Communications to the Editor

Chemical Shift Anisotropies from Nuclear Magnetic Resonance Studies of Oriented Molecules

Sir:

It is now well known that anisotropy in nuclear magnetic shielding can be obtained through measurement of a shift due to partial molecular alignment.[1-3] If the molecule is linear, or if the bond containing the nucleus has an axis of symmetry, it is possible to determine $\sigma_{\parallel} - \sigma_{\perp}$, the difference in the shielding for fields parallel and perpendicular to the bond. If the mean shielding constant, $(\sigma_{\parallel} + 2\sigma_{\perp})/3$, is also known through measurements on an isotropic sample, both $\sigma_{\parallel}$ and $\sigma_{\perp}$ are then available.

Recently the shifts and splittings in the proton and fluorine spectra of CH_3F in *p,p'*-di-*n*-hexyloxyazoxybenzene were observed.[4] It was reported that $(\sigma_{\parallel} - \sigma_{\perp})^{F} = -179 \pm 15$ ppm and that the difference in the mean proton shielding parallel and perpendicular to the threefold axis is -28 ± 4 ppm; if the bond angles are tetrahedral and the CH bonds axially symmetric, the latter result entails $(\sigma_{\parallel} - \sigma_{\perp})^{H} = +84 \pm 12$ ppm, a value rightly described[4] as "unexpectedly large." The actual shifts were evidently about -195 cps (-2.08 ppm) and -32 cps (-0.32 ppm) for the F and H resonances.

The purpose of this communication is to point out that a small nmr shift between the nematic and isotropic phases of a liquid crystal solution (relative to an external reference) cannot easily be related to shielding anisotropy. The difficulty is due to shifts arising from the environment of the solute. The isotropic → nematic transition is a first-order phase change, and there is a small decrease in the mean volume susceptibility of the medium leading to a downfield shift. However, there is a more important effect due to the anisotropy in the bulk susceptibility brought about by the more-or-less complete molecular alignment in the nematic phase in the strong magnetic field. If the sample is in a cylinder at right angles to a magnetic field H_z, the volume susceptibility is $\chi_{\parallel}$ in the direction of the field, and $\chi_{\perp}$ at right angles to it, and the field strength inside the cylinder is

$$H_z[1 + 2\pi\chi_{\parallel}]^{-1} \approx H_z\left[1 - 2\pi\chi - \frac{4\pi}{3}\Delta\chi\right]$$

where $\chi = {}^1/_3(\chi_{\parallel} + 2\chi_{\perp})$ is the mean volume susceptibility and $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$. In a spherical sample, the field inside is

$$H_z\left[1 + \frac{4\pi}{3}\chi_{\parallel}\right]^{-1} \approx H_z\left[1 - \frac{4\pi}{3}\chi - \frac{8\pi}{9}\Delta\chi\right]$$

The "effective field" acting on a molecule is $(1 + {}^4/_3\pi\chi_{\parallel})$ times the actual field in the medium, so there is no bulk susceptibility shielding in a spherical sample, but the equivalent shielding constant in a cylinder is

$$\sigma_b = \frac{2\pi}{3}\chi_{\parallel} = \frac{2\pi}{3}\chi + \frac{4\pi}{9}\Delta\chi$$

The shift $(2\pi/3)\chi$ is well known,[5] but the second term appears to be new and gives rise to an upfield shift when the solution goes nematic. Measurements of the difference in the field strength needed to produce resonance in a cylinder and a sphere would yield σ_b and hence valuable information about the volume susceptibility.[6]

There are other environmental contributions to the shielding that might change significantly when the medium undergoes the isotropic → nematic transition. In particular, there is the "solvent anisotropy effect," σ_a,[7] which arises from the link between the shape of the solvent molecules and their magnetic susceptibilities. Thus in benzene, the large diamagnetic susceptibility in the direction perpendicular to the ring, coupled with the fact that solute molecules can approach a benzene molecule most closely in this direction, leads to a high-field shift of about ${}^1/_3$ ppm.[7] But if the benzene molecules were aligned with the ring planes parallel to the magnetic field, this high-field shift would be converted into a shift $-{}^3/_2\chi_{11}(\chi_{33} - \chi_{11})^{-1}$ times as large, where $\chi_{11} = \chi_{22}$ is the magnetic susceptibility in the plane of the ring and χ_{33} that at right angles to it; this ratio is approximately -0.9 for benzene, and the resulting change in σ_a is about -0.6 ppm.

It is not possible to prescribe definite values for $\Delta\sigma_b$ and $\Delta\sigma_a$ in the isotropic → nematic transition in solutions in *p,p'*-di-*n*-hexyloxyazoxybenzene. Although it is apparently a first-order phase change, the decrease in volume, and hence in χ, is small and probably less than 1%.[8] However, $\Delta\chi$ may be about 0.13 ppm (its value for *p*-azoxyanisole[9]) so that $\Delta\sigma_b \sim +0.18$ ppm. The change in σ_a is doubtless much smaller than that calculated above for benzene, and a figure of -0.3 ppm is reasonable. Thus we would expect a downfield shift when the solvent goes nematic, and this could greatly reduce $(\sigma_{\parallel} - \sigma_{\perp})^{H}$. If it is assumed that $(\sigma_{\parallel} - \sigma_{\perp})^{H}$ is zero, the solvent shift is -0.32 ppm and the corrected anisotropy $(\sigma_{\parallel} - \sigma_{\perp})^{F}$ is -150 ppm.

From the point of view of evaluating shielding anisotropies, it would seem to be preferable to use an *internal* reference comprising a molecule of high symmetry; thus CH_4 would be appropriate for proton spectra, and CF_4 or SF_6 for F resonances. Even with internal referencing, special care may be needed in interpreting small shifts, for the change in the environment could affect the solute and reference differently.

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Received April 11, 1967