# Multiple-Quantum NMR Spectra of Partially Oriented Indene: A New Approach to Estimating Order in a Nematic Phase

Leslie D. Field,*,[1] Saadallah A. Ramadan,* and Gregory K. Pierens†

*School of Chemistry, University of Sydney, Sydney, New South Wales 2006, Australia; and †AstraZeneca R&D Griffith University,
Mount Gravatt Research Park, Nathan, Queensland 4111, Australia

Multiple-quantum proton NMR spectra of the 8-spin system of indene partially oriented in a nematic mesophase were acquired using a magnetic field gradient (MFG) method. Six-, seven- and eight-quantum spectra were solved to yield all intramolecular dipolar couplings ($D_{ij}$) which were used to determine the molecular shape. The spectral widths of multiple-quantum spectra are dependent on molecular orientation and geometry and a novel method was developed to estimate the Saupe order parameters from the observed spectral widths of the high-order multiple-quantum spectra. © 2002 Elsevier Science (USA)

*Key Words*: multiple-quantum NMR; liquid crystal solvent; magnetic field gradient; dipolar coupling; order parameters.

## 1. INTRODUCTION

NMR spectra of compounds partially oriented in a nematogen provide a unique type of structural information that other methods cannot provide (*1*). The rod-like molecules of liquid crystal align so that the axis of minimum magnetic susceptibility is parallel to the applied magnetic field (*2*). As a result of the solvent alignment, partial alignment is imposed on the solute molecules dissolved in the liquid crystalline solvent and consequently intramolecular dipole–dipole couplings ($D_{ij}$) within the solute molecules are not averaged to zero and complex spectra are observed even for relatively simple spin systems. Solute molecules are sufficiently mobile in the anisotropic phase to average solute–solvent and solute–solute intermolecular dipole–dipole interactions to zero. The $^1$H NMR spectrum of the neat liquid crystal is typically observed as a few relatively featureless broad humps. Single-quantum NMR spectra of solutes dissolved in liquid crystalline solvents exhibit relatively sharp and well resolved lines; however, single-quantum spectra of all but the simplest spin systems are complex and, in most cases, solving the single-quantum spectrum is a challenge.

Multiple-quantum (MQ) NMR spectra (*3–8*) afford the same type of spectral information as the single-quantum spectrum but the spectra are far less complex. MQ spectra contain many

fewer transitions than conventional single-quantum spectra, and this greatly simplifies assignment of spectral lines and spectral analysis. Generally, in an *n*-spin system of spin-1/2 nuclei, the ($n - 1$)- and ($n - 2$)-quantum spectra contain sufficient transitions to determine order parameters, dipolar couplings, and the chemical shifts. The *n*-quantum spectrum of an *n*-spin system of spin-1/2 nuclei consists of a single resonance whose chemical shift is the algebraic sum of the chemical shifts of the *n* nuclei. The number of transitions in the *m*-quantum spectrum of an *n*-spin system (of spin-1/2 nuclei) with no simplifying symmetry can be calculated using (*9*)

$$\text{number of transitions} = (2n!)/[(n - m)!(n + m)!]. \quad [1]$$

When *m* is 1 (i.e., for a single-quantum spectrum) there would be 11,440 transitions in an 8-spin system. There would be 120 and 16 transitions in the 6-, and 7-quantum spectra, respectively. The presence of symmetry in the spin system decreases the number of transitions by increasing transition degeneracy.

In obtaining the dipolar couplings from the spin system of any molecule aligned in nematic solution by an iterative analysis of spectra, the initial stages involve obtaining reasonable estimates of chemical shifts of the nuclei and an estimate of molecular alignment. In this paper we describe a method by which the molecular order parameters can be estimated from high-order MQ spectra and the chemical shifts can be estimated from the *n*− and *n* − 1 quantum spectra. The MQ spectra of the 8-spin system of indene are analysed as an illustrative example.

## 2. CALCULATED MQ SPECTRA

MULTQ is a simulative and iterative computer program that was developed originally by Field and Pierens (*8*). MULTQ, which is based on the iterative NMR analysis program UEA (*10*), digests dipolar couplings, scalar couplings, and chemical shifts and calculates the energy levels and sorts them according to their Zeeman quantum number ($\Delta M$) and irreducible symmetry representation. Only energy levels relevant to the required MQ order(s) are considered in the calculation and this dramatically reduces computational time. MULTQ alternatively accepts the

approximate atomic coordinates, scalar couplings, order parameters, and chemical shifts as input data and simulates MQ spectra according to these values. The program iteratively fits chemical shifts and dipolar couplings until the transition frequencies in the simulated spectra match those in the experimental spectra.

## 3. THE SPECTRA OF INDENE ALIGNED IN NEMATIC SOLUTION

Indene is a bicyclic, semirigid molecule (*11*) containing 8 protons. The aromatic ring of the molecule is flat and the fused 5-membered ring is puckered but there is very low barrier to inversion so the system can be regarded as a planar with protons 7 and 8 symmetrically disposed above and below the plane. The spin system has $C_s$ symmetry and there are 22 independent dipolar couplings between the protons.
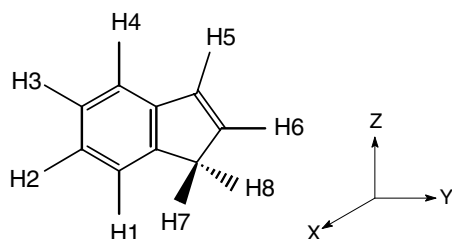


A sample of indene was purified by distillation and a solution (15% w/w) in nematic liquid crystal (Merck 11865, ZLI-1083) (*12*) was prepared and gave the $^1$H spectrum (600 MHz) shown in Fig. 1. A one-dimensional single-quantum $^1$H spectrum of partially oriented indene in a nematic mesophase (*13*) has been analyzed previously.
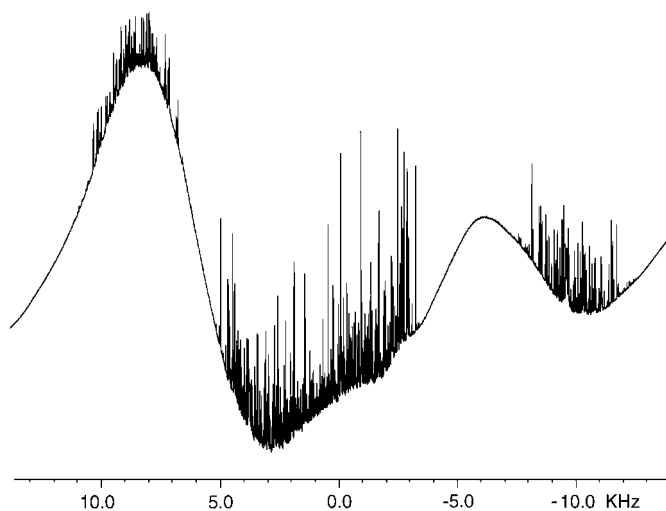


**FIG. 1.** The 1Q $^1$H spectrum of indene partially aligned in a liquid crystalline solvent (814 scans with 2 s between scans and 32K data points acquired; 600 MHz at 295K).
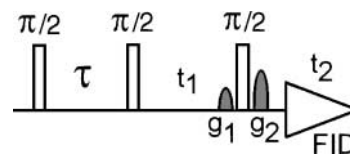


**FIG. 2.** Typical MQ gradient enhanced pulse sequence. ($\pi/2$) are 90° RF pulses (with equal and constant phase), $\tau = 20$ ms, MFG pulse = 1 ms, while $g_1$ and $g_2$ are magnetic field gradients, with $g_2 = ng_1$ for selection of the selected coherence order, $n$.

## 4. MULTIPLE-QUANTUM SPECTRA

The 6Q, 7Q, and 8Q nonrefocussed spectra were acquired at 290K using the gradient-assisted pulse sequence (Fig. 2) (*14*). With this sequence, the desired order of coherence, $n$, is selected by the ratio of the gradients $g_1$ and $g_2$, where $g_2/g_1 = n$. The maximum field gradient was 53 Gauss cm$^{-1}$ and $g_1$ and $g_2$ were expressed as percentage ratios of the maximum field gradient with a duration of 1 ms and a sine gradient shape. The preparation period, $\tau$, was set to 20 ms, and typically FIDs of 1K data points were acquired. Spectra were processed with 1K points in $F_2$ and 4K points (zero-filled) in $F_1$. The data were weighted with a sine-bell weighting function prior to two-dimensional transformation. Magnitude spectra were calculated and the multiple-quantum spectra obtained as $F_1$ sum projections of the 2D data set (*8*), with an average linewidth of approximately 45 Hz.

## 5. CHEMICAL SHIFT DETERMINATION

The 8Q spectrum of indene is a singlet resonance whose frequency is the sum of the shift of the 8 spins in the spin system. The 7-quantum spectrum of indene consists of 7 doublets, and each doublet is centered approximately at the sum of chemical shifts of the protons that contribute to the coherence. The identity of which transitions mate to each other to form the doublets in the 7Q spectrum was confirmed in a shift refocussed experiment (*15*) where the 7-doublets in the 7Q spectrum are all centred about 0 Hz. In the refocused spectrum, the peak separation for each doublet can be measured easily and accurately and this separation uniquely identifies the doublets in the nonrefocussed spectra (Fig. 3).
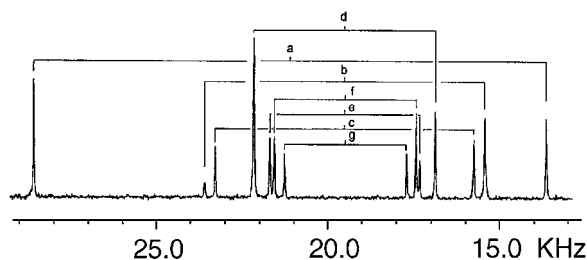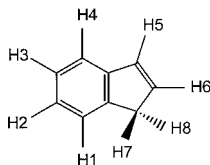


**FIG. 3.** The 7Q $^1$H spectrum of indene partially aligned in a liquid crystalline solvent (pulse sequence given in Fig. 2).

| Chemical shift (Hz)[a] | Assignment |
|---|---|
| 3259 | H(1) |
| 3248 | H(2) |
| 3250 | H(3) |
| 3269 | H(4) |
| 3238 | H(5) |
| 3237 | H(6) |
| 1681 | H(7) and H(8) |

[a] Referenced arbitrarily, positive shifts to low field.

With no knowledge or assumptions about the 7 chemical shifts in the indene spin system, there are 7! (5040) possible sets of 7 linear simultaneous equations that can be constructed to describe the shifts of the midpoints of the doublets (labelled a–g) in Fig. 3 (21,185, 19,629, 19,628, 19,597, 19,616, 19,618, 19,607 Hz). These sets of simultaneous equations were solved analytically by computer using MATLAB (16) and 720 solutions gave a satisfactory match to the frequency of the 8Q spectrum (22,857 Hz which corresponds to the sum of the 8 shifts of the spins in the spin system). These satisfactory solutions all provide the chemical shifts correctly but differ in the assignment of the shifts to nuclei. With the assumption that the chemical shifts of

the nuclei in a partially oriented medium fall in the same order as the shifts in isotropic solution (17), the shifts can be notionally assigned to protons in the indene spin system (Table 1).

Note that in this spin system, all the aromatic and vinyl protons are predicted to fall in a relatively narrow spread of chemical shifts. The assumption that shifts follow the same sequence as in isotropic solution is not necessarily correct, however, this is not critical and the chemical shifts estimated in this way are an excellent starting point for an iterative analysis of the spectra.

## 6. ESTIMATING THE ORDER PARAMETERS

As with any spectral analysis, the better the quality of the initial estimate of spectral parameters, the easier the final iterative analysis. In practice this means that a simulated spectrum must be obtained with the estimated dipolar coupling values such that there is a reasonable match between the experimental and simulated MQ spectrum in sweep width (left-most peak to right-most peak) and approximate line positions. The dipolar couplings depend on the molecular geometry according to the following equation (18) (using Cartesian coordinates),

$$D_{ij} = -[\gamma_i \gamma_j h/(4\pi^2)](S_{xx}\Delta x^2 + S_{yy}\Delta y^2$$
$$+ S_{zz}\Delta z^2 + 2S_{xy}\Delta x \Delta y + 2S_{xz}\Delta x \Delta z$$
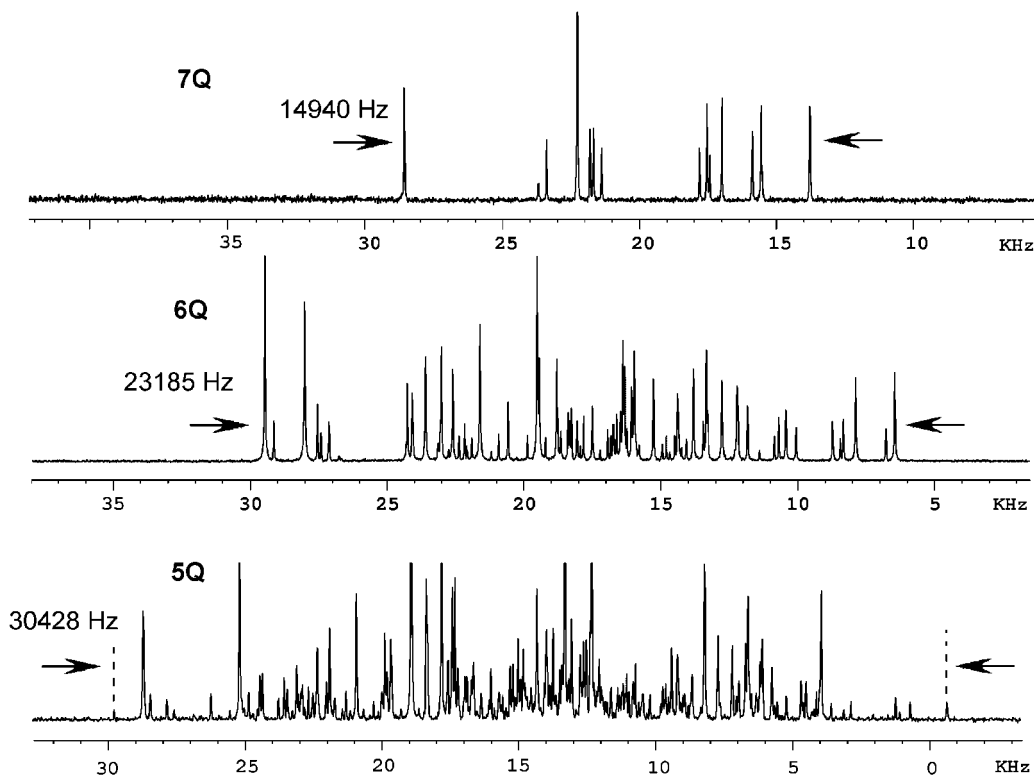$$+ 2S_{yz}\Delta y \Delta z)/(\Delta x^2 + \Delta y^2 + \Delta z^2)^{2.5} \qquad [2]$$



FIG. 4.  The 5Q, 6Q, and 7Q ¹H spectra of indene partially aligned in a liquid crystalline solvent showing the observed spectral widths (pulse sequence given in Fig. 2).
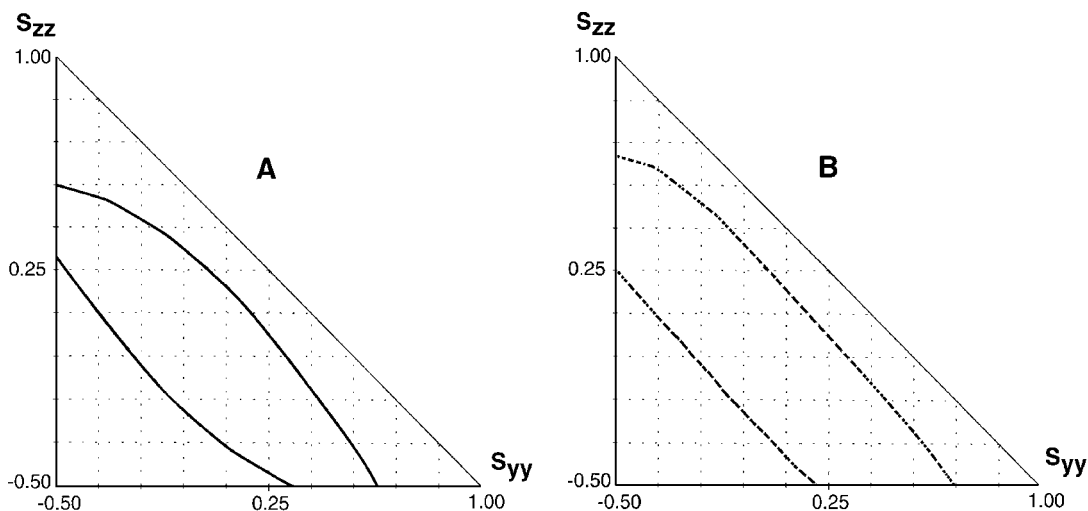
**FIG. 5.** (A) Plot of the simulated width of the 6Q spectrum of indene as a function of $S_{zz}$ and $S_{yy}$; (B) plot of the simulated width of the 7Q spectrum of indene as a function of $S_{zz}$ and $S_{yy}$. $S_{yz}$ was fixed at a value of 0; the geometry of indene was taken from Hyperchem (*20*). Chemical shifts used are given in Table 1.

where $\gamma_i \gamma_j$ are gyromagnetic ratios of spins $i$ and $j$, respectively; $h$ is Planck's constant; $S_{xx}$, $S_{yy}$, $S_{zz}$, $S_{xy}$, $S_{xz}$, $S_{yz}$ are the elements of the Saupe order matrix; and $\Delta x$, $\Delta y$, and $\Delta z$ are the differences of the $x$, $y$, and $z$ coordinates of nuclei $i$ and $j$.

The diagonal order parameters ($S_{xx}$, $S_{yy}$, and $S_{zz}$) can have any value between $-0.5$ and $1.0$, whereas the off-diagonal order parameters ($S_{xy}$, $S_{yz}$, and $S_{xz}$) vary between $-0.75$ and $+0.75$ (*19*).

The total spectral width of any MQ spectrum is dominated by the values of the dipolar couplings in the spin system. The dipolar couplings in turn are a function of the order parameters and the internuclear distances. A reasonable starting estimate of molecular geometry can usually be obtained from model compounds or by using molecular modelling. It is, however, much more difficult to obtain reasonable estimates of orientation parameters.

A general procedure was developed to estimate the Saupe order parameters for spin systems aligned in liquid crystal media by iteratively fitting the spectral widths of the high-order multiple-quantum spectra. For indene, the observed spectral widths of the 5Q, 6Q, and 7Q spectra are 30,428, 23,185, and 14,940 Hz, respectively (Fig. 4).

The proton spin system of indene has $C_s$ symmetry (since the molecule has a plane of symmetry that goes through a plane of the benzene ring). $H_7$ and $H_8$ are out of plane and three nonzero independent order parameters ($S_{yy}$, $S_{zz}$, and $S_{yz}$) are required to define the molecular orientation. Approximate atomic coordinates for the protons of indene were obtained from a molecular simulation program (e.g., HyperChem (*20*), Spartan (*21*)) and estimates of scalar couplings were taken from an NMR spectral parameters reference (*17*). The program MULTQ was used to simulate MQ spectra and to calculate the spectral widths while systematically varying the order parameters through all possible values. Figure 5 shows plots of the simulated spectral width of

the 6Q (Fig. 5A) and 7Q (Fig. 5B) spectra of indene as a function $S_{yy}$ and $S_{zz}$ (with $S_{yz}$ fixed arbitrarily at 0). The graphs clearly indicate that, given an estimated geometry, there is a continuum of combinations of $S_{yy}$ and $S_{zz}$ which can give a 6Q spectrum whose width is 23,185 Hz; likewise there is a continuum of combinations of $S_{yy}$ and $S_{zz}$ which can give a 7Q spectrum whose width is 14,940 Hz. However, if the graphs are superimposed (Fig. 6), there are only few combinations of $S_{yy}$ and $S_{zz}$ which can simultaneously fit the observed widths of both the 6Q and 7Q spectra. This immediately provides reasonable estimates of the possible order parameters that can provide a match to the experimental data.
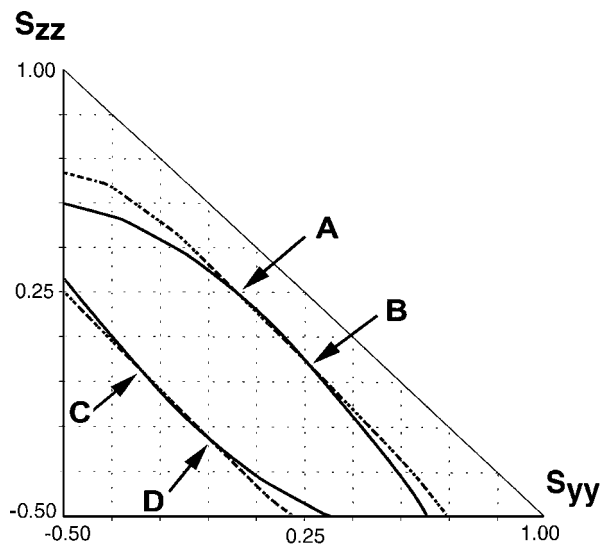


**FIG. 6.** Superposition of the graphs in Figs. 5A and 5B showing the range of $S$ values which can simultaneously fit the widths of both 6Q and 7Q spectra.

The analysis was done more accurately by automating the search procedure for the regions where the order parameters simultaneously fit the widths of the 6Q and 7Q spectra (22) by iteratively using MULTQ to refine all three required order parameters. Although only the sweep widths of the $(n-1)$ and $(n-2)$ orders were needed to find a suitable set of order parameters, the analysis could be refined to simultaneously fit more MQ orders. This approach does not necessarily provide a unique set of order parameters for the spin system; however, the set of possible solutions obtained using this approach is typically small and these serve as excellent starting points for a full iterative analysis of the spectrum to proceed.

The automated analysis for indene gave four sets of $S$ values that give rise to sweep widths within a few hundred Hz of the experimental sweep width of both the 6Q and 7Q spectra:

A. $S_{yy} = 0.034$     $S_{zz} = 0.25$
B. $S_{yy} = 0.268$     $S_{zz} = -0.0156$
C. $S_{yy} = -0.247$    $S_{zz} = -0.0219$
D. $S_{yy} = -0.05$     $S_{zz} = -0.237$

The 6Q and 7Q spectra were simulated using the above $S$ values, plotted, and compared visually to the experimental 6Q and 7Q. Solutions B and C gave spectra that were a much better visual match to the experimental spectra than solutions A and D. Solution B, however, gave a negative $S_{xx}$ ($S_{xx} + S_{yy} + S_{zz} = 0$) as expected for a flat aromatic molecule in the direction of the axis perpendicular to the aromatic ring (23). The dipolar couplings from solution B were used as a starting point for the iterative process.

## 7. SPECTRAL ANALYSIS

Indene belongs to the molecular symmetry subgroup (MS) $G_2$ (24). $G_2$ has only 2 symmetry classifications, A and B, depending on whether the permutation of equivalent spins ($78 \rightarrow 87$) is symmetric or antisymmetric. To calculate the 6Q, 7Q, and 8Q spectra, 74 wavefunctions for describing the indene spin system were checked for their symmetries. A total of 60 wavefunctions was symmetric and 14 were antisymmetric upon the permutation of protons 7 and 8. The 8Q spectrum has only one transition between symmetric levels, the 7Q spectrum has 14 transitions between symmetric levels, and the 6Q spectrum has 93 transitions between symmetric levels and 1 transition between antisymmetric levels. There are no degenerate transitions.

## 8. CHEMICAL SHIFTS AND DIPOLAR COUPLINGS

Iterative analysis of the 6Q, 7Q, and 8Q spectra simultaneously using MULTQ gave the values for chemical shifts and dipolar couplings listed in Table 2. A plot of the simulated solutions of the 6Q, 7Q, and 8Q spectra is given in Fig. 7. Note that MULTQ only simulates line frequencies and all transitions

### TABLE 2
Chemical Shifts and Dipolar Couplings for Indene Partially Oriented in a Nematic Liquid Derived by Solving[a] the 6Q, 7Q, and 8Q Spectra

| Parameter | Value (Hz) | Parameter | Value (Hz) |
|---|---|---|---|
| Shift (1)[b] | $3206.2 \pm 3.2$ | $D_{36}$ | $-84.8 \pm 3.9$ |
| Shift (2) | $3276.0 \pm 3.2$ | $D_{37}$ | $-112.6 \pm 4.4$ |
| Shift (3) | $3329.2 \pm 4.3$ | $D_{45}$ | $-1162.3 \pm 6.9$ |
| Shift (4) | $3235.7 \pm 3.9$ | $D_{46}$ | $-177.3 \pm 5.7$ |
| Shift (5) | $3306.5 \pm 4.2$ | $D_{47}$ | $-80.4 \pm 3.4$ |
| Shift (6) | $3164.5 \pm 4.4$ | $D_{56}$ | $-785.4 \pm 2.7$ |
| Shift (7) | $1673.9 \pm 1.0$ | $D_{57}$ | $-65.3 \pm 3.3$ |
| Shift (8) | $1673.9 \pm 1.0$ | $D_{67}$ | $-516.6 \pm 4.3$ |
| $D_{12}$ | $-1475.8 \pm 4.2$ | $D_{78}$ | $6094.2 \pm 2.0$ |
| $D_{13}$ | $-135.0 \pm 8.6$ | $J_{12}{}^{c}$ | 6.91 |
| $D_{14}$ | $-46.4 \pm 5.6$ | $J_{13}{}^{c}$ | 1.28 |
| $D_{15}$ | $-62.5 \pm 7.3$ | $J_{14}{}^{c}$ | 0.54 |
| $D_{16}$ | $-169.1 \pm 7.4$ | $J_{15}{}^{c}$ | 0.80 |
| $D_{17}$ | $-799.5 \pm 4.5$ | $J_{23}{}^{c}$ | 7.48 |
| $D_{23}$ | $-371.2 \pm 5.8$ | $J_{24}{}^{c}$ | 1.38 |
| $D_{24}$ | $-153.0 \pm 6.8$ | $J_{34}{}^{c}$ | 6.74 |
| $D_{25}$ | $-97.8 \pm 6.4$ | $J_{56}{}^{c}$ | 5.60 |
| $D_{26}$ | $-83.8 \pm 5.4$ | $J_{57}{}^{c}$ | 2.10 |
| $D_{27}$ | $-204.7 \pm 3.5$ | $J_{67}{}^{c}$ | 2.00 |
| $D_{34}$ | $-1468.1 \pm 6.0$ | $J_{78}{}^{d}$ | $-15.0$ |
| $D_{35}$ | $-204.9 \pm 3.9$ | | |

[a] Number of lines assigned: 94 out of 109. RMS error, 5.1 Hz. All chemical shifts and dipolar couplings were fitted.
[b] All chemical shifts were assigned relative to an arbitrary fixed transmitter offset.
[c] Scalar couplings (17) were fixed during the analysis.
[d] See Ref. (25).

were taken to have the same intensity in the spectral simulation so variations in signal intensity in the simulations arise only from signal overlap and spectral digitisation.

If the signs of all dipolar couplings are inverted, the RMS error obtained would be 5.7 Hz. The set of dipolar couplings that provided a negative value for $S_{xx}$ was taken to be the correct solution (23).

## 9. THE SHAPE OF THE INDENE SPIN SYSTEM

The dipolar couplings that were obtained from MULTQ were analyzed using the program SHAPE (26), which varied the order parameters and the atomic coordinates, until a match between experimental and simulated dipolar couplings was obtained. Optimized parameters, with an RMS error of 3.7 Hz, are listed in Table 3.

In determining the structure of indene, the following assumptions were made:

(i) The indene carbon skeleton is flat and H(7) and H(8) are symmetrically disposed with respect to the YZ plane that contains the carbon atoms.

(ii) Vibrational effects are negligible.

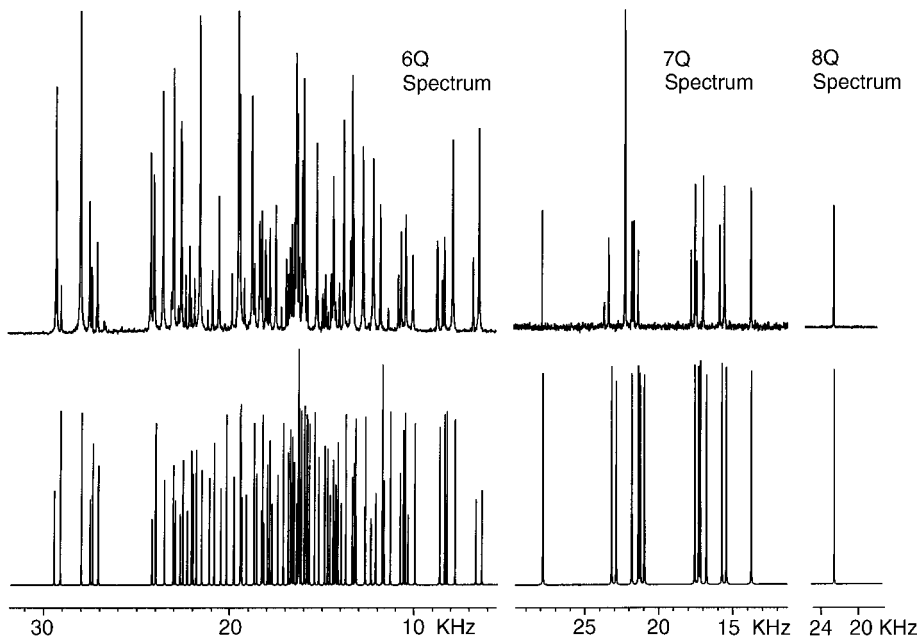(iii) The distance between H(2) and H(3) is 2.481 Å (as in benzene (27)).

**FIG. 7.** Simulated (bottom) and experimental (top) MQ spectra of indene partially aligned in a nematic phase (ZLI-1083). Experimental details for 6Q, $\tau = 30$ ms, 3K $t_1$ increments, 15 scans per increment, 57 KHz in $F_1$ and 27.3 KHz in $F_2$, $g_1/g_2 = 16/96$. For 7Q, $\tau = 20$ ms, 3K $t_1$ increments, 15 scans per increment, 57 KHz in $F_1$ and 27.3 KHz in $F_2$, $g_1/g_2 = 14/98$. For 8Q, $\tau = 20$ ms, 1.5K $t_1$ increments, 15 scans per increment, 60 KHz in $F_1$ and 27.3 KHz in $F_2$, $g_1/g_2 = 12.5/100$, 600 MHz at 290K. Average linewidth is 45 Hz. All simulations assume transitions have the same intensity so variations in signal intensity arise only from signal overlap and spectral digitization.

(iv) The contribution of anisotropic scalar coupling to dipolar coupling is negligible.

Based on the above assumptions, 3 dipolar couplings are required to determine the molecular orientation parameters and 11 dipolar couplings for the molecular geometry (a total of 14 $D$'s out of 22 $D$'s) and the system is overdetermined. A comparison of distance ratios obtained by MQ analysis and single-quantum analysis (*13*) is shown in Table 4.

### TABLE 3

**Proton Atomic Coordinates (Å) and Order Parameters Calculated Using the Program SHAPE, Using the Dipolar Coupling Obtained from MULTQ**

| Nucleus (H) | X | Y | Z |
|---|---|---|---|
| 1 | $0.000 \pm 0.000$ | $0.000 \pm 0.000$ | $0.000 \pm 0.000$ |
| 2 | $0.000 \pm 0.000$ | $-2.10 \pm 0.04$ | $1.20 \pm 0.05$ |
| 3 | $0.000 \pm 0.000$ | $-2.11 \pm 0.05$ | $3.68 \pm 0.05$ |
| 4 | $0.000 \pm 0.000$ | $0.000 \pm 0.000$ | $4.89 \pm 0.05$ |
| 5 | $0.000 \pm 0.000$ | $2.80 \pm 0.05$ | $4.62 \pm 0.08$ |
| 6 | $0.000 \pm 0.000$ | $4.4 \pm 0.1$ | $2.6 \pm 0.1$ |
| 7 | $0.87 \pm 0.01$ | $2.68 \pm 0.06$ | $0.71 \pm 0.05$ |
| 8 | $-0.87 \pm 0.01$ | $2.68 \pm 0.06$ | $0.71 \pm 0.05$ |
| $S_{yy}$ | $0.22 \pm 0.01$ | | |
| $S_{zz}$ | $0.0475 \pm 0.0007$ | | |
| $S_{yz}$ | $0.001 \pm 0.007$ | | |
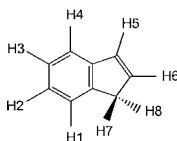
*Note.* H(1) was taken to be at the origin of coordinate axis systems.

### TABLE 4

**Interproton Distance Ratios for Indene Determined by MQNMR and One-Dimensional NMR Methods[a]**

| | MQ NMR (this work) | 1D NMR |
|---|---|---|
| $r_{12}/r_{23}$ | $0.97 \pm 0.01$ | $1.025 \pm 0.005$ |
| $r_{13}/r_{23}$ | $1.71 \pm 0.02$ | $1.765 \pm 0.006$ |
| $r_{14}/r_{23}$ | $1.97 \pm 0.02$ | $2.062 \pm 0.009$ |
| $r_{15}/r_{23}$ | $2.17 \pm 0.02$ | $2.285 \pm 0.011$ |
| $r_{16}/r_{23}$ | $2.06 \pm 0.03$ | $2.162 \pm 0.014$ |
| $r_{17}/r_{23}$ | $1.17 \pm 0.01$ | $1.260 \pm 0.007$ |
| $r_{24}/r_{23}$ | $1.71 \pm 0.02$ | $1.765 \pm 0.007$ |
| $r_{25}/r_{23}$ | $2.41 \pm 0.03$ | $2.512 \pm 0.012$ |
| $r_{26}/r_{23}$ | $2.68 \pm 0.04$ | $2.803 \pm 0.016$ |
| $r_{27}/r_{23}$ | $1.97 \pm 0.02$ | $2.099 \pm 0.011$ |
| $r_{34}/r_{23}$ | $0.98 \pm 0.01$ | $1.028 \pm 0.005$ |
| $r_{35}/r_{23}$ | $2.01 \pm 0.02$ | $2.120 \pm 0.011$ |
| $r_{36}/r_{23}$ | $2.66 \pm 0.04$ | $2.787 \pm 0.016$ |
| $r_{37}/r_{23}$ | $2.30 \pm 0.03$ | $2.435 \pm 0.012$ |
| $r_{45}/r_{23}$ | $1.13 \pm 0.01$ | $1.205 \pm 0.007$ |
| $r_{46}/r_{23}$ | $2.00 \pm 0.03$ | $2.112 \pm 0.014$ |
| $r_{47}/r_{23}$ | $2.03 \pm 0.02$ | $2.170 \pm 0.012$ |
| $r_{56}/r_{23}$ | $1.04 \pm 0.03$ | $1.093 \pm 0.008$ |
| $r_{57}/r_{23}$ | $1.61 \pm 0.02$ | $1.711 \pm 0.009$ |
| $r_{67}/r_{23}$ | $1.08 \pm 0.03$ | $1.130 \pm 0.008$ |
| $r_{78}/r_{23}$ | $0.699 \pm 0.007$ | $0.740 \pm 0.004$ |

[a] $r_{23}$ was assumed to be 2.481 Å.

**TABLE 5**
**Interproton Distance Ratios within the Cyclopentadiene Ring of Indene**

|            | Electron diffraction (28) | 1D NMR          | MQNMR (this work) |
| ---------- | ------------------------- | --------------- | ----------------- |
| $r_{56}/r_{57}$ | $0.642 \pm 0.011$    | $0.639 \pm 0.008$ | $0.64 \pm 0.02$   |
| $r_{67}/r_{57}$ | $0.672 \pm 0.016$    | $0.660 \pm 0.008$ | $0.67 \pm 0.02$   |

Only the cyclopentadiene fragment in indene has been characterized by electron diffraction (28) and a comparison of distance ratios within this fragment is shown in Table 5.

The distortion of the aromatic fragment from hexagonal geometry can be deduced if one compares $r_{12}/r_{23}$ and $r_{34}/r_{23}$ ($0.97 \pm 0.01$ and $0.98 \pm 0.01$) and $r_{13}/r_{23}$ and $r_{24}/r_{23}$ ($1.71 \pm 0.02$ and $1.71 \pm 0.02$) with 1.000 and 1.732 (ratios for perfect hexagonal geometry).

## 10. EXPERIMENTAL

The commercially available liquid crystal Licristal-1083 was dried by heating at 90°C for 3 h under vacuum (Kugelrohr) prior to sample preparation. Proton NMR spectra were recorded on a Bruker AMX-600 (600-MHz) NMR spectrometer fitted with a gradient accessory. Spectra were recorded in 5-mm sample tubes fitted with a concentric insert (2-mm o.d., Wilmad Cat No. WGS-5BL) containing benzene-$d_6$ to provide lock signal.

## 11. CONCLUSIONS

MQNMR spectroscopy of partially oriented compounds can provide structural data in the liquid phase and high-order MQ spectra of good quality can be obtained using a gradient-filtered MQ pulse sequence. Chemical shifts of the nuclei in the spin system can be estimated from the $n$-1 quantum spectrum. A good estimate of molecular orientation and order parameters can be obtained by analysis of the spectral widths of high-order MQ spectra. The ability to determine order parameters from MQ spectra relies on the fact that the spectral widths of high-order spectra depend on molecular orientation and only a small set of orientation parameters can simultaneously satisfy the widths of 2 or more orders of MQ spectra.

The higher order MQ spectra are relatively simple although the linewidths that can be achieved in reasonable acquisition times are still large. The spectral parameters obtained from analysis of high-order spectra could easily be used as input parameters to simulate and solve the more complex single-quantum spectrum (where linewidths are not acquisition limited) should higher resolution be required.

## REFERENCES

1. J. W. Emsley (Ed.), "Nuclear Magnetic Resonance of Liquid Crystals," Reidel, Dordrecht (1985); J. W. Emsley and J. C. Lindon, "NMR Spectroscopy Using Liquid Crystal Solvents," Pergamon, London (1975).

2. G. W. Gray, "Molecular Structure and Properties of Liquid Crystals," Academic Press, New York (1962).

3. G. Drobny, A. Pines, S. Sinton, D. Weitekamp, and D. Wemmer, *Farady Symp. Chem. Soc.* **13,** 49 (1979); S. Sinton and A. Pines, *Chem. Phys. Lett.* **76,** 263 (1980); W. S. Warren and A. Pines, *J. Am. Chem. Soc.* **103,** 1613 (1981); D. P. Weitekamp, J. R. Garbow, and A. Pines, *J. Chem. Phys.* **77,** 2870 (1982).

4. C. P. Slichter, "Principles of Magnetic Resonance," 3rd ed., Springer-Verlag, Berlin/New York (1990).

5. R. R. Ernst, G. Bodenhausen, and A. Wokaun, "Principles of Nuclear Magnetic Resonance in One and Two Dimensions," Oxford Univ. Press, London (1988).

6. G. Bodenhausen, *Prog. NMR Spectrosc.* **14,** 137 (1981).

7. D. P. Weitekamp, *Adv. Magn. Reson.* **11,** 111 (1983).

8. L. D. Field, G. K. Pierens, K. J. Cross, and M. L. Terrry, *J. Magn. Reson.* **97,** 451 (1992); G. K. Pierens, Ph.D. thesis, University of Sydney (1992).

9. S. W. Sinton, D. B. Zax, J. B. Murdoch, and A. Pines, *Mol. Phys.* **53,** 333 (1984); S. Sinton, Ph.D. thesis, University of California, Berkeley (1982).

10. J. A. Ferretti, R. K. Harris, and R. B. Johannesen, *J. Magn. Reson.* **3,** 84 (1970).

11. K. Ziegler and F. Grossmann, *Ber. Deut. Chem. Ges.* **62,** 1768 (1929); J. Meisenheimer and W. Theilacker, *Liebigs Ann. Chem.* **469,** 26 (1929).

12. G. Drobny, A. Pines, S. Sinton, D. Weitekamp, and D. Wemmer, *Faraday Div. Chem. Symp.* **13,** 49 (1979).

13. P. Diehl and J. Vogt, *Org. Magn. Reson.* **7,** 81 (1974).

14. G. K. Pierens, T. A. Carpenter, L. D. Colebrook, L. D. Field, and L. D. Hall, *J. Magn. Reson.* **97,** 398 (1992).

15. The shift refocussed spectrum was obtained by inserting a 180° pulse at the midpoint of the evolution period in the pulse sequence (Fig. 2). The quality of refocussed spectra was invariably poorer than non-refocussed spectra. See, for example, J. C. T. Rendell and E. E. Burnell, *Mol. Phys.* **90,** 541 (1997).

16. MATLAB Version 5.3, MathWorks, Inc.

17. W. Brugel, "Handbook of NMR Spectral Parameters," Heyden, London (1979).

18. P. Diehl and C. L. Khetrapal, "NMR, Basic Principles and Progress," Vol. 1, Springer-Verlag, New York (1969).

19. E. E. Burnell and C. A. De Lange, *Chem. Rev.* **98,** 2359 (1998).

20. HyperChem™ Realease 4.5 for SGI, Molecular Modeling System, Hypercube, Inc.

21. SPARTAN SGI Version 5.0.2 OpenGl, Wavefunction Inc., California.

22. In an automated analysis, the range of all possible $S$ values was scanned coarsely and systematically to locate regions where there were suitable matches to experimental data. The procedure was then repeated focussing

the range on the narrower ranges of $S$ values. The process was again repeated until the search converged on sets of $S$ values.

23. A. Saupe and G. Englert, *Phys. Rev. Lett.* **11,** 462 (1963).

24. P. R. Bunker, "Molecular Symmetry and Spectroscopy," Academic Press, New York (1979).

25. C. G. MacDonald, J. S. Shannon, and S. Sternhell, *Aust. J. Chem.* **17,** 38 (1964).

26. P. Diehl, P. M. Heinrichs, and W. Niedergerger, *Mol. Phys.* **20,** 139 (1971).

27. A. Langseth and B. P. Stoicheff, *Can. J. Phys.* **34,** 350 (1956); E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. R. Soc. London Ser. A* **1,** 247 (1958).

28. J. F. Southern, L. Schafer, K. Brendhaugen, and H. M. Seip, *J. Chem. Phys.* **55,** 2418 (1971).