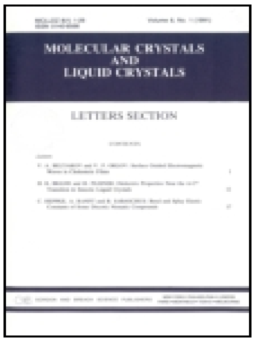

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^{129}Xe NMR Investigation of the Anisotropic Environment of a Thermotropic Nematic Liquid Crystal 4-Cyano-4′-Pentylbiphenyl

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The anisotropic environment of the thermotropic nematic liquid crystal (LC), 4-cyano-4′-pentylbiphenyl (5CB), is probed by using ^{129}Xe NMR spectroscopy. The temperature versus ^{129}Xe nuclear shielding of the xenon gas dissolved in 5CB LC has clearly shown the nematic-isotropic phase transition. The observed linear and non-linear behavior of ^{129}Xe chemical shifts in the isotropic and nematic phases, respectively, are explained by using the pair-wise additive model. Furthermore, the parameters such as ^{129}Xe shielding constant (σ_0), the anisotropy of the shielding tensor (σ_0), the temperature dependence of the isotropic shielding (ε), and the shielding anisotropy (χ), are derived.

Keywords Pair-wise additive model; phase transition; xenon shielding-anisotropy; ^{129}Xe NMR, 5CB liquid crystal

Introduction

The intrinsic anisotropic properties of liquid crystals [1]: long-range molecular orientational order and optical birefringence, and the ability to control their molecular alignment on confined surfaces [2], are basis for developing these materials for display applications [3]. The new advanced applications also include liquid crystal based biosensors [4], tunable lenses [5] and muscle-like actuators [6], have further enhanced the potential of these remarkable liquid crystals. However, in order to employ them for specific applications, a prior understanding of the morphological features and anisotropic parameters in bulk state is essential. In this regard, the early extensive ^{1}H, ^{2}H and ^{13}C NMR studies of different LC molecules have provided information about molecular order, dynamics and phase transitions at the molecular level. Subsequently, the advent of ^{129}Xe NMR spectroscopy of xenon (spin 1/2, natural abundance 26.44%) gas dissolved in LC phases [Fig. 1], has offered a unique means of probing the anisotropic environment [7, 8]. The important physical properties of xenon gas, for example, (1) mono atomic and small in diameter (∼4Å), which allows the xenon atoms to easily occupy the inter-molecular spaces and (2) sensitive to the physical environment in which the xenon atoms are dissolved, resulting in a wide ^{129}Xe chemical shift range (∼300 ppm), have led the ^{129}Xe NMR spectroscopy to probe into

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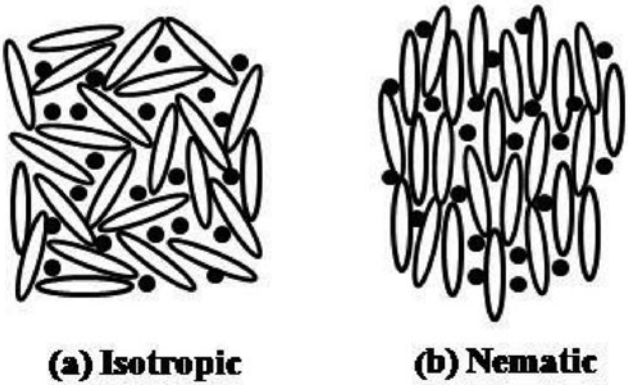

Figure 1. Schematic representation of the occupancy of xenon atoms (●) in the isotropic and nematic phases in 5CB. For the sake of clarity, the molecular arrangement as well as the occupancy of xenon atoms is exaggerated and is not to scale.

the mesophases of thermotropic liquid crystals [9–17]. Furthermore the ^{129}Xe chemical shifts in anisotropic systems carry information about the average molecular ordering and shielding anisotropy that can be analyzed in the framework of mean-field approximation. The recent developments of theoretical models: phenomenological model [9] and pair-wise additive model [11] to account for the temperature dependence of ^{129}Xe nuclear shielding behavior in nematic/smectic and nematic phases, respectively, have enabled to obtain more quantitative details about the morphology and anisotropic parameters of these systems. Particularly, the *pair-wise additive* model [11] reported by Ylihautala et al. for nematic phases, which takes into account the LC-density, orientational order parameter and the contribution due to Xe-LC pair correlations, could successfully explain the temperature dependence of the ^{129}Xe nuclear shielding behavior in these LCs. Subsequently, relying on both the phenomenological [9] and the pair-wise-additive [11] models, our group has explained ^{129}Xe nuclear shielding in the smectic liquid crystal, n,n-diheptyl-azoxy-benzene, HAB [15]. Diehl and co-workers have reported the ^{129}Xe chemical shift data for 4-cyano-4'-pentylbiphenyl (5CB) LC [17]. However, a detailed analysis of the ^{129}Xe shielding behavior by using the pair-wise additive model, has not been reported for this LC. It has been well established by various theoretical and experimental studies that the 5CB serves as an important model system to understand the physics of the isotropic-nematic phase transition, cooperative molecular ordering and anisotropic dynamics in bulk as well as in two-dimensional films (in confined geometries) [18, 19]. Furthermore, for newer applications/demonstrations [20], the utility of 5CB is continued to be high. Hence, it is important to have a complete account of the temperature dependence of isotropic and anisotropic parts of ^{129}Xe shielding in the 5CB LC, and the present work fulfills this requirement.

Theoretical Background

In free xenon gas, the Xe atoms possess spherical distribution of electronic cloud and hence exhibit only isotropic part of the chemical shift. Upon dissolving the xenon gas in the LC solvent, the solute (Xe) atoms experience the solvent induced change in their nuclear shielding. In the nematic phase, the anisotropic interactions cause partial orientation of the xenon atoms that leads to the deformation of the spherical symmetry and results in ^{129}Xe shielding anisotropy. In their phenomenological model, Lounila et al. [9] have attributed the observed temperature dependence of the ^{129}Xe chemical shifts in LCs solely to the variation of the density and the local orientational order. Furthermore, the isotropic (σ_0) and the anisotropic ($\Delta\sigma_0$) parts of the shielding tensor were treated as independent of temperature. Ylihautala et al. in their improved *pair-wise additive* model [11], have considered that σ_0 and $\Delta\sigma_0$ to be temperature dependent and have also incorporated another important term that takes into account the interaction between LC molecules and Xe atoms through a molecular pair correlation function. According to this model, the shielding tensor of the solute atom depends on the solute-solvent pair configuration i.e., the relative positions and orientations of the solute and solvent molecules. As the changes in solute-solvent pair configurations are thermally activated, any change in the pair correlation results in change in the solute nuclear shielding. Accordingly, the total solute ^{129}Xe shielding is a sum over all the shielding perturbations induced by the individual Xe-LC pairs. Nevertheless, while the contributions of LC density and order parameter to the ^{129}Xe shielding are realized directly, the contribution due to the change of pair correlation function is seen only indirectly through the changes of configurational averages of the local ^{129}Xe shielding elements, σ_0 and $\Delta\sigma_0$. As the orientational order in the isotropic phase is absent, it is assumed that the ^{129}Xe shielding in this phase is a linear function of temperature, and is predominantly due to the variation in the LC density. The temperature dependence for σ_0 and $\Delta\sigma_0$ is considered by approximating them around a point T_0, by the linear functions

$$\sigma(T) = \sigma(T_0) + \left(\frac{\partial\sigma}{\partial T}\right)_{T_0} (T - T_0) \tag{1}$$

$$\Delta\sigma(T) = \Delta\sigma(T_0) + \left(\frac{\partial\Delta\sigma}{\partial T}\right)_{T_0} (T - T_0) \tag{2}$$

By applying the *pair-wise additive* model for the uniaxial nematic phase, the temperature dependence of the xenon shielding tensor element in the direction of the external magnetic field is written as [11]

$$\sigma_{(T)} = \rho_{(\mathrm{T})}\{\sigma_0[1 - \varepsilon(T - T_0)] + \frac{2}{3}\Delta\sigma_0[1 - \Delta\varepsilon(T - T_0)]\, S(T)P_2(\cos\beta)\} \tag{3}$$

here, $\rho_{(T)} = \rho_0[1 - \alpha(T - T_0)]$ (for the isotropic phase) or $\rho(T) = \rho_0[1-\alpha(T - T_0)+\Delta\rho/\rho_0]$ (for the nematic phase, where $\Delta\rho$ is a small jump in the density at the isotropic-nematic phase transition) is the temperature dependent density of LC that acts as a scaling factor for the ^{129}Xe shielding parameters, where ρ_0 is the density of the liquid crystal at the reference temperature, α is the thermal expansion coefficient and T_0 is the reference temperature (T_{NI}). The isotropic shielding constant σ_0 describes the spherically symmetric part of the distortion, while $\Delta\sigma_0$ describes the deviation of the electron density distribution from spherical symmetry. The factors ε and $\Delta\varepsilon$ describe the temperature dependence of the isotropic shielding and shielding anisotropy, respectively. They also carry important but indirect information about the changes in the Xe-LC pair correlations, with respect to the temperature. The factor $P_2(cos\beta) = 1/2\ (3\cos^2\beta - 1)$ is the second-order Legendre polynomial, and β is the angle between the director of the liquid crystal and the direction of magnetic field B_0. Since the anisotropy of diamagnetic susceptibility of the uniaxial 5CB LC is positive, the term $P_2(cos\beta)$ in Eq. (3) is approximated to 1. It is well-known that the variation of the order parameter with temperature can be fitted to Haller's function [21]

$$S_{(T)} = \left[1 - y\left(\frac{T}{T_0}\right)\right]^z \tag{4}$$

where, y and z are adjustable parameters. However, as the orientational order is absent in the isotropic phase, by substituting $S_{(T)} = 0$ in the Eq. (3), the isotropic phase can be analyzed. A detailed mathematical treatment of the model can be found in the reference [11].

Experimental Section

5CB (K15) liquid crystal is a gift from Merck and is used without further purification. Xenon gas (99.999%) was obtained from Hydrogas, India. About 1.0 g of 5CB is transferred to a 10 mm o.d., medium wall Pyrex tube and evacuated by several freeze-pump-thaw cycles to remove free oxygen. After the sample is evacuated to $\sim 10^{-6}$ Torr, 2 atm of xenon gas is loaded into the sample tube, which is then flame sealed. The ^{129}Xe chemical shift measurements are carried out on a Varian UNITY-400 spectrometer operating at 110.6 MHz. A broadband 10 mm probe with variable temperature capability is employed. A single 90° excitation pulse (pulse width 16 μs) with a 30 s recycle delay is used to obtain the spectra for chemical shift measurements. To ensure orientational order in the magnetic field, the sample was first heated to its isotropic phase and then cooled in steps.

Results and Discussion

Initially, in order to estimate the effect of the bulk density on ^{129}Xe shielding, the parameters ρ_0 and α in Eq. (3) are determined from the density data of 5CB [22]. The density is found to vary linearly with temperature in both the isotropic and nematic phases. The data is fitted to the linear functions, $\rho_{(T)} = \rho_0\,[1 - \alpha\,(T - T_0)]$ in the isotropic phase and $\rho_{(T)} = \rho_0\,[1 - \alpha\,(T - T_0) + \Delta\rho/\rho_0]$ in the nematic phase. The values of ρ_0 (g/cm^3) and α (K^{-1}) derived from the fits in the isotropic and nematic phases are, 1.0067 and 7.65×10^{-4}; 1.0067 and 9.17×10^{-4}, respectively. The 5CB sample loaded with xenon gas is initially heated to 333 K (isotropic phase) in the presence of magnetic field and allowed to stabilize for 30 min. Subsequently, the ^{129}Xe shielding is measured as a function of temperature, and at every temperature the sample is allowed to stabilize for 15 min. Only one peak corresponding to the xenon gas dissolved in 5CB is observed. The corresponding ^{129}Xe chemical shifts are referenced to an external sample of low pressure xenon gas (0 ppm, at 295 K). For this reason, a bulk susceptibility correction (σ_b) is applied to get the effects due to the medium alone. For cylindrical samples parallel to the external magnetic field, the expression for the correction σ_b [23] is,

$$\sigma_b\,(T) = -\frac{1}{3}\left[\chi + \frac{2}{3}\Delta\chi\,S_{(T)}\right]\frac{\rho_{(T)}}{M} \tag{5}$$

where χ (-2.10×10^{-9} m^3/mol) and $\Delta\chi$ (0.55×10^{-9} m^3/mol) are the isotropic part and anisotropy of the molecular susceptibility tensor, respectively, which are typical values for molecules with two benzene rings [24]. The molar mass of 5CB is 249.35×10^{-3} kg/mol.

After making the bulk susceptibility correction ($\sigma_{(T)=}\sigma_{m(T)} - \sigma_{b(T)}$) to the ^{129}Xe chemical shifts and incorporating the temperature dependent order parameter ($S_{(T)}$) represented by the Haller's function, into the Eq. (3), the temperature dependence of ^{129}Xe chemical

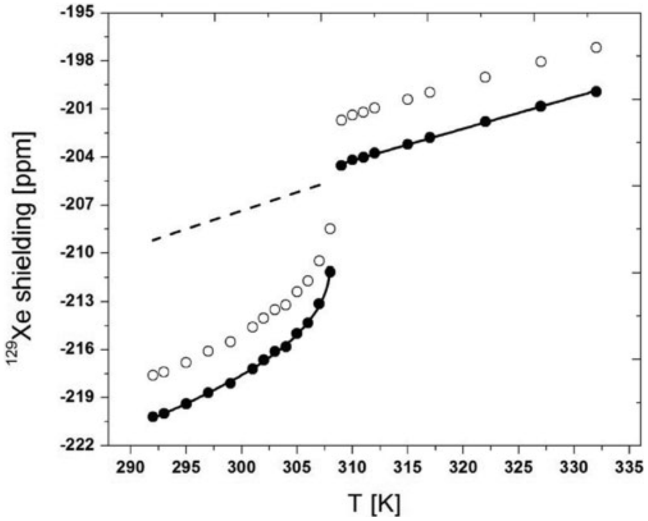

Figure 2. Temperature dependence of the ^{129}Xe chemical shifts of xenon gas dissolved in 5CB. Medium induced shielding σ_m of ^{129}Xe in 5CB (○) and the bulk susceptibility corrected value $\sigma_{m-}\sigma_b$ (●). The solid lines represent least-squares fits to Eq. (3). The dashed line indicates the variation of the chemical shifts in the nematic phase due to density alone, as explained in the text.

shielding in both isotropic and nematic phases is analyzed independently and is shown in Fig. 2. The results show a clear signature of nematic-isotropic (NI) phase transition at 308 K (T_{NI}). In the isotropic phase, the variation of ^{129}Xe chemical shift is linear with temperature (0.188 ppm/K). At T_{NI}, the data exhibits a down field jump of about 6.6 ppm (N-I transition) and the ^{129}Xe chemical shifts exhibit non-linear variation with temperature in the nematic phase.

In the isotropic phase, $S_{(T)} = 0$ in Eq. (3) and the resultant expression is linear in ρ and ε. Since ρ_0 and α are known from density measurements, the only adjustable parameters in the least-squares fit are σ_0 and ε, which are evaluated to be -203.25 (ppm cm^3 g^{-1}) and 2.06×10^{-4} (K^{-1}), respectively. The higher value of α (7.65×10^{-4} K^{-1}) as compared to ε (2.06×10^{-4} K^{-1}) in the isotropic phase indicates that the solvent density alone has profound effect on the temperature dependence of ^{129}Xe shielding. Moreover, the ε value falls within the range of observed values in other liquid crystals [10, 11].

In the nematic phase, the experimental average shielding data is non-linear, whereas the extrapolated data from the isotropic phase is linear (shown as dotted line in Fig. 2). These findings suggest that there could be other contributions stronger than the density effects in this phase. The jump (~6.6 ppm) in the chemical shift at T_{NI} to a less shielded value is marginally due to the increase in density but mainly due to the deviation of the electron cloud from spherical symmetry, leading to shielding anisotropy. Considering the contribution of orientational order parameter to the xenon nuclear shielding, the nematic phase is analyzed by using Eq. (3). The parameters σ_0 and ε are kept fixed at the values determined in isotropic phase with $T_0 = T_{NI}$ and the coefficients y and z for $S_{(T)}$ are constrained to the values (table 1) obtained from Eq. (4). Then the only adjustable parameters left for fitting the nematic phase data are $\Delta\sigma_0$ and $\Delta\varepsilon$, which are refined to be -31.17 (ppm cm^3 g^{-1}) and -62.0×10^{-4} (K^{-1}), respectively. The fit looks good throughout the range of the analysis (Fig. 2). The negative value of $\Delta\sigma_0$ is consistent with the case that director lies along the

Table 1. Values of the parameters derived from the least-squares fits of Eq. (1) to the experimental ^{129}Xe chemical shielding data

Parameter	Isotropic phase	Nematic phase
$T_0 = T_{NI}$ (K)	308[a]	308[a]
ρ_0 (g cm^{-3})	1.0067[b]	1.0067[b]
α (10^{-4} K^{-1})	7.65 [b]	9.17 [b]
σ_0 (ppm cm^3 g^{-1})	−203.25	−203.25[c]
ε (10^{-4} K^{-1})	2.06	2.06[c]
$\Delta\sigma_0$ (ppm cm^3 g^{-1})		−31.17
$\Delta\varepsilon$ (10^{-4} K^{-1})		−62.0
y of $S_{(T)}$		0.9991
z of $S_{(T)}$		0.1867

[a]Fixed during the analysis. [b]Obtained from density data. [c]Fixed to the value obtained in the isotropic phase.

direction of B_0 and also falls within the range of observed values in other liquid crystals [9, 10]. The observed $\Delta\varepsilon$ (-62.0×10^{-4} K^{-1}) is much larger in magnitude and opposite to α (9.17×10^{-4} K^{-1}) indicating that Xe-LC pair correlations have significant contribution to the anisotropic shielding.

At this instant, one can determine the specific contributions of the effective isotropic deformation ($\sigma_{\mathrm{iso}(T)}$) and the shielding anisotropy ($\Delta\sigma_{\mathrm{aniso}(T)}$) to the temperature dependence of ^{129}Xe shielding in the nematic phase of 5CB, by using the parameters presented in Table 1. These individual contributions in the nematic phase can be expressed as

$$\sigma_{\mathrm{iso}(T)} = \rho_0 \left[1 - \alpha\,(T - T_0)\right]\left[\sigma_0 \left[1 - \varepsilon\,(T - T_0)\right]\right] \qquad (6)$$

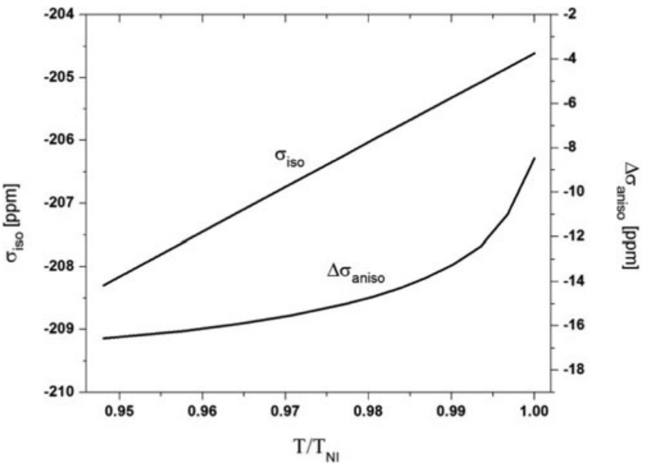

Figure 3. Variation of the isotropic deformational part (σ_{iso}) and the anisotropic shielding part ($\Delta\sigma_{\mathrm{aniso}}$) of ^{129}Xe shielding as a function of reduced (T/T$_{\mathrm{NI}}$) temperature in the nematic phase of 5CB. The contributions are estimated by using eqs. 6 and 7.

and

$$\Delta\sigma_{\mathrm{aniso}(T)} = \rho_0\left[1-\alpha\left(T-T_0\right)\right]\left[\Delta\sigma_0\left[1-\Delta\varepsilon\left(T-T_0\right)\right]\right]\left[S_{(T)}\right] \tag{7}$$

and are shown in Fig. 3.

From Fig. 3, it is inferred that the linear behavior of $\sigma_{\mathrm{iso}(T)}$ in the nematic phase, is mainly due to the variation of the LC density with temperature. On the other hand, the increase of $\Delta\sigma_{\mathrm{aniso}(T)}$ from -8.5 to -16.6 ppm is non-linear, as expected from the Eq. (7). A detailed analysis of $\Delta\sigma_{\mathrm{aniso}(T)}$ suggest that the orientational ordering, ($S_{(T)}$), and Xe-LC molecular pair correlation function are primarily responsible for the increase in $\Delta\sigma_{\mathrm{aniso}(T)}$ in the nematic phase of 5CB.

Conclusions

We have explored the isotropic and anisotropic environments of the 5CB liquid crystal by recording ^{129}Xe nuclear shielding of xenon gas dissolved in the liquid crystal medium and the results are analyzed by using the *pair-wise additive* model. The down field jump in ^{129}Xe shielding at 308 K is attributed to the nematic-isotropic phase transition. It is inferred from the analysis that the temperature dependence of the ^{129}Xe chemical shifts in the isotropic phase is exclusively due to the density of the medium alone, whereas, in the nematic phase, the orientational order and Xe-LC molecular pair correlation function have significant contribution to the ^{129}Xe shielding anisotropy.

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