales roughly with molecular dimensions, and thus it is difficult in practice to distinguish between long-range models based on the molecular polarizability and short-range models based on the molecular size and shape. In this sense, calculations based on the polarizability tensor elements might be thought of as models for short-range interactions which are expected to be functions of molecular size and shape anisotropy.

Other intermolecular interactions, such as those involving the molecular quadrupole or the reaction field of the molecular dipole, can also be cast in terms of eq 17. Thus the parameters ϵ and λ describe a generalized second-rank interaction tensor, and need not be associated with a particular anisotropic intermolecular interaction. A given anisotropy λ in the interaction can be used to calculate a universal curve (calculated as a function of ϵ) of the asymmetry of the order matrix $S_{xx}-S_{yy}$ versus S_{zz}. Comparison of such universal curves with experimental values of $S_{xx} - S_{yy}$ and S_{zz} gives the asymmetry of the interaction tensor λ directly. The value of ϵ varies with the experimental temperature, and comparison between experimental and calculated curves provides a test for the second-rank nature of the interaction represented by eq 17.

An extension of the potential of mean torque is to assign a “potential of mean torque” to each bond or group of atoms in a molecule. This model assumes that a molecule is built of rigid subunits, each of which independently interacts with the liquid-crystal mean field to produce an orientational torque.[115,116] In this picture there is no division of interactions into long- and short-range. This model has been used to calculate the order parameter tensors as a function of conformational motion in hydrocarbon chains, especially those in liquid-crystal molecules. A drawback that has been pointed out for this model is that it takes no account of the overall shape of the molecule.[64] In Figure 7 molecules of very different shapes but identical potentials of mean torque are indicated; because of the shape differences, very different orientation parameters would be expected.

In an attempt to better incorporate short-range interactions, Photinos, Samulski, and co-workers have extended the “potential of mean torque” idea to a “chord” model which attempts to account for the size and shape of the molecule,[64,65,72] see Figure 8. This mean field model for molecular orientation in a uniaxial phase is specially tailored for molecules comprised of repeating identical units.[64,65] Thus, it is not surprising that this model gives remarkably good results in the analysis of ^{1}H dipolar coupling constants of oriented hydrocarbons.[71,75,118]. This potential is derived from the leading terms in a rigorous expansion of the mean-field interaction. Photinos et al.[71] write

$$U_n^{\mathrm{aniso}}(\Omega) = -\sum_{i=1}[\tilde{w}_0 P_2(\mathbf{s}^i,\mathbf{s}^i) + \tilde{w}_1 P_2(\mathbf{s}^i,\mathbf{s}^{i+1})] \qquad (19)$$

where $\mathbf{s}^i$ (see Figure 8) is a unit vector describing the orientation of the i-th C−C bond of the hydrocarbon chain, and where the sum is over all of the bonds in the chain. The factors $P_2(\mathbf{s}^i,\mathbf{s}^{i+m})$ are given by

$$P_2(\mathbf{s}^i,\mathbf{s}^{i+m}) = {}^3/_2\cos\theta_Z^i\cos\theta_Z^{i+m} - {}^1/_2\mathbf{s}^i\cdot\mathbf{s}^{i+m} \qquad (20)$$

where θ_Z^i is the angle between the i-th bond and the nematic director. The parameters $\tilde{w}_m$ are proportional to the liquid-crystal order parameter. The first term in eq 19 corresponds to the independent align-

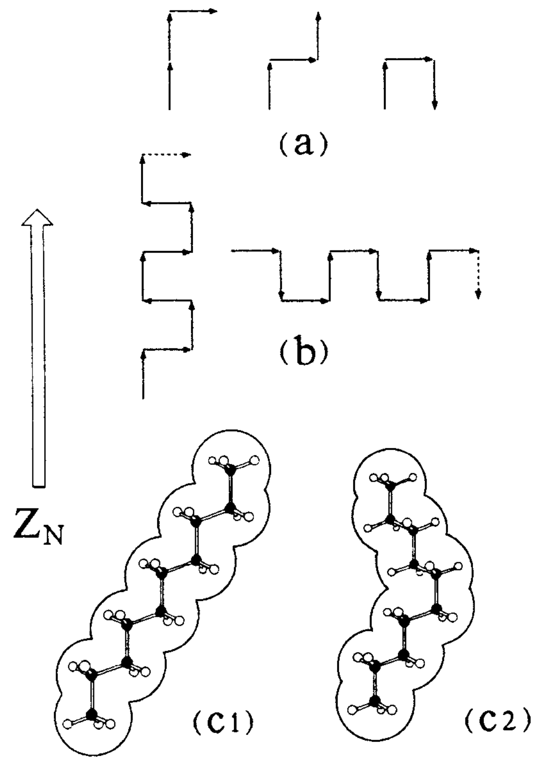

Figure 7. Examples of chain conformations and orientations with different shapes and identical bond orientational energy according to the group-additive potential of mean-torque approach. Panels a and b refer to freely jointed chains, and panel c refers to fixed valence angle chains. Z_N is the nematic director. (Reproduced with permission from ref 64. Copyright 1990 American Chemical Society.)

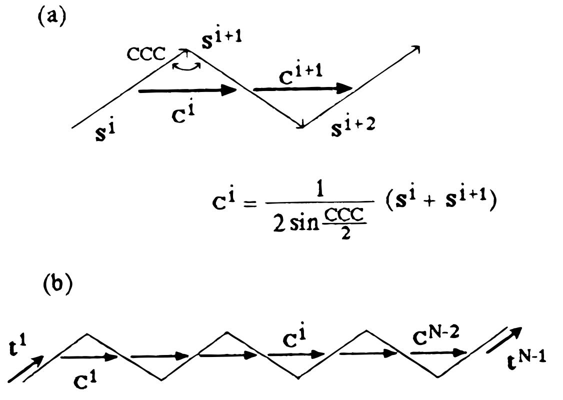

Figure 8. (a) Chord segment geometry in relation to C−C bond geometry and (b) schematic representation of the elementary units in the chord representation of the anisotropic interaction. (Reproduced with permission from ref 64. Copyright 1990 American Chemical Society.)

ment of separate C−C bonds that may arise, for example, from the anisotropy of the polarizability of the bonds.[119] The second term incorporates correlations between adjacent bond orientations, and therefore distinguishes between conformations that may have equal numbers of trans and gauche bonds but significantly different shapes; thus, it accounts for shape-dependent excluded-volume interactions. The specific case $\tilde{w}_0 = \tilde{w}_1$ is called the "chord model", since it can be shown to be equivalent to a model in which the chords c^i (see Figure 8) connecting the midpoints of the C−C bonds are the elemental submolecular units interacting with the external field. The chord model tries to describe both the long-range and short-range parts of the anisotropic intermolecular pseudopotential.

In potential of mean torque treatments, the interaction parameters are simply fitting parameters, and no attempt is made to relate them to molecular properties. For molecules which are made from a number of chemically different "rigid" groups, this leads to a multitude of undefined adjustable fitting parameters. For a more complete treatment the reader is again referred to Dong's book.[8]

Recently a theory has been developed which calculates the orientational distribution of a probe molecule in a nematic solvent in terms of an intermolecular potential describing steric, dispersional, and electrostatic interactions with the solvent.[19] The theory includes both short-range hard body and long-range contributions. A central approximation in this statistical theory consists of replacing the average of the distribution function for several solvent molecules by the product of averages of intermolecular pair terms. An important conclusion of this research is that the solute orientational order is not only due to short-range interactions, but that electrostatic contributions are of similar importance in "magic mixtures" and "pure" liquid crystals. Both solute and solvent molecular dipole and quadrupole moments are claimed to be important contributors to the electrostatic interactions. The theory is applied to a small number of solutes ranging in size from molecular hydrogen to anthraquinone. This study criticizes the notion that an important contributor to solute orientational order in "pure" liquid crystals is the interaction between an average electric field gradient experienced by the solute and the solute quadrupole moment. In a follow-up paper,[78] a series of closely related cyclic aliphatic solutes have been studied. The theory including only the hard-body short-range interactions (to be reviewed in section VII) has been used to analyze results for these "magic solutes".

The notion that molecular dipoles make an important contribution to molecular orientational order is still an open question.[19,20] In this context it is interesting to note that, when the three different methyl and chloro *para*-substituted benzenes with virtually identical size and shape but with different molecular dipole and quadrupole moments are dissolved in a "magic mixture", their experimental orientation parameters are essentially the same, suggesting that electrostatic contributions to the overall solute order in this nematic phase are unimportant. The order parameters of these solutes in other liquid crystal solvents are consistent with quadrupolar, but *not* dipolar, contributions to the molecular orientational order.[20]

With the advent of significantly greater computer power in recent years a different approach to the study of orientational order in anisotropic environments has become increasingly popular. These "computer experiments" include Monte Carlo (MC) and molecular dynamics (MD) simulations. Early work involved simulations of pure liquid crystalline phases. Two extreme approaches have been used. In the first, a lattice model is employed. The liquid crystal molecules are points, placed on lattice sites, which interact via some electrostatic potential. No short-range, repulsive interactions are included in the calculation which can be thought of as modeling only the long-range part of the pseudopotential.[120] In the other approach the liquid-crystal molecules are modeled as hard convex bodies that are allowed to both translate and rotate but not to overlap.[121−125] Such a calculation models only the short-range part of the molecular pseudopotential. It is amazing that such simple approximations of the liquid crystal molecular structure yield a very reasonable description of observed macroscopic properties. Some calculations attempt to incorporate a more realistic potential by utilizing “soft” ellipsoids, and using e.g. the Gay−Berne potential.[126−130] A rather complete study of a pure liquid crystal is that by Wilson and Allen[131,132] where conformational freedom is taken into account in a simulation of the nematic liquid crystal 5CB. In principle, the incorporation of such greater complexity is very powerful, but the calculation time required for such a full treatment is prohibitive.

It is interesting that most work has concentrated on the liquid crystal itself,[131−134] and that only a few simulations account for the presence of a solute.[38,98,135−142] The solutes that have been studied with these techniques until now are hydrogen,[38] benzene,[135,137,142] hexane,[136,138,140] biphenyl,[139] and a series of solutes modeled by hard ellipsoids of various lengths and widths.[98,141] The simulations have been used to explore to what extent conformational probabilities of the solute were affected by the liquid-crystal environment.

As discussed in section IV, there exist at least two orientation mechanisms in most liquid crystals. Most mean field studies of liquid crystals and of solutes in liquid crystals have assumed either that there exists only one mechanism, or that the efg/molecular quadrupole moment interaction can be neglected in the specific case under investigation. Such assumptions are dangerous. Of course, the simple Maier−Saupe mean field model[12,13] assumes a $P_2(\cos\theta)$ potential as given in eq 16, and the quadrupole interaction for axially symmetric solutes has precisely this form. Note that the quadrupole interaction is nonzero only when the averaging implicit in the Maier−Saupe theory is over the nonspherical distribution of the intermolecular vector.[97] It is anticipated that such a model could fit experimental NMR results for a given molecule, or type of molecule, in any liquid-crystal environment. In this case the parameter ϵ' must account for all interactions that have a $P_2(\cos\theta)$ form, including the efg/molecular quadrupole moment term.

However, when two or more interactions are operative, it is quite likely that they will contribute unequally to the anisotropic intermolecular potential in different liquid crystals, and that their relative importance among solutes will depend on differences in solute properties. Thus, there is no a priori way to transfer results between the same solute in different liquid crystals, or between different solutes in the same liquid crystal. That is, a single-mechanism theory that explains the orientational order of a set of molecules in a given liquid crystal will normally provide a disastrous prediction of results obtained in a different liquid crystal (see Figure 5). To fit the results obtained in the second liquid crystal, quite different model parameters are normally needed.

In section IV we reviewed the considerable evidence that there are two and only two main contributions to the anisotropic intermolecular interactions that lead to orientational ordering in nematic liquid crystals. One of these contributions is a long-range interaction involving the nonzero efg which most solutes experience in ordinary liquid crystals, and the other is most likely short-range in nature. An important advance of recent years is the use of “magic mixtures” for which an important part of the long-range anisotropic interaction has been removed. There is strong evidence that a single, probably short-range, orientation mechanism is operative in such mixtures, and thus they provide an excellent medium for examining this mechanism.[43−46] Because of the inherent difficulty in dealing with short-range interactions, it is sensible to ask whether some phenomenological description, mean field or otherwise, can be found to account for the order parameters observed in these mixtures. In the next section we shall review several of the most successful models that have been used in the interpretation of data obtained from these “magic mixtures”. Of course these short-range models are equally applicable to “magic solutes”.

VII. Phenomenological Descriptions of Short-Range Interactions—Size and Shape Models

The first MC and MD simulations of nematic liquid crystals that employed hard ellipsoids or spherocylinders included no electrostatic interactions. This description, which involves only short-range interactions, was remarkably successful in that it predicts the existence of nematic phases on the basis of hard-body interactions alone. The idea that the most important contribution to the single-molecule anisotropic pseudopotential must arise from short-range interactions has been incorporated into several mean-field descriptions both of small solutes in nematic phases and of liquid-crystal molecules themselves. These descriptions account in an often somewhat crude manner for the size and shape of the solute or liquid crystal molecule under consideration. In some cases, the size and shape is accounted for by the moment of inertia, or by the overall dimensions, of the molecule. In other cases the molecule is portrayed as a collection of van der Waals spheres that interact in some way with the liquid-crystal mean field.

We note that for a mean field potential $U(\Omega)$ the order parameters are calculated by taking the appropriate Boltzmann averages as the molecule is rotated through all possible orientations $\Omega \equiv \theta_\alpha,\theta_\beta$

$$S_{\alpha\beta} = \frac{\int ({}^{3}\!/_{2}\cos\theta_{\alpha}\cos\theta_{\beta} - {}^{1}\!/_{2}\delta_{\alpha\beta})\exp\left(\frac{-(U(\Omega) - \langle U\rangle)}{k_{\mathrm{B}}T}\right)\mathrm{d}\Omega}{\int \exp\left(\frac{-(U(\Omega) - \langle U\rangle)}{k_{\mathrm{B}}T}\right)\mathrm{d}\Omega} \quad (21)$$

This equation should be regarded as the defining equation of the potential of mean torque acting on a solute particle. The isotropic component $\langle U\rangle$ that is inherent in some of the potentials employed below has been subtracted to ensure that the potential is totally anisotropic. This subtraction has no effect on calculations for rigid molecules, but it is particularly important to realize that, when treating molecules which exist in more than a single conformation, both the anisotropic and isotropic parts of the potential affect the conformer probabilities.[76,143]

Below we shall review some of the phenomenological mean field models that have been proposed for the investigation of short-range interactions. The zero-efg mixtures and the "magic solutes" represent excellent conditions for testing the models, and results from NMR experiments will be reviewed in section VIII.

A. Early Models

There have been several attempts to model the anisotropic short-range interactions in liquid crystals in a phenomenological way. In these models, the molecular size and shape was taken into account in a simplified manner, using parameters such as overall molecular dimensions which were sometimes estimated from moments of inertia.

It long has been realized that in many cases molecules, in the anisotropic environment of rodlike liquid crystals, tend to orient with their longest dimension along the director axis. Already in 1971 an attempt was made to put this idea on a quantitative basis by observing that, for several substituted benzenes of C_s symmetry, the principal axes of the order tensor and the moment of inertia tensor did not deviate much, and that a reasonable correlation existed between the different orientation parameters and the corresponding moments of inertia.[48] A few years later a simple model of interacting liquid molecules which lack an axis of rotational symmetry was developed in which the molecules were approximated by rectangular parallelepipeds.[49] Surprisingly, excluded volume considerations led to a mean field model and to a phase diagram showing both uniaxial and biaxial phases. This idea, after some slight modifications,[144,145] was exploited by approximating alkane conformers with such rectangular shapes.[57,75,76,89] The linear dimensions of length, breadth, and width were then estimated from the three moments of inertia. However, there are serious problems associated with the manner in which this model has been applied to solutes in nematic solvents.[146] First, the model is developed in terms of the volume excluded by two identical particles, and the equations do not apply for the volume excluded by dissimilar particles such as the two different liquid crystals of a mixture or of a solute and a liquid crystal. If we follow the prescription in the literature[57,75,76,89] we predict positive order parameters for the symmetry axes of both prolate and oblate objects. This is consistent with a collection of oblates forming a discotic phase, but is not consistent with the negative order parameter anticipated, and observed, for such oblate objects as solutes in a nematic phase. In addition, the second-rank part of the interaction tensor introduced by Straley (equivalent to the $\epsilon D^{2}_{00}(\Omega)$ term of eq 17) is not in the correct spherical tensor form, and contains a nonzero trace. This also applies to the various corrections of the original equation,[57,75,76,89,144,145] and leads to incorrect Boltzmann factors for orientational probabilities. Hence, comparisons based on the Straley model should be viewed with caution.

In an independent development[47] the linear dimensions of molecular solutes were approximated by Stuart's "Wirkungsradien".[147] Later the linear dimensions were estimated on the basis of van der Waals radii.[56,59,61,63] The predictions of the above early models have been compared to experimental orientation parameters obtained in "pure" liquid crystals. Since it is now known that in these "pure" liquid crystals more than one orientation mechanism is usually operative, it is not surprising that comparisons between theory and experiment were often not very satisfactory. In a later paper[70] naphthalene-d_8 was studied in EBBA, 1132 and the 55 wt % 1132/EBBA "magic mixture". The results were analyzed by including both long-range quadrupolar and short-range size and shape interactions for the 1132 and EBBA solvents, and only short-range interactions for the mixture. Satisfactory agreement between model and experimental order parameters was obtained.

B. Models That Incorporate the Detailed Molecular Structure

The early models, discussed above in section VII.A, all recognized the importance of size and shape in the description of anisotropic intermolecular forces. For example, in some of these models the inertial tensor is simply used as a crude measure of size and shape anisotropy. These descriptions have largely been superseded by models that employ a more complete description of the solute or liquid-crystal molecule, and which attempt to incorporate some of the physics that may be involved in the short-range anisotropic intermolecular forces. In the newer models the solute is approximated by a collection of van der Waals spheres that are centered on the nuclei. It is the anisotropy in the shape of the solute interacting with the uniaxial nematic field that gives rise to the orientational dependence of the potential energy.

In the original model from the Burnell group the liquid crystal is taken to be an elastic tube that must stretch to accommodate the solute. The Z or long axis of the tube is coincident with the nematic director. Thus there is a restoring force due to this stretching that is taken to be given by Hooke's law

$$F = -k\,\mathrm{d}C(\Omega) \quad (22)$$

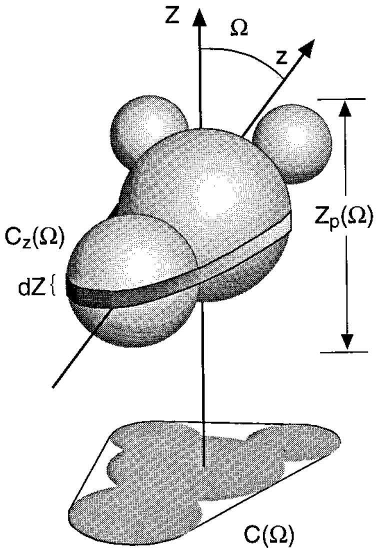

Figure 9. The potentials given by eqs 23−25 and 28 depend on the solid angles Ω which describe the orientation of the director (the Z axis) in a molecular fixed coordinate system (the z axis is shown here). The size and shape of the molecule are characterized by $Z_P(\Omega)$, $C(\Omega)$, and $C_Z(\Omega)$. $Z_P(\Omega)$ is the length of the projection of the molecule onto the Z axis. $C(\Omega)$ is the length of the “minimum” circumference (the solid line) around the projection of the molecule onto the plane perpendicular to the director. $C_Z(\Omega)$ is the “minimum” circumference obtained by including only the projections of the atoms where they intersect a plane located at Z. The potential in eq 25 is obtained by integrating $C_Z(\Omega)\,dZ$ (represented by the “ribbon” around the molecule) along $Z_P(\Omega)$. (Reproduced with permission from ref 74. Copyright 1993 Taylor & Francis Ltd.)

where $C(\Omega)$ is the circumference about the tube perimeter for the solute oriented at angle Ω (see Figure 9). The energy associated with this distortion is

$$U(\Omega) = {}^1/_2 kC^2(\Omega) \qquad (23)$$

This potential will be referred to as model C (for circumference).[55]

As we shall see below, despite its simplicity, model C has met with a great deal of success. While adjusting only the single parameter k, this model has been quite adequate in fitting simultaneously results for a variety of chemically unrelated solutes of varying symmetries and shapes in the “magic mixture” liquid crystals. However, it was noted early on that longer solutes preferred a smaller value of the parameter k than did shorter solutes. One way of approaching this problem is the addition to the potential of a term that depends on the solute length. This has been done by modifying the potential to

$$U(\Omega) = {}^1/_2 k[1 - \xi Z_P(\Omega)/C(\Omega)]C^2(\Omega) \qquad (24)$$

where $Z_P(\Omega)$ is the projection of the length of the solute along the tube axis for solute orientation Ω. This will be referred to as the CZ model.[66]

Equation 24 has an interesting physical interpretation. The first term is proportional to the area of the end of a cylinder with the same circumference as that projected by the solute; the second term is the area of the side of the tube. Thus eq 24 is a crude two-parameter representation of an anisotropic interaction between the solute surface and the liquid-crystal mean field. This realization motivated the search for better models for this anisotropic surface interaction. Note that the physical interpretation of the leading term has changed from an elastic-restoring force to an interaction between the cylinder ends and the liquid-crystal mean field.

The possibility that the dominant anisotropic short-range interactions are those between the solute surface and the liquid-crystal mean field is exciting, and has motivated two independent descriptions, both of which involve a single parameter. The first is in essence an expansion of the second term of the CZ model. Instead of using the projection of the entire molecule, the circumference $C_Z(\Omega)$ is calculated at various positions along the length of the molecule in the Z direction (see Figure 9). The potential is then calculated from the integral of this circumference along Z, giving

$$U(\Omega) = -{}^1/_2 k_s \int_{Z_{\min}}^{Z_{\max}} C_Z(\Omega)\, dZ \qquad (25)$$

Note that the area of a segment of the ring $C_Z(\Omega)\,dZ$ is $|\sin \theta_{\hat{n}}|$ times the area of the surface of the molecule within the same C and Z limits. Thus the physical interpretation of this model, to be referred to as the I (for integral) model,[74] is that it accounts for the anisotropic interaction between the solute surface and the liquid-crystal mean field. Indeed, eq 25 can be written as

$$U(\Omega) = -{}^1/_2 k_s \int dS_{\hat{n}}\, |\sin \theta_{\hat{n}}| \qquad (26)$$

where $\hat{n}$ is the unit vector normal to a surface area element $dS_{\hat{n}}$, and $\theta_{\hat{n}}$ is the angle between $\hat{n}$ and the nematic director.

A second and elegant treatment of the anisotropic surface interaction was proposed by Ferrarini et al.[73] In this model, referred to hereafter as N, the interaction between the solute surface normal and the liquid-crystal mean field, in analogy with the surface anchoring potential in a bulk nematic, is taken to vary as $P_2(\cos \theta_{\hat{n}})$. The orientation potential is then

$$U(\Omega) = k_B T \epsilon \int_S dS_{\hat{n}}\, P_2(\cos \theta_{\hat{n}}) \qquad (27)$$

This potential can be expanded in terms of second-rank spherical harmonics, and written in terms of a second-rank surface tensor which can be calculated from a description of the solute surface. Despite the fact that the angle dependencies ($P_2(\cos \theta_{\hat{n}})$ of model N and $|\sin \theta_{\hat{n}}|$ of model I) appear to be very different, use of the models does not lead to significant differences in order parameters calculated for the same solute; as will be discussed in more detail in the next section, both models account quite well for the experimental data.[79] Indeed, the angle-dependence of the singlet orientational distribution functions and the corresponding mean field potentials for calculations of prolate ellipsoids are similar.[141] While greater deviations are anticipated for more complicated solute shapes, the main differences between calculations involving the I and N models can be

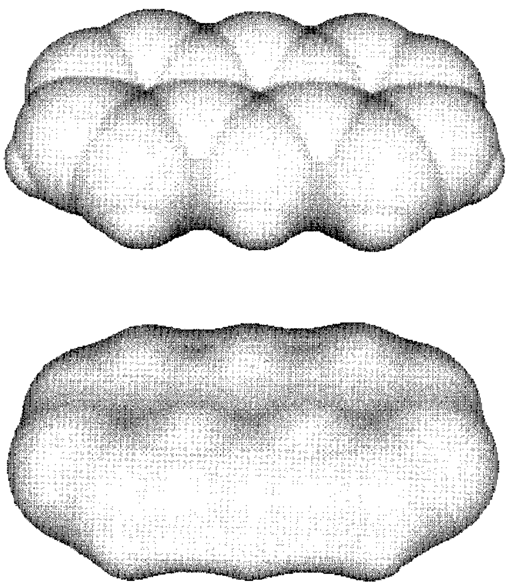

Figure 10. Anthracene surfaces generated by rolling sphere radii $R = 0$ (top) and $R = 3$ Å (bottom). Reproduced with permission from ref 80.

traced to the different schemes used for integrating over the solute surface—otherwise they give essentially identical results.[79] In recent work Ferrarini et al.[80] have introduced a rolling sphere algorithm in order to achieve a realistic representation of the molecular surface that is accessible to the solvent. The radius of the sphere is a new adjustable parameter, making this a two-parameter model. The anthracene surfaces generated with rolling spheres of diameters 0 and 3 Å are shown in Figure 10.

A different approach to a two-parameter model is to combine two successful one-parameter potentials. Of the two one-parameter C and I potentials, the I model gives better fits to the experimental order parameters calculated from the NMR experiments. However, for longer solutes the C model tends to overestimate, and the I model underestimate, the experimental order parameters. Perhaps the most successful description of the experimental order parameters is provided by combining the C and I potentials, model CI

$$U(\Omega) = {}^{1}/_{2}kC^{2}(\Omega) - {}^{1}/_{2}k_{\mathrm{s}}\int_{Z_{\min}}^{Z_{\max}} C_{Z}(\Omega)\,\mathrm{d}Z \quad (28)$$

One can think of this potential as describing both an elastic distortion of the liquid crystal and an anisotropic interaction between a liquid-crystal mean field and the solute surface.[74]

As we shall see in section VIII, the CI potential provides excellent fits to the experimental results. The CI and CZ models each involve two adjustable parameters, and there is no physical basis to choose the relative values of these parameters. Indeed, the success of these models is judged partly on the basis that the ratios of the two parameters appear to be stable when fitting to different solutes.

As mentioned in section VI, Terzis and Photinos have developed a theory that contains both short- and long-range contributions.[19] In the spirit of our review, we shall concentrate on the short-range part only. This component is written as a solute's shape function, $g^{H}(\Omega,\mathbf{r})$, where $\mathbf{r}$ and Ω are the position vector and the orientation of the solvent molecule relative to the solute. The $g^{H}(\Omega,\mathbf{r})$ is a hard-body function whose value is one or zero depending on whether the solute and solvent particles overlap. The orientation potential experienced by a solute molecule is then proportional to the orientational average of its excluded volume with respect to the solvent molecules

$$\frac{U(\Omega)}{k_{\mathrm{B}}T} = \frac{N}{V}\int \mathrm{d}\mathbf{r}\ \mathrm{d}\Omega'\ \tilde{f}(\Omega')[1 - g^{H}(\Omega,\mathbf{r})] \quad (29)$$

where N/V is the number density of the solvent molecules, and $\tilde{f}(\Omega')$ is their orientational distribution function, with Ω' denoting the orientation of the solvent molecule relative to the director. To relate predictions of the theory to experimental results, a scaling parameter which is proportional to the solute orientational order is introduced and adjusted in the fitting procedure.[78]

VIII. Orientational Order and Short-Range Interactions: A Summary of Experimental Results

In this section we shall compare experimental order parameters, measured by NMR, of solutes in "magic mixtures" and of "magic solutes" in arbitrary liquid-crystal solvents with predictions of some of the models presented above. One of these molecular solutes forms a nematic phase itself. The hypothesis is that, as argued in section V, there exists only a single short-range anisotropic interaction in such cases. The quality of the comparisons will indicate to what extent the short-range modeling can be seen as successful. There are two distinct ways of proceeding, being either to explore sets of different solutes in the same liquid-crystal solvent, or for solutes of low symmetry, to examine the two or more independent components of the order matrix of a single solute.

It is convenient to discuss the results in terms of increasing complexity of the molecule under investigation. First we shall examine "rigid" solutes of various symmetries. Here the word "rigid" implies that we shall neglect the effects due to small-amplitude molecular vibrations, and especially their correlation with reorientation. We shall then examine the much more complicated problem posed by molecular flexibility and the associated large-amplitude internal motions. A review of work on relatively simple "floppy" solutes that can exist in a small number of well-defined conformations is followed by a discussion of the more complicated liquid-crystal molecules themselves. The problems inherent in studies of liquid crystal molecules are akin to those presented by the flexibility of the simpler, floppy solutes. A typical example that has received a lot of attention is the liquid-crystal molecule 5CB whose hydrocarbon chain, due to the rotation about C−C bonds, can be thought of as existing in 27 different conformers, most of which require the maximum of

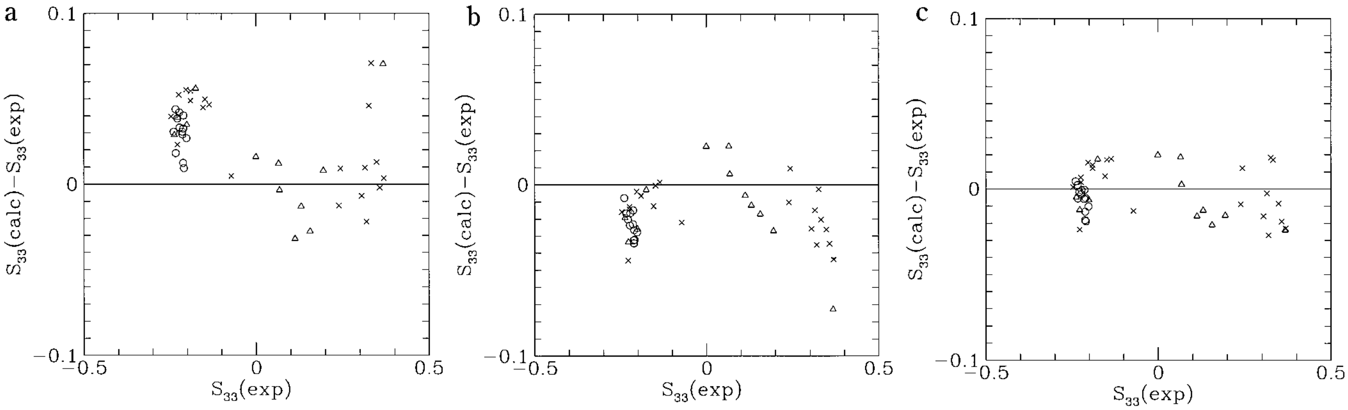

Figure 11. (a) The difference between the calculated and experimental values of S_{33} versus the experimental values of S_{33} where S_{33} is the diagonal element of the experimental $S_{\alpha\beta}$ with the largest absolute value. The △, ×, and ○ correspond to the group of molecules with C_{3v} or higher symmetry, the group with C_{2v} or D_{2h} symmetry, and the group with C_s symmetry, respectively. These values were calculated using eq 23 with $k = 5.44$ dyn/cm. (b) As in a but the values were calculated using eq 25 with $k_s = 76.7$ dyn/cm. (c) As in a but the values were calculated using eq 28 with $k = 2.04$ dyn/cm and $k_s = 48.0$ dyn/cm. (Reproduced with permission from ref 74. Copyright 1993 Taylor & Francis Ltd.)

five independent order parameters to describe the second-rank order matrix. We shall review a study of 5CB as a solute in "magic mixtures".

A fair comparison of different solutes in the same liquid crystal solvent is only possible if variations in experimental conditions are taken properly into account. These variations arise because order parameters for different solutes are often measured in separate sample tubes. Thus variations in sample temperature and concentration will affect the liquid-crystal mean orientation potential. As discussed in section V, a reasonable way of taking these differences into account is to choose some solute as an "orientational reference".

A. "Rigid" Solutes

Before attempting to explain results obtained with flexible solutes and liquid crystals, we shall examine a set of simpler "rigid" solutes. There are several studies in the literature in which comparisons between experimental order parameters and those calculated from some model for the short-range intermolecular interactions have been presented.

Many solutes, including those with C_{3v} and higher symmetry, require only one second-rank orientation parameter.[10] For molecules that have less than C_3 or D_{2d} symmetry, two or more parameters are required to specify the average second-rank order matrix. In the following, the diagonal elements of the experimental order parameter matrix $S_{\alpha\beta}$ are chosen such that

$$|S_{11}| \leq |S_{22}| \leq |S_{33}| \tag{30}$$

and the asymmetry of the order matrix is given as

$$\eta = \frac{S_{11} - S_{22}}{S_{33}} \tag{31}$$

For solutes of lower symmetry, more orientation parameters are required.

In the following, we review several studies in which models for the short-range interactions have been fitted to experimental results obtained under conditions where short-range interactions are thought to dominate.[74,78−80] We shall start by discussing results obtained for series of rigid solutes in "magic mixtures".

In one comprehensive study[74] order parameters from 46 different solutes in the 55 wt % "magic mixture" have been used to test the various models presented in section VII. The results analyzed and fitted in ref 74, using a least-squares minimization procedure based on the C and I models, are compared graphically in Figure 11, parts a and b. Differences between experimental and calculated values of the principal order parameter S_{33} values for a large variety of chemically unrelated solutes with widely varying sizes and shapes are plotted versus the experimental order parameters. Different symbols are used for molecules of unlike symmetry. The results for the less symmetrical solutes coalesce with those for the more symmetrical ones, and solutes of all symmetries exhibit the same general trends. Thus the models fit the largest magnitude principal order parameter equally well for solutes of any symmetry. The points with negative S_{33} correspond to mainly flat, oblate-shaped molecules such as substituted benzenes. The points with the largest positive S_{33} correspond to elongated molecules such as 2,4-hexadiyne and *para*-substituted aromatics. A variety of molecules is included in the fitting, and the reader is referred to ref 74 for details of the solutes studied and their order parameters. For a perfect fit, all points would have to lie on the horizontal axis at $S(\text{calc}) - S(\text{exp}) = 0$. The fits to the C and I one-parameter models show an interesting trend. For the very long solutes (those associated with a very positive S_{33} value) and the very flat solutes (those associated with a very negative S_{33} value), the order parameters recalculated from these two models differ in opposite ways from the experimental values. Another way of interpreting this result is that long solutes tend to require a smaller k in the C model, or a larger k_s in the I model, than do shorter molecules. An excellent fit is provided by the CI model (Figure 11c) that incorporates both the C and I interactions. The combination of the two

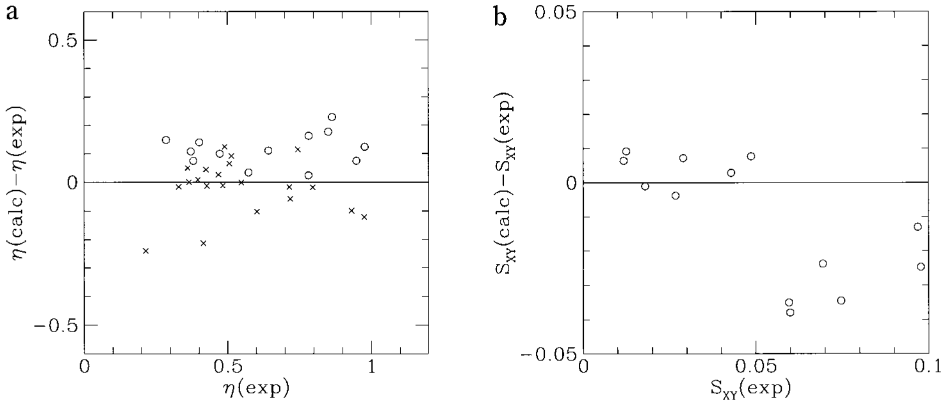

Figure 12. (a) As in Figure 11c for $\eta = (S_{11} - S_{22})/S_{33}$ where S_{11}, S_{22}, and S_{33} are the diagonal elements of the experimental $S_{\alpha\beta}$ with the smallest, intermediate, and largest absolute values, respectively. (b) As in a for the off-diagonal element S_{xy}. See ref 74 for details of molecular axes. (Reproduced with permission from ref. 74. Copyright 1993 Taylor & Francis Ltd.)

terms removes the undesirable correlation with molecular length noted above.

For those molecules that have less than C_3 or D_{2d} symmetry, one or more additional order parameters are required to specify the average second-rank order matrix. The use of molecules that require more than one order parameter to specify their average orientational order leads to an exciting possibility: it is feasible to examine the relative values of order parameter elements arising from a single solute. In this case it is certain that the mean potential needed for calculation of all the parameters within a given molecule is identical. In Figure 12, parts a and b, we present comparisons between experiment and predictions for the CI model introduced in section VII. There are many ways to present the comparison—we show in Figure 12a the difference between the experimental and recalculated values of the asymmetry in the order matrix η as defined in eq 31. For molecules whose lack of symmetry requires more than two independent order parameter elements, we show in Figure 12b the off-diagonal element S_{xy} where x,y,z is some chosen molecule-fixed axis system.[74] The results presented in Figures 11 and 12 are for the global fit to all order parameter elements of all solutes. With the CI model the scatter of order parameter differences about the best-fit zero line appears random, and the experimental values are fit to about the 10% level. Such fits represent excellent agreement between model calculations and NMR experiment and provide strong support for the use of a simple-minded approach to model the short-range interactions.

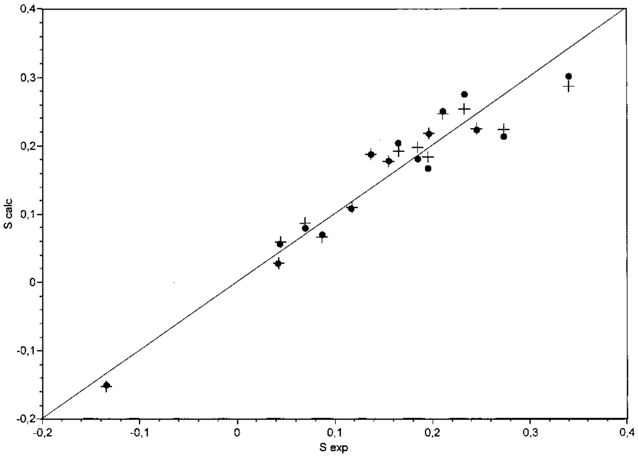

Figure 13. Comparison between experimental and calculated values of order parameters of solutes according to the N (+) and I (●) models of section VII. (Reproduced with permission from ref 79. Copyright 1997 Taylor & Francis Ltd.)

In a recent study,[79] a series of 10 C_{2v} and higher symmetry solutes in “magic mixtures” were investigated at the same reduced temperature in order to facilitate comparisons of orientational order measured in different sample tubes. The experimental data were analyzed in terms of a potential that includes both short- and long-range contributions. The one-parameter N and I models of section VII were used separately for the short-range interactions. The long-range part of the orientation potential was described in terms of the reaction field experienced by the solute which polarizes the surrounding medium. The separate contributions that are included in the reaction field involve the solute electric dipole and quadrupole moments and its molecular polarizability. It was found that calculations in which one contribution to the orientation potential was optimized at a time produced acceptable fits only for the short-range interaction potential. The addition of terms arising from the various long-range contributions did not improve significantly the quality of the fits. In a few cases the quality of the fit was slightly improved by the addition of extra terms, but the associated fitting parameters showed standard errors higher than their actual values, and the resulting long-range contributions were of the same order of magnitude as uncertainties in the short-range contributions arising from uncertainties in solute structures. The results of the fitting procedures involving the N and I models are presented in Figure 13.

An interesting result of this study[79] is that the fits obtained with the N and I models for the short-range interaction in terms of an anisotropic surface potential are virtually identical. The points recalculated from both models and shown in Figure 13 are practically superimposed. This demonstrates that the N and I models both lead to essentially the same orientation parameters, and hence that their different angular dependencies are of little consequence.

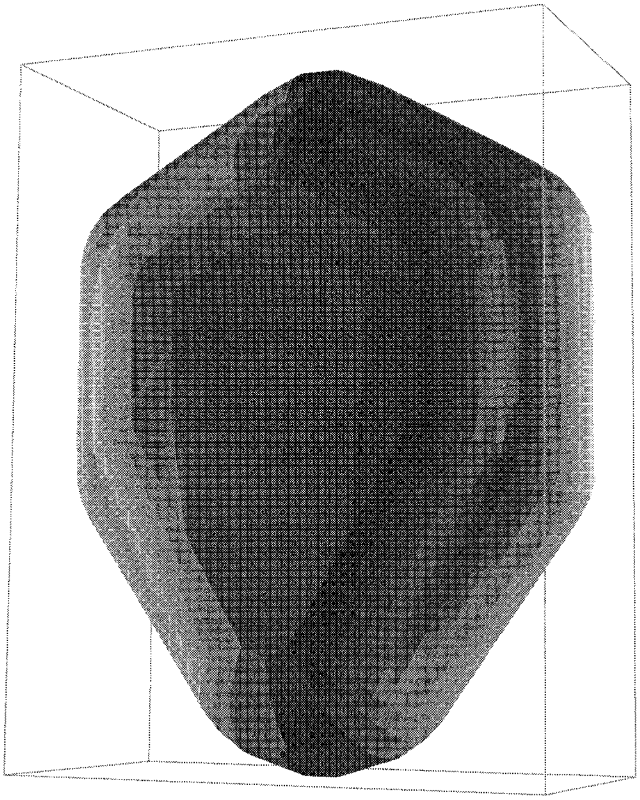

Figure 14. Surface of the chlorobenzene molecule. (Reproduced with permission from ref 79. Copyright 1997 Taylor & Francis Ltd.)

It should be noted that the description of the solute surface used in ref 79 is different from that used in the original N model of ref 73. The original model for the surface included all surface elements that resulted by replacing every atom by a van der Waals' sphere. Since the surfaces of these van der Waals' spheres are not entirely accessible to the surrounding medium, the concept of a smoothed surface was introduced, as shown for chlorobenzene in Figure 14. In the comparisons of results obtained from the N and I models, the agreement was excellent provided that the same description of the surface was used. This study demonstrates once more that there are no substantial long-range contributions to the ordering potential in the "magic mixtures".

In an attempt to obtain a better description of the smoothed solute surface accessible to the solvent, required to model the short-range interactions, a rolling-sphere algorithm[148] has been introduced.[80] The radius of the rolling sphere represents a second adjustable parameter of the model. A typical example of the solute surface employed is shown in Figure 10 for anthracene. The rolling-sphere approach has been utilized to reanalyze data for several solutes in nematic solvents. In this case, instead of examining results for a collection of solutes in different sample tubes, the full set of orientation parameters obtained for a single solute are used for comparison. In particular, this approach has been applied to the data[46] for *o*- and *m*-dichlorobenzene as solutes in two "magic mixtures", and the results are presented in Figure 15. The two-parameter fit of the rolling-sphere model agrees quite well with the experimental points. Note that these data were analyzed earlier with the C, I, and CI models.[46] The fit to the one-parameter I model is essentially the same as that for the two-parameter rolling-sphere approach.

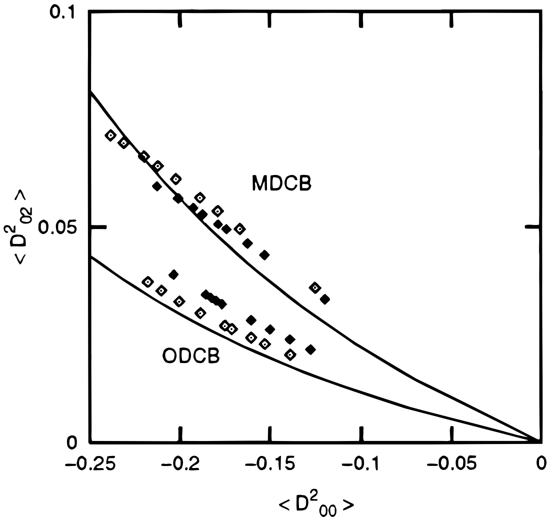

Figure 15. Biaxiality order parameter $\langle D^2_{02}\rangle = 1/\sqrt{6}(S_{xx} - S_{yy})$ plotted as a function of $\langle D^2_{00}\rangle = S_{zz}$ for *o*-dichlorobenzene (ODCB) and *m*-dichlorobenzene (MDCB). Open and filled squares denote experimental values reported in ref 46 for two "magic mixtures". The continuous lines represent the surface model results for a rolling sphere radius of 3 Å. (Reproduced with permission from ref 80.)

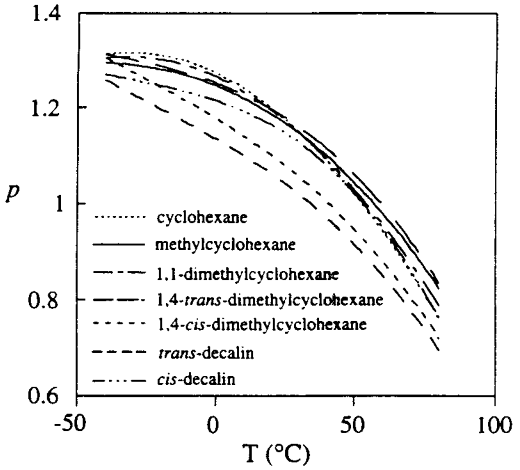

Figure 16. Plots of the temperature dependence of the optimal values of the solvent parameter *p* as determined from the fits to the measured order parameters of saturated cyclic hydrocarbons. (Reproduced with permission from ref 78. Copyright 1996 American Chemical Society.)

A recent ^{2}D NMR study of deuterated cyclic hydrocarbons dissolved in an arbitrary nematic solvent provides an example of work utilizing "magic solutes".[78] The results were analyzed in terms of the Terzis/Photinos theory for short-range interactions, reviewed in section VII. The fitting involves a single adjustable parameter, *p*, whose maximum value in the theory is 1. Excellent agreement between experimental and recalculated orientation parameters was obtained. As shown in Figure 16, *p* was temperature- and solute-dependent, and values of $p > 1$ were required. Nevertheless, the spread of *p* values at a particular temperature for different molecules is not excessive, and the model provides a reasonable phenomenological description of short-range interactions.

As required for a test of a good model, the values of the fitting parameters obtained should be roughly independent of the collection of molecules chosen for the fitting. Although some fits discussed above provide better results than others, the picture that emerges indicates that adequate fits are obtained with any of the phenomenological models for the short-range orientation potential.

A totally different approach to obtaining information about orientational order, either for liquid crystals themselves or for solutes in liquid crystals, is provided by MC and MD computer simulations. A paper in which both nematogen and solute molecules were modeled as hard ellipsoids has specifically addressed the question to what extent the various short-range size and shape models discussed in section VII and the potential of mean torque calculations in section VI were supported by MC simulations. When the degree of solute orientational order was calculated as a function of solute length and width, remarkable agreement with the predictions of the two-parameter anisotropic surface model (CI) was found.[141] An important aspect of MC simulations is that they start from the full interaction Hamiltonian and are thus capable of testing theories in which approximations had to be invoked. This has been exemplified in an MC paper[98] in which the theories developed by Emsley and Luckhurst[54,62,68] and by Terzis and Photinos[19] were considered, by taking into account both short- and long-range interactions between hard nematogens and solute molecules which did or did not possess a quadrupole moment. It was found that in the purely hard-core systems, the theory of Terzis and Photinos[19] was seriously underestimating the solute ordering, a phenomenon ascribed to the complete neglect of solvent−solvent correlations. In the quadrupolar systems it was found that the calculated average efg was highly sensitive to the properties of the solute, in contrast to what has been assumed in experimental work on efg's in nematic phases.[27,28,30,31,34,35,41,55,58,99] However, the point quadrupole approximation which was used may provide too simple a picture. In addition it was observed that the Emsley−Luckhurst prediction for the orientational order of spherical solutes, where only electrostatic interactions can play a role, was quantitatively poor.[98] This was again ascribed to the severity of the approximations made in the theory.

B. Flexible Molecules

In principle, all molecules are flexible in the sense that they vibrate. The treatment of small-amplitude, high-frequency vibrational normal modes has been dealt with in the literature,[149−151] including the interaction between vibrational and rotational motions.[28,32,81,82,92,108] Fortunately, the effect of such vibrations on the order parameters determined from the dipolar and quadrupolar couplings measured in NMR spectroscopy is normally quite small, and of no consequence for the comparisons of order parameters presented here. In this section we will examine the problem posed by large-amplitude internal motions, and especially those that involve interconversion among different conformers of the same molecule. The molecule may be either a solute or one of the solvent molecules that comprise the liquid-crystalline phase. The problem will be treated on two levels. The first is to simplify the problem and to assume that there exists rapid interconversion among discrete, rigid conformers. In the case of hydrocarbon chains, this becomes the “rotamer isomeric state” (RIS) model of Flory.[152] The second level is to attempt to account for the extra nonrigidity which results from the librational motions within the potential well of each conformer. The main difference among the various treatments at this level is the method of incorporating the dependence of order parameter elements on librational amplitude.

The study of flexible solutes is motivated by the notion that the molecules which give rise to the liquid crystal phase can be thought of simply as just another solute. A component of one of the “magic mixtures” is 5CB, and it has been studied as a solute in several “magic mixtures”.[44] A technical problem associated with large, flexible molecules such as long hydrocarbon chains or liquid-crystal molecules is that they often exhibit a very complicated proton NMR spectrum. For example, the normal proton NMR spectrum of a molecule such as butane, partially oriented in a nematic phase, contains over 1000 lines (see Figure 17). For larger molecules the number of transitions becomes even greater. In the case of a typical liquid crystal the overlap of lines leads to a broad, rather featureless spectrum. Clearly, under these circumstances, analysis of the normal single-quantum spectrum is not practical.

For such complicated molecules alternative approaches have been used. One method that has been quite successful is the use of multiple-quantum (MQ) NMR. The high-order MQ spectra contain relatively few transitions and the parameters resulting from their analysis can be used in a number of ways. In the case of butane, the seven- and eight-quanta spectra were measured and analyzed in order to provide estimates of dipolar couplings and chemical shifts which were then used as the starting point for analysis of the much more accurate single-quantum spectrum.[76] In studies of the hydrocarbon chains hexane to nonane, partly deuterated species were used in conjunction with MQ methods in order to measure directly the dipolar couplings between all proton spin pairs.[75,89] In the case of chain perdeuterated 5CB the multiple quantum NMR of the ring protons was used and estimates of the dihedral angle between the two benzene rings were obtained.[153,154]

Another method that has been widely used in studies of partially oriented fluids is deuteron NMR of partially or completely deuterated molecules. The deuteron NMR spectra are dominated by quadrupolar couplings $\Delta\nu$ which are related to order parameters by

$$\Delta\nu = \frac{3}{2}\frac{eQV_{bb}}{h}\left(S_{bb} + \frac{1}{3}\eta(S_{aa} - S_{cc})\right) \qquad (32)$$

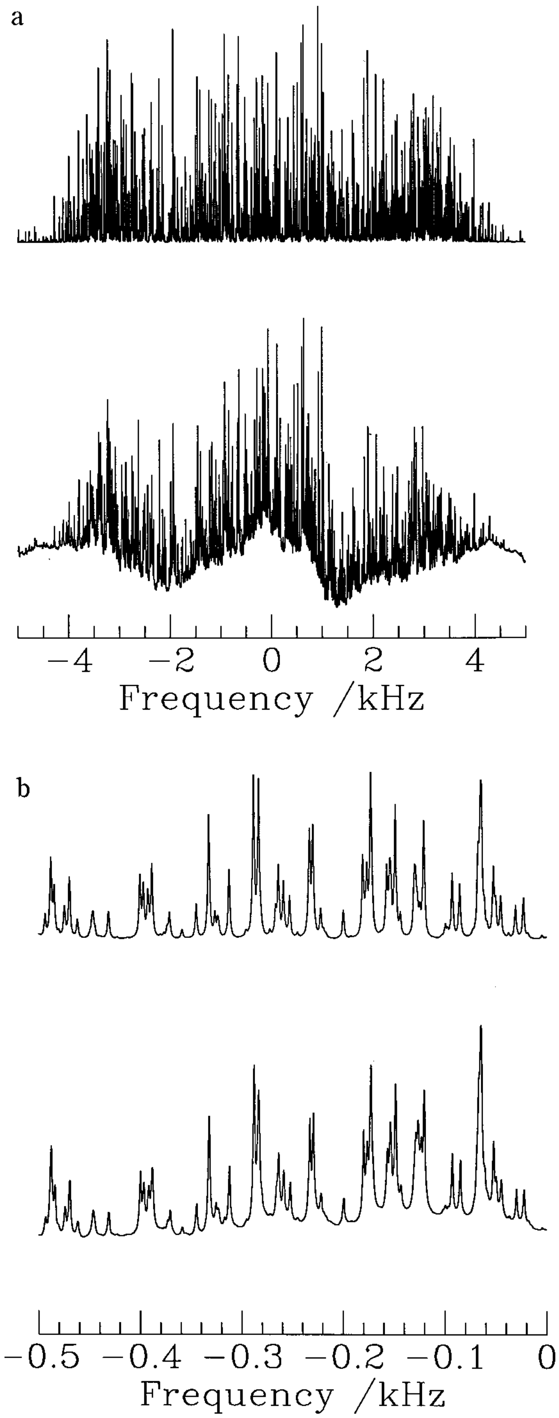

Figure 17. (a) Experimental (bottom) and simulated (top) NMR spectra of butane dissolved in the 55 wt % “magic mixture” at 301.4 K and (b) expanded region of the spectra in a. (Reproduced with permission from ref 76. Copyright 1995 American Institute of Physics.)

where eQ is the nuclear quadrupole moment, V_{bb} is minus the bb principal component of the electric field gradient at the nucleus, S_{bb} is the order parameter for the b direction, normally taken to be along the C−D bond, with axes a and c perpendicular to that direction, and η is the asymmetry in the quadrupole coupling constant, which is often taken to be zero for a C−D bond.

1. Solute and Solvent Molecules Undergoing Conformational Change—Rigid Conformers

In this section we shall discuss solutes which are considered to interconvert between a limited number of “rigid” conformers. This corresponds to the situation where each conformer exists at the bottom of a deep potential well.

Symmetry-Related Conformers. A particularly simple case arises when it is possible to generate all conformers from symmetry operations applied to one of them; the order matrixes for all conformers are then related, and the spectrum can be described using essentially a single order matrix whose off-diagonal elements may change sign with change of conformer. The spectral observables are averages of those for all conformers, and this averaging frequently reduces the number of independent dipolar and quadrupolar couplings. The solute 2,6-dichloroethenylbenzene (DCEB) was analyzed in this way.[111] The five independent elements of the order matrix determined for this solute were compared with predictions from several of the models for short-range intermolecular interactions. The CI and I models provided particularly good predictions for results obtained for DCEB dissolved in the 55 wt % “magic mixture”.[146]

Symmetry-Unrelated Conformers. Next, we shall examine the much more complicated problem posed by molecules that can exist in a number, n, of symmetry unrelated, “rigid”, rapidly interconverting conformers. One then needs up to five independent order parameters (or two order parameters and three diagonalization angles) for each of the n independent conformers.[7] In such cases, not only is the number of independent order parameters a problem, but also the relative conformer probabilities may be unknown. To gain insight into the inherent problems, it is sensible to start with the simplest case possible, being that of two symmetry unrelated conformers in “magic mixtures”.[76,103,105]

To understand the problems posed by molecular flexibility, we note that the observable NMR interactions can be written in the form

$$O = \sum_i P_i \sum_{\alpha,\beta} S^{(i)}_{\alpha\beta} C^{(i)}_{\alpha\beta} \qquad (33)$$

where O is the dipolar or quadrupolar coupling, P_i is the probability, $S^{(i)}_{\alpha\beta}$ is the $\alpha\beta$ element of the order tensor, and $C^{(i)}_{\alpha\beta}$ is some appropriate constant for conformer i. One problem is that it is impossible to separate the individual contributions to the products $P_i S^{(i)}_{\alpha\beta}$. In principle these products can be determined from the observables. However, when this is attempted in studies of the three solutes 2-chlorobenzaldehyde, 2,2′-dithiophene, and furfural in a “magic mixture”, in each case the parameters for the two different symmetry unrelated conformers end up highly correlated, and the $P_i S^{(i)}_{\alpha\beta}$ products obtained have large errors associated with them.[105] It appears very difficult to obtain such products with any great accuracy.

Even if these products could be determined accurately, some method of separating the probability from the order parameter would still be needed if one wished independent information about either. To do this, some way of relating either the probabilities or the order parameters of different conformers must be devised. In general, there is no unambiguous solution to this dilemma. Thus, at first sight the investigation of the potential involved in conformer interconversion in the anisotropic liquid-crystal phase seems hopeless. However, as we have seen above, there exist quite reasonable models for the orientational order of "rigid" solutes in zero-efg magic mixtures and of "magic solutes" in arbitrary liquid-crystal solvents, and these can be used to provide the necessary link between order parameters of different conformers.

In some early work involving conformers of differing symmetry, including that on simple solutes and on liquid crystals that contain hydrocarbon chains, the simple scheme that was employed assumed that the order parameter remains constant in some rigid segment of the flexible molecule; however, there is no physical justification for such a picture. A more rigorous approach involves determining the complete order parameter matrix for each conformer. This method accounts for the possibility that both (i) the principal values of the order parameter matrix, and (ii) the Euler angles relating the principal ordering axes to some molecular frame, may vary with conformation.[7] Such an approach was used, in conjunction with the models of section VII, to estimate relative conformer probabilities of the three solutes 2-chlorobenzaldehyde, 2,2′-dithiophene, and furfural in a "magic mixture".[105] In the analysis, each solute was assumed to switch rapidly between two symmetry-unrelated, rigid conformers. The NMR results for 2,2′-dithiophene were also analyzed using a maximum entropy (ME) approach, and the results agree with the rigid-conformer analysis.[155]

An alternative, perhaps simpler calculation neglects the dependence on conformation of the principal order parameter values, assuming that they are the same in some principal ordering frame which is often approximated by the principal inertial frame. In many cases this yields reasonable results—probably because there is only a relatively small change in principal order parameter elements associated with the internal motion. However, it has been argued that there is no physical justification for this approximation for large-amplitude conformational changes that involve movement of large molecular segments.[7]

The factor that governs the intramolecular contribution to relative conformer probabilities is the energy difference associated with conformational change. In liquids this energy difference may have intra- and intermolecular contributions, and thus may differ from values found in gas-phase studies. In the case of hydrocarbon chains the intramolecular trans—gauche energy difference E_{tg} is either chosen to have some reasonable value, or is treated as an adjustable parameter in the fit. In addition, one or more model parameters associated with the prediction of the geometrical dependence of the order parameters may be adjusted to fit the calculated dipolar and quadrupolar couplings to the experimental NMR observables. As was the case for the three solutes described above, the model is used to scale the order parameters between the different conformers.

Analyses of experimental NMR results have been performed for several liquid crystals and for hydrocarbon solutes, and sometimes the results are quite impressive. In some cases the model parameters that are adjusted are purely phenomenological and there is no clear connection between the scheme used and the real physical interactions. In the case of hydrocarbon chains, either as solutes or as part of a liquid-crystal molecule, the value used for E_{tg} has a pronounced effect on the analysis—if E_{tg} is a free parameter, the value derived varies with the scheme employed for the analysis.

Flexible saturated straight-chain hydrocarbons are an interesting class of compounds because long-range electrostatic interactions with the environment are expected to play a minor role compared to size- and shape-dependent short-range interactions. Hence, the models discussed in section VII should be applicable to these "magic solutes" dissolved in arbitrary liquid crystals. Although this approach has been quite successful, a word of caution is in order: measurements of the order parameter asymmetry η, eq 31, of propane dissolved in the different liquid crystals 1132 and in EBBA resulted in the quite different values 0.42 and 0.24.[156] In the following we shall review results for hydrocarbons whose interactions with the anisotropic environment are assumed to be entirely short range in nature.

The simplest flexible hydrocarbon is butane. In the RIS approximation butane exists in three conformers, two of which are symmetry unrelated. In a recent study of butane in a "magic mixture", comparisons were made using eight of the models for the orientation potential presented in sections VI and VII to calculate changes in order parameters with conformational change. The value realized in the fitting for E_{tg} was dependent on the precise assumptions made about the molecular structure. For example, increasing the dihedral angle from 112° to 120° led to a 10% increase in the value of E_{tg}. There was an even larger dependence of the value obtained in the fitting for E_{tg} on the model chosen to describe the orientation potential.[76] Also, it should be realized that even for this simplest of the flexible hydrocarbons there remains ambiguity between gas-phase and condensed-phase values of E_{tg}.[44,76]

Several workers have employed the RIS approximation in proton and deuteron NMR studies of longer *n*-alkanes, ranging from pentane to hexadecane, as solutes in nematic phases. Photinos and co-workers have used both the extended Straley model[57] (despite the problems associated with its use indicated in section VII[146]) and the more sophisticated chord model[64,65] to analyze their deuteron NMR results. In addition, they used the chord model[71] to analyze the proton NMR results of *n*-hexane obtained by Gochin et al.[89] Also proton NMR experiments on *n*-alkanes have been interpreted[90] using the Terzis/Photinos model for short-range interactions. In all cases they observed good agreement between experimental and calculated couplings. In addition, reasonable values for the trans-gauche energy difference, E_{tg}, were obtained. Because the *n*-alkanes contain only two different types of chemical bonds, they are ideally suited for an analysis using a bond-additive approach such as the chord model which then requires a minimum of adjustable parameters.

Pines and co-workers have measured proton NMR dipolar couplings between all proton pairs for the *n*-alkanes from hexane to decane dissolved in the nematic liquid crystal Kodak EK 11650 (*p*-pentylphenyl-2-chloro(4-benzylbenzoyloxy)benzoate).[75,89] They analyzed their experimental couplings in terms of the C, CZ, Straley, and chord models for the orientation potential reviewed in sections VI and VII above. They claimed that the chord model provided the best description of their results. The C, CZ, and Straley models were considered less adequate, mainly because they predicted values for E_{tg} which were deemed to be too large or too small. It would be interesting to reanalyze Pines and co-workers' results in terms of the CI model which has generally been found to provide the best fit between experimental and predicted order parameters. We note that MC calculations of hexane in a liquid crystal have been performed, and the results compared with the NMR experiments and with predictions of various mean field models. The chord model does not appear to give the best agreement.[136]

The ultimate solute molecule is the liquid-crystal molecule itself. Liquid-crystal molecules generally contain a roughly rigid core and a flexible hydrocarbon chain. In most cases the chain has many minima in the conformational potential. Thus analysis is normally limited to the "rigid" conformer approximation, and the RIS model is used.

Most investigations of liquid crystals involve samples in which there is an average gradient in the electric field that is experienced by the liquid-crystal molecules. Usually the details of the intermolecular forces are not specified, and the interaction is written in terms of some generalized mean field expansion. Such studies are beyond the scope of this review. For an authoritative overview of the large literature relevant to this topic, the reader is referred to the excellent monograph by Dong.[8]

The only liquid-crystal molecule that has been examined in detail as a solute in "magic mixtures" is the deuterated liquid crystalline molecule 4-*n*-pentyl-4′-cyanobiphenyl, 5CB. In a temperature-dependent study, 5CB was investigated in two quite different zero-efg phases.[44] In one of the phases employed, the 5CB is itself one of the of liquid crystals used as a constituent of the zero-efg mixture. The observed quadrupolar splittings were fitted using the CI and CZ two-parameter models for the short-range interactions, and excellent agreement between experiment and calculation was obtained. What is more important is that the models fit the results in the two quite different zero-efg liquid crystal mixtures in precisely the same way. For a given value of the α methylene group quadrupolar splitting, which was employed in the study as a measure of reduced temperature, the adjustable parameters could be transferred from one liquid crystal to the other. Reasonable fits were obtained for values of $E_{tg} \approx 700$ cal/mol. This result is in line with that obtained for pure 5CB using the chord model where an E_{tg} of 500 cal/mol is required.[69] Values for E_{tg} between 400 and 700 cal/mol are generally considered acceptable by workers in the field.[152] An interesting aspect is that spectra which correspond to the same values of adjustable parameters are in fact quite dissimilar in the two mixtures. The reason is that the spectra are for different real temperatures, and the spectral variations arise from unequal populations of conformers because of the effect that unequal temperatures have on the Boltzmann probabilities. This study is important because it demonstrates that phenomenological models that have been most successful in explaining solute orientational order can also be applied very successfully to the zero-efg liquid crystal mixtures themselves.[44]

2. Solute and Solvent Molecules Undergoing Conformational Change—Librations

We now turn to the more general situation in which the effects of librational motion may play a significant role. Examples that we shall discuss in some detail are the solutes DCEB, biphenyl and straight-chain hydrocarbons.

In the previous section we discussed conformational changes in the simplified context of deep potential wells. In contrast, librational motion allows appreciable probability for conformer geometries which are significantly different from those at the potential energy minima. A possible way to treat this problem is to expand the idea of discrete conformers to include all possible structures, and to sum quasi-continuously over these structures for the calculation of spectral properties. As all the structures are not now related by symmetry operations, the problem of describing the conformer dependence of order parameters is again important. This is an interesting problem, and several quite reasonable, but quite different, approaches are possible. Of course, one can use one's favorite means of analysis of the rigid conformer problem above, and expand it to the present treatment.

In one approach, equivalent to the alternative calculation discussed in the section above, one thinks of these librational motions as vibrations. In the case of a free molecule in the gas phase, the vibrations would occur about the so-called Eckart axes, which essentially implies that there be no change in the rotational angular momentum during the vibration. The Eckart axes are often approximated by the principal inertial axes. It has been argued that for fast vibrational motions the order parameters, referred to the Eckart axes, would be invariant.[157,158] This approximation, labeled EA, circumvents the need to calculate the geometrical dependence of order parameter elements.

Among the cases of solutes in magic mixtures, the spectra of DCEB and biphenyl were treated using the EA approximation. The resulting analysis of DCEB led to a very deep minimum in the potential energy curve at a dihedral angle of 45.4°. In this case no information about the dihedral angle dependence of the order parameter matrix is available, because the NMR observables are dominated by their value at the potential minimum.[111]

Biphenyl has been the subject of two recent investigations.[110,159] In this case the assumption of interconversion between four "rigid" conformers does not yield a particularly satisfactory fit to the experimental dipolar couplings.[110] To incorporate effects of librational motion, it is necessary to calculate order parameters as a function of changes in molecular shape associated with internal motions. As well as the EA approximation, several additional schemes have been used to calculate the geometrical dependence of order parameters. The additive potential (AP) approach employs the potential of mean torque to relate order parameters to molecular geometry.[159] In another method (CT) which is similar to the AP approach, the value of $S_{xx}-S_{yy}$ is allowed to vary as the cosine of the dihedral angle. Finally, a maximum entropy (ME) method was used which provides an interesting alternative approach because it makes no assumptions about the intramolecular potential.[155,159−161] In essence the ME method attempts to maximize the number of different geometries involved in the internal motion, i.e. to flatten their distribution.

In the first study biphenyl was investigated as a solute in two different liquid-crystal solvents and the AP and ME methods were used for analysis.[159] The ME method yielded a value for the dihedral angle at the internal potential minimum that was smaller than the one obtained using the AP method. The ME and AP methods give different results only because they allow differences in the form of the intramolecular potential. However, a recent MD simulation of biphenyl as a solute in a nematic phase found that the AP approach was in better agreement with the simulation results than was the ME method.[139]

In the second study of biphenyl as a solute in three liquid crystals, one of which is a "magic mixture", both the EA and CT methods were employed in a joint fit to the results from all three experiments.[110] The two methods gave precisely the same result. Apparently, the NMR dipolar couplings are not sensitive to precise details of the dependence of the order parameter elements on changes in molecular structure. However, the calculations show that the parameters which describe the intramolecular potential do depend on liquid-crystal solvent, the variation being of order 10%.

The study of butane, reviewed in terms of the RIS approximation in the previous section, also investigated the effect of librational motions on the conformer probabilities and trans−gauche energy difference E_{tg}. The effects of librations were incorporated by using a total of nine different conformer structures in the analysis, rather than the three used in the RIS approach. To obtain order parameters associated with each independent conformer geometry, a total of eight different models were used for the orientation potential. The results obtained did not differ much from those based on the three-conformer RIS approximation. When librational motions were included, the value of E_{tg} increased by at most 4%, and the orientation potential parameter changed by at most 2%. Moreover, an important observation was that much larger differences in these parameters arose when different models for the intermolecular orientation potential were used. It appears that results obtained with flexible molecules depend strongly on the detailed description of this potential.

Two recent papers[162,163] have used the ME method to reanalyze the available proton dipolar couplings for hydrocarbons in a liquid-crystal solvent[75,89] and have come up with quite different pictures. In the first paper,[162] the method is constrained by the proton dipolar couplings and an assumed form for the potential of intramolecular rotation about C−C bonds. The authors find that the proton dipolar coupling data are rather insensitive to the internal bond rotational potential and that no reliable conclusions about conformer probabilities can be extracted. In contrast, in the second paper[163] the ME method is constrained by the proton dipolar couplings and the gas-phase RIS approximation with E_{tg} taken to be 2.1 kJ/mol. In this work seemingly reasonable values for conformer probabilities are obtained. It appears that the manner in which the ME method is constrained has a distinct effect on the outcome. Obviously more work is needed to resolve the discrepancies that can arise when the ME method is used.

In summary, for solutes in "magic mixtures" and for "magic solutes" a variety of schemes for modeling short-range interactions is available. Since the average orientational order appears to be dominated by such interactions, with longer-range electrostatic contributions playing an insignificant role, models for short-range interactions provide an excellent means of relating the conformer order parameters to their size and shape. Moreover, of the models discussed, the CI model is not only the best predictor of solute order parameters in "magic mixtures", but also generates order parameters that are in excellent agreement with those calculated from Monte Carlo simulations of a solute in a liquid crystal environment where both solute and liquid crystal are modeled as hard ellipsoids.[141]

For situations that do not involve "magic mixtures" or "magic solutes" the short-range interaction is no longer the only orientation mechanism; in addition, electrostatic interactions, such as that between the solute molecular quadrupole moment and the nonzero average efg experienced by the solute, should be considered. In such cases, a treatment of the orientational problem in terms of short-range interactions alone is inappropriate. Moreover, in contrast to the situation for "magic mixtures" and "magic solutes", there currently exists no a priori way to transfer results between the same solute in different liquid crystals, or between different solutes in the same liquid crystal.

IX. Conclusions

We have reviewed research which focuses on the measurement and interpretation of orientational order in anisotropic environments under conditions

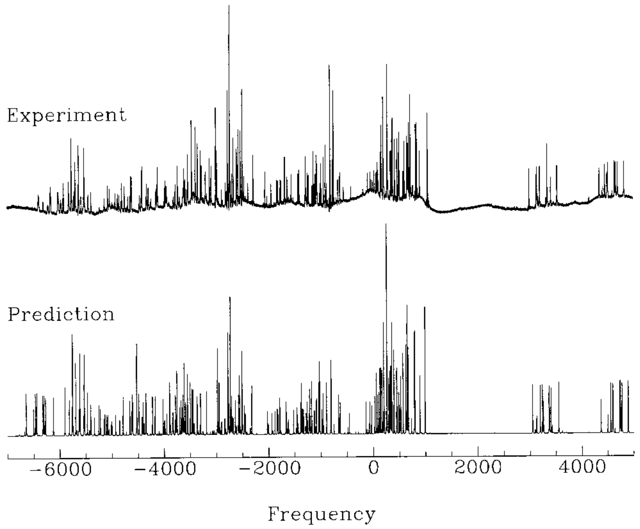

Figure 18. Experimental NMR spectrum of *m*-chlorotoluene (dilute) dissolved in the 55 wt % "magic mixture" at 300 K. The CI model with the parameters of Figure 11c was used for the prediction. This prediction was sufficiently close to the experimental spectrum that a fit to all the lines was obtained within 2 h. The order parameters predicted from the CI model, and those calculated from the fit to the spectrum, are as follows: S_{xx}, 0.0737 (prediction), 0.0795 (experiment); S_{zz}, −0.2150 (prediction), −0.2166 (experiment); S_{xy}, −0.0846 (prediction), −0.0796 (experiment).

where short-range anisotropic interactions are expected to dominate and where long-range electrostatic interactions can be neglected. These studies involve the use of "magic mixtures" as well as "magic solutes". The simplest successful description of short-range interactions involves phenomenological models which are only concerned with size- and shape-dependent hard-body interactions. With the phenomenological models now available to emulate the short-range interactions, order parameters for a large variety of chemically unrelated solutes are predictable to about the 10% level. Solutes which have been studied are of very different sizes and shapes, either "rigid" or showing large-amplitude internal motions, and include some which themselves form nematic phases. An example of the predictive power of the models is given in Figure 18,[164] where we show a predicted and an experimental spectrum of *m*-chlorotoluene as a dilute solute in the 55 wt % "magic mixture". It is obvious that the spectrum, predicted from the CI model (using the parameters of Figure 11c) is quite close to the experimental spectrum from the dilute solution.

The notions obtained from extensive studies in the nematic mixtures can be extended to "pure" nematic liquid crystals. A first approximation for the treatment of nematic liquid crystals in general is to add to the hard-body potential the interaction of the molecular quadrupole moment with the average electric field gradient experienced by the liquid crystal. If such an approach can be justified and further substantiated, it allows for the interesting possibility to estimate molecular quadrupole moments in the condensed phase with some degree of confidence.

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XI. References

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