

Variable angle spinning (VAS) NMR study of solvent effects in liquid crystalline solutions of ^{13}C -iodomethane

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Abstract

NMR spectra of ^{13}C -iodomethane oriented in three different liquid crystalline solvents have been collected and analyzed under spinning at various angles with respect to the static magnetic field. For each sample the ratio of homonuclear (^1H - ^1H) to heteronuclear (^{13}C - ^1H) dipolar couplings, which is a function of the geometry of the solute molecule, does not change significantly with the scaling of the dipolar couplings due to spinning at different angles. This result implies that the ‘apparent bond angle deviations’ ($\Delta\theta_a$), previously calculated from thermotropic liquid crystals, arise from a solvent effect and are not an artifact from scaling the anisotropic interactions.

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1. Introduction

Dipolar couplings, which are directly observed only in anisotropic environments such as solids or solute molecules aligned in liquid crystalline solvents, can be used to calculate structures of both small and large molecules [1–4]. However, molecular structures calculated from NMR spectra of small molecules oriented in liquid crystals have often shown noticeable variation. Such structures have typically been calculated using an ideal uniaxial model for the liquid crystalline medium, which assumes that the biaxial fluctuations do not exist, or they do not affect the results of the averaging of NMR parameters even if they do exist. Especially in thermotropic liquid crystals, the magnitude of this apparent

variation in structural parameters, e.g., the ‘apparent bond angle deviation’ ($\Delta\theta_a$) in iodomethane, is inversely proportional to the molecular ordering [5]. Although there have been many attempts to rationalize the apparent distortions of many simple molecules [6–9], still the true origin of these deviations and their $1/S$ -dependence cannot be readily explained.

In the case of ^{13}C -iodomethane, the ratio of the homonuclear (^1H - ^1H) to heteronuclear (^{13}C - ^1H) dipolar couplings can be used as an index for this spectral aberration. Although this value is a function of the geometry of the solute molecule and should not change in a uniaxial nematic solvent, the measured ratio usually shows deviation from the ideal value. When molecular structure parameters such as bond angles are calculated using this ratio, the induced errors result in an apparent deviation from known values. Discussing the solvent effects in terms of the calculated bond angles could lead to ambiguity about whether the solvent has a distorting effect on the molecule itself rather than imposing a

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systematic error on the measurement of the dipolar couplings. Therefore, we define a scaling factor ξ , which is the ratio of the ideal $D_{\text{CH}}/D_{\text{HH}}$ value to the experimentally measured $D_{\text{CH}}/D_{\text{HH}}$ value. This parameter can be regarded as a measure of the nonideality of the solvent relative to the simple traditional uniaxial model [5].

With decreasing molecular ordering, average dipolar couplings are also scaled down, and the relative error in the magnitude of dipolar couplings increases; this might be responsible for the increase of $\Delta\theta_a$ at low molecular ordering. However, in this case the deviations would have random signs, whereas the observed deviations are always in one direction. This suggests that the artifacts are due to solvent–solute interactions and the corresponding changes in molecular motions and the averaged resulting tensors.

Scaling of dipolar couplings can also be achieved by using the variable angle spinning (VAS) experiment [10–21]. By spinning the sample around an axis at an angle that ranges from 0° to the magic angle (54.7°) relative to the static magnetic field and thereby reorienting the directors of the liquid crystal solvent without changing the chemical properties of the sample, thus without changing the molecular motional averaging mechanisms, the dipolar couplings can be scaled and even reduced to zero. If the simple decrease in the values of the dipolar couplings causes the increase in $\Delta\theta_a$, the same effect should occur with scaling of dipolar couplings in VAS experiments. If the magnitude of $\Delta\theta_a$ does not change for a series of VAS experiments with the same sample, we can conclude that $\Delta\theta_a$ is a consequence of the molecular properties of the sample.

2. Experimental

For the liquid crystals under examination we have chosen: (a) *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline (EBBA; Sigma–Aldrich, St. Louis, Missouri, USA), (b) I52 (EM Industries, Hawthorne, New York, USA), and (c) ZLI1132 (EM Industries, Hawthorne, New York, USA). As with ^{13}C -iodomethane (99% ^{13}C ; Isotec, Miamisburg, Ohio, USA), these liquid crystals were used without further purification.

A Varian Mercury 300BB spectrometer and a Varian CMX Infinity 500 NMR spectrometer were used for the static and VAS NMR experiments, respectively. The latter was equipped with an extensively modified Varian/Chemagnetics double resonance DAS/VAS probe with a split solenoid coil. Spectra of oriented ^{13}C -iodomethane samples were collected under spinning at various angles with respect to the static magnetic field. The shims were manually readjusted at each angle used in the experiments to correct for the change in magnetic field inhomogeneity caused by the magnetic susceptibility of the cylindrical sample at different orientations. All

measurements were performed at room temperature (15°C).

The reference value for the H–C–H bond angle is taken from the microwave spectroscopy data [22]. Before the calculation of the molecular structure or the scaling factor ξ [5] all the data were corrected for harmonic vibrations. The correction factors were taken from the literature [23].

3. Results and discussions

^{13}C -iodomethane has been traditionally chosen as a model system because of the simplicity of its spectrum. For ^{13}C -iodomethane, the H–C–H bond angle is expressed by the ratio of two dipolar couplings, D_{CH} and D_{HH} . We performed variable angle spinning (VAS) experiments for ^{13}C -iodomethane samples, in which dipolar couplings were scaled down without any change in sample composition. In this case, we expect the apparent deviations of the H–C–H bond angle from the known structure to remain constant and stable within this experimental error range and indeed they are equal in each case to the value for nonspinning sample, oriented along the magnetic field. The VAS result shown in Fig. 1 shows that even though both D_{CH} and D_{HH} are scaled down with the change of sample spinning angle, their ratio remains the same as that of the nonspinning sample for all three liquid crystal solvents used, in contrast to the reduction in couplings induced by decreased ordering in different solvent mixtures.

Fig. 2 shows the correlation between the value of D_{HH} and the aberration of ^{13}C -iodomethane spectra, from both our own VAS data and the data compiled from the literature with different liquid crystal solvents [24–27]. It has been long known that with the change of the solute order parameter, which is usually achieved by the use of different liquid crystal solvents, the apparent structural deviation of small molecules (e.g., $\Delta\theta_a$ of iodomethane) is inversely proportional to the solute order parameter. However, our data show that when the size of the dipolar couplings is scaled using VAS, the ratio between the two dipolar couplings, and thus the structural deviation of the sample, remains the same as that of the nonspinning sample.

While the VAS experiments can explicitly rule out the possibility of increased experimental error from the ratios of small coupling values, the exact origin of the apparent structural deviation is still under investigation. Photinos and coworkers studied the relative contribution of various ordering mechanisms to the biaxiality of the hydrocarbon chain in a smectic liquid crystal [28]. In a recent Letter, the difference in averaging of biaxiality was suggested as a possible mechanism for the different behaviors of the deviations observed in thermotropic and lyotropic liquid crystals [5]. Although the VAS

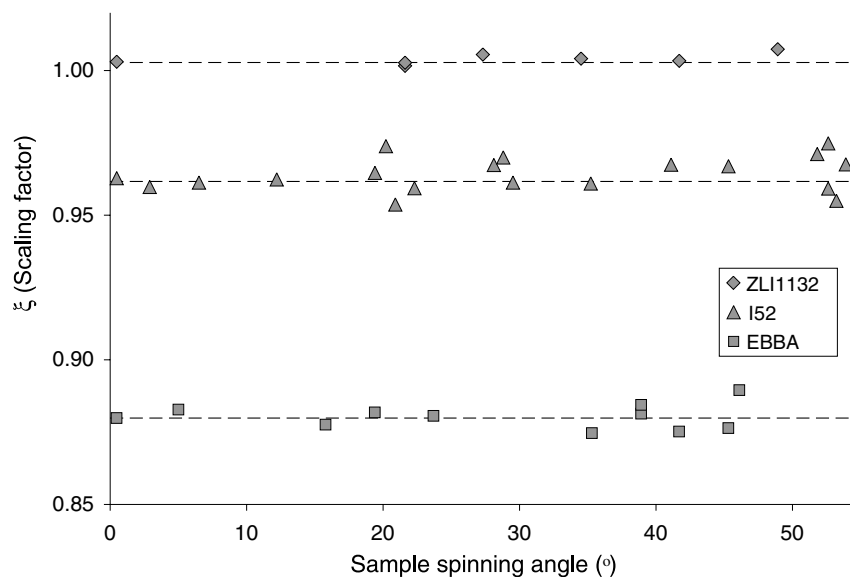


Fig. 1. Comparisons of the scaling factor ζ for VAS NMR spectra of ^{13}C -iodomethane in three different thermotropic liquid crystals with the change of the sample spinning angle.

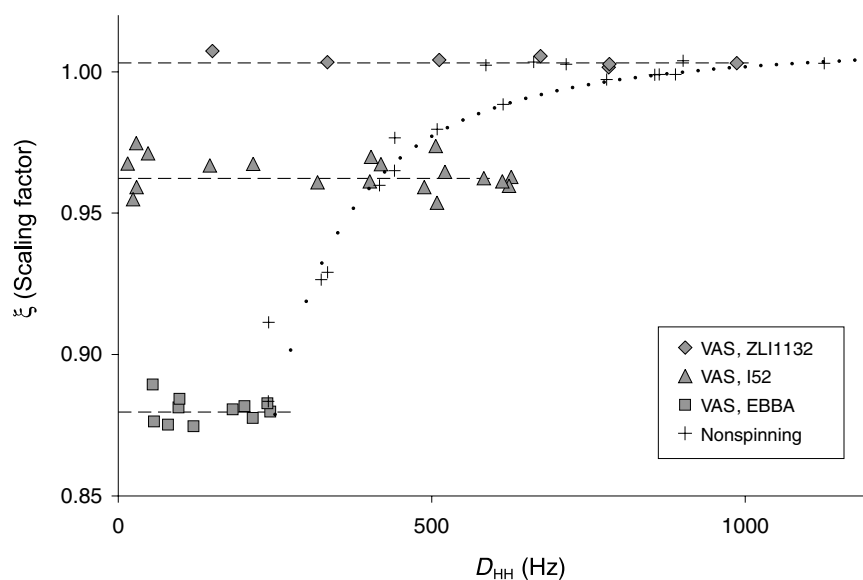


Fig. 2. Comparisons of the scaling factor ζ for VAS NMR spectra of ^{13}C -iodomethane in three different thermotropic liquid crystals versus the magnitude of the dipolar coupling D_{HH} . Reference data for static NMR sample are also presented.

experiment may be in principle used to characterize the phase symmetry of liquid crystals, the detailed theory of the effect of various orientational order mechanisms on the phase symmetry of liquid crystals is beyond the scope of this work. NMR spectra of less symmetric molecules are also known to show similar order dependence of apparent structural deviation [5], and further study of these solute molecules would give additional information for the behaviors of liquid crystals.

Using the technique proposed in [16], we have also measured the indirect spin–spin coupling $^1J_{\text{CH}}$ for each

solvent from each series of VAS data. The isotropic values of $^1J_{\text{CH}}$ were 149.48 ± 0.23 , 150.18 ± 0.38 and 151.09 ± 0.11 Hz in ZLI1132, I52 and EBBA, respectively. These values were found to be slightly different from the previously reported VAS result [16], and among the three solvents the differences behaved in a similar manner to the deviations of the ratio between the two dipolar couplings. Although scaling of dipolar couplings by successive dilution have been widely used to separate J couplings from dipolar couplings and thus to determine molecular structures from dipolar cou-

plings, our experimental results imply that the isotropic values of J couplings themselves are also significantly affected by the solvent effects in the same way as the dipolar couplings, and this method should be used with appropriate attention to possible solvent effects. On the contrary, when VAS and switched angle spinning (SAS) experiments are performed on the same sample, the molecular properties of the sample do not change and the isotropic J couplings should also remain the same as those in nonspinning samples.

4. Conclusion

We compared the scaling of dipolar couplings by VAS experiments to the scaling by using different liquid crystal-line samples, and found that the VAS experiments did not alter the relative ratio between dipolar couplings. This result shows that the apparent bond angle deviations do not arise from a general property of the low alignment regime, but are related to the liquid crystal solvents themselves. We also illustrated that the isotropic J couplings are also affected by the solvent effects in a similar manner to the dipolar couplings among different solvents.

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