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On Measuring Nuclear Magnetic Shielding Anisotropies in Liquid Crystal Solvents

Abstract: Up to the present time nuclear magnetic shielding anisotropies ($\Delta\sigma$) have been determined in nematic liquid crystal solutions by comparing the chemical shifts in the isotropic and nematic phases. Unknown changes in solvent-induced shifts arising from the isotropic → nematic phase transition constitute a serious problem in the interpretation of the results. To avoid the ambiguities inherent in these shifts, a method is described for measuring $\Delta\sigma$ in the nematic phase alone. This technique has been used to determine $\Delta\sigma$ in a variety of ^{1}H- and ^{19}F-containing molecules and the results are compared with those obtained by the two-phase method.

Introduction

The magnetic shielding at a nucleus due to the surrounding electrons is a sensitive probe of molecular electronic structure. In conventional NMR experiments in isotropic liquids only the mean value of the shielding tensor is measured; consequently, no information is obtained about the details of shielding (and of electron distribution) along various molecular axes. Although other techniques have been used in special cases, the experiments of Saupe and Englert [1] using nematic liquid crystal solvents provided the first generally useful technique for obtaining the anisotropic part of the nuclear magnetic shielding tensor. That method requires a measurement of the chemical shift in both the isotropic and the nematic phases. To obtain the shielding anisotropy the assumption is made that the isotropic part of the shielding is the same in both phases. The results of some early experiments [2] raised doubts about the validity of this assumption, and it was subsequently postulated [3] that a solvent shift originating in the nematic ordering could qualitatively explain the observations. The purpose of the present paper is to describe a method for determining the nuclear magnetic shielding anisotropy in a single phase, thereby avoiding the assumption (and concomitant uncertainties) inherent in a two-phase measurement.

Two-phase measurements and resultant solvent shift

The isotropic chemical shift of a given nucleus relative to a reference nucleus is defined [4] by

$$\delta^{iso} \equiv \sigma^{iso} - \sigma^{iso}_{ref} = (\nu^{iso}_{ref} - \nu^{iso})/\nu_0, \qquad (1)$$

where σ^{iso} and σ^{iso}_{ref} are the mean values of the nuclear magnetic shielding tensor in the isotropic phase for the sample and reference nuclei, respectively. In Eq. (1) $(\nu^{iso}_{ref} - \nu^{iso})/\nu_0$ is the difference between resonant frequencies of the reference and sample nuclei at fixed magnetic field strength (normalized to the spectrometer frequency ν_0 and usually expressed in ppm). In isotropic solutions the chemical shift includes the difference between local fields at solute and reference nuclei due to the solvent [5] as well as the difference between nuclear magnetic shielding effects in the isolated molecules, δ^{iso}_0 [see Figs. 1(a) and (b)]. The chemical shift in the nematic phase [6] is

$$\delta^{nem} \equiv (\nu^{nem}_{ref} - \nu^{nem})/\nu_0 = \delta^{nem}_{iso} + S_\alpha \Delta\sigma - S_{\alpha,ref} \Delta\sigma_{ref}, \qquad (2)$$

where $(\nu^{nem}_{ref} - \nu^{nem})/\nu_0$ is the difference between resonant frequencies of the reference and sample nuclei at fixed field (normalized to ν_0), and $\delta^{nem}_{iso} \equiv \sigma^{nem} - \sigma^{nem}_{ref}$ [see Fig. 1(c)] is the difference in mean shielding between the sample and reference nuclei in the nematic phase. Any difference between δ^{nem}_{iso} and δ^{iso} is due only to solvent effects [see Figs. 1(b) and (c)]. In Eq. (2), $\Delta\sigma$ and $\Delta\sigma_{ref}$ are the shielding anisotropies of the sample and reference nuclei, respectively. For molecules with a C_n ($n \geq 3$) axis of symmetry, one such parameter is sufficient to describe the anisotropic part of the nuclear shielding tensor. The results reported in this paper pertain to molecules with C_{3v} symmetry. Similarly, S_α and $S_{\alpha,ref}$ are the ordering parameters of the molecules [7]. The ordering parameter is defined by

$$S_\alpha = \tfrac{1}{2}(3\cos^2\alpha - 1)S_0, \qquad (3)$$

where α is the angle between the optic axis of the nematic solvent and the external field and S_0 is given by

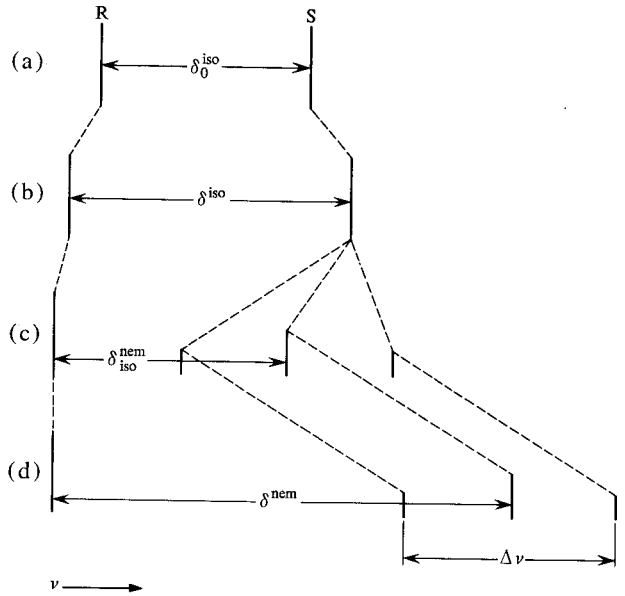


Figure 1 Hypothetical NMR spectra of nuclei in a spherical reference molecule (R) and of a system of three equivalent spin-$\frac{1}{2}$ nuclei (S) with C_{3v} point symmetry in (a) the gas phase, showing the difference in intramolecular shielding between R and S nuclei; (b) solution, showing the difference in the effect of an isotropic solvent on R and S resonances; (c) nematic solution with $\Delta\sigma = 0$, showing the difference in the effect of an ordered solvent on R and S resonances, and also the appearance of splitting due to dipolar interactions among the S nuclei; and (d) nematic solution, showing the shifts in the S resonances due to a nonzero $\Delta\sigma$.

$$S_0 = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle, \tag{4}$$

where θ is the angle between the symmetry axis of the solute molecule and the optic axis of the solvent. The angular brackets in Eq. (4) signify an average over molecular motion. Experimentally, S_α is obtained from the nuclear dipole splittings that characterize NMR spectra in nematic solutions. The NMR spectrum of an oriented system of three magnetically equivalent spin-$\frac{1}{2}$ nuclei located at the vertices of an equilateral triangle (e.g., the ^{19}F nuclei in CF_3CCl_3) is shown in Figs. 1(c) and (d). The ordering parameter [6] is given by

$$S_\alpha = \Delta\nu\left(\frac{9}{4}\frac{\gamma^2\hbar}{\pi r^3}\right)^{-1},$$

where $\Delta\nu$ is the observed splitting, γ is the nuclear gyromagnetic ratio, and r is the internuclear distance. Since the results of several studies [8] on a variety of molecules have shown that the gas-phase geometry is maintained in the nematic phase, r may be evaluated from the gas-phase studies and S_α determined from the measured splitting. If 1) a spherical reference molecule is used ($S_{\alpha,ref} = 0$) and 2) it is assumed that the isotropic shifts in the isotropic and nematic phases are the same (i.e., that $\delta^{iso} = \delta_{iso}^{nem}$), then $\Delta\sigma$ can be obtained from Eqs. (1) and (2):

$$\Delta\sigma = (\delta^{nem} - \delta^{iso})/S_\alpha. \tag{5}$$

The assumption of equal isotropic shifts in both phases became a matter of controversy after unreasonably large values were obtained for ^1H anisotropies [2]. Subsequently it was shown [3] that the data could be explained, at least qualitatively, by a solvent shift that affects the solute and reference nuclei differently when going from the isotropic to the nematic phase. Briefly, this effect arises as follows: In solution the solute and reference nuclei experience different local magnetic fields due primarily to diamagnetic currents induced in the benzene rings of the nematic solvent [5]; see Fig. 1(b). The magnitudes of these currents depend on the relative orientation of the rings and the external field; therefore, when the isotropic $\rightarrow$ nematic phase transition occurs and the rings become aligned parallel to the external field, the solvent fields at the solute and reference nuclei differ from their values in the isotropic phase (in which the rings tumble randomly); see Fig. 1(c). The important point, however, is that the change in solvent field at the phase transition is not expected to be identical for the solute and the reference nuclei because of 1) the differences in size and shape of the solute and reference molecules and 2) the fact that the solute molecules show preferred orientation while the reference molecules do not.

Single-phase measurements

The technique proposed avoids the problem associated with a phase change because the entire experiment is done in the nematic phase. If a spherical molecule is used as an internal reference [9], $S_{\alpha,ref} = 0$ and Eq. (2) can be written

$$\delta^{nem} = \delta_{iso}^{nem} + S_\alpha\,\Delta\sigma. \tag{6}$$

The experiment simply involves measuring δ^{nem} as a function of S_α. A plot of δ^{nem} vs S_α then yields $\Delta\sigma$ directly *if* δ_{iso}^{nem} *is independent of* S_α.

It is crucial to be able to change S_α without affecting δ_{iso}^{nem}. That S_α can be changed readily by varying the temperature of the sample was considered initially [10]. Although this method may be useful in special cases [11], it is known that chemical shifts are also temperature dependent [12]; see Tables 1 and 2. A more general approach is to spin the nematic solution about an axis perpendicular to the direction of the external field [13]. Spinning will result in a frictional torque on the solvent molecules that rotates the optic axis about the molecular center of mass in the direction of spinning. If the angular speed of rotation, ω, is less than a critical value ω_c (which is determined by sample characteristics—viscosity, tem-

Table 1 Shielding anisotropy of ^{19}F.

Molecule	*T (°C)*	$\Delta\sigma_F$ *(ppm)*	*Method*[a]	S_α	$d\delta^{iso}/dT$ *(ppm/°C)*
CF_3CCl_3	91	-72.9 ± 0.9	Spinning	0.01448–0.01646[b]	-0.0077 ± 0.0002
CF_3CCl_3	91	-74.6 ± 1.0	Two-phase	0.01646[c]	-0.0077 ± 0.0002
CH_3F	90	-123.92 ± 0.09	Spinning	0.00908–0.01152[b]	$+0.0101 \pm 0.0004$
CH_3F	90	-111.0 ± 0.08	Two-phase	0.01152[c]	$+0.0101 \pm 0.0004$
CH_3F	[d]	−157	Two-phase	0.01060[c]	[d]

[a] In all experiments CF_4 was used as the internal reference.
[b] Range of S_α covered by spinning the nematic solution.
[c] Value of S_α when the sample is stationary ($\alpha = 0$).
[d] R. A. Bernheim, D. J. Hoy, T. R. Krugh and B. J. Lavery, *J. Chem. Phys.* **50**, 1350 (1969); bis-hexyloxyazoxybenzene solvent; δ^{iso} measured at 125°C, δ^{nem} measured at 80°C; no temperature dependence reported for δ^{iso}.

Table 2 Shielding anisotropy of ^1H in CH_3CCl_3.

T (°C)	$\Delta\sigma_H$ *(ppm)*	*Method*[a]	S_α	$1/S_\alpha$	$d\delta^{iso}/dT$ *(ppm/°C)*
60	−63.4	Two-phase	0.0008[b]	1250	-0.00660 ± 0.00005
70	−60.4	Two-phase	0.0006[b]	1667	-0.00660 ± 0.00005
80	−87.4	Two-phase	0.0004[b]	2500	-0.00660 ± 0.00005
60–80	0	Spinning	0.000486–0.000760[c]		

[a] In all experiments CH_4 was used as the internal reference.
[b] Value of S_α when the sample is stationary ($\alpha = 0$).
[c] Range of S_α covered by spinning the nematic solution.

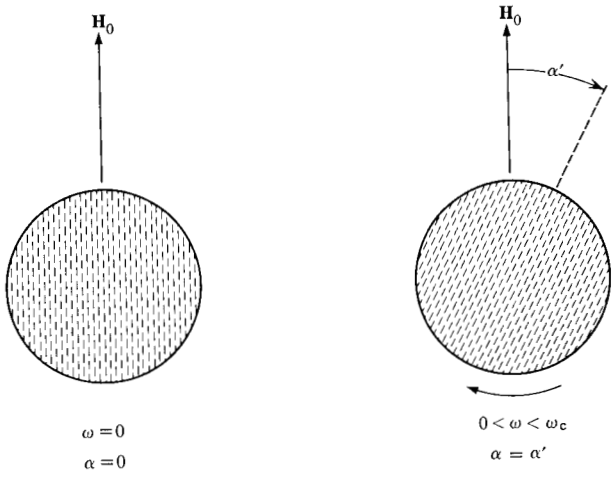
perature, diamagnetic anisotropy), the frictional moment is balanced by the diamagnetic torque that aligns the long axis with the external field. The result of this equilibrium is that the angle between the external field and the long molecular axes assumes a new value α' (see Fig. 2), and the solute molecules attain a new ordering parameter $S_{\alpha'}$ [14]. Experimental results indicate that δ_{iso}^{nem} does remain constant when S_α is varied by spinning the sample. The following relation is then valid [see Eq. (6)]:

$$d\delta^{nem}/dS_\alpha = \Delta\sigma. \tag{7}$$

Experiment

All spectra were taken on a Varian Associates HA-60-IL spectrometer operated in the frequency-sweep mode. Since the commercially available air-driven spinners could not be controlled at spinning rates less than 15 rps, a mechanical spinner was built. The output shaft of a motor was coupled through gears to a vertical drive shaft centered above the NMR probe and a cylindrical coupling with two ball-tipped pins 180° apart provided point contact to a slotted delrin cylinder that held the NMR tube. The speed of the motor was controlled electronically and the maximum spinning rates in the experiments described here were 1.5 rps.

Figure 2 Horizontal section illustrating the effect on the orientation of the optic axes of the solvent when a nematic sample is spun in the magnetic field.



Results

Data for the ^{19}F resonance in CF_3CCl_3 (referred to CF_4 internal reference) in bis-heptyloxyazoxybenzene are shown in Fig. 3. Each point corresponds to a different sample rotation rate. A linear-least-squares fit was used

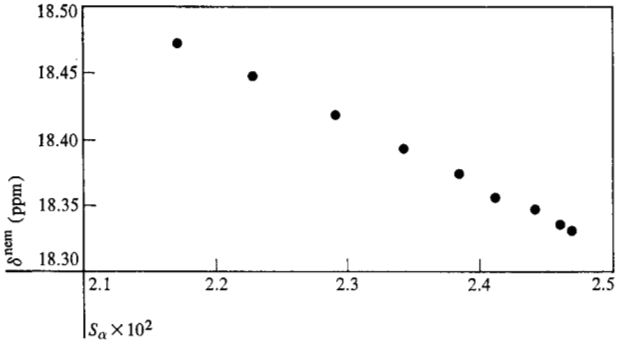


Figure 3 ^{19}F chemical shift of CF_3CCl_3 at 91°C (with CF_4 as internal reference) in the nematic phase of bis-heptyloxyazoxybenzene as a function of the ordering parameter.

to obtain the slope and intercept. The results of several similar single-phase determinations of $\Delta\sigma$ for ^{19}F and ^1H are shown in Tables 1 and 2, respectively. The values of $\Delta\sigma$ obtained by the two-phase measurement are included for comparison. When the isotropic chemical shift was temperature dependent, the value of δ^{iso} used in the two-phase technique [Eq. (5)] was obtained from a linear extrapolation to the temperature at which the nematic-phase measurement was made.

In the spinning experiment, it is imperative that the change in δ^{nem} (as the sample is rotated) arise only from a nonzero shielding anisotropy for the solute nuclei. It is possible to test for changes in δ^{nem} from other sources by observing the NMR signal of nuclei in a spherical ($S_\alpha = 0$) molecule. The absolute resonance frequency for such nuclei [4] is given by

$$\nu^{nem} = \gamma H_0(1 - \sigma^{nem})/2\pi. \tag{8}$$

The mean value σ^{nem} of the shielding tensor in the nematic phase includes solvent, as well as intramolecular, effects. Since $S_\alpha = 0$, the contribution of $\Delta\sigma$ to δ^{nem} vanishes [see Eq. (2)], so that any change observed in ν^{nem} as the sample is spun must be due to a change in the solvent shift. The absolute measurement is made in the following way: The output of the spectrometer is fed to the y axis of an oscilloscope having a high-persistence trace. The x-axis sweep is driven in synchronism with a linear dc sweep of the external field; the extrema of this sweep bracket the values of the resonant field. Thus the absolute position of the signal can be monitored visually. The drift of the field was minimized and the signal was observed on a carefully calibrated scale (10.3 Hz/cm) so that changes of 1 Hz (0.016 ppm at 60 MHz) were easily detected. The shifts of both tetramethylsilane (TMS) and CH_4 in bis-hexyloxyazoxybenzene were studied this way. No change in signal position was observed until the speed of rotation was well above that used in the foregoing experiments (less than or about 1.5 rps). This result establishes that no solvent shift is due to rotation, at least not for nuclei in molecules the size and shape of TMS and CH_4.

Discussion

• *CF_3CCl_3*

If we assume that the ^{19}F shielding tensor is axially symmetric about the C–F bond, the observed shielding anisotropy (see Table 1) can be transformed to the bond axis system:

$$(\sigma_\parallel - \sigma_\perp)_{bond} = \tfrac{1}{2}\Delta\sigma_{obs}(3\cos^2\phi - 1), \tag{9}$$

where ϕ is the angle between the C–F bond and the threefold axis of CF_3CCl_3. Taking ϕ from the same structural data used to obtain S_α [15], we find $(\sigma_\parallel - \sigma_\perp)_{bond} = +224$ ppm, in close agreement with the results of NMR studies on similar molecules in the solid state [16]. Good agreement between results from single- and two-phase methods is also evident in Table 1.

• *CH_3F*

The value of $\Delta\sigma_F$ for CH_3F oriented in a clathrate, -66 ppm [17], is much lower than any of the liquid crystal results (Table 1). The single-phase measurement yielded a value (-124 ppm) 21 percent smaller than the original two-phase measurement value (-157 ppm). However, this two-phase value was calculated without correcting for the temperature dependence of the isotropic chemical shift [18]. If such a correction is made to the original data, using the value for $d\delta^{iso}/dT$ shown in Table 1, we obtain $\Delta\sigma_F = -120$ ppm, in good agreement with the single-phase result.

• *1, 3, 5-$C_6H_3Cl_3$*

Using the spinning method we found $\Delta\sigma_H = -5.86 \pm 0.13$ ppm with CH_4 as internal reference, and -4.34 ± 0.18 ppm using TMS. This shielding anisotropy had previously been measured by several workers using both two-phase [1, 18] and single-phase [11] techniques. The results are all in agreement, but are consistently higher (by 0.8 to 1.5 ppm) when CH_4, rather than TMS, is used as the internal reference. Even though TMS is known to orient very slightly [19], this orientation does not introduce significant error since it is estimated that the product $S_{\alpha,ref}\,\Delta\sigma_{ref}$ for TMS [see Eq. (2)] is only about 0.003 ppm [20, 21]. However, it is known that there is a discontinuity at the isotropic → nematic phase transition when the CH_4-TMS chemical shift is measured as a function of temperature [22]. This discontinuity could be used to explain the difference between values of $\Delta\sigma_H$ obtained with CH_4 and with TMS in the two-phase measurements. The problem is that single-phase measurements [11, this work], which involve no phase transition and therefore no

discontinuity, lead to the same difference between CH_4 and TMS measurements of $\Delta\sigma_H$. These puzzling results must be explained before a choice can be made between CH_4 and TMS as a reference molecule. In the meantime, it is probably more reliable, as suggested elsewhere [11], to use CH_4 as an internal reference.

• *CH_3CCl_3*

Data for this molecule provide an example of how the two-phase measurement can go awry. Even when the temperature dependence of the isotropic shift is accounted for, the results given in Table 2 show unreasonably large values for $\Delta\sigma_H$. Yet no detectable change in δ^{nem} (referred to CH_4 as internal reference) can be observed when the sample is spun in the nematic phase, although the ordering parameter can be reduced by 30 percent. This results shows that $\Delta\sigma_H \approx 0$, as expected for aliphatic C—H bonds [21]. The reason for the large discrepancy between the two methods can be explained as follows: CH_3CCl_3 is an almost spherical molecule, since the covalent radii of a methyl group and a chlorine atom are nearly equal. Accordingly the orientation is small and the large values of $1/S_\alpha$ (Table 2), coupled with seemingly insignificant solvent shifts of 0.035 to 0.05 ppm, account for the large values of $\Delta\sigma_H$ observed in the two-phase measurements.

Conclusions

For nuclei such as ^{19}F, ^{13}C, ^{14}N and ^{31}P, which have large shielding anisotropies [23], the relative error resulting from a two-phase measurement is small unless the molecule is only slightly oriented (i.e., $S_\alpha < 0.01$). It should be noted, however, that if the isotropic chemical shift is temperature dependent, an extrapolation must be made so that both δ^{iso} and δ^{nem} are given at the same temperature. The most important use for the single-phase technique is for measurements of ^1H shielding anisotropies, especially in molecules that are only slightly oriented. These molecules are among the most interesting ones for which $\Delta\sigma$ should be accurately determined.

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