# Nuclear Magnetic Resonance Spectra in Liquid Crystals and Molecular Structure

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High-resolution nuclear magnetic resonance (nmr) is now a familiar tool in the chemical laboratory. Recently a variant of this technique, characterized by the use of a nematic liquid crystalline solvent for the solute molecules to be studied, has gained importance. The spectra obtained by this technique are very different from those obtained in the conventional way. For instance, whereas the proton nmr spectrum of benzene in a solvent such as CCl_4 is a sharp singlet, the spectrum of benzene dissolved in the nematic liquid crystalline solvent 4,4'-di(n-hexyloxy)azoxybenzene (1) is complex,

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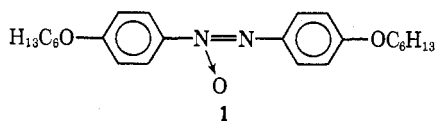
as shown in Figure 1. This difference results from the fact that in the liquid crystalline solvent the direct magnetic interactions between the nuclei become important. Determination of these interactions from the nmr spectrum provides quantitative information about the molecular geometry. The theory needed in interpreting an nmr spectrum in a liquid crystalline solvent in terms of molecular geometry is the principal concern of this Account.

The pioneering work on high-resolution nmr spectroscopy in liquid crystalline solvents is that of Saupe and Englert,[1] published in 1963. In subsequent years, this technique has been applied in determination of the structure and conformation of simple organic molecules in the liquid phase.[2,3] In its present state of development the technique has two major limitations: (a) for molecules containing more than seven or eight magnetic

nuclei, the nmr spectrum in a liquid crystalline solvent has so many lines that extensive overlap occurs, and theoretical interpretation becomes impractical; (b) the accuracy of the method is reduced by a failure to take molecular vibrations and pseudodipolar couplings into account. There are prospects that both difficulties can be met, at least in part, the first by an isotope substitution technique and the second by the development of suitable theoretical corrections. The present state of these developments will be outlined in this Account.

In the next section, an exposition of the principles on which the method is based is given. This is intended to serve both as an introduction for the nonspecialist and as an opportunity to formulate the basic assumptions underlying the method. It will be followed by a section giving the formal theory, a section on corrections for molecular vibrations and pseudodipolar interactions, and finally a section on results, specifically of the isotope substitution technique as applied to cyclohexane.

Principle of the Method

Basically the technique differs from ordinary high-resolution nmr only in that the compound studied is dissolved in a liquid which is in the nematic liquid crystalline phase. Compounds exhibiting a nematic phase consist in general of elongated, rod-shaped molecules. Much of the nmr work has been done with 4,4'-di(n-hexyloxy)azoxybenzene (1). This compound melts at about 80° to form the nematic phase, while a first-order transition from nematic to isotropic (normal) liquid occurs at 125°. Many other compounds exhibiting a nematic phase have been used in the nmr technique, including some that are nematic at room temperature. A list is given in ref 2.

The nematic phase is characterized by a high degree of long-range orientational order; that is, the long axes of the molecules tend to orient parallel to each other. As a consequence, the bulk properties of these materials are anisotropic; for instance, under the microscope they show double refraction of light (hence the term "liquid

(1) A. Saupe and G. Englert, *Phys. Rev. Lett.*, 11, 462 (1963).
(2) An excellent long review has recently been published: P. Diehl and C. L. Khetrapal in "NMR—Basic Principles and Progress," Vol. 1, P. Diehl, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, New York, N. Y., 1969. We refer to this article, as well as those in ref 3, for references to articles published up to 1969.
(3) (a) A. Saupe, *Angew. Chem., Int. Ed. Engl.*, 7, 107 (1968); (b) G. R. Luckhurst, *Quart. Rev., Chem. Soc.*, 22, 179 (1968); (c) S. Meiboom and L. C. Snyder, *Science*, 162, 1337 (1968); (d) A. D. Buckingham and K. A. McLauchlan, *Progr. NMR Spectrosc.*, 2, 63 (1967).
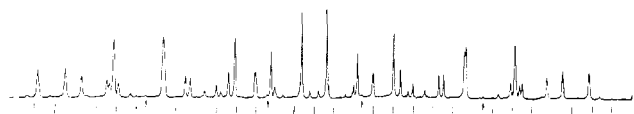
Figure 1. Spectrum of benzene dissolved in nematic 4,4'-di(*n*-hexyloxy)azoxybenzene. The arrows indicate lines due to molecules containing one ^{13}C nucleus. The markers below the trace are spaced by 100 Hz. Spectrometer frequency was 60 MHz and sample temperature 80°. The trace is a time average of 100 scans.

crystal"). In other respects, the microscopic picture of the nematic state can be thought of as quite similar to that of the normal (isotropic) liquid state. Specifically, the translational mobility of the molecules in the nematic phase is quite comparable to that in the normal liquid, and thus the nmr relaxation times are of similar magnitude in the nematic and normal liquids.

As a result of disturbing influences, such as caused by the presence of boundaries, temperature gradients, flow, etc., the direction of molecular orientation will not necessarily be uniform over a macroscopic sample. However, the presence of even a modest magnetic field will establish a uniform orientation. Even though the magnetic interaction energy of a single molecule is small compared to kT, the local orientational order is large enough for the magnetic field to effect orientation through the anisotropy of the magnetic susceptibility. The magnetic field present in an nmr spectrometer is more than sufficient to produce the necessary uniform orientation of the sample.

As already mentioned, the nmr spectrum of a solute molecule dissolved in a nematic liquid crystal is very different from that observed in a normal (isotropic) solvent. Figure 1 shows the proton spectrum of benzene dissolved in **1**. All the sharp lines are due to benzene; the liquid crystalline solvent gives much broader lines, which are not apparent at the sweep width of the figure. The key to the spectrum interpretation is in the orientation of the nematic solvent, which provides an anisotropic environment for the solute molecules. If the latter have lower than cubic symmetry, they too will be partially oriented. This fact has decisive consequences for the nmr spectrum.

We have become so used to the interpretation of high-resolution nmr spectra in terms of chemical shifts and indirect (electron-coupled) spin–spin couplings that we tend to forget that by far the strongest coupling between nuclear magnetic dipoles is through the direct dipolar interaction. The latter is simply the energy of each nuclear dipole in the magnetic field produced by the dipoles of other nearby nuclei. This interaction is of course dominant in the nmr spectra of solids, but in ordinary liquids its average value is zero. Because of the rapid tumbling of the molecules in a nonviscous liquid, one must average the dipolar interaction isotropically over all molecular orientations, with the well-known result of a zero value of the average interaction energy. In a nematic solvent, on the other hand, different molecular orientations are no longer equally

probable, and thus the average value of the dipolar interaction is no longer zero. In fact, for neighboring protons, a typical value for this coupling is of the order of a few kilohertz, and it is thus dominant in determining the character of the nmr spectrum.

It should be stressed that this nonzero average in nematic solvents applies only to the *intra*molecular interactions. As a result of the high molecular mobility mentioned above, the *inter*molecular interactions do average to zero, as in a normal liquid. This is in contrast to the situation in solids, where both the *intra*- and the *inter*molecular interactions are of importance. It is the presence of direct *intra*molecular interactions, combined with the absence of *inter*molecular interactions, that give the nematic-solvent nmr spectrum its unique properties.

The basis for the interpretation of the nematic-solvent nmr spectrum in terms of a molecular structure will now be outlined. A more formal treatment will be given in the next section.

The interpretation of ordinary high-resolution nmr spectra in terms of a spin Hamiltonian containing chemical shifts and indirect spin–spin interactions as parameters is well known. The same approach is used for nematic solvent spectra, except that a suitable additional term, accounting for the direct dipolar interaction, is added. This term contains parameters D_{ij}^{dir}, characterizing the magnitude of the direct interaction between the ith and jth nuclei in a molecule. The D_{ij}^{dir}, as well as the chemical shifts and indirect interactions, are determined from the experimental spectra. In the simplest cases, involving only a few magnetic nuclei, closed formulas are available, but in most cases a trial and error method, using computer diagonalization of the Hamiltonian, is required.

It should be pointed out in passing that some of the familiar features of interpretation of high-resolution spectra, such as the multiplet rules and the rule to the effect that the indirect spin–spin coupling is not effective for equivalent nuclei, are a result of the particular (scalar) form of the indirect coupling. These rules do not apply to the direct dipolar coupling. The benzene spectrum in Figure 1 contains many lines, though all the protons are equivalent. Also, no simple rules to replace the multiplet rules seem to exist for an intuitive qualitative understanding of the spectra.

Once the dipolar coupling constants, D_{ij}^{dir}, have been obtained, they can be related to the geometry of the molecule. The D_{ij}^{dir} measure the direct magnetic interaction between two nuclear dipoles and can thus be calculated from simple magnetostatics. (This is in contrast to the indirect spin–spin couplings, a calculation of which involves a knowledge of the electronic wave functions.) There is, however, a fly in the ointment: the D_{ij}^{dir} do not measure a static interaction, but rather a weighted average over the tumbling movement of the molecule. As explained in the next section, this averaging process can be characterized by one to five orientational parameters (the actual number depending on the symmetry of the molecule). It turns

out that the ratio of these parameters can be obtained from the observed nmr spectrum, but not their absolute values. Accordingly, one can determine the shape of a molecule, but not its absolute size. In practice, one adopts one suitable internuclear distance, obtained by another method or an educated guess, in order to obtain a complete structure.

We shall terminate this section with a general discussion of the limits of applicability of the method. First, the method, as described, is applicable to determine the positions of nuclei with spin $1/2$ only. Nuclei with larger spin exhibit a large quadrupolar interaction. Although this effect can give interesting information on electric field gradients in the molecule,[4,5] a discussion of this aspect is outside the scope of this review.

Most of the work has been done on proton spectroscopy, although ^{19}F spectra have also been studied. The position of carbon nuclei, relative to hydrogen, has been studied from the $^{13}C-^1H$ coupling in proton spectra.

For a successful structure determination, the molecule must contain neither too few nor too many magnetic nuclei. Obviously, the number of parameters describing the geometry of the molecule, plus the number of orientational parameters required, must be smaller than the number of measured D_{ij}^{dir}. This will not be the case in molecules containing only a few magnetic nuclei. On the other hand, the number of lines in the spectrum increases rapidly with the number of magnetic nuclei, and one soon reaches a point where extensive overlap of lines occurs and interpretation becomes impossible. Organic molecules for which a structural interpretation has been made have between four and nine magnetic nuclei. There is hope that deuterium substitution will extend the applicability to larger molecules. Preliminary results of such a study in cyclohexane (12 protons) will be presented in the last section.

Theory

It will be assumed that the reader is familiar with the interpretation of regular high-resolution nmr spectra in terms of a spin Hamiltonian containing chemical shifts and indirect spin–spin couplings as parameters. This approach can easily be generalized to include dipolar interactions as well. The general form of the high-field spin Hamiltonian in frequency units for a set of interacting nuclei of spin $1/2$ is given by eq 1.[6,7]

Here γ_i is the magnetogyric ratio of the ith nucleus, σ_i is its shielding constant, H_z is the applied magnetic field, and I_{xi}, I_{yi}, I_{zi} are the components of the angular

$$\mathcal{H} = -\frac{1}{2\pi} \sum_i \gamma_i (1 - \sigma_i) H_z I_{zi} +$$
$$\sum_{i>j} J_{ij}(I_{xi}I_{xj} + I_{yi}I_{yj} + I_{zi}I_{zj}) +$$
$$\sum_{i>j} D_{ij}(-1/2 I_{xi}I_{xj} - 1/2 I_{yi}I_{yj} + I_{zi}I_{zj}) +$$
$$\sum_{i>j} G_{ij}(I_{xi}I_{yj} - I_{yi}I_{xj}) \quad (1)$$

momentum operator of the ith nucleus. The parameters J_{ij}, D_{ij}, and G_{ij} characterize the interactions between nuclei i and j.

In Hamiltonian 1 the first term represents the Zeeman energy, while the other three terms represent the interaction energy. The separation into three terms is convenient. If the average environment of the nuclei has cylindrical symmetry about the applied magnetic field direction, then the parameters G_{ij} must vanish because that term of the Hamiltonian is odd upon reflection of the nuclear moments in any plane parallel to the applied field. This is the case in nematic and isotropic solvents. The first interaction term, containing J_{ij}, is scalar, which implies that it is invariant for coordinate rotations. Only the indirect coupling contributes to this term; the direct magnetic dipolar coupling has a zero isotropic average, and thus cannot contribute to a scalar term. The remaining term, with D_{ij} as coefficients, is the only one containing the direct magnetic dipolar coupling and is thus the one of primary interest here. Unfortunately, one cannot equate this term rigorously with the direct coupling: the indirect coupling is, in general, a tensor quantity and its anisotropic part will make a contribution of exactly the same form as the direct coupling.[6]

One must, therefore, write

$$D_{ij} = D_{ij}^{dir} + D_{ij}^{ind} \quad (2)$$

The D_{ij}^{ind} is also referred to as the pseudodipolar coupling. Since the spectrum interpretation gives the D_{ij}, while a molecular structure interpretation is based on the D_{ij}^{dir}, some estimate of the D_{ij}^{ind} is required. Theoretical estimates indicate that D_{ij}^{ind} is very small relative to D_{ij}^{dir} for H–H and C–H interactions.[8,9] Experimental results as to their magnitude will be discussed in the next section.

The direct dipolar coupling is related to the geometry of the molecule by[6]

$$D_{ij}^{dir} = K_{ij} \langle (1 - 3 \cos^2 \Theta_{ij}) r_{ij}^{-3} \rangle_{av} \quad (3)$$

where $K_{ij} = [1/(2\pi)]\gamma_i\gamma_j\hbar$. Here the distance between nuclei i and j is r_{ij}, and Θ_{ij} is the angle between a vector from nuclei i to j and the applied-field direction. If distances are specified in ångströms, then for a pair of protons $K_{ij} = 120.067$ Hz Å^3. The angular brackets indicate an average taken over all the molecular mo-

(4) J. C. Rowell, W. D. Phillips, L. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).

(5) W. J. Caspary, F. Millett, M. Reichbach, and B. P. Dailey, *ibid.*, **51**, 623 (1969).

(6) (a) A. D. Buckingham and J. A. Pople, *Trans. Faraday Soc.*, **59**, 2421 (1963); (b) A. Saupe, *Z. Naturforsch. A*, **19**, 161 (1964); (c) L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).

(7) The restriction to spin $1/2$ is made because for nuclei of larger spin an electric quadrupolar term must be added. While this is zero in an isotropic solvent, it is often dominant in an anistropic one. See ref 4 and 5.

(8) A. D. Buckingham and I. Love, *J. Mag. Resonance*, **2**, 338 (1970).

(9) (a) M. Barfield, *Chem. Phys. Lett.*, **4**, 518 (1970); (b) H. Nakatsuji, H. Kato, I. Morishima, and T. Yonezawa, *ibid.*, **4**, 607 (1970).

tions. These include vibrations as well as the anisotropic tumbling of the molecule in the liquid crystalline solvent.

In the derivation of the expressions which follow, it has been assumed that the molecular equilibrium geometry and vibrations, as well as the indirect couplings, are independent of the orientation of the solute molecule relative to the optical axis of the liquid crystal. To relate $D_{ij}{}^{\text{dir}}$, $D_{ij}{}^{\text{ind}}$, and σ_i to the anisotropic motion of a molecule in a liquid crystalline solvent, we employ the function $P(\theta,\Phi)$, defined as the probability per unit solid angle of a molecular orientation specified by the angles θ and Φ, the polar coordinates of the applied magnetic field direction relative to a molecule-fixed Cartesian coordinate system.

We expand $P(\theta,\Phi)$ in real spherical harmonics (eq 4).

$$P(\theta,\Phi) = (1/4\pi) + c_x P_x + c_y P_y + c_z P_z +$$
$$c_{3z^2-r^2}D_{3z^2-r^2} + c_{x^2-y^2}D_{x^2-y^2} + c_{xz}D_{xz} +$$
$$c_{yz}D_{yz} + c_{xy}D_{xy} \dots \quad (4)$$

The P spherical harmonics have been included for generality. In the absence of an electric field, they will vanish in liquid-crystal solvents.

If a molecule is symmetrical, one can choose a molecule-fixed coordinate system in which a minimum number of D spherical harmonics contribute to expansion 4. For example, if the molecule has a threefold or higher axis of symmetry, the choice of this axis as the z axis causes only $c_{3z^2-r^2}$ to be nonzero. If a molecule has two perpendicular planes of symmetry, then taking the z axis parallel to both, the x axis in one plane and the y axis in the other, causes only $c_{3z^2-r^2}$ and $c_{x^2-y^2}$ to be nonzero.

It may be shown that the coefficients in the expansion of $P(\theta,\Phi)$ are closely related to the elements of the order matrix defined by Saupe.[6b]

Written explicitly, the average of eq 3 becomes eq 5.

$$\langle (1 - 3\cos^2\Theta_{ij})r_{ij}{}^{-3}\rangle_{\text{av}} = \iint P(\theta,\Phi)(1 - 3\cos^2\Theta) \times$$
$$r_{ij}{}^{-3}P(q_1 \dots q_n)\mathrm{d}\theta\mathrm{d}\Phi\mathrm{d}q_1 \dots \mathrm{d}q_n \quad (5)$$

Here the coordinates q_k describe the internal molecular motions as displacements from the equilibrium geometry, and $P(q_1 \dots q_n)$ is the configurational probability density.

If we disregard the vibrations by setting the configurational probability density equal to a δ function for the equilibrium geometry, the integration of eq 5 gives the equilibrium value for the direct interaction, $(D_{ij}{}^{\text{dir}})^{\text{e}}$, expressed explicitly in terms of the internuclear distances

$$(D_{ij}{}^{\text{dir}})^{\text{e}} = -K_{ij}5^{-1/2}[c_{3z^2-r^2}(2z_{ij}{}^2 - x_{ij}{}^2 - y_{ij}{}^2)r_{ij}{}^{-5} +$$
$$c_{x^2-y^2}\sqrt{3}(x_{ij}{}^2 - y_{ij}{}^2)r_{ij}{}^{-5} + c_{xz}2\sqrt{3}(x_{ij}z_{ij})r_{ij}{}^{-5} +$$
$$c_{yz}2\sqrt{3}(y_{ij}z_{ij})r_{ij}{}^{-5} + c_{xy}2\sqrt{3}(x_{ij}y_{ij})r_{ij}{}^{-5}] \quad (6)$$

Here $z_{ij} = z_i - z_j$, $x_{ij} = x_i - x_j$, and $y_{ij} = y_i - y_j$, where x_i, y_i, and z_i are the coordinates of the ith nucleus in the molecule-fixed system in the equilibrium geometry.

We should note that the motional constants c and the nuclear coordinates always enter eq 6 in products of the first power in c and the inverse third power of the coordinates. For this reason only ratios of nuclear coordinates can be determined by analysis of nmr spectra in anisotropic media. A linear expansion or contraction of an assumed molecular geometry, with a compensating change in the orientational constants, will leave the $D_{ij}{}^{\text{dir}}$ unchanged.

To take account of vibrations we have to replace the above expression by the average

$$D_{ij}{}^{\text{dir}} = \int D_{ij}{}^{\text{dir}}(q_1 \dots q_n)P(q_1 \dots q_n)\mathrm{d}q_1 \dots \mathrm{d}q_n \quad (7)$$

Here $D_{ij}{}^{\text{dir}}(q_1 \dots q_n)$ are the direct dipolar interactions for the molecular configuration specified by $q_1 \dots q_n$.

The pseudodipolar contribution expressed in terms of the components of the indirect coupling tensor is

$$D_{ij}{}^{\text{ind}} = \frac{1}{\sqrt{15}}[c_{3z^2-r^2}(2J_{zzij} - J_{xxij} - J_{yyij}) +$$
$$c_{x^2-y^2}(J_{xxij} - J_{yyij}) + c_{xz}(J_{xzij} + J_{zxij}) +$$
$$c_{yz}(J_{yzij} + J_{zyij}) + c_{xy}(J_{xyij} + J_{yxij})] \quad (8)$$

The magnitude of these interactions is of current interest. We will note experimental evidence on their importance in the next section.

The Effect of Vibrations and Pseudodipolar Coupling

The problem of correcting for molecular vibrations consists in principle of the evaluation of the integrals given in eq 7. This could be done in terms of normal coordinates, but these are rarely available for molecules of interest. Moreover, as will be shown, anharmonicity of the vibrations gives an important contribution. It is therefore appropriate to explore whether simplified models can be found which give reasonable estimates of the vibrational corrections.

A very simple model is obtained if one takes into account only the vibrations of the hydrogen atoms and neglects those of heavier ones. As a compound of accurately known molecular geometry on which to test the adequacy of this approach, we have chosen benzene. The model assumes that only C–H bond stretching and bending is important. The hydrogen is considered to vibrate and oscillate against an infinitely massive and rigid carbon framework. As coordinates we take Δr, $\alpha_{\parallel}$, and $\alpha_{\perp}$, which represent, respectively, the stretching of the C–H bond, its bending in the plane of the ring, and its bending perpendicular to that plane.

To evaluate eq 7, $D_{ij}(q_1 \dots q_n)$ is expanded in a Taylor series about the equilibrium geometry, neglecting terms higher than quadratic. Assuming that motions in the coordinates adopted are independent of each other, cross terms can be neglected and one obtains eq 9.

$$D_{ij} = D_{ij}{}^{\text{e}} + \sum_k \left(\frac{\partial D_{ij}}{\partial q_k}\right)^{\text{e}} \overline{q_k} + \frac{1}{2}\sum_k \left(\frac{\partial^2 D_{ij}}{\partial q_k{}^2}\right)^{\text{e}} \overline{q_k{}^2} \quad (9)$$

The derivatives of the direct coupling parameters at the equilibrium configuration can easily be evaluated

numerically. The mean-square amplitudes are computed for a harmonic oscillator of $\frac{1}{2}h\nu$ energy. Using a mean C–H stretching frequency of 3066 cm^{-1} for benzene,[10] one calculates a root-mean-square amplitude of the C–H stretch $(\overline{\Delta r^2})^{1/2} = 0.074$ Å. Similarly the mean in-plane bending frequency of 1136 cm^{-1} and a 1.08-Å bond length gives $(\overline{\alpha_\parallel^2})^{1/2} = 6.44°$. The mean out-of-plane bending frequency of 760 cm^{-1} gives $(\overline{\alpha_\perp^2})^{1/2} = 7.87°$. The C–H bond is anharmonic with a mean extension from the equilibrium length of $\overline{\Delta r} = 0.01$ Å.[11,12]

Using these numbers, the fractional changes in the direct coupling parameters due to vibrations, $(D_{ij} - D_{ij}{}^e)/D_{ij}{}^e$, were computed from eq 9. The contributions of the individual terms of this equation are summarized in Table I. We note that the entries in Table I are sums for the motions of the hydrogen atoms involved in the D_{ij} calculated.

Our main conclusion is that the vibrational effect on the C–H dipolar interaction is far greater than for the proton–proton interactions. D_{CH} is reduced $\sim$5.5% relative to H–H interactions. An interpretation without corrections for vibrations will thus produce a C–H bond length 1.8% too large relative to the H–H distances. Carefully measured nmr spectra of benzene containing carbon-13 in natural abundance have satellite proton resonances due to molecules containing one ^{13}C nucleus. Agreement between calculated and observed positions of these lines is obtained if a C–H bond length, in terms of H–H distance, is adopted which is 2.5% larger than the accepted value of benzene. This is in rough agreement with the figure of 1.8% derived above. For protons the same spectra show D_{ortho} to be 0.5% smaller relative to D_{para} than expected for a rigid hexagon. Table I predicts a 0.4% reduction, in good agreement with measurements. We conclude that the main effects of vibrations in benzene are fairly well described by our model. It is not clear whether or not an appreciable pseudodipolar contribution is present for the C–H interaction, because of uncertainty in the large vibrational effect.

A similar analysis for hexafluorobenzene[13] indicates that a pseudodipolar interaction is required for F–F couplings. The observed ratio of the ortho:para dipolar interactions is 6.5% less than for a rigid hexagon, and the meta:para ratio is 9% less. These fractional changes are far greater than can be attributed to vibrations, for these should be smaller than in benzene.

Krugh and Bernheim[14] have analyzed the spectrum of CH$_3$F and concluded that a pseudodipolar contribution is important. However, no adequate account of vibrations was given, and our calculations suggest that

Table I
Computed Fractional Changes of D_{ij} in Benzene Due to Vibrations

Interaction	Contributions				
	$\overline{\Delta r}$	$\overline{\Delta r^2}$	$\overline{\alpha_\parallel}^2$	$\overline{\alpha_\perp}^2$	Total
D_{CH}	−0.028	+0.029	0	−0.056	−0.055
D_{ortho}	−0.012	+0.001	+0.028	−0.020	−0.003
D_{meta}	−0.012	+0.002	+0.009	+0.002	+0.001
D_{para}	−0.012	+0.003	+0.006	+0.004	+0.001

the use of an electron diffraction geometry different from the one adopted by these authors could well account for the observed discrepancy.

Recently, Gerritsen and MacLean[15] have used a different approach in trying to estimate the importance of pseudodipolar interactions. They studied 1,2-difluorobenzene in a number of different liquid crystalline solvents. It was found that, although the ratio of the orientational parameters, $c_{3z^2-r^2}/c_{x^2-y^2}$, varied over nearly a factor of two, the same molecular geometry could account for the spectra in different solvents. They note that the direct and pseudodipolar couplings, given by eq 6 and 8, respectively, would be expected to vary in a different manner with orientational parameters. From this they conclude that the pseudodipolar F–F coupling appears to be very small in this case.

From the scarce and partially contradictory evidence available, we tentatively conclude that the pseudodipolar interaction is negligible for H–H couplings, small or negligible for C–H couplings, and probably important for F–F couplings.

Applications

We refer to ref 2 and 3 for a review of compounds which have been investigated by nematic solvent nmr. Here we shall summarize results for two compounds only: (1) bicyclobutane, which provides a good example of the kind of structural information obtainable and illustrates the complexity of the nematic-solvent nmr spectrum even for a relatively simple compound containing six protons; (2) cyclohexane, which with 12 protons gives, for practical purposes, an uninterpretable nmr spectrum and illustrates the great simplification resulting from partial deuteration.

Bicyclobutane. The experimental spectrum of this compound is shown in the lower trace of Figure 2. The upper trace is a computer simulation of the spectrum, obtained by diagonalization of the Hamiltonian, with values of the coupling and orientational parameters adjusted for optimum fit between calculated and experimental line positions. A Lorentzian line shape with a width at half-height of 4 Hz has been assumed.

The spectrum evident in Figure 2 is due to molecules having only nonmagnetic ^{12}C nuclei. Superposed on it is a much weaker and even more complex spectrum due to molecules containing one ^{13}C nucleus (this isotope has a spin of $^1/_2$ and is present at 1% natural abundance). This spectrum is somewhat wider than that

(10) G. Hertzberg, "Molecular Spectra and Molecular Structure II," Van Nostrand, New York, N. Y., 1945.

(11) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1954, Table 11.5.

(12) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Elsevier, Amsterdam, 1968, Chapter 10.

(13) L. C. Snyder and E. W. Anderson, J. Chem. Phys., 42, 3336 (1965).

(14) T. R. Krugh and R. A. Bernheim, ibid., 52, 4942 (1970).

(15) J. Gerritsen and C. MacLean, Abstracts, Third International Liquid Crystal Conference, Berlin, Aug 1970.

Table II

Structure of Bicyclobutane, as Determined by Nmr, Electron Diffraction, and Microwave Spectroscopy

Method	Angle, deg^a				Distance, Å^a				
	α	β	γ	δ	C1–C2	C2–C3	C1–H2	C2–H4	C2–H6
Nmr	120.2	110.2	128.0	126.3	(1.507)^b	1.507	1.167	1.194	1.142
Electron diffraction^c	122.8	116.0	125.5	~122	1.507	1.502	~1.106	~1.106	1.108
Microwave^d	122° 40′	115° 34′	128° 22′	121° 34′	1.498	1.497	1.093	1.093	1.071

^{a} See Figure 3. ^{b} Electron diffraction result. ^{c} Reference 16. ^{d} Reference 17.
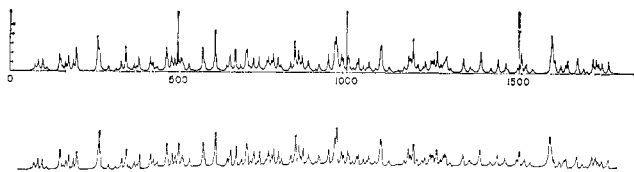

Figure 2. Spectrum of bicyclobutane. The top spectrum is a computer simulation, calculated from an optimum set of coupling parameters. The bottom trace is an observed spectrum. The frequency scale is in hertz. Experimental conditions as for Figure 1.
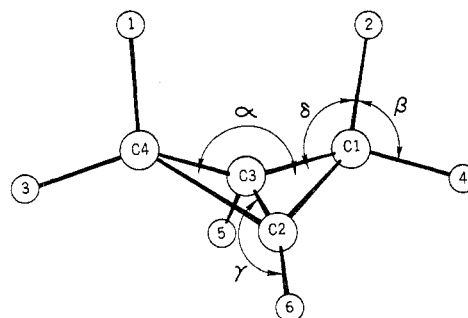

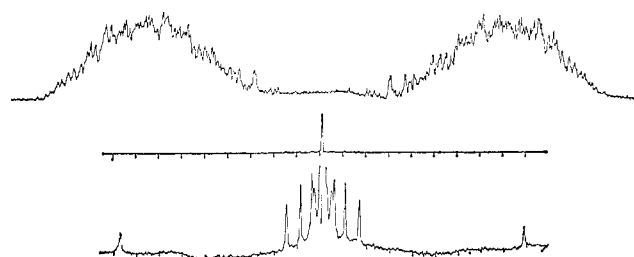Figure 3. Molecular model of bicyclobutane showing the notation used for Table II.

Figure 4. The upper trace is the spectrum of regular cyclohexane. The center and bottom traces both show the spectrum of cyclohexane-d_{11} with 98% deuterium abundance. The bottom trace has been recorded with its y scale magnified by a factor of 32 relative to that of the center trace. The short downward lines on the center and bottom traces are frequency markers, spaced 100 Hz apart; they also apply to the upper trace. The spectrometer frequency was 100 MHz, the nematic solvent 4,4′-di(n-hexyloxy)azoxybenzene, and the temperature 102°. The sample used in recording the upper trace had somewhat higher solute concentration than that used in the lower traces, with resulting lower orientation and spectral width. The top trace is the average of 50 scans, the lower traces of about 1000 scans.

due to ^{12}C-only molecules, and although most of its lines are masked by the stronger spectrum, a few that are beyond the outermost lines of the strong spectrum can be detected by extensive signal averaging. From the positions of these lines, carbon–proton coupling parameters can be determined.

Interpretation of the dipolar coupling parameters in terms of molecular geometry results in the numbers given in Table II. The notation used in this table is defined in Figure 3. For comparison, the results of structure determinations by electron diffraction[16] and by microwave spectroscopy[17] are also given in the table. As mentioned previously, only ratios of internuclear distances, rather than absolute values, can be determined by the nmr method. Accordingly, the C1–C2 distance of the electron diffraction results has been adopted, as indicated by parentheses in the table.

At the time of this writing we have not attempted to correct for vibrations, and the results given in Table II should not be considered as final.

Cyclohexane. The upper trace in Figure 4 shows the nematic-solvent nmr spectrum of cyclohexane. Overlap of lines in this spectrum is so extensive that an amorphous background appears, with only the peaks of the stronger lines sticking out. A detailed interpretation of this spectrum is clearly impossible. A way out is to reduce the number of magnetic nuclei involved by partial isotopic substitution. In the case of hydrogen, the deuteron is the only practical replacement for the proton. It has spin 1, and decoupling by means of strong radio-frequency irradiation at the deuteron frequency is necessary. In the nematic solvent this cannot be achieved by conventional methods, because the deuteron resonance exhibits a major splitting into two peaks, separated by a few kilohertz, due to the interaction of

the nuclear electric quadrupole with the electric field gradient in the molecule.[4,5] However, it was found that decoupling can be achieved by irradiation at the exact center frequency of the two lines to induce double quantum transitions.[18] The center and bottom traces in Figure 4 show the proton spectrum of cyclohexane-d_{11} obtained in this way. The material used had an isotopic abundance of about 98% deuterium. Thus about 78% of the molecules have one proton, about 20% a pair of protons, and the remaining 2% three or more protons. It is generally accepted that cyclohexane inverts rapidly between chair forms at the temperature used in the experiment (102°). This implies that the protons alternate rapidly between axial and equatorial positions and that the nmr frequencies must be averaged

(16) O. Bastiansen, private communication.
(17) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, J. Chem. Phys., 50, 1976 (1969).
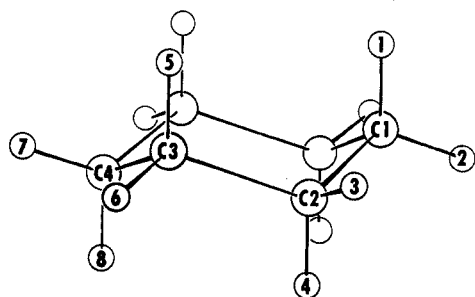
(18) S. Meiboom and R. C. Hewitt, to be published.

Figure 5. Molecular model of cyclohexane showing the notation used in Table III.

Table III
Experimental and Theoretical Proton nmr of Cyclohexane-$d_{10,11}$

Lines	Spacing, Hz	
	Experimental[a]	Theoretical[b]
(1,2)	1798.9 ± 5	(+1798.9)
(1,C1)	871.8 ± 2	+998.4[c]
(1,5)	326.3 ± 2	−392.9
(1,3)	200.0 ± 2	−169.2
(1,7)	99.7 ± 2	−107.4
(1,6)	98.1 ± 2	−107.0
(1,4)	78.4 ± 2	−88.1
(1,C3)	33.9 ± 1	−42.1
(1,C2)		−28.1
(1,C4)	20.0 ± 1	−21.2
(1,8)	16.0 ± 1	−8.8

[a] Experimental spacings at 102° in 4,4'-di-n-hexyloxyazoxybenzene. [b] Theoretical spacings are computed for rapidly interconverting chair forms with tetrahedral bond angles at the carbon and $r_{CH}/r_{CC} = 0.714$. The motional constant is scaled to make the (1,2) line coincident with experiment. [c] Equals the sum of D_{CH} of 875.4 and J_{CH} of 123 Hz (J. H. Goldstein and G. S. Reddy, J. Chem. Phys., **36**, 2644 (1962)). The other indirect couplings have been neglected.

accordingly. On this model, one expects a single strong peak from the molecules containing one proton and a symmetrical pair of lines for each molecular species

containing two protons. There are seven such species, which we shall denote by (1,2), (1,3), ... (1,8), the numbers referring to the positions of the protons according to the numbering in Figure 5. The center trace in Figure 4 shows the strong single line due to molecules containing one proton. The bottom trace, which gives the spectrum at higher sensitivity, shows the symmetrical pairs of lines due to species with proton pairs. In traces with an expanded frequency scale, not reproduced here, additional lines near the center, as well as lines due to molecules containing one ^{13}C nucleus, can be identified. The first two columns of Table III give the observed frequency spacing for each line pair and their assignment. In the third column of this table are theoretical spacings, calculated on the assumption of tetrahedral bond angles at the carbon and a ratio of C–H to C–C distances of 0.714. The agreement between experimental and calculated line positions is sufficiently good to indicate that this simple model is not far from the actual structure. A detailed quantitative interpretation is at present in progress.

Conclusion

Up to now molecular structure determination from nematic-solvent nmr has been restricted to very simple molecules. We believe, however, that the technique of deuterium substitution may extend its usefulness significantly. One can even envision that quite complicated compounds of special interest could be studied by preparing a number of deuterated species, each with a proton at a different specific site. In this way a large amount of structural information could be obtained, though the labor involved would be far from trivial. Fourier transform nmr spectroscopy, which is rapidly evolving at this time, can be expected to provide the improvement in sensitivity which would be required for such a project.
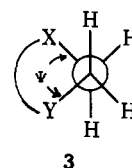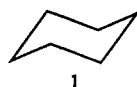
Structural Chemistry in Solution.   The R Value

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Six-membered rings that lack endocyclic double bonds are not restricted in conformation to the classic tetrahedral[1] chair (**1**) and twist-boat (**2**) forms. By

1   **2**

appropriate choice of substituent or heteroatom, internal dihedral (torsional) angles (Ψ), defined in structure

(1) H. Sachse, *Ber.*, **23**, 1363 (1890).

3

3, may range from 70° down to 45° within the basic chair form and even lower in boat and intermediate forms. For cyclohexane, Ψ is about 56° all around the ring;[2] for the puckered 1,4-dithiane **4**, the S–C–C–S tor-