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LETTERS

NMR Studies of ^{13}C-Iodomethane: Different Behavior in Thermotropic and Lyotropic Liquid Crystals

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High-resolution NMR spectra of ^{13}C-iodomethane dissolved in thermotropic and lyotropic liquid crystalline solvents have been used to measure ^{1}H−^{1}H and ^{13}C−^{1}H dipolar couplings. The ratio of these two couplings, which is a function of the H−C−H bond angle in ^{13}C-iodomethane, is, in general, different from that expected from the known molecular structure; solvent−solute interactions in liquid crystalline solutions are responsible for this difference. In thermotropic liquid crystalline solutions, the apparent bond angle deviation ($\Delta\theta_a$) increases with decreasing molecular ordering. In contrast, in lyotropic liquid crystals, no significant spectral aberration has been observed. These results indicate a fundamental physicochemical difference between the intermolecular interactions that prevail in thermotropic and lyotropic liquid crystals.

Introduction

Historically, structural NMR spectroscopists have used thermotropic liquid crystals rather than lyotropic ones due to the high solubility and alignment of many small molecules in these solvents. However, in recent studies, the three-dimensional structures have been calculated from orientation-dependent NMR parameters, such as residual dipolar couplings (RDC), of weakly aligned biomolecules in lyotropic liquid crystalline solvents.[1−3] In general, these structures, calculated using the simplest RDC interpretation models, show good agreement with their X-ray counterparts.[3−6]

In contrast, structural parameters calculated from NMR spectra of small molecules in thermotropic liquid crystalline solvents sometimes display substantial disagreement with one another, despite the use of more advanced interpretation schemes and the high precision of the individual measurements. Moreover, they sometimes show large discrepancies from the expected values, either from theoretical predictions or from other structural methods, such as diffraction experiments and microwave spectroscopy.

There have been many attempts to explain and overcome these anomalous results.[7−10] These anomalies have been attributed to solute−solvent interactions leading to perturbation effects, which can result in systematic errors in simple theoretical models used for NMR data interpretation. Often, this perturbation effect can be large and must be taken into account in the calculation of molecular structures. Theoretical models of solvent effects have been developed, but most of them are very sophisticated and require extensive calculations and their use in structural NMR is limited.

One of these approaches involves a search for an ideal solvent in which solvent effects are absent or minimal. This search is based on the observed intercorrelation of discrepancies of different molecules. In this approach, a series of spectra is collected for a small, well-characterized molecule in different liquid crystalline solvents and their mixtures, and solvent effects

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are deduced from the spectra. Ideal solvents are made from a mixture of two liquid crystals, having opposite signs of $\Delta\theta_a$. Typical probe molecules include methane and its monosubstituted derivatives, as well as benzene.[11−14] In particular, D_{CH} of methane is often used as an index of the nonideality of a solvent;[15−18] a solvent is regarded as ideal when D_{CH} of dissolved methane is zero. A similar approach involves interpolation of structural data measured in different liquid crystals to a hypothetical neutral solvent, using the value of D_{CH} of methane in each solvent as the characteristic index of apparent distortion of the solute in each solvent.[19,20]

However, no known thermotropic liquid crystalline solvent exhibits ideal behavior for all small solute molecules investigated. Also, this nonideal behavior intensifies in these solvents, whereas lyotropic liquid crystals of the type used in NMR spectroscopy of large biomolecules display more ideal behavior at low levels of molecular alignment. The lack of a consistent model to eliminate this solvent-induced apparent bond-angle deviation has hindered the use of weakly oriented thermotropic liquid crystals for the determination of accurate molecular structures by NMR spectroscopy.

In this work, we obtained high-resolution NMR spectra of ^{13}C-iodomethane dissolved in different thermotropic and lyotropic liquid crystals and compared the patterns of their spectral aberrations. These measurements show the existence of fundamental differences of the physicochemical properties between thermotropic and lyotropic liquid crystalline media.

Experimental Details

Cetylpyridinium bromide monohydrate (CPBr), cetylpyridinium chloride monohydrate (CPCl), cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), sodium dodecyl sulfate (SDS), *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline (EBBA), and ^{13}C-iodomethane (99%) were purchased from Sigma−Aldrich Chemical Co. (St. Louis, MO). Liquid crystals ZLI1132 and ZLI1695 were purchased from EM Industries (Hawthorne, NY) and used without further purification. 1-Hexanol and all the other reagents used for the sample preparations were of the highest purity commercially available.

The procedure for lyotropic sample preparation is described elsewhere in detail.[21−23] More than 40 samples with different compositions were prepared.

NMR spectra were recorded on a Varian Mercury-300 spectrometer equipped with a broadband probe. ^{2}H spectra were acquired with the deuterium frequency lock turned off. The values of ^{2}H quadrupolar splittings of solvent D_2O ranged from 7 to 70 Hz in various samples. Digital resolution in spectra did not exceed 0.1 Hz, and the line widths for the solute peaks did not exceed 3 Hz.

Results and Discussion

Table 1 shows the list of experimental data for ^{1}H−^{1}H and ^{13}C−^{1}H dipolar couplings of ^{13}C-iodomethane dissolved in thermotropic and lyotropic liquid crystalline solvents, as well as those compiled from the literature.[11,24−26]

In most of the literature of structural NMR spectroscopy in liquid crystals, the molecular structure of iodomethane has been represented in terms of H−C−H bond angle. Assuming that the C−H bond length does not change, solvent effect is often discussed in terms of a distortion of the H−C−H bond angle. However, we adopt a different representation in this work; we assume that the molecular geometry of iodomethane in liquid crystals is the same as that derived from the microwave spectroscopy data and does not change. The H−C−H bond angle is calculated from the ratio of two dipolar couplings, D_{CH} and D_{HH}, and in order to obtain the correct bond angle, we need to scale the ratio by a scaling factor, ξ. Figure 1 shows the correlation between this scaling factor and the order parameter with respect to the liquid crystal director. We will discuss the origin of this scaling factor ξ later.

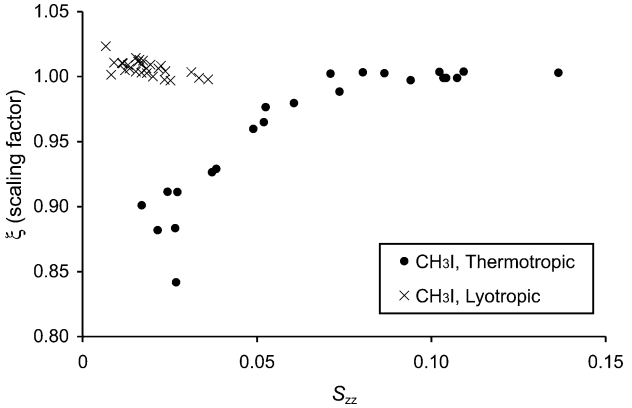

Figure 1. Variation of the scaling factor ξ with respect to the solute order parameter S in a series of thermotropic and lyotropic liquid crystalline solutions. H−C−H bond angles were assumed to be 111.40° for $^{13}CH_3I$.

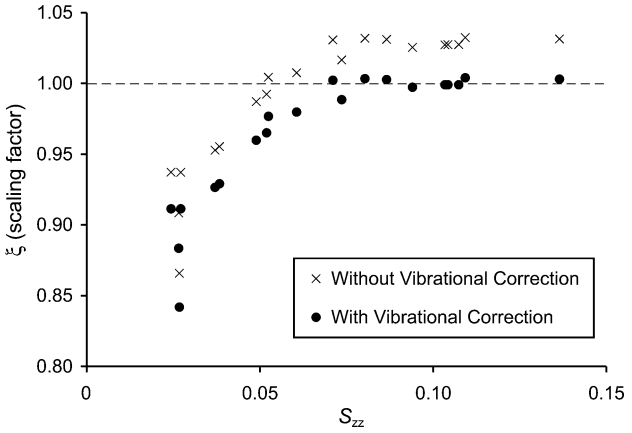

Figure 2. Comparisons of the variation of the scaling factor ξ with respect to the solute order parameter S for ^{13}C-iodomethane in thermotropic liquid crystals without and with vibrational correction.

Before the calculation of the scaling factor ξ, all of the data were corrected for harmonic vibrations using vibrational correction factors found in the literature.[26,27] The temperature dependence of the vibrational correction factors was neglected. The reference values for the H−C−H bond length and bond angle were also taken from the literature.[28]

In thermotropic liquid crystals, the scaling factor ξ is smaller than unity and its value further decreases with decreasing order parameter. For weakly aligned molecules, we need significant scaling to obtain correct molecular structures from the observed dipolar couplings. In nematic thermotropic liquid crystals, this effect has been observed for many molecules of different symmetry. At a first glance, this effect is consistent regardless of the thermotropic liquid crystals used, the temperature, and the solute concentration for a given solute molecule. Figure 2 shows that vibrational correction only slightly shifts all data points along the vertical axis, without changing their general pattern. Spectra of bromomethane and chloromethane also exhibit similar behaviors.

This effect could be detrimental to accurate determination of molecular structures by NMR spectroscopy. For example, with S_{zz} below 0.03, if we used our spectrum of ^{13}C-iodomethane without scaling by $\xi \approx 0.85$, the resulting molecular structure

TABLE 1: Dipolar Coupling Constants and Calculated Apparent H−C−H Bond Angles (in Degrees) for ^{13}C-iodomethane in Thermotropic and Lyotropic Liquid Crystalline Solutions.

solvent	D_{HH} (Hz)	D_{CH} (Hz)	S_{zz}[a]	$\angle(HCH)_{NMR} - \angle(HCH)_{mw}$[b]	note[c]
EBBA	168.71	150.70	0.0169	+1.73	
	213.07	194.50	0.0215	+2.10	
	243.20	214.80	0.0243	+1.53	ref 24
	262.87	239.51	0.0265	+2.07	ref 11
	271.67	239.95	0.0272	+1.54	ref 24
HAB	261.47	250.00	0.0268	+2.93	ref 24
	889.86	714.40	0.0865	−0.04	ref 11
Phase 997	385.25	333.78	0.0383	+1.21	ref 11
Phase 1221	1070.96	862.91	0.1043	+0.02	ref 11
Phase 1291	1062.42	856.07	0.1034	+0.02	ref 11
Phase IV	372.40	323.53	0.0371	+1.26	ref 11
ZLI1132	990.40	794.29	0.1023	−0.06	
	1123.86	901.15	0.1093	−0.06	ref 11
ZLI1167	−701.65	−563.12	0.1364	−0.05	ref 11
ZLI1695	−365.31	−293.39	0.0710	−0.04	
	−413.05	−331.36	0.0803	−0.05	
79.7% ZLI1167 + 20.3% Phase IV	−551.52	−444.36	0.1074	+0.02	ref 11
57.6% ZLI1167 + 42.4% Phase IV	753.99	613.99	0.0736	+0.19	ref 11
39.1% ZLI1167 + 60.9% Phase IV	618.98	508.59	0.0606	+0.33	ref 11
19.9% ZLI1167 + 80.1% Phase IV	496.73	416.55	0.0489	+0.67	ref 11
78.0% ZLI1167 + 22.0% EBBA	−482.79	−389.68	0.0940	+0.04	ref 11
30.4% ZLI1167 + 69.6% EBBA	528.47	440.82	0.0520	+0.58	ref 11
40.8% ZLI1132 + 59.2% Phase IV	535.28	441.18	0.0525	+0.38	ref 11
CTAB	−34.20	−26.90	0.0066	−0.37	55 °C, $\Delta\nu_Q$ = 7.1 Hz
	−57.97	−46.18	0.0112	−0.17	55 °C, $\Delta\nu_Q$ = 15 Hz
	−94.55	−75.90	0.0184	−0.04	40 °C, $\Delta\nu_Q$ = 32.7 Hz
CTAC	−81.93	−65.20	0.0159	−0.18	60 °C, $\Delta\nu_Q$ = 40.2 Hz
	−86.47	−68.95	0.0168	−0.15	55 °C, $\Delta\nu_Q$ = 39.6 Hz
	−115.47	−92.17	0.0224	−0.08	30 °C, $\Delta\nu_Q$ = 52.1 Hz
CPBr	−42.14	−33.87	0.0082	−0.02	55 °C, $\Delta\nu_Q$ = 9.6 Hz
	−46.41	−36.96	0.0090	−0.17	60 °C, $\Delta\nu_Q$ = 16.1 Hz
	−59.51	−47.42	0.0115	−0.16	60 °C, $\Delta\nu_Q$= 20.2 Hz
	−67.04	−53.48	0.0130	−0.14	50 °C, $\Delta\nu_Q$ = 20.4 Hz
	−78.47	−62.92	0.0153	−0.06	30 °C, $\Delta\nu_Q$ = 19.6 Hz
	−83.95	−66.70	0.0163	−0.21	50 °C, $\Delta\nu_Q$ = 37.5 Hz
	−93.98	−75.16	0.0183	−0.10	40 °C, $\Delta\nu_Q$ = 41.2 Hz
CPCl	−62.35	−49.95	0.0121	−0.08	30 °C, $\Delta\nu_Q$ = 11.1 Hz
	−78.86	−62.58	0.0153	−0.23	60 °C, $\Delta\nu_Q$ = 49.8 Hz
	−89.23	−70.95	0.0173	−0.19	50 °C, $\Delta\nu_Q$ = 50.4 Hz
	−100.16	−79.89	0.0194	−0.15	40 °C, $\Delta\nu_Q$ = 50.4 Hz
	−112.13	−89.70	0.0218	−0.10	30 °C, $\Delta\nu_Q$ = 50 Hz
	−121.97	−97.77	0.0237	−0.07	23 °C, $\Delta\nu_Q$ = 49.5 Hz
SDS	−69.37	−55.49	0.0135	−0.10	60 °C, $\Delta\nu_Q$ = 32 Hz
	−86.87	−69.72	0.0169	−0.05	50 °C, $\Delta\nu_Q$ = 34 Hz
	−103.45	−83.26	0.0201	0	40 °C, $\Delta\nu_Q$ = 37.4 Hz
	−120.68	−97.37	0.0235	+0.04	30 °C, $\Delta\nu_Q$ = 39 Hz
	−129.95	−104.36	0.0252	+0.05	25 °C, $\Delta\nu_Q$ = 39.8 Hz
	−160.40	−128.65	0.0312	−0.05	25 °C, $\Delta\nu_Q$ = 68 Hz
	−171.20	−137.95	0.0333	+0.02	20 °C, $\Delta\nu_Q$ = 69.7 Hz
	−184.66	−148.96	0.0360	+0.03	13.5 °C, $\Delta\nu_Q$ = 70.3 Hz

[a] Order parameters are given with respect to the liquid crystal director. [b] Microwave spectroscopy values for the C−H bond length and the H−C−H angle of CH_3I are 1.0819 Å and 111.40°, respectively.[28] All the dipolar coupling constants have been corrected for harmonic vibrations using correction factors of ρ_{HH} = 1.0229 and ρ_{CH} = 1.0519[27] before the calculation of the H−C−H bond angles, assuming that the C−H bond lengths are the same as the microwave spectroscopy value. [c] ^{2}H quadrupole splitting of D_2O, which changes with sample composition.

would be equivalent to an H−C−H bond angle deviation of more than 3°, assuming that the C−H bond length is constant.

The trivial explanation that the relative error in the experimental values of the dipolar couplings increases with the decreasing molecular ordering cannot fully account for the sharp increase of deviations near $S = 0$. In that case, the direction of the fluctuations would be random, whereas the observed deviations are all in one direction, indicating the existence of a systematic error. Many other molecules in thermotropic liquid crystals, including fluoromethane,[29] acetylene,[30] benzene, and thiophene, also show increasing deviation in one consistent direction at low molecular order.

Scaling of dipolar couplings without changing the chemical properties of the solution can be achieved using Variable Angle Spinning (VAS) experiments.[31−34] In this experiment, dipolar couplings can be scaled or even reduced to zero by varying the sample spinning axis angle relative to the static magnetic field

from 0° to the magic angle (54.7°). ^{13}C-iodomethane dissolved in three different liquid crystalline solvents was chosen as a model system for the VAS experiments. These experiments show that, for a sample of the same composition at different angles, the values of the $\Delta\theta_a$ remained constant and did not show any significant difference from that of the nonspinning sample oriented along the magnetic field, within the range of the experimental error. This result indicates that the apparent deviations arise from the molecular properties of the thermotropic liquid crystals and are not a systematic error induced by scaling down the dipolar couplings.[34]

Figure 1 also shows that, in contrast to thermotropic liquid crystals, the spectral data for iodomethane in five different lyotropic liquid crystals need only a small correction, if any; this is equivalent to the accuracy of the H−C−H bond angle within 0.3°. Moreover, this deviation looks independent of the degree of molecular alignment. We observed similar behaviors for bromomethane and chloromethane generated in situ in these lyotropic systems. The scaling factor needed to get the correct distance ratio between ortho and para proton pairs in benzene follows a similar trend.[35] This result is striking in contrast to that of many "ideal solvents" from mixtures of thermotropic liquid crystals, which give the expected results only under limited experimental conditions.

Different ordering mechanisms of thermotropic and lyotropic liquid crystals may contribute to different averaging of the NMR parameters in those systems in both space and time, resulting in the different behavior of thermotropic and lyotropic liquid crystals. Diehl and co-workers have previously pointed out that in lyotropic liquid crystalline phases the NMR spectra of methanol showed constant and consistent results, whereas they showed anomalous results in thermotropic ones.[36] Our literature search also shows that the molecular structures determined in lyotropics are, in general, closer to the expected values than those determined in thermotropics. However, to our knowledge, these phenomena have not previously been systematically investigated.

For molecules of high symmetry (with C_3 or higher), the dipolar couplings between nuclei μ and ν in a solvent n can be expressed as[37]

$$D_{\mu\nu}^{(n)} = S^{(n)} g_{\mu\nu}(1 + p_{\mu\nu}^{h} + p_{\mu\nu}^{d(n)})$$

in which p^h, $p^{d(n)}$, and g denote a correction factor for harmonic vibration, another correction factor for the correlated deformation in a solvent n, and a function of the equilibrium molecular geometry, respectively. Applying this to the case of halomethane gives

$$\frac{D_{CH}}{D_{HH}} = \frac{g_{CH}}{g_{HH}}\left(\frac{1 + p_{CH}^{h} + p_{CH}^{d(n)}}{1 + p_{HH}^{h} + p_{HH}^{d(n)}}\right) = \frac{g_{CH}}{g_{HH}}\,\xi_{CH,HH}^{(n)}$$

where (g_{CH}/g_{HH}) is the "ideal" analytic expression with the equilibrium molecular geometry, and ξ is the empirical scaling factor required to get the correct molecular geometry. This scaling factor, ξ, contains all the information about solvent−solute interaction and other nonideality. Moreover, $p_{CH}^{d(n)}$ and $p_{HH}^{d(n)}$ have the terms inversely proportional to the order parameter, S, which contribute to the large $\Delta\xi$ and $\Delta\theta_a$ near $S = 0$. Our result in thermotropics agrees quite well with this theoretical framework.

However, the situation in weakly aligned lyotropics is quite different. Unlike the case of typical thermotropic liquid crystals, in these lyotropics, the spectral data do not need significant scaling to give correct molecular structures, even with the order parameter near 0. This also implies that the traditional vibration−rotation correlation theory cannot be used for these lyotropics. Currently, there is no established consensus about the structure and behavior of these lyotropics, even for the most widely used ones, such as the cetylpyridinium/hexanol/salt system.[21−23,38] The derivation of the scaling factor ξ to account for the apparent bond angle θ_a is predicated on a uniaxial molecular order tensor, i.e., a single order parameter. One possible explanation for the behavior of ξ and θ_a is a biaxial order tensor. In thermotropic solvents, the biaxial order tensor appears to be homogeneous in the solution; as the order decreases (by using different kinds of solvents or mixtures thereof), the biaxiality increases, and consequently, ξ and θ_a show more anomalous behavior. In lyotropic solvents, the biaxial order tensor appears to be the average of a biaxial component (induced by the vicinity of the dilute lyotropic molecules) and an isotropic component (characteristic of the water). Thus, the biaxiality and, consequently, ξ and θ_a remain constant as the order parameter decreases. In this case, the change of the composition of the lyotropic components modulates the overall order but not the biaxiality. These interesting differences between the two types of solvents are being investigated in ongoing studies.

Conclusion

We have shown that NMR spectra of oriented molecules exhibit entirely different behavior in thermotropic and lyotropic liquid crystalline phases. In thermotropic liquid crystalline solvents, the dipolar coupling data usually need significant scaling in order to obtain the correct molecular structures. Moreover, the spectral data need more scaling at low molecular ordering; this order dependence is common for different solutes and thermotropic liquid crystalline solvents. On the contrary, in weakly aligned lyotropics, no significant solvent effects are observed, regardless of the degree of molecular ordering. Comparisons of the different behaviors of small-molecule NMR spectra in thermotropic and lyotropic liquid crystals can provide an insight into the fundamental molecular properties of these systems.

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