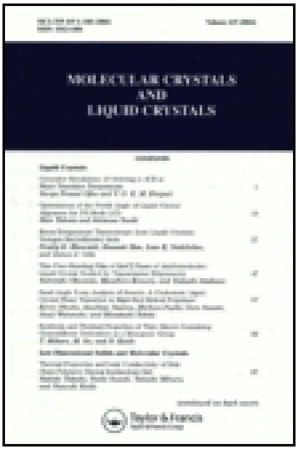

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Molecular Motions of 4-*n*-alkyl-4′-cyanobiphenyls in Liquid Crystal Phases

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On the basis of a model which takes into account the couplings of the conformational transitions in the alkyl chain with the orientational diffusion of the molecule, the outcome of various experiments performed in the liquid crystal phases of *n*-alkyl-cyanobiphenyl (*n*CB) systems can be analyzed and interpreted. The relaxation rates for the various positions in the flexible chain and in the biphenyl core, derived from ^{2}H and ^{13}C NMR experiments, and the frequency dependence of the complex dielectric permittivity, obtained from dielectric relaxation data, have been considered in detail.

Keywords: molecular motions, chain dynamics, NMR relaxation, dielectric relaxation

INTRODUCTION

A dynamical model has been recently developed for molecular systems with internal motions superimposed to overall reorientations.[1] Both kinds of motions are assumed to be diffusive in character. The internal transitions are described by a master equation for jumps among configurational sites, derived by projecting the multidimensional diffusion equation for the torsional variables onto a suitable set of site functions, located at the minima of the torsional potential. The rate constants for the conformational changes are then obtained by an extension of the Kramers theory to the multidimensional case.[2,3] The coupling with the overall diffusion is explicitly taken into account, by considering the conformational dependence of both the molecular diffusion tensor and the mean-field potential, which acts in the liquid crystal phase.

The theoretical model has been applied to interpret the detailed NMR relaxation data obtained in the nematic phase of 5CB.[4–6] Although a satisfactory understanding of the relevant factors which influence the complex dynamics of these systems was certainly reached, the relatively high number of physical parameters necessary to give a full description of the system seemed to prevent the possibility of optimizing all parameters to obtain quantitative estimates. In order to attempt quantitative predictions, one should first have a detailed knowledge of hydrodynamical and energetic properties such as diffusion tensor anisotropy, frictional effects for the chain motions, potential profiles for the torsions about the chain bonds, mean-field forces exerted by the anisotropic environment.

The analysis of experimental data available from different techniques, deuteron[4,5] and carbon-13[6] NMR relaxation, and dielectric relaxation,[7–9] supplies some of the parameters entering into the theory and confirms the validity of a unified description.

DYNAMICS

If the cyanobiphenyl group is treated as a single rigid unit, the motions of the flexible molecule can be described in terms of the variables Ω and α. The Ω variables are the Euler angles which give the orientation of a molecular frame, fixed in the aromatic cores, with respect to the laboratory axis system. The α variables are the torsional angles of the alkyl chain, defining the relative orientation of the various CH_2—CH_2 segments. In the following, they will be referred to as *external* and *internal* coordinates, respectively.

The probability distribution function of the system, $P(\alpha, \Omega, t)$, evolves in time according to

$$\frac{\partial P(\alpha, \Omega, t)}{\partial t} = -[\hat{R}^i(\alpha, \Omega) + \hat{R}^e(\alpha, \Omega)]P(\alpha, \Omega, t) \tag{1}$$

where the operators $\hat{R}^i$ and $\hat{R}^e$, internal and external time evolution operators, describe the effects of overall reorientations, and torsions about the chain bonds. If the motions are assumed to be diffusive in character, these operators can be written as:

$$\hat{R}^e(\alpha, \Omega) = \hat{\mathbf{L}} \cdot \mathbf{D}^w(\alpha)P(\alpha, \Omega) \cdot \hat{\mathbf{L}}P(\alpha, \Omega)^{-1} \tag{2}$$

and

$$\hat{R}^i(\alpha, \Omega) = -\left(\frac{\partial}{\partial\alpha}\right) \cdot \mathbf{D}(\alpha)P(\alpha, \Omega) \cdot \left(\frac{\partial}{\partial\alpha}\right) P(\alpha, \Omega)^{-1}. \tag{3}$$

In the above equations $\mathbf{D}^w$ and $\mathbf{D}$ represent the diffusion tensors for the whole molecule and for the flexible tail, $\hat{\mathbf{L}}$ is the generator of infinitesimal rotations about the molecular axes, and $P(\boldsymbol{\alpha}, \Omega)$ is the equilibrium distribution function, i.e., the stationary solution of Equation (1), defined as

$$P(\boldsymbol{\alpha}, \Omega) = \exp[-V(\boldsymbol{\alpha}, \Omega)/k_BT]/\int d\boldsymbol{\alpha} \int d\Omega \exp[-V(\boldsymbol{\alpha}, \Omega)/k_BT]. \tag{4}$$

$V(\boldsymbol{\alpha}, \Omega)$ is the potential acting on the molecule with orientation Ω and conformation specified by the set of torsional angles $\boldsymbol{\alpha}$; it can be written as

$$V(\boldsymbol{\alpha}, \Omega) = V^{\text{tors}}(\boldsymbol{\alpha}) + V^{mf}(\boldsymbol{\alpha}, \Omega), \tag{5}$$

where $V^{\text{tors}}(\boldsymbol{\alpha})$ is a torsional contribution, while $V^{mf}(\boldsymbol{\alpha}, \Omega)$ is a mean-field potential, describing the interactions with the anisotropic environment.

Note that both frictional and potential couplings are explicitly considered by Equation (1), given the dependence of the diffusion tensors upon the chain conformation, and the form of the equilibrium distribution function $P(\boldsymbol{\alpha}, \Omega)$, where internal and external contributions cannot be factorized. Only the recoil effects produced by the internal rotations are neglected, but this is a minor approximation, if the frictional resistance of the flexible chain is small in comparison with that of the rigid fragment.[1,10]

According to the usual procedures, the dynamical problem can be solved by expanding the diffusion operator, $\hat{R}^i + \hat{R}^e$, on a basis of functions $f(\boldsymbol{\alpha}, \Omega)$. The easiest choice, the representation of the operator in a space which is the direct product of basis functions for the different degrees of freedom, is actually unpracticable, because of the rapid increase of the dimension of the matrices to be handled, with increasing chain length. A convenient set of basis functions is given by the products $\phi^l_{mk}(\Omega)g_J(\boldsymbol{\alpha}, \Omega)$, where $\phi^l_{mk}(\Omega) = \sqrt{(2l+1)/8\pi^2}\mathcal{D}^l_{mk}(\Omega)$ are modified Wigner functions, and $g_J(\boldsymbol{\alpha}, \Omega)$ is a set of "site functions," localized at the minima of the torsional potential corresponding to the stable chain conformers.[3]

The introduction of the localized functions for the torsional variables, which is justified by the relatively high barriers separating the potential minima, can be viewed as an extension to the time domain of the RIS approximation.[11] After projection onto the subspace of the site functions $g_J(\boldsymbol{\alpha}, \Omega)$, the time evolution of $P_J(\Omega, t)$, the probability distribution function for the J-th conformer, is described by the master equation:

$$\frac{\partial P_J(\Omega, t)}{\partial t} = -\sum_{J'} \{\hat{W}_{JJ'}(\Omega) + \hat{R}_J(\Omega)\delta_{J,J'}\}P_{J'}(\Omega, t) \tag{6}$$

where $\hat{R}_J(\Omega)$ and $\hat{W}_{JJ'}(\Omega)$ are still operators in the Euler angles space. The former is given by

$$\hat{R}_J(\Omega) = \hat{\mathbf{L}} \cdot \mathbf{D}^w_J \cdot [\hat{\mathbf{L}} + \hat{\mathbf{L}}V^{mf}_J(\Omega)] \tag{7}$$

where $\mathbf{D}_J^w \equiv \mathbf{D}^w(\alpha_J)$ is the rotational diffusion tensor of the molecule in the J-th configuration. The operator $\hat{W}_{JJ'}$ for the transition from the J'-th to the J-th conformation has the following expression, obtained by generalizing to the multidimensional case the Kramers theory in the overdamped regime[2]:

$$\hat{W}_{JJ'}(\Omega) = (|\lambda_1|/2\pi)\exp\{-[E_S(\Omega) - E_{J'}(\Omega)]/k_BT\} \tag{8}$$

where $E_{J'}(\Omega)$ and $E_S(\Omega)$ are free energies, evaluated at the J'-th configuration and at the saddle point connecting the two adjacent minima J and J'. The parameter λ_1, related to the reaction pathway for the $J' \rightarrow J$ conformational jump, depends upon both the energetics of the transition, and the frictional resistances opposing the rotating bond. The operator $\hat{W}_{JJ}(\Omega)$, describing the loss of population from the J-th state, is determined by the detailed balance condition.

In the usual approaches, the couplings among internal and overall variables are completely neglected.[4,12–14] The overall diffusion tensor $\mathbf{D}^w$ is assumed to be independent of the configuration, and the potential is separated as

$$V(\alpha, \Omega) = V^e(\Omega) + V^i(\alpha) \tag{9}$$

where $V^e(\Omega)$ describes the anisotropic interaction exerted on the rigid core, and $V^i(\alpha)$ takes into account both the torsional potential and the orientation pseudopotential acting on the alkyl chain. The latter is assumed to be independent of the orientation of the molecule relative to the director; this means that the flexible tail tends to orient with respect to a molecular frame. This is hardly justified from a physical point of view, the wide use of such an approximation being uniquely due to the substantial reduction of the mathematical complexity of the dynamical problem.

GEOMETRY AND ENERGETICS

The carbon positions in the alkyl chain of a nCB molecule are labeled as $C_1, \ldots, C_n$, moving away from the aromatic core towards the free end. The ring carbon bearing the aliphatic chain and those bound to hydrogen atoms are denoted by C_0 and C_R respectively.

The chain is described by an "extended atom" model, with fixed bond lengths l_{CC}, and bond angles δ_C. The aromatic moiety is taken as a rigid body. Each methylene-methylene bond can exist in one of the three conformational states: gauche$_-$ (g_-), trans (t) and gauche$_+$ (g_+). The values of geometric and energetic parameters are taken from Reference 15.

In the absence of unambiguous data about the internal potential around the aromatic-aliphatic C_0—C_1 bond, different choices have been considered:

1. A single conformation, with the C_1—C_2 bond on the plane perpendicular to the attached phenyl ring.
2. Two equivalent states, with the C_1—C_2 bond lying on the plane perpendicular to the attached phenyl ring, above or below the ring plane.

3. Four equivalent states, with the C_0—C_1—C_2 plane making a dihedral angle $\bar{\alpha}$ with the attached phenyl ring, above (states *a* and *a'*) and below the ring plane (states *b* and *b'*).

The results obtained from these various options are discussed elsewhere,[1] so we shall concentrate here on case 3, with $\bar{\alpha} = 45°$, which appears the most promising for the best agreement with the experimental data.

In order to define the energetic parameters, let's first consider that, if the RIS model is assumed for the tail conformations, the potential acting on the *J*-th conformer can be written as:

$$V_J(\Omega) = V_J^{\text{tors}} + V_J^{mf}(\Omega) \tag{10}$$

where $V_J^{\text{tors}} \equiv V^{\text{tors}}(\alpha_J)$ is[11]:

$$V_J^{\text{tors}} = n_g V_g + n_{g\pm g\mp} V_p \tag{11}$$

with n_g the number of gauche states, V_g the gauche-trans energy difference, $n_{g\pm g\mp}$ the number of $g_\pm g_\mp$ sequences and V_p a contribution accounting for the so called "pentane effect." Longer range effects are taken into account by rejecting the configurations in which parts of the chain would overlap. In the case of the 5CB molecule this leads to the exclusion of the conformers containing $g_\pm g_\mp g_\pm$ sequences.

The nematic mean-field potential acting on the molecule in the *J*-th configuration is written as a sum of contributions describing the interactions of the rigid molecular sub-units with the environment.[15] In the simplest approach, the units composing the molecule are the aromatic core (the whole cyanobiphenyl group), and the segments of the aliphatic tail. Then we can write

$$V_J^{mf}(\Omega) = V^{core}(\Omega) + \sum_{i=0}^{n} V_J^i(\Omega) \tag{12}$$

where V^{core} represents the potential acting on the core, and V_J^i the contribution of the *i*-th segment, corresponding to the C_i—C_{i+1} bond, when the molecule is in the *J*-th configuration. The interactions of the various units with the environment are described by second rank tensors, with axial symmetry about the para axis for the aromatic core, and along the C—C bonds for the chain segments.[15] If the director is assumed to be parallel to the laboratory *Z* axis, the two kinds of contributions are expressed by

$$V^{core}/k_B T = -\eta \mathcal{D}^2_{00}(\Omega) \tag{13}$$

and

$$V_J^i/k_B T = -\varepsilon \mathcal{D}^2_{00}(\Omega_i^J) \tag{14}$$

where the parameters η and ε are the major principal components of the interaction tensors for the core and the chain respectively, and Ω^J_i are the Euler angles which relate the laboratory frame to a local frame having the z axis along the C_i—C_{i+1} bond, for the molecule in the J-th configuration.

Actual calculations have been performed for the 5CB system, and in this case the ratio η/ε has been kept equal to 3.3,[15] the η values being chosen in such a way to reproduce the experimental order parameters. It is interesting to calculate the value η would assume for an aliphatic chain with N segments in the all-trans configuration. According to the definition given in Equation (13), η is related to the difference in potential energy for the chain with the long axis parallel or perpendicular to the mesophase director, and so one finds

$$\begin{aligned}\eta &= N\varepsilon\left\{\cos^2\frac{\pi-\theta_T}{2} - \cos^2\frac{\theta_T}{2}\right\}\\ &= -N\varepsilon\cos\theta_T = N\varepsilon/3\end{aligned} \tag{15}$$

where θ_T is the tetrahedral angle. It follows therefore that the intensity of the mean-torque acting on the cyanobiphenyl moiety is the same as that acting on an extended aliphatic chain of approximately the same dimension ($N \approx 10$). This conclusion may indicate that the orientational torques originate mainly from steric interactions.

The internal dynamics of the nCB molecule can be specified in terms of the parameter w, corresponding to the $g_\pm \rightleftharpoons t$ transition rate for a chain with a single degree of freedom. The transition rates for the intermethylenic bonds are calculated by explicitly considering the frictional drag opposing the displacement of the rest of the chain, and the cooperativity in the barrier crossings.[1,3] The particular dynamics about the C_0—C_1 bond is taken into account by assigning a frequency c_1w to the transitions $a \rightleftharpoons a'$ and $b \rightleftharpoons b'$, and c_2w to the transitions $a \rightleftharpoons b$ and $a' \rightleftharpoons b'$.

NMR RELAXATION

The experimental determination of static order parameters and dynamical behaviour from NMR data are related to the presence of magnetic interactions described by second-rank tensors. In the most interesting cases (^{13}C—H dipolar interactions, ^{2}H quadrupolar interactions) the tensors are assumed to be axially symmetric, with the symmetry axis along a specific C_i—H bond. The relevant theoretical quantities are then the equilibrium averages of Wigner functions $\overline{\mathcal{D}^2_{m0}(\Omega_{F_i})}$, and the spectral densities for the corresponding correlation functions,

$$\mathcal{J}^{C_i}_m(\omega) = Re\int_0^\infty dt\,\exp(-i\omega t)\overline{(\mathcal{D}^2_{m0}(\Omega_{F_i},t)\mathcal{D}^2_{m0}(\Omega_{F_i},0)^*} - |\overline{\mathcal{D}^2_{m0}(\Omega_{F_i})}|^2 \tag{16}$$

where the Euler angles Ω_{F_i} describe the transformation from the laboratory frame to the local frame F_i having the z axis along the C_i—H bond.

Tables I–III show numerical results for 5CB molecules, with reference to the experimental data reported in Reference 5. Note that only the methylene carbons have been considered, the methyl group being characterized by motional processes of different nature. The spectral densities $\mathcal{J}_1$ and $\mathcal{J}_2$ have been collected in the nematic phase at T = 303.5 K from deuteron relaxation times at the two Larmor frequencies ω_D = 12.0 MHz and ω_D = 30.7 MHz. All entries in Table II and III are scaled by the factor $3\pi^2 q_{CD}^2/2$, where the quadrupole coupling constant q_{CD} = (e^2qQ/h) has been taken equal to 168 kHz for alkyl deuterons, and 185 kHz for those bound to the aromatic ring carbons.

In the calculations, an axially symmetric diffusion tensor $\mathbf{D}_J^{\mathrm{w}}$ has been taken, with a principal axis system obtained by diagonalization of the mean-field potential for each conformer. Alternatively, the principal diffusion axes can be obtained by diagonalizing the inertia tensor of the molecule for each configuration. Calculations performed with the two choices show only minor differences. The principal values $D_\perp$ and $D_\parallel$ are taken independent of the conformation. The following set of parameters have been used: $D_\perp = 8 \cdot 10^7\ \mathrm{s}^{-1}$, $D_\parallel/D_\perp = 20$, w $= 8 \cdot 10^9\ \mathrm{s}^{-1}$, $c_1 =$ 0.5 and c_2 = 0.005. The value of $D_\perp$ has been taken from dielectric relaxation measurements,[7] by extrapolating the reported data to 303:5 K. The other param-

TABLE I

C_i—H order parameters for 5CB, [a]experimental, [b]calculated. In parenthesis, values obtained under decoupling approximation

	R	1	2	3	4
$\lvert\overline{\mathcal{D}^2_{00}(\Omega_{F_i})}\rvert$ [a]	0.038	0.185	0.123	0.133	0.089
$\overline{\mathcal{D}^2_{00}(\Omega_{F_i})}$ [b]	-0.056	-0.183	-0.125	-0.124	-0.087
	(-0.055)	(-0.146)	(-0.090)	(-0.090)	(-0.056)

TABLE II

Spectral densities $\mathcal{J}_m$, [a]experimental, [b]calculated, in ps units. In parenthesis, values obtained under decoupling approximation

	R	1	2	3	4
$\mathcal{J}_1$(12.0MHz) [a]	85	79	44	41	18
$\mathcal{J}_1$(30.7MHz) [a]	79	54	35	29	15
$\mathcal{J}_1$(0) [b]	95	67	40	26	11
	(94)	(75)	(49)	(35)	(17)
$\mathcal{J}_2$(24.0MHz) [a]	58	40	19	12	9
$\mathcal{J}_2$(61.4MHz) [a]	54	30	15	11	7
$\mathcal{J}_2$(0) [b]	56	41	29	20	10
	(57)	(37)	(28)	(20)	(11)

TABLE III

Relaxation times $\mathcal{R}(\omega) = \mathcal{J}_1(\omega) + 4\mathcal{J}_2(2\omega)$ at a Larmor frequency of 30.7 MHz, [a]experimental, [b]calculated, in ps units. In parenthesis, values obtained under decoupling approximation

	R	1	average (2 , 3 , 4)
$\mathcal{R}^{a}$	295	174	70
$\mathcal{R}^{b}$	310	213	103
	(315)	(205)	(106)
$\mathcal{R}^{iso\ a}$	280	310	120
$\mathcal{R}^{iso\ b}$	359	284	122

eters have been chosen to obtain good agreement with the experiments. All values are quite acceptable on physical ground, except perhaps $D_{\parallel}/D_{\perp}$, which appears a little too high. It is possible that this value accommodate for the neglect in the model of recoil effects, which would flip the aromatic ring as a consequence of conformational transitions in the tail. The conformational jump rate w should be compared with the accepted value of 10^{10} for a butane-like system at liquid viscosities of 0.5 ÷ 1 cP.[3,16] The values of c_1 and c_2 indicate that the delete rotation about the first methylene segment of the chain is strongly hindered, so that the motions about this bond can be visualized as large amplitude fluctuations of the chain, followed by relatively rare π-jumps. If this motion is completely frozen, an unrealistically high ratio $D_{\parallel}/D_{\perp}$ is required to reproduce the spectral densities at the various positions of the chain.[1]

As an outcome of the calculations we see that, according to the physical intuition, the isomerization constants for the intermethylene bonds increase moving towards the free end of the chain, the higher mobility being a consequence of the diminishing frictional effects and of the cooperativity of the transitions. As an example, the $g \rightarrow t$ transition rate goes from $3 \cdot 10^9\ \mathrm{s}^{-1}$ for the C_1—C_2 bond, to $1.6 \cdot 10^{10}\ \mathrm{s}^{-1}$ for the C_3—C_4 bond.

As shown by a comparison of experimental and calculated quantities, the theoretical analysis accounts rather well for the values of the order parameters and the spectral densities $\mathcal{J}_1$ and $\mathcal{J}_2$, at the ring positions and along the chain. In the Tables, only zero frequency values of the calculated spectral densities are reported; actually, some frequency dependence is predicted, more pronounced for the less mobile chain bonds.[1]

The theoretical model gives also an explanation of the behaviour of the deuteron relaxation times $\mathcal{R}(\omega) = \mathcal{J}_1(\omega) + 4\mathcal{J}_2(2\omega)$ at the isotropic-nematic transition; in particular, the dramatic discontinuity of the relaxation rate for the first chain bond[4] can be reproduced. The numerical results, especially those concerning the carbon atom C_1, are strongly influenced by the choice of the torsional potential about the aromatic-aliphatic bond, for which little information is available.

As shown in the Tables, the results are only slightly affected by the use of the decoupling approximation, at least in the calculation of the dynamical quantities.

This depends essentially on the relative timescales characterizing conformational transitions and overall reorientations in the 5CB case, the agreement between coupled and uncoupled calculations getting worse as the motions of the molecule as a whole slow down.[1]

DIELECTRIC RELAXATION

The alkylbiphenyl series has been subjected to extensive investigations by dielectric relaxation techniques, both in the isotropic[7] and in the liquid crystal phases.[8,9] The main characteristics exhibited by the Cole-Cole presentation of the data, where imaginary versus real part of the complex permittivity is displayed, are the following:

i) In the isotropic case, small deviations from semicircular plots are observed in the high-frequency region of the spectra.
ii) Almost perfect semicircles are obtained in the liquid crystal phases when the monitoring electric field is directed along the optical axis (parallel arrangement), with the maxima centered at frequency values (1–10 MHz) lower than in the isotropic phase.
iii) Very broad Cole-Cole plots are obtained in the L.C. phases for the perpendicular arrangement. Three frequency regions can be roughly identified: a low frequency region similar to that characterizing the parallel arrangement, an intermediate one analogous to the isotropic case, and a third one two decades higher in frequency.

The theoretical analysis proceeds as follows. The correlation function $G_e(t)$ for the component of the molecular dipole in the direction of the applied field is calculated and the Cole-Cole plots are obtained as graphs of imaginary versus real part of the Fourier-Laplace transform $\mathcal{L}[-\dot{\gamma}_e(t)]$, $\dot{\gamma}_e(t)$ being the time-derivative of the normalized correlation function

$$\gamma_e(t) = G_e(t)/G_e(0) \tag{17}$$

We avoid in this way to go into the problem of the correct relation between $\dot{\gamma}_e(t)$ and the dielectric permittivity tensor, which is out the scope of this work.[17-19] In the anisotropic phases, if (X, Y, Z) is the laboratory coordinate system with the Z-axis in the direction of the optical axis, and (xyz) is the molecular diffusion principal system, one finally obtains[20] that the approximate expressions for $G_e(t)$ in the two experimental geometries are

$$\langle\mu_Z(t)\mu_Z(0)\rangle = g_1\mu_z^2 G^1_{00}(t) + g_2(\mu_x^2 + \mu_y^2)G^1_{01}(t) \tag{18}$$

and

$$\langle\mu_X(t)\mu_X(0)\rangle = g_1\mu_z^2 G^1_{10}(t) + g_2(\mu_x^2 + \mu_y^2)G^1_{11}(t) \tag{19}$$

for the parallel and perpendicular arrangements respectively, $G^1_{pq}(t)$ denoting correlation functions of first-rank Wigner components. The coefficients g_1 and g_2 are Kirkwood factors which take into account antiparallel correlation between molecular dipoles.[21,22] These effects are expected to be of importance in the pure *n*CB phases, because of the interactions between nitrile groups.

In the isotropic phases, the correlation functions are independent of the index p, and so the two expressions become equivalent, as expected.

In the *n*CB systems, a perpendicular component of the molecular dipole can result from the deviations of the major diffusion axis from the para axis, due to the alkyl tail in the different conformational states. This situation is accounted for by our model, where a configuration dependent diffusion tensor is explicitly considered.

Calculations for 5CB have been performed with the same set of parameters used for Tables I–III. Kirkwood factors $g_1 = 0.5$ and $g_2 = 1$, suggested from the experimental values of the static permittivities[21,22] have been adopted.

The numerical results confirm that the low frequency shift of the dielectric absorption and dispersion curves at the isotropic-nematic transition is well rationalized by the diffusion equation. The frequency shift is related to the hindering of the dipole reorientations due to the onset of the mean-field potential in the L.C. phase. The theory correctly predicts an increase of the dipole correlation time by a factor of 5, going from the isotropic fluid to a nematic state characterized by an order parameter $\overline{P_2} = 0.34$, at constant viscosity. This factor amounts to almost 20, when the order parameter reaches the value 0.56. In agreement with the experimental findings, a perfectly circular Cole-Cole plot is obtained for the parallel arrangement.

There is no simple way, however, to interpret the broad Cole-Cole plots reported for the experimental geometry with the electric field perpendicular to the mesophase optical axis. By using the standard set of physical parameters, barely perceptible deviations from the semicircle shape result. In order to obtain more pronounced effects, the average tilt angle β_0 between the molecular dipole vector, directed along the C≡N bond, and the major diffusion axis, should have a value of at least 20°. Such a value is roughly twice as large as that obtained by the theoretical analysis, where instantaneous tilt angles result from the dependence of the diffusion tensor $\mathbf{D}^{w}_{j}$ upon the chain conformation. A value of 10° is also suggested by the experimental data. Even if this discrepancy does not appear too dramatic, one should note that the higher value of β_0 brings about deviations from the semicircular plot also for the parallel geometry, in contrast with the experiment. The Cole-Cole plots calculated for $\beta_0 = 20°$ and for the two experimental geometries, in an oriented phase with $\overline{P_2} = 0.44$, are shown in Figure 1.

The most serious difficulty is concerned with the high frequency component of the dielectric relaxation. The correlation function $\langle \mu_X(t)\mu_X(0)\rangle$ is described by a multiexponential decay,[8,20] but the highest decay rates are of the order of $D_\parallel$. Therefore, contributions due to the conformational jumps cannot be invoked to justify relaxation frequencies two order of magnitude larger than $D_\perp$. In addition, the high frequency relaxation component appears to have similar weights in *n*CB homologs of different chain length, and this observation is in contrast with the

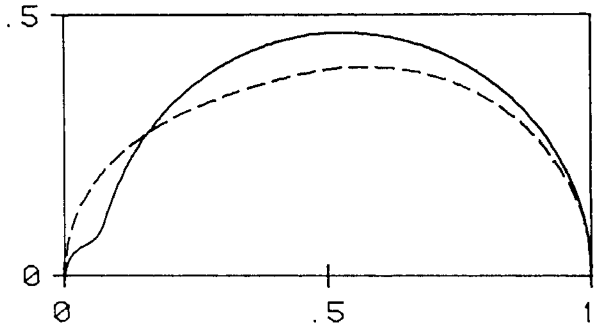

FIGURE 1 Imaginary vs. real part of the Fourier-Laplace transforms of the time derivatives $\langle \dot{\mu}_Z(t)\mu_Z(0)\rangle / \langle \mu_Z(0)^2\rangle$ (full line) and $\langle \dot{\mu}_X(t)\mu_X(0)\rangle / \langle \mu_X(0)^2\rangle$ (dashed line). The Cole-Cole plots are calculated for an average tilt angle of the chain $\beta_0 = 20°$, in an oriented phase with $\overline{P_2} = 0.44$.

hypothesis that recoil effects are actually operating, because they should vary with the chain length.

In view of the very satisfactory interpretation offered by the theory for all other aspects of the NMR and dielectric relaxation behaviour, the unexplained characteristics of the Cole-Cole plots in the perpendicular arrangement remain an intriguing problem. Possible solutions may emerge either from novel experimental data, or by an extension of the theory to include specific interactions between the probe dipole and the surrounding polar molecules.[23]

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