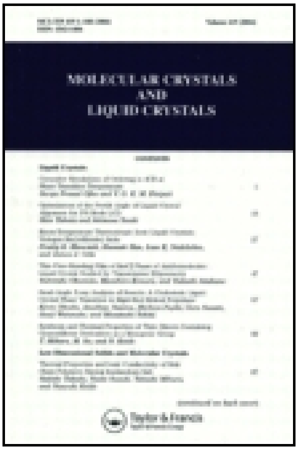

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Orientational Order of Long-Chain Molecules in the Nematic Phase

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Version of record first published: 17 Oct 2011.

To cite this article: S. K. Ghosh (1983): Orientational Order of Long-Chain Molecules in the Nematic Phase, Molecular Crystals and Liquid Crystals, 98:1, 375-384

To link to this article: http://dx.doi.org/10.1080/00268948308073488

Mol. Cryst. Liq. Cryst., 1983, Vol. 98, pp. 375–384
0026-8941/83/9804–0375/$18.50/0

Printed in the United States of America

Orientational Order of Long-Chain Molecules in the Nematic Phase†

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(Received February 17, 1983)

It is shown here that the quadrupole splittings arising from the different deuterium sites of long-chain molecules constituting nematic liquid crystal phases can be well understood with a single order parameter tensor **S** defined for the whole molecule by its long molecular axis, as has been suggested elsewhere. This is demonstrated explicitly for *p*-cyanobenzylidene-*p*'-d_{17}-octyloxyaniline and *p*-butyloxybenzylidene-*p*'-d_{17}-octyl-2,6-d_2-aniline. The role of molecular conformations in relation to the observed splittings has been made evident by recovering the average quadrupole coupling constants and orientations of different C—D bonds for both molecules. These values are in reasonable agreement.

INTRODUCTION

It is generally observed that the quadrupole splittings arising from the different deuterium sites of long-chain molecules constituting nematic liquid crystals do not follow a temperature independent simple proportionality relation expected for the nematic phase.[1] Such an expectation is based on the fact that the orientational order parameter tensor **S** in the uniaxial nematic phase has only one independent component S in its principal axes system, and the averaged electric field gradient tensor at any molecular site responsible for observed splitting could be expressed simply as proportional to **S**. With the accumulation of experimental data in contradiction of this expectation, various proposals have been put forward, and a unified viewpoint is yet to emerge.[2] These different proposals can be broadly divided into two groups with the following essential ideas: (1) a single

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†Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

order parameter tensor **S** for the whole molecule, and (2) an order parameter tensor **S** for each rigid segment of the molecule or multiple order parameters for the whole molecule. The concept of a single order parameter **S** is very attractive, particularly from the point of view of defining a phase, as is very essential to our current understanding of phase transitions. This **S**, the characteristic of the phase, has to be unique and should not depend upon the methods of measurement; it can even be a quantity that is not directly accessible, as in superfluid helium.[3] It seems that a lot of the discrepancies between the two viewpoints arise from the lack of a precise definition of **S**, and without this we cannot expect to obtain a satisfactory relation between **S** and the averaged tensor responsible for observed splittings. This averaged tensor must contain local information for any local probe, as we encounter in NMR and EPR methods, in addition to **S** which is a long range quantity but has a microscopic origin at the molecular level. Hence, the need arises for a microscopic definition of **S**.

There is no disagreement that **S** is a traceless second rank symmetric tensor. Such a tensor can be generated by any unit vector **n** attached to the molecular frame so that $\mathbf{S} = \langle \mathbf{nn} - \mathbf{1}/3 \rangle$, where the angular brackets denote the thermodynamic average and **1** a unit tensor. We can always find a coordinate system in which it is diagonal. Since **S** is to be a long range quantity characteristic of the phase, it is natural to assume that such an **S** has not only the symmetry of the phase, but also the same principal axes as that of the system under consideration. For simplicity, let us consider a uniaxial system and hence restrict ourselves to uniaxial **S**. It is apparent then that we have to choose **n** in conformity with the principal axes system of the phase and *vice versa*. We know the director axis is the only axis that can be defined uniquely in the uniaxial system and hence for **S**. Thus the unique choice of **n** falls on a unique axis of the molecule, if we want to define it from the standpoint of some microscopic properties. We choose this unit vector $\boldsymbol{\zeta}$ along the long molecular axis. This is in conformity with the general form of intermolecular interaction, the first term of which is[4,5] $(\boldsymbol{\zeta}_1 \cdot \boldsymbol{\zeta}_2)^2$ This form of interaction ensures that the director, which is the direction of the molecular field in the molecular field approximation, remains invariant with reversal of $\boldsymbol{\zeta}$. Particularly, we would like to note in this connection that the well known Maier-Saupe[6] form is the special case of the above in the presence of a defined director axis required to have long range order for a rotationally invariant potential. Maier-Saupe calculations show clearly the connection between the definition of **S** and the principal axes of the uniaxial system. Consider XYZ as these principal axes with Z as the director. Obviously X and Y can be any two orthogonal axes in the plane normal to Z but they must be well defined in biaxial systems. Hence, if we define an order parameter $\mathbf{S}^n$ with a unit vector $\mathbf{n}$ other than ζ, as is usually done in experimental situations, then we expect to have five independent components in general. The problem is to relate this $\mathbf{S}^n$ with $\mathbf{S}$ and this relation is expected to be conformation dependent if $\mathbf{n}$ is so related to ζ. Conformation dependence of $\mathbf{S}$ cannot be determined without a rigorous theory and that is lacking at the moment. Yet the effects of conformations on splittings can be observed when a proper relation of $\mathbf{S}^n$ and $\mathbf{S}$ can be established. We have shown elsewhere[7] that the splitting in the uniaxial phase, when can be expressed as proportional to S^n_{ZZ}, is given by a very simple relation. Such a situation is fairly well satisfied by the different C—D bonds of the long-chain molecules of compounds that form liquid crystals, with the assumption that the electric field gradient tensor at the D-site has cylindrical symmetry about the bond axis. With these considerations, and identifying $\mathbf{n}$ with different C—D bonds, the quadrupole splitting for any bond can be expressed as

$$\delta\nu_i = m_i S + b_i \tag{1}$$

where

$$m_i = C^{(i)}_{eff} \frac{3\cos^2\overline{\theta}_i - 1}{2}\left(1 + \frac{\langle \sin^2 \delta\theta_i \rangle}{(3\cos^2\overline{\theta}_i - 1)\langle \cos 2\,\delta\theta_i \rangle}\right),$$

$b_i = 3C^{(i)}_{eff} \sin 2\overline{\theta}_i \langle \sin 2\beta \rangle / 2\pi$, $C^{(i)}_{eff} = 3e^2\overline{q}_i Q/2h$, and $\overline{q}_i = q_i \langle \cos 2\,\delta\theta_i \rangle$. Here i is the bond index and the other quantities have the following significance: e^2qQ/h is the quadrupole coupling constant, $\delta\theta = \overline{\theta} - \theta_p$ with θ_p the angle between ζ and the bond axis in the p^{th} conformation, and $\overline{\theta}$ is its average value, i. e., $\langle \delta\theta \rangle = 0$ on averaging over all conformations. The angle between ζ and Z is β so that $S = \langle 3\cos^2\beta - 1 \rangle / 2$; the angular brackets here represent the statistical average taken with the molecular distribution function under the condition $0 \leqslant \beta \leqslant \pi$. On the other hand, $\langle \sin 2\beta \rangle$ in term b also indicates averaging over the molecular distribution function but for $0 \leqslant \beta \leqslant \pi/2$ or $\pi/2 \leqslant \beta \leqslant \pi$. Hence, it is not zero as we expect for $\mathbf{S}$, being uniaxial in XYZ. This term appears here since the bond axis does not lie along ζ, but makes with it an average angle $\overline{\theta}$. This simplification has been obtained by symmetry arguments given elsewhere[7] and will not be repeated. It is to be noted here that b is zero for the isotropic liquid phase by the same symmetry arguments. Furthermore, very simple arguments show that the temperature dependence of $\langle \sin 2\beta \rangle$ must be very weak in comparison with that of S. This has been well supported by our calculations of these quantities using the intermolecular potential noted earlier. Preliminary calculations with higher order terms do not significantly change this conclusion except in giving some minor variations in magnitudes.

The purpose of the present communication is to show that the quadrupole splittings arising from different deuterium sites of long-chain molecules constituting the nematic phase can be well understood by Eq. 1. We have observed excellent confirmation of this relation using various nematic systems. Here we present results obtained with *p*-cyanobenzylidene-*p*'-d_{17}-octyloxyaniline (CBOOA-d_{17}) and *p*-butyloxybenzylidene-*p*'-d_{17}-octyl-2,6-d_2-aniline (BOBOA-d_{19}) using the data of Deloche and Charvolin.[8]

RESULTS AND DISCUSSIONS

In the absence of any reliable data on S, we cannot directly use Eq. 1 to understand the observed splittings. Later on, we shall see that this limitation can be reasonably overcome. Hence, to check the validity of our approach, we use first the following relation between any two splittings for i and j bonds obtained with the help of Eq. 1:

$$\delta\nu_i = m_{ij}\delta\nu_j + b_{ij} \tag{2}$$

where $m_{ij} = m_i/m_j$, and $b_{ij} = b_i - m_{ij}b_j$. Eq. 2 suggests that the plot of two splittings should be a straight line if m_{ij} and b_{ij} are temperature independent. Such plots together with the least squares fits to Eq. 2 are shown in Figures 1 and 2 for CBOOA-d_{17} and BOBOA-d_{19}, respectively. All the fits are quite good, with correlation coefficient better than 0.99 in every case except for CD_3 in BOBOA-d_{19}. At least two straight lines can be drawn for this particular case as shown in the figure. We shall come back to this point later.

From the rigorous point of view, the temperature dependences of $\bar{\theta}$ and $\langle\sin^2 \delta\theta\rangle$ involved in m and b cannot be excluded, but can be expected to be very weak over the small temperature range involved. These temperature dependencies become weaker from the further considerations that the angles are defined with respect to ζ, and ζ itself is a quantity to be obtained by averaging over all conformations at any temperature. Such a theory has not been developed yet. But the form of the intermolecular potential noted earlier and suggested from symmetry arguments directs us to this picture. The temperature dependence of b due to $\langle\sin 2\beta\rangle$, as we have noted earlier, is expected to be small in comparison with S. From these considerations, the straight line representations of two splittings shown in Figures 1 and 2 seem reasonable.

In the absence of any exact values of S for different temperatures, either from theory or experiment, we have estimated S for the two compounds

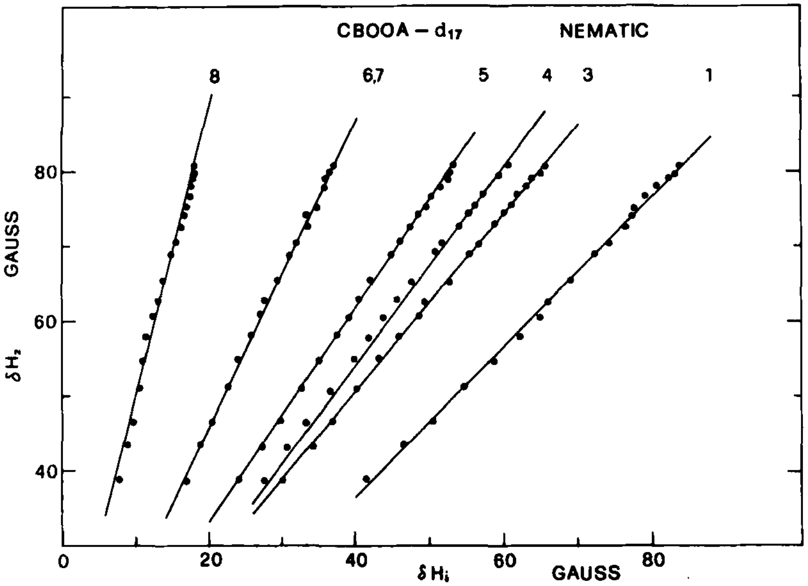

FIGURE 1 Plots of deuterium quadrupole splittings of different C—D bonds measured by Deloche and Charvolin[8] using the nematic phase of CBOOA-d_{17}. The straight lines represent the least squares fits to Eq. 2.

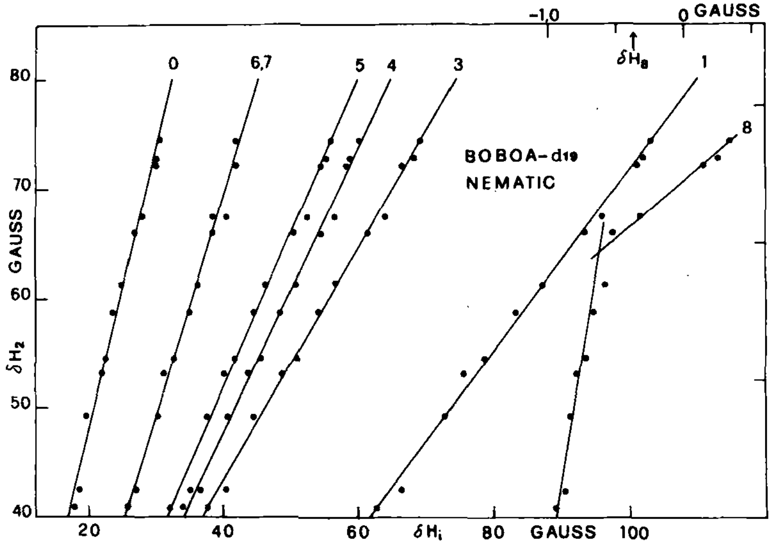

FIGURE 2 Similar plots to those in Figure 1 from the data of the same authors obtained with the nematic phase of BOBOA-d_{19}. The number zero for the first straight line on the left refers to the splittings of ring deuterons. Note that the methyl deuterium splittings cannot be represented by a single straight line.

from an empirical curve of S vs $1 - T/T_C$ obtained from the data of Boilini[9] for PAA corrected with $\langle \sin\beta \cos\beta \rangle = 0.358 \pm 0.002$ computed in the temperature range studied with a Maier-Saupe potential. Here T_C stands for the nematic-isotropic liquid transition temperature. On the other hand, S calculated with the same potential shows a change of ±7–8% in the same temperature range. The plots of the splitting $\delta\nu$ for both the compounds with S obtained as above are shown in Figures 3a and 4a, together with the least squares fits to Eq. 1. It can be noticed that all $\delta\nu$ except $\delta\nu_8$ in BOBOA-d_{19} (see also Figure 2) give excellent fits in spite of using S estimated at different temperatures from an empirical curve. We have also determined $e^2\overline{q}_iQ/h$ and $\overline{\theta}_i$ for different bonds of each molecule using the corresponding m_i and b_i obtained from the least squares fits, and the expressions given in Eq. 1. In such determinations we have neglected first the second term of m_i inside the brackets. These results for different C—D bonds in the alkyloxy and alkyl chains of CBOOA-d_{17} and BOBOA-d_{19}, respectively, are shown in Figures 3b and 4b. It should be noticed that the values of $e^2\overline{q}Q/h$ for those bonds, in each case known to be close to the rigid parts of molecules, are very similar to those obtained with solids.[10] The decrease of $e^2\overline{q}_iQ/h$ along a chain length can be easily understood from simple considerations of conformations[11] according to which $\delta\theta_i$ is expected to increase and consequently to decrease $\langle \cos 2\,\delta\theta_i \rangle$ as i moves away from the rigid part of a molecule. It should be pointed out that $\overline{\theta}_i$ obtained here is slightly greater than that usually used for these molecules. This is not surprising when we note that these angles are estimated from molecular geometries without taking any account of molecular conformations. We would like to note here that the angles obtained can be well reconciled with the observation that the splittings for C—D bonds attached to a C-atom are identical and the bonds have tetrahedral angles between them. Considering the structural differences of the alkyloxy and alkyl chains existing here (particularly the number of C—C bonds), both $e^2\overline{q}_iQ/h$ and $\overline{\theta}_i$, except for $i = 8$, obtained here seem to be in reasonable agreement. One interesting point to note in this connection is that $e^2\overline{q}_1Q/h$ is lower than $e^2\overline{q}_2Q/h$ for CBOOA-d_{17} in spite of the larger splitting observed for the former; such an anomaly, if we want to identify it in that way, does not occur with BOBOA-d_{19}. These observations seem to suggest the lowering of the deuterium quadrupole coupling constant due to sp^3 hybridization[12] in O—CD$_2$—C in comparison with C—CD$_2$—C bonds.

To neglect the second term in m_i inside the brackets is not completely justified, in particular for large i. The effects of this approximation on the different bonds have also been estimated and the results are included in Figures 3b and 4b (denoted corrected). In such estimations, we have used

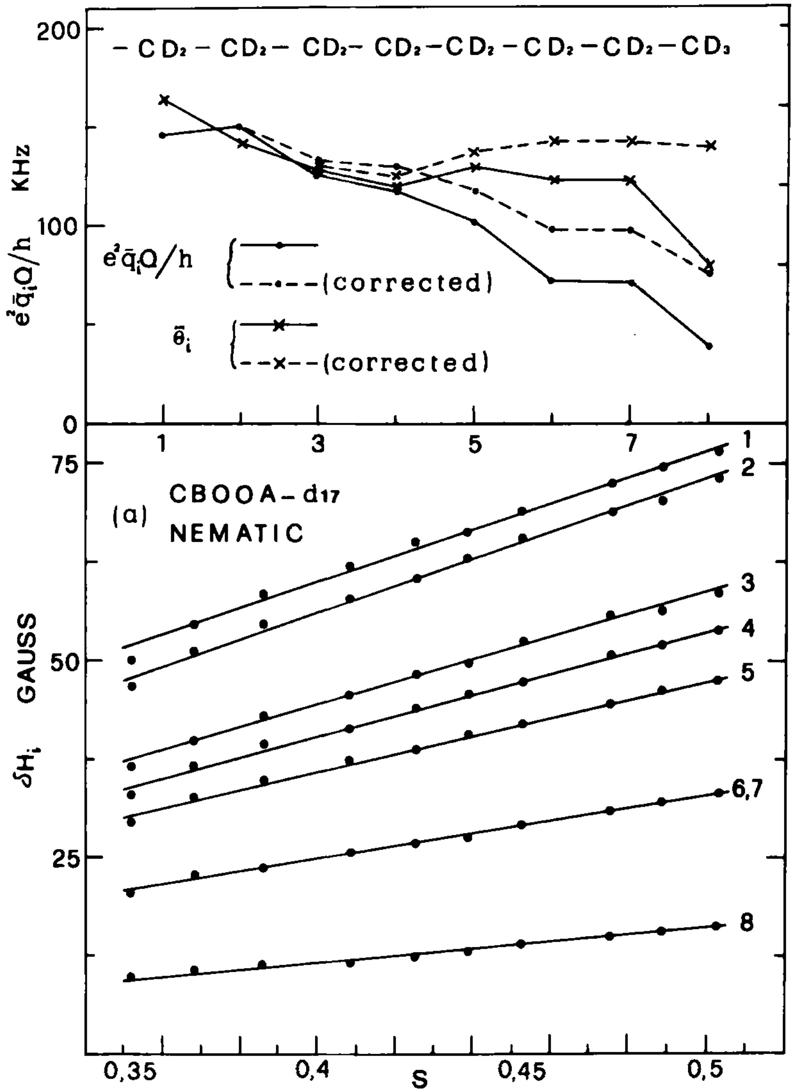

FIGURE 3 (a) Plots of the same splittings as those shown in Figure 1, together with the least squares fits to Eq. 1. Given above (a) are the bond parameters $e^2\bar{q}_iQ/h$ and $\bar{\theta}_i$ for different bonds i obtained from the best fit parameters. See the text for details.

the maximum value of e^2qQ/h observed for a C—D bond in a chain. Similar results for the CD_3 bonds in BOBOA-d_{19} have been obtained by fitting the observed splittings with two straight lines shown in Figures 2 and 4a. The two straight lines are obtained from low and high temperature data

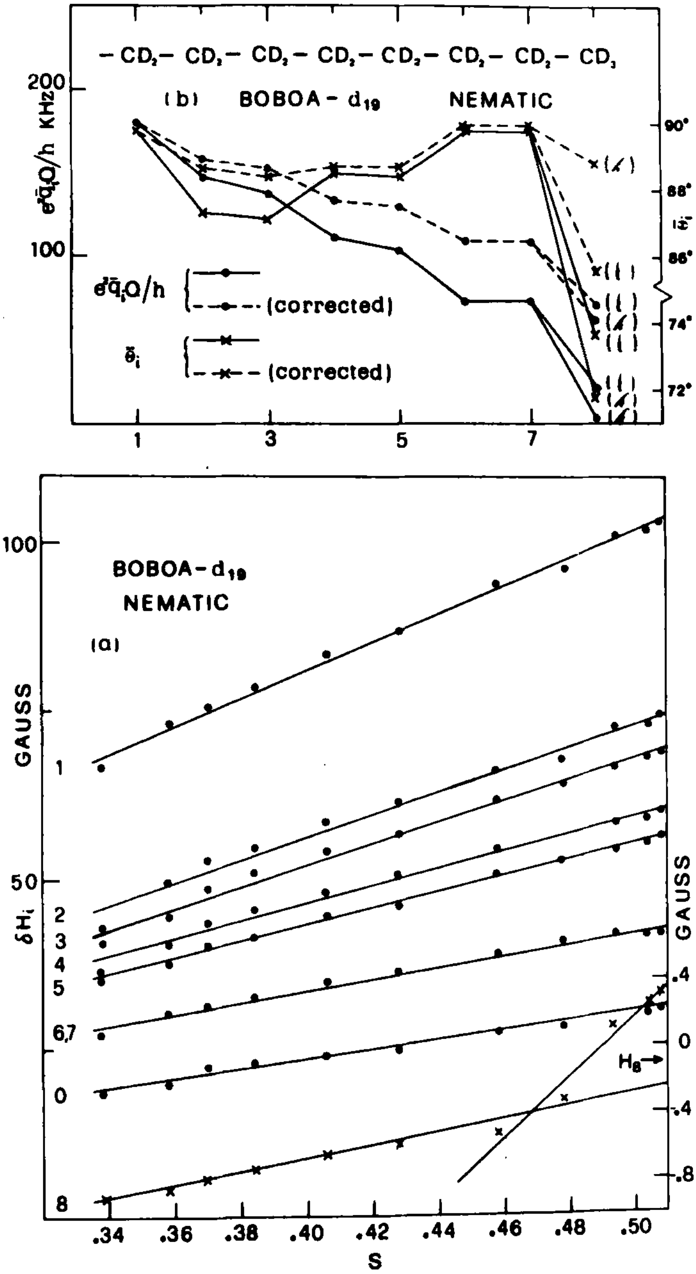

FIGURE 4 (a) and (b) are similar plots to those in Figure 3, and were obtained with data shown in Figure 2. Note here again that methyl deuterium splittings cannot be represented by a single straight line.

and denoted by *l* and *h* inside parentheses in Figure 4b. It should be noticed that the bond parameters for CD_3 for both the molecules also become very close after such corrections; this is particularly true when we consider the low temperature values for BOBOA-d_{19}.. The two-straight-line representation followed here is a simplification. In fact, a continuous change of bond parameters with temperature can be easily thought of. Our studies show that this temperature dependence arises from conformations and is not negligible in the temperature range.

Finally, we would like to bring out the essential points in which our approach differs from earlier ones summed up in the two broad groups. The difference with the group having the concept of multiple order parameters, if these refer to a phase, is fundamental, as we have pointed out earlier. On the other hand, their viewpoints can be easily understood from ours, if their order parameters refer to local molecular properties. The difficulties of such an approach would be to separate the truly long range *S* from the exact local properties using the available experimental data. In this connection, we would like to stress again the absence of any theory for the nematic phase itself where molecular conformations have been taken into account to calculate *S*. This approach and its associated difficulties noted above can be appreciated when viewed in the following way: the order parameter tensor here is generated by a unit vector along the director axis in the principal axes system of the tensor quantity of experimental interest, and these axes are local and fixed in the molecular frame. The order parameter tensor defined in such a way will have five independent components[13] and only two of these will be available for any fixed principal axes frame noted above;[14] the information on the other three components will be lost. The principal axes, which are local axes, are expected to change with conformations, and hence two different independent components are available at each conformation. It is not clear that these two parameters contain all the information on the five independent components on averaging over the conformations. But it is quite apparent that the parameters contain information on the long range order and the local molecular properties in an inseparable way. The difference with the group having the concept of a single order parameter tensor for the whole molecule as presented by Doane and coworkers[15] is not that clear, particularly their definition of this order parameter tensor. However, it is clear from their calculation that they have transformed this order parameter tensor in the principal axes system fixed at some part of a molecule. As discussed above, this is a local frame and is subjected to change with conformations. Moreover, the splittings will contain information on two of the five independent components of the order parameter tensor. Hence the information is incomplete, and probably this is the reason why they get two or three independent components which are expected to be strongly temperature dependent. All these difficulties have been avoided in our approach.

CONCLUSIONS

We have shown here that the quadrupole splittings arising from different parts of a long-chain molecule can be well understood with a single order parameter tensor defined by a unique molecular axis which we call long-molecular axis $\boldsymbol{\zeta}$. This long range order parameter tensor **S** has the uniaxial symmetry of the nematic phase and hence has only one independent component in its principal axes system. No effort has been made here to establish any relation between this independent component S and molecular conformations. On the other hand, we have shown here that all the splittings can be well understood with a simple relation of the form: $\delta\nu_i = m_i S + b_i$, derived elsewhere[7] with m_i and b_i containing bond parameters averaged over conformations. It is argued that these bond parameters are expected in general to be weakly temperature dependent. No general theoretical arguments could be offered at this stage where strong temperature dependencies of these parameters could be expected. It has been shown that such cases can be identified experimentally. Finally, we would like to note that the bond parameters particularly $e^2\bar{q}_i Q/h$ or $\langle \sin^2 \delta\theta_i \rangle$ for any bond i could be very useful in studying conformational statistics.

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