The relationship between molecular symmetry and second-rank orientational order parameters for molecules in chiral liquid crystalline solvents

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From group theoretical arguments, we demonstrate that the effective molecular symmetry is reduced in a chiral liquid crystalline phase. This reduction changes the location of the principal axes of the orientational order matrices for four molecular point groups, namely C_s, C_{2v}, S_4, and D_{2d}. These symmetries correspond to compounds which have prochiral faces, groups, or directions. The change in effective molecular symmetry can be detected by NMR spectroscopy, and this is illustrated by the example of acenaphthene dissolved in a chiral nematic solvent. © *1999 American Institute of Physics.* [S0021-9606(99)51937-5]

I. INTRODUCTION

The problem that we shall address is of a general nature, but it can be described simply by referring to a particular example. The NMR spectrum from a molecule dissolved in a liquid crystalline phase is affected by both isotropic interactions, such as scalar spin–spin couplings, J_{ij}, and anisotropic interactions, such as dipolar couplings, D_{ij}, or quadrupolar splittings, Δ_i. The magnetic field of the spectrometer, $\mathbf{B}_o$, is sufficiently intense to align the directors, $\mathbf{n}$, of a nematic liquid crystalline phase to be uniformly aligned either along $\mathbf{B}_o$ if $\Delta\chi$, the anisotropy in the magnetic susceptibility is positive, and in the plane perpendicular to $\mathbf{B}_o$ if it is negative.[1] We will consider the case of $\Delta\chi$ positive. The result of analyzing the NMR spectrum of a sample dissolved in a uniaxial liquid crystalline phase is to obtain the tensor components, T_{zz}, of the different interactions along the direction of the magnetic field, which is also the component along the mesophase director. This component is related to components, $T_{\alpha\beta}$, in a frame fixed in the molecule by[2]

$$T_{zz} = \Sigma_{\alpha,\beta} T_{\alpha\beta} S_{\alpha\beta}. \tag{1}$$

The $S_{\alpha\beta}$ are elements of the Saupe order matrix, $\mathbf{S}$, whose values are

$$S_{\alpha\beta} = \langle 3\cos\theta_\alpha \cos\theta_\beta - \delta_{\alpha\beta}\rangle/2. \tag{2}$$

The angles θ_α and θ_β are between the director and the axes α and β, respectively. $\delta_{\alpha\beta}$ is the Kronecker function and takes the value 1 if $\alpha = \beta$ and zero otherwise; the brackets $\langle ... \rangle$ denote an ensemble average. For a general choice of molecular axes, there will be five independent elements of $\mathbf{S}$, but there is one set of principal axes (abc) for which the

order matrix is diagonal, and since it is always traceless, the number of independent elements reduces to just two, S_{aa} and $S_{bb} - S_{cc}$.

Now let us consider a particular molecule, CH_3CD_2OH, and its deuterium spectrum in a nematic liquid crystalline solvent. To simplify matters we will decouple the protons so that the spectrum is just that from two deuterons. The spectrum observed shows just one splitting from the quadrupolar interaction, and one interdeuteron dipolar coupling. This we interpret as being because the molecule has an effective plane of symmetry which contains the two carbons and the oxygen atom. This is consistent with Eq. (1) when we note that the presence of the mirror plane means that one of the principal axes for $\mathbf{S}$ will be the normal, a, to the molecular mirror plane, and the other two principal axes, b and c, must lie in the plane. It has been observed recently that the deuterium spectrum of CD_3CD_2OD dissolved in the chiral nematic phase of a solution of poly-(γ-benzyl-L-glutamate) (PBLG) in chloroform consists of two quadrupolar doublets for the methylene group.[3] This means that the two C-D directions in the molecule have become nonequivalent. Note that this phenomenon has been observed for some other molecules of symmetry C_s.[4] The PBLG/CHCl$_3$ solution in the absence of an external constraint forms a cholesteric phase, that is the directors twist into helices. In the magnetic field of the NMR spectrometer, the phase helices unwind and the phase is now like a normal nematic, except that the PBLG molecules are chiral. The question that we will address here is why are the two C-D bond directions nonequivalent when ethanol is dissolved in the chiral nematic phase? There are clearly three possible reasons why there is an apparent reduction in symmetry of the molecule. First, the solute might indeed be distorted in some way so that the molecular symmetry plane is lost. Second, ethanol has an effective molecular symmetry plane only if the motion about the C–O bond has twofold symmetry, and so perhaps there is a change in

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the symmetry of the bond rotation in the PBLG/CHCl$_3$ solution? Third, the reduction in effective molecular symmetry could be a general consequence stemming from the reduced symmetry of the phase. We will show that the latter phenomenon does explain the observation of a reduction in effective molecular symmetry of ethanol in the chiral nematic phase. We will also demonstrate that this effect occurs for a solute, acenaphthene, which is rigid, thus eliminating a conformational change as a cause of the phenomenon. Finally, we apply these considerations for chiral smectic A and C, and conclude that this phenomenon is general for all chiral liquid crystalline phases.

II. THEORY

The way in which symmetry affects the result of making a measurement of a physical property of a molecule depends on both the molecular symmetry point group, G'_M, and on the symmetry group of the phase, G_P. Thus this leads to the concept of the effective symmetry point group, G_M, of a molecule in the phase. For NMR spectra the distinction must also be made between G'_M and the effective symmetry group of the interacting spins, G'_S, for the spins in an isolated molecule, and G_S for a molecule in a phase. G'_S is a subgroup of G'_M, and G_S is a subgroup of G_M. Isotropic liquid phases belong to the full orthogonal group O$_3$,[5,6] of which all the G'_M are subgroups, and G_M is equivalent to G'_M. The relationships between the G'_M and G'_S for isotropic phases are given by Corio.[7]

All the liquid crystalline phases have lower rotational symmetry than O$_3$. This group is the direct product of two groups, the group of rotation in 3-space, SO$_3$, and the two elements group C_i consisting of the inversion operation and the identity. In other words, this group is composed of all the proper and improper rotations.[5] Some phases also have translational periodicities, but these do not affect the form taken by NMR spectra, and so we will confine our discussions to rotational symmetry alone. The nematic phase has symmetry $D_{\infty h}$.[8,9] Because a rotation about the director, or a 180° rotation perpendicular to the director, does not change the physical properties, this phase is apolar, and uniaxial. Moreover, when the phase is composed of nonchiral molecules, or a racemic mixture, then it is centrosymmetric. The consequences for NMR spectroscopy, and for the orientational order parameters of molecules in the phase, have been discussed before,[2,10,11] but will be revisited here to set the scene for the changes which occur when the phase is chiral.

The phase and molecular symmetries do affect the number of order parameters required to describe the orientationally dependent properties of molecules dissolved in the nematic phase. The effect that symmetry has on order parameters is seen most simply by using the spherical tensor formalism and defining a general order parameter of the rigid molecules as

$$\langle D^L_{m,n}\rangle = \int D^L_{m,n}(\alpha,\beta,\gamma)P_{LC}(\alpha,\beta,\gamma)d\alpha \sin\beta d\beta d\gamma, \quad (3)$$

where $D^L_{m,n}(\alpha,\beta,\gamma)$ is an Lth rank Wigner function, and α, β, and γ are the Euler angles describing the orientation of the director in the molecule-fixed frame. $P_{LC}(\alpha,\beta,\gamma)$ represents the singlet orientational distribution function.

Before discussing the effect that the symmetry operations of the phase and of the solute have on the $D^L_{m,n}(\alpha,\beta,\gamma)$ functions, we note that these operations have to leave $P_{LC}(\alpha,\beta,\gamma)$ unchanged. In all nonchiral liquid crystalline media, $P_{LC}(\alpha,\beta,\gamma)$ is invariant to all rotation and reflection operations which compose the full orthogonal group O$_3$. Because the symmetry group operations of the phase, G_P, and of the molecules, G'_M, leave the singlet distribution unchanged, then these groups are subgroups of the O$_3$ group. Consequently, the molecular effective symmetry group, G_M, is identical to the symmetry point group, G'_M, because all the point groups, G'_M, are subgroups of O$_3$. In conclusion, the reduction in phase symmetry does not affect the equivalencies between the G_M and G'_M, and the relationships between $G'_S + G_S$ and G'_M are unchanged from the case of an isotropic environment.

We turn our attention now to the effect of symmetry on the order parameters. The uniaxial symmetry about the director makes α redundant and restricts m to being zero in Eq. (3). The reflection plane perpendicular to the director restricts L to being even. Thus, for a nematic phase, the $\langle D^L_{0,n}\rangle$ are the only nonzero order parameters. For $L=2$, the allowed values of n are ±1, ±2, and 0; however, there is a set of principal axes for which n is restricted to just 2 and 0. The order matrices are traceless, and so in principal axes there are just two independent elements, $\langle D^2_{0,0}\rangle$ and $[\langle D^2_{0,2}\rangle = \langle D^2_{0,-2}\rangle]$, which in Cartesian coordinates translate into being S_{aa} and $S_{bb} - S_{cc}$. Thus, for a molecule of any symmetry in a nematic phase, or a uniaxial phase of the same rotational symmetry such as the SmA and SmB, there are just two independent elements of **S** in the principal frame, but this is of direct help, for example in using Eq. (1), only if the principal axes can be located. The location of the principal axes is related to the molecular symmetry, as discussed by Zannoni,[10] and with the results shown in Table I.

Chiral nematic phases contain chiral molecules, which have the distinguishing character that they are different from their mirror image. This property of the molecules eliminates any reflection symmetry for the phase. Therefore $P_{LC}(\alpha,\beta,\gamma)$ cannot be invariant under inversion or reflection,[12,13] and it is unchanged only by proper rotations and so belongs to the SO$_3$ group. Consequently, the symmetry groups of the solute, G_M, and of the mesophase, G_P, have also to be subgroups of SO$_3$. The molecular asymmetry is transmitted to a phase comprised of chiral molecules of one enantiomeric form. The consequence for a chiral nematic phase is that the mirror plane perpendicular to the director is lost, and the phase symmetry is reduced to D_∞. The uniaxial symmetry about the director is preserved and so m is still restricted to being zero. There is an infinite set of twofold axes in the plane perpendicular to the director, and so the order parameters are still restricted to those with L even. Thus, for $L=2$ there are still only just two principal order parameters for a molecule dissolved in a chiral nematic phase.

TABLE I. Location of the principal axes *abc* of the second-rank orientational order parameters $\langle D^2_{m,n}\rangle$ for molecules of different point group symmetries dissolved in nonchiral uniaxial phases.

Molecular point group	Location of axes *abc*	Independent order parameters (in terms of Wigner elements)	Independent order parameters (in terms of Saupe elements)
C_1, C_i	not special	$\langle D^2_{0,0}\rangle$, Re($\langle D^2_{0,1}\rangle$), Im($\langle D^2_{0,1}\rangle$), Re($\langle D^2_{0,2}\rangle$), Im($\langle D^2_{0,2}\rangle$)	$S_{aa}, S_{bb}-S_{cc}, S_{bc}, S_{ab}, S_{ac}$
C_s, C_2, C_{2h}	*a* normal to the plane or parallel to the twofold axis; *a* parallel to the twofold axis	$\langle D^2_{0,0}\rangle$, Re($\langle D^2_{0,2}\rangle$), Im($\langle D^2_{0,2}\rangle$)	$S_{aa}, S_{bb}-S_{cc}, S_{bc}$
C_{2v}	*b* normal to the mirror plane	$\langle D^2_{0,0}\rangle, \langle D^2_{0,2}\rangle$	$S_{aa}, S_{bb}-S_{cc}$,
D_2, D_{2h}	*a,b,c* parallel to the twofold axes		
$D_{2d}, C_3, C_{3v}, C_{3h}, D_3, D_{3h}, D_{3d}, C_4, C_{4v}, C_{4h}, D_4, D_{4h}, D_{4d}, S_4, C_5, C_{5h}, C_{5v}, D_5, D_{5h}, D_{5d}, C_6, C_{6h}, C_{6v}, D_6, D_{6h}, D_{6d}, S_6, C_\infty, C_{\infty v}, C_{\infty h}, D_{\infty h}$	*a* parallel *p*-fold axis or intersection of mirror planes	$\langle D^2_{0,0}\rangle$	S_{aa}

Thus far the chiral and nonchiral nematic phases present the same situation, but a difference emerges when the effect on the spin permutation symmetry and the choice of principal axes for **S** are considered. Both these phenomena are related to the change in the relationship between G_M and G'_M. The absence of inversion symmetry, for the effective symmetry group leaving $P_{LC}(\alpha,\beta,\gamma)$ invariant, means that the G_M also cannot contain improper rotation operations. This implies that G_M for some molecular symmetry groups is different than G'_M. Thus this means that the rules for identifying the location of the principal axes can change for some of the molecular point groups. For example, in the case of ethanol, with point group symmetry C_s, which contains a mirror plane and the identity operator, the effective molecular point group is lowered to C_1. The loss of the mirror symmetry also lowers the permutation spin symmetry, G_S, and the two deuterons of the methylene group in CD_3CD_2OD when dissolved in a chiral nematic phase are not symmetrically equivalent. The lower effective point group symmetry means that none of the principal axes is identifiable by symmetry. That is, the normal to the mirror plane of the molecular point group is a principal axis for **S** when ethanol is dissolved in a normal nematic, but not for a chiral nematic solvent. Table II gives the relationship between G_M and G'_M for molecules in a chiral nematic phase. From a comparison between the Tables I and II, we can observe that several symmetry groups do not have G_M equivalent to G'_M when the molecules are in a chiral uniaxial liquid crystalline phase. When the point group contains an *n*-fold rotation axis with $n>2$, this axis is a principal axis, *a*, for the order matrix, and also $S_{bb}=S_{cc}$. This situation is not changed by the loss of reflection symmetry. Thus, reducing the effective symmetry from C_{3v} to C_3 does not change either the location of the

principal axes of **S** or the uniaxial symmetry. When the point group does not contain a threefold or higher rotation axis, the loss of reflection symmetry may lead to a change in the location of the principal axes of **S**. This occurs for four groups, C_S, S_4, C_{2v}, and D_{2d}. Note that in the terminology of stereochemistry, compounds possessing these symmetries are said to have prochiral faces, groups, or directions.[14] Thus, the enantiotopic faces, groups, or directions in molecules with these symmetries can be identified by comparing the NMR spectra of samples dissolved in nematic and chiral nematic phases.

It is worth noting at this point the necessary criteria for a phase to be chiral. It is not necessary for all the molecules in the phase to be identical, that is the same enantiomer of a particular molecular species. In fact, a phase in which all the molecules are achiral except one would in principle not have inversion symmetry and would be chiral. In practice, the case of most interest so far for NMR spectroscopy has been the **N*** phase produced by PBLG dissolved in organic solvents. The effects of the phase chirality have been observed either on the spectrum from the solvent molecules, or from that of an additional solute.[15–19]

Cholesteric phases are examples of chiral nematics with the directors arranged in helices. The symmetry about the director is still D_∞, and so solutes in such a phase will have the same properties as for chiral nematics. It has been shown[20] that the quadrupolar splittings of deuterons in some pairs of optical isomers dissolved in cholesteric phases are different, and so it is probable that these solvents will also reveal the presence of prochirality in solutes.

Chiral SmA and SmB phases have the same symmetry as chiral nematics, and so the NMR spectra of pairs of optical isomers dissolved in these phases in principle should be

TABLE II. Location of the principal axes *abc* of the second-rank orientational order parameters $\langle D^2_{m,n}\rangle$ for molecules of different point group symmetries dissolved in chiral uniaxial phases.

Molecular point group	Effective molecular point group in chiral liquid crystal	Location of axes *abc*	Independent order parameters (in terms of Wigner elements)	Independent order parameters (in terms of Saupe elements)
C_1, C_i, C_S[a]	C_1	not special	$\langle D^2_{0,0}\rangle,$ $\mathrm{Re}(\langle D^2_{0,1}\rangle), \mathrm{Im}(\langle D^2_{0,1}\rangle),$ $\mathrm{Re}(\langle D^2_{0,2}\rangle), \mathrm{Im}(\langle D^2_{0,2}\rangle)$	$S_{aa}, S_{bb}\text{-}S_{cc},$ S_{bc}, S_{ab}, S_{ac}
$C_2, C_{2h}, S_4,$[a] C_{2v}[a]	C_2	*a* parallel to the twofold axis	$\langle D^2_{0,0}\rangle,$ $\mathrm{Re}(\langle D^2_{0,2}\rangle), \mathrm{Im}(\langle D^2_{0,2}\rangle)$	$S_{aa}, S_{bb}\text{-}S_{cc}, S_{bc}$
$D_2, D_{2h}, D_{2d},$[a]	D_2	*a,b,c* parallel to the twofold axes	$\langle D^2_{0,0}\rangle, \langle D^2_{0,2}\rangle$	$S_{aa}, S_{bb}\text{-}S_{cc},$
$C_3, C_{3v}, C_{3h}, D_3,$ $D_{3h}, D_{3d}, C_4, C_{4v},$ $C_{4h}, D_4, D_{4h}, D_{4d},$ $C_5, C_{5h}, C_{5v}, D_5,$ $D_{5h}, D_{5d}, C_6, C_{6h},$ $C_{6v}, D_6, D_{6h}, D_{6d},$ $S_6, C_\infty, C_{\infty v}, C_{\infty h},$ $D_{\infty h}$	C_n or D_n with $n>3$	a parallel *n*-fold axis	$\langle D^2_{0,0}\rangle$	S_{aa}

[a]Molecules with these point groups have a lower effective symmetry and a change in the location of the principal axes of the order matrix.

different, but there seem to be no reported examples of this phenomenon. These phases should also produce a reduction in effective symmetry of molecules possessing prochiral faces, groups, or directions, but again this has not yet been observed. By analogy with the case of cholesteryl nematic phases, the effect should be detectable in those cholesteryl esters which form SmA phases.

A. Smectic *C* phases

As yet the lowering of the effective molecular point group symmetry because of phase symmetry has been detected only for the uniaxial, chiral nematic phase; however, the same possibility exists for the biaxial, tilted smectic phases. An unconstrained SmC phase has symmetry C_{2h} with the mirror plane containing the director and layer normal.[2] Note this symmetry group is a subgroup of O_3 and all the symmetry operations leave $P_{LC}(\alpha,\beta,\gamma)$ unchanged. These operations, apart from the identity operator, are $C_2(z)$, i and σ_{xy}. The effect that these operations have on the Wigner functions, and hence on the orientational order parameters, has been given by Zannoni, and for the $\langle D^L_{m,n}\rangle$ to be invariant under these operations we have the relations[10]

$$\langle D^L_{m,n}\rangle = (-)^m\langle D^L_{m,n}\rangle \tag{4}$$

under the $C_2(z)$ operation,

$$\langle D^L_{m,n}\rangle = (-)^L\langle D^L_{m,n}\rangle \tag{5}$$

under the inversion operation,

$$\langle D^L_{m,n}\rangle = (-)^{L+m}\langle D^L_{m,n}\rangle \tag{6}$$

under the σ_{xy} operation. Thus the invariance restricts L and m to being even. The second-rank order parameters for a molecule in a SmC phase are

$$\langle D^2_{0,n}\rangle \quad \text{and} \quad \langle D^2_{2,n}\rangle = (-)^n\langle D^{2*}_{-2,n}\rangle.$$

We see clearly, that even if the particles have cylindrical symmetry, we still have two principal nonzero independent order parameters corresponding to the biaxiality of the phase. The allowed values of *n* for a general choice of the axes fixed in the molecule are $0, \pm 1, \pm 2$, so that there are ten independent order parameters in the principal frame of the director. The molecular symmetry may lead to the identification of some of the principal axes for the $\langle D^L_{m,n}\rangle$, as shown in Table III.

If the location of the molecular principal axis frame is known, then *n* can only be 0 or 2, and the principal order parameters are just four in number,

$$\langle D^2_{0,0}\rangle, \langle D^2_{0,2}\rangle = \langle D^2_{0,-2}\rangle, \langle D^2_{2,0}\rangle = \langle D^2_{-2,0}\rangle,$$

and

$$\langle D^2_{2,2}\rangle = \langle D^2_{2,-2}\rangle = \langle D^2_{-2,2}\rangle = \langle D^2_{-2,-2}\rangle.$$

The remaining question for a SmC phase is how does molecular symmetry assist in locating the principal axes, and in particular is G_M equivalent to G'_M? The two molecular symmetry groups are equivalent because in the nonchiral liquid crystal all the molecular groups are subgroups of the full orthogonal group O_3, and so the situation is identical to that for the nonchiral uniaxial phases and all operations of the molecular point groups are allowed.

When deciding how many order parameters are required to relate the tensor components measured in an NMR experiment to the molecular components of the relevant second-rank tensors, it is also necessary to remember that usually only the tensor component along the magnetic field direction is measured. For nematic samples, either the field is parallel or perpendicular to the director, but other possibilities exist for smectic phases. It is now much more useful to write the general form of Eq. (1) for a second-rank interaction in irreducible tensor form,

TABLE III. Independent orientational order parameters in smectic C phases for molecules of various symmetry in the principal axis system of the phase.

Molecular point group	Number of independent order parameters	Independent order parameters (in terms of Wigner elements)
C_1, C_i	10	$\langle D_{0,0}^2 \rangle$, $\mathrm{Re}(\langle D_{0,1}^2 \rangle), \mathrm{Im}(\langle D_{0,1}^2 \rangle)$, $\mathrm{Re}(\langle D_{0,2}^2 \rangle), \mathrm{Im}(\langle D_{0,2}^2 \rangle)$, $\langle D_{2,0}^2 \rangle$, $\langle \mathrm{Re}\langle D_{2,1}^2 \rangle\rangle, \mathrm{Im}(\langle D_{2,1}^2 \rangle)$, $\mathrm{Re}(\langle D_{2,2}^2 \rangle), \mathrm{Im}(\langle D_{2,2}^2 \rangle)$
C_s, C_2, C_{2h}	6	$\langle D_{0,0}^2 \rangle$, $\mathrm{Re}(\langle D_{0,2}^2 \rangle), \mathrm{Im}(\langle D_{0,2}^2 \rangle)$, $\langle D_{2,0}^2 \rangle$, $\mathrm{Re}(\langle D_{2,2}^2 \rangle), \mathrm{Im}(\langle D_{2,2}^2 \rangle)$
C_{2v}	4	$\langle D_{0,0}^2 \rangle$, $\langle D_{0,2}^2 \rangle, \langle D_{2,0}^2 \rangle$, $\langle D_{2,2}^2 \rangle$
D_2, D_{2h} $D_{2d}, C_3, C_{3v}, C_{3h},$ $D_3, D_{3h}, D_{3d}, C_4,$ $C_{4v}, C_{4h}, D_4, D_{4h}$ D_{4d}, S_4, C_5, C_{5h} $C_{5v}, D_5, D_{5h}, D_{5d}$ C_6, C_{6h}, C_{6v}, D_6 $D_{6h}, D_{6d}, S_6, C_\infty,$ $C_{\infty v}, C_{\infty h}, D_{\infty h}$	2	$\langle D_{0,0}^2 \rangle, \langle D_{0,2}^2 \rangle$

$$\langle (T_{2,0})_{\mathrm{mag}} \rangle = \sum_m D_{0,m}^2(0, \beta_{B_o}, \gamma_{B_o}) \cdot \sum_n \langle D_{m,n}^2 \rangle (T_{2,n})_{\mathrm{mol}}. \tag{7}$$

Uniaxial symmetry about $\mathbf{B}_0$ is assumed, so that α_{B_0}, but not β_{B_0} and γ_{B_0}, is redundant when describing the orientation of the field in the director frame by $D_{0,m}^2(0, \beta_{B_0}, \gamma_{B_0})$. This will be an effective symmetry at large fields (the ''high field approximation''), but may be an exact symmetry for some special, but common, cases. When there is uniaxial symmetry about the director then m is zero and Eq. (7) reduces to the irreducible tensor equivalent of Eq. (1).[21] There are two special cases which lead to a simplification of Eq. (7). One case is when the directors are all uniformly aligned either along, or perpendicular to $\mathbf{B}_0$. Samples with this arrangement are produced when cooled from a nematic phase, either directly, or via an intervening SmA phase.[21] In the absence of a constraint acting on the minor axes of the director there will be uniaxial symmetry about $\mathbf{B}_0$ and the directors, and m is zero. This means that Eq. (7) reduces to Eq. (1) in Cartesian form, and the NMR experiments yield only the appropriate elements of **S**. This situation also occurs when the sample is prepared with the layer normals uniformly aligned along $\mathbf{B}_0$. In this case the directors are uniformly distributed about $\mathbf{B}_0$.

B. Chiral SmC phases

In these phases the symmetry is reduced to being C_2, which is a subgroup of SO_3, and the only restriction on the order parameters is that given by Eq. (4), so that m has to be even, but there are no restrictions on L. The phase is polar, which means that it can be ferroelectric. However, by NMR

it is still only possible to measure the second-rank interactions, and so only the order parameters with $L = 2$ need to be considered, and there are still only four independent principal order parameters. The lowered phase symmetry means that molecules with the molecular point group symmetries C_s, C_{2v}, S_4, and D_{2d} have the same special properties as they do in chiral uniaxial phases, that is their effective molecular symmetry in the SmC* phase is lowered, and the location of the principal axes of the order matrices is changed, as shown in Table IV. The SmC* phase, therefore, can in principle be used just like the uniaxial chiral phases to reveal the presence of enantiotopic faces, elements, groups, or directions in dissolved molecules by NMR, or any other physical method which is sensitive to solute orientational order. The magnitude of the phenomenon will depend on the strength of the asymmetric interaction between the chiral solvent and the solute molecules, and it remains to be discovered whether this is sufficiently strong in particular cases to produce an observable effect.

III. EXPERIMENT

A sample of 100 mg of acenaphthene-d_{10} in the chiral nematic solvent produced by dissolving 100 mg of PBLG ($DP = 562$, Sigma) in 350 mg of CHCl$_3$ was prepared. Its deuterium spectrum, shown in Fig. 1, was recorded on a Bruker DRX 400 spectrometer at 295 K using a 5 mm diameter inverse broadband probe. A solution of 100 mg of acenaphthene-d_{10} in the compensated nematic solvent produced by dissolving 50 mg of PBLG ($DP = 562$, Sigma) and 50 mg of PBDG ($DP = 914$, Sigma) in 300 mg of CHCl$_3$ was prepared. The deuterium spectrum of this solution is shown in Fig. 1(b). The deuterium signals in both spectra were assigned first by their chemical shifts, which distinguish aromatic from aliphatic deuterons, and then by two-dimensional Q-COSY experiments.[14,22]

IV. DISCUSSION

The structure of acenaphthene has been determined by a neutron diffraction study on single crystals to have the aromatic nuclei and the two aliphatic carbons to be coplanar, and for the aliphatic protons to be placed symmetrically above and below this plane.[23] This means that the molecule belongs to the C_{2v} point group. In the nonchiral nematic solvent, the PBLG-PBDG racemic mixture, the deuterium nuclei give the spectrum shown in Fig. 1(b). The aromatic deuterons produce a doublet for each site and the aliphatic deuterons produce one doublet. It is obvious that all four aliphatic nuclei have the same quadrupolar splitting. In orientation terms, it is clear that the axes a, b, and c shown in Fig. 2 are the principal axes for the solute order matrix in this phase, and in the frame (abc) the nonzero, independent order parameters are S_{aa} and $S_{bb} - S_{cc}$.

In the chiral nematic solvent, the spectrum [Fig. 1(a)] from the aliphatic deuterons has just four resolved lines, which can be confidently interpreted as being the result of there being two different quadrupolar splittings, which is consistent with a lowering of effective molecular symmetry to C_2, as predicted by the rules shown in Table II. Thus, in

TABLE IV. Independent orientational order parameters in smectic C^* phases for molecules of various symmetry in the principal axis system of the phase orientation.

Molecular point group	Effective molecular point group in chiral liquid crystal	Number of independent order parameters	Independent order parameters (in terms of Wigner elements)
C_1, C_i, C_s [a]	C_1	10	$\langle D_{0,0}^2 \rangle$, $\mathrm{Re}(D_{0,1}^2)$, $\mathrm{Im}(\langle D_{0,1}^2 \rangle)$, $\mathrm{Re}(\langle D_{0,2}^2 \rangle)$, $\mathrm{Im}(\langle D_{0,2}^2 \rangle)$, $\langle D_{2,0}^2 \rangle$, $\mathrm{Re}(\langle D_{2,1}^2 \rangle)$, $\mathrm{Im}(\langle D_{2,1}^2 \rangle)$, $\mathrm{Re}(\langle D_{2,2}^2 \rangle)$, $\mathrm{Im}(D_{2,2}^2)$
C_2, C_{2h}, S_4 [a], C_{2v} [a]	C_2	6	$\langle D_{0,0}^2 \rangle$, $\mathrm{Re}(\langle D_{0,2}^2 \rangle)$, $\mathrm{Im}(\langle D_{0,2}^2 \rangle$, $\langle D_{2,0}^2 \rangle$, $\mathrm{Re}(\langle D_{2,2}^2 \rangle)$, $\mathrm{Im}(\langle D_{2,2}^2 \rangle)$
D_2, D_{2h}, D_{2d} [a]	D_2	4	$\langle D_{0,0}^2 \rangle$, $\langle D_{0,2}^2 \rangle, \langle D_{2,0}^2 \rangle$, $\langle D_{2,2}^2 \rangle$
$C_3, C_{3v}, C_{3h}, D_3,$ $D_{3h}, D_{3d}, C_4, C_{4v},$ $C_{4h}, D_4, D_{4h}, D_{4d},$ $C_5, C_{5th}, C_{5v}, D_5,$ $D_{5h}, D_{5d}, C_6, C_{6h},$ $C_{6v}, D_6, D_{6h}, D_{6d},$ $S_6, C_\infty, C_{\infty v}, C_{\infty h},$ $D_{\infty h}$	C_n or D_n with $n > 3$	2	$\langle D_{0,0}^2 \rangle, \langle D_{0,2}^2 \rangle$

[a] Molecules with these point groups have a lower effective symmetry and a change in the location of the principal axes of the order matrix.

a chiral nematic medium, the two deuterons of the methylene group are clearly not equivalent. The reduction in the effective molecular symmetry means that the axes b and c shown in Fig. 2 are no longer principal axes for the solute order matrix in this phase. The twofold rotation axis, a, remains a principal axis, and in the frame (abc) the nonzero, independent order parameters are S_{aa}, $S_{bb} - S_{cc}$, and S_{bc}. In order to determine the magnitudes of these order parameters it is necessary to know the quadrupolar coupling constants for the deuterons in acenaphthene-d_{10}, and the signs of the quadrupolar splittings. Experiments to measure these parameters are in progress.

V. CONCLUSIONS

We have shown that symmetry arguments predict that in principle the effective molecular point group of solutes dissolved in any chiral liquid crystalline solvents may differ from their molecular point groups. When the molecules have
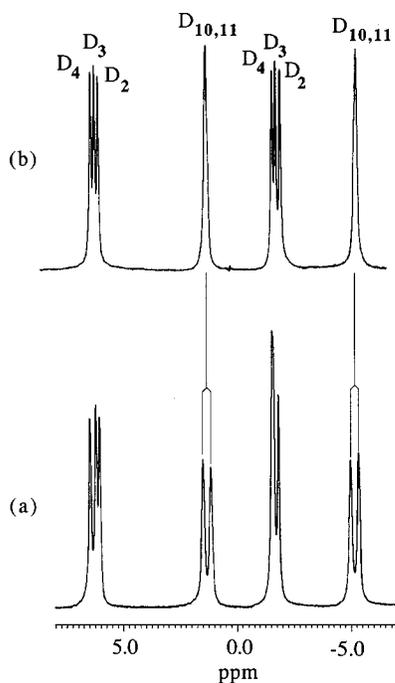

FIG. 1. 61.4 MHz deuterium NMR spectra of acenaphthene-d_{10} at 295 K: (a) in PBLG/CHCl$_3$ liquid crystal; (b) in (PBLG-PBDG)/CHCl$_3$ liquid crystal.
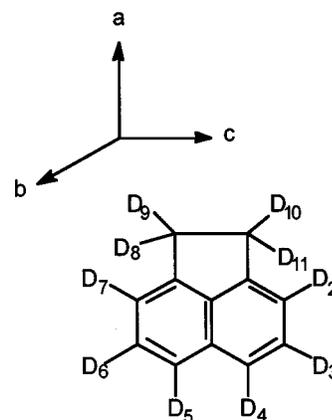

FIG. 2. Molecular reference frame of acenaphthene-d_{10} and numbering system.

a point group symmetry of either C_s, C_{2v}, S_4, or D_{2d}, then this symmetry reduction can be observed by NMR experiments, and indeed it is the reason why the pair of deuterons are nonequivalent in molecules like CH_3CD_2OH dissolved in the chiral nematic phase produced when PBLG is dissolved in organic solvents. Molecules like ethanol, which is flexible, and contains a labile proton, are not ideal candidates for demonstrating this symmetry reducing effect since they may be affected in other ways by the solvent so as to produce a spectral nonequivalence. We have demonstrated unequivocally that the symmetry reduction does occur by examining the deuterium spectrum of a rigid solute, acenaphthene, with C_{2v} point group symmetry.

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