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STUDY OF THE ISOTROPIC-NEMATIC-SOLID TRANSITIONS
IN A LIQUID CRYSTAL BY CARBON-13-PROTON DOUBLE RESONANCE*

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ABSTRACT

Carbon-13 nmr spectra have been obtained for p-methoxy
benzylidene p-n-butylaniline (MBBA) in the isotropic, nematic
and solid phases. Sharp, resolved spectra are obtained in the
nematic phase with high power proton spin-decoupling. The
isotropic-nematic transition is accompanied by a discontinuous
change in $^{13}$C absorption frequencies due to the molecular ordering
and anisotropic chemical shielding. It is concluded that the
benzene rings reorient rapidly about the para axes. The angle
between the molecular director and the para axes is calculated
to be 9°. Employing average values from studies of $^{13}$C chemical
shielding tensors in model aromatic solids, values of the order
parameter $S$ are estimated. The nematic-solid transition is
accompanied by sudden and severe line broadening due to anisotropic
chemical shielding.

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Science Foundation, and by the U.S. Atomic Energy Commission
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Berkeley Laboratory.
Study of the Isotropic-Nematic-Solid Transitions
in a Liquid Crystal by Carbon-13-Proton Double Resonance

Although nuclear magnetic resonance (nmr) has featured prominently in the study of liquid crystals, its application has not been straightforward. The reason for this is readily appreciated: the molecules comprising liquid crystal systems are normally long, rod-like in character. In isotropic liquid phase rapid molecular reorientation takes place and thus averages to zero the direct magnetic dipolar couplings between nuclear spins. In the liquid crystalline phase, motion about the long axes is rapid, but the axes (the molecular directors) are aligned preferentially along the magnetic field and reorientation is inhibited. This leads to complicated, normally intractably broadened nmr spectra. Thus, most studies have resorted to the use of small probe molecules, wide-line spin relaxation times and second moments, partial deuteration, etc, and no general useful approach has been available.

In this letter we report the observation of $^{13}$C nmr spectra in the isotropic, nematic and solid phases of p-methoxy benzylidene p-n-buty laniline (MBBA). This work provides the first high resolution $^{13}$C nmr study of the phase transitions in a liquid crystal and opens the way for a detailed study of structure and dynamics in liquid crystals on a microscopic scale. The advantages of observing $^{13}$C derive from the absence of $^{13}$C-$^{13}$C
dipolar splittings due to its low natural isotopic abundance (\(\sim 1\%\)), the large range of chemical shifts and thus sensitivity to molecular ordering, and the dominant dependence of the \(^{13}\)C spectra and spin relaxation times upon local intramolecular effects.

Figure 1 shows Fourier transform \(^{13}\)C nmr spectra of neat MBBA under different conditions. At high temperature (46°), the system exhibits normal isotropic liquid behavior and spectra are shown for experiments with and without proton spin decoupling. The line splittings from spectrum (a) to (b) are due to electron-coupled interactions between \(^{13}\)C and \(^{1}\)H nuclear spins and have aided us in the assignment of lines to specific carbon nuclei. Since, in this phase, the molecules are reorienting rapidly, the chemical shifts \(\sigma_i\) correspond to an isotropic average over the chemical shielding tensors \(\mathbf{\sigma}\)

\[
\sigma_i = \frac{1}{3} \text{Tr} \mathbf{\sigma}
\]

In the nematic phase, the molecules are aligned preferentially with the long axis (the molecular director \(\mathbf{D}\) in figure 1) along \(\mathbf{H}_0\) and thus shifts in the line positions are expected. For aromatic \(^{13}\)C nuclei the heaviest shielding occurs perpendicular to the aromatic plane, whereas for the attached aliphatic group the lightest shielding occurs in this direction. Thus we expect a downfield shift of the aromatic lines and an upfield shift of the aliphatic lines in the isotropic-nematic transition.
exactly as observed in spectrum (d). Without proton decoupling, at this temperature, a broad structureless resonance is obtained. Spectrum (c) taken at the isotropic-nematic transition point (40.6°) shows sharp lines from both the high and low temperature regimes indicating that the transition is discontinuous and first order within our temperature resolution (0.4°). As the temperature is lowered in the nematic phase the proton decoupled $^{13}$C spectra remain sharp (e) down to -2° where the nematic-solid transition induces a broadening due to the large $^{13}$C chemical shielding anisotropy (g). On increasing the temperature, the spectrum remains broad (f) until 17°C thus exhibiting hysteresis in the nematic-solid transition. We observe no hysteresis in the nematic-isotropic transition, in agreement with the low free energy barrier found by light scattering.

Figure 2 depicts the $^{13}$C line positions over a wide temperature range in MBBA. The six sets of points below 18° were taken with temperature decreasing from the nematic phase; above this temperature, points were taken both with temperature increasing and with temperature decreasing, giving similar behavior. From our results a number of conclusions can be drawn:

1. In the nematic phase only one line is observed from each pair of ortho carbon positions. This demonstrates unequivocally that the benzene rings reorient rapidly about their para axes.

2. The single line at 75 ppm is due to the O-CH$_3$ group and changes only by 1.5 ppm from the isotropic phase to the nematic phase at 10°C. This indicates that the angle between the O-CH$_3$
axis and the director (D) is close to 54.7°, the 'magic angle'.

In solid p-azoxy dianisole (PAA) we have found \( \sigma_{\parallel} - \sigma_{\perp} \approx 70 \) ppm for the O-CH\(_3\) group. (11) Taking this value for MBBA and assuming (a) that \( \sigma_{\parallel} \) is along the O-CH\(_3\) bond as in methanol, (b) the order parameter \( S \) at 10°C = 0.6, (12) we can calculate the angle between D and the para axis and find \( \phi = 9^\circ \).

3. Since the molecules reorient rapidly about D, each \(^{13}\)C tensor \( \sigma \) yields a motionally averaged tensor \( \bar{\sigma} \) with components \( \sigma_{\parallel} \) along D and \( \sigma_{\perp} \) perpendicular to D:

\[
\sigma_{\parallel} = \cos^2 \phi \sigma_{11} + \sin^2 \phi \sigma_{22} \\
\sigma_{\perp} = \frac{1}{2} [\sin^2 \phi \sigma_{11} + \cos^2 \phi \sigma_{22} + \sigma_{33}] 
\]

for the aromatic \(^{13}\)C nuclei on the para axis, and:

\[
\sigma_{\parallel} = \frac{1}{2} [1 + 2 \sin^2 \phi] \sigma_{11} + (1 + 2 \cos^2 \phi) \sigma_{22} \]

\[
\sigma_{\perp} = \frac{1}{2} [(1 + 2 \cos^2 \phi) \sigma_{11} + (1 + 2 \sin^2 \phi) \sigma_{22} + \sigma_{33}] 
\]

for the aromatic \(^{13}\)C nuclei in ortho positions, where \( \sigma_{ii} \) are the principal elements of \( \sigma \). The observed chemical shifts \( \Delta \sigma \) from the isotropic to nematic phase are given by:

\[
\Delta \sigma = \sigma_{\perp} - \frac{2}{3} S (\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp})
\]

where \( S \) is the order parameter. We have used average data for \( \sigma \) from studies of model aromatic solids, (7) taking \( \sigma_{11} = -98, \sigma_{22} = -13, \sigma_{33} = 108 \) ppm to calculate values of \( S \) from the data in figure 2 and equations (1) - (4) with \( \phi = 9^\circ \). We
estimate, for example, $S = 0.58$ at $10^\circ\text{C}$ in the nematic phase
and $S = 0.29$ just below the clearing point ($40.6^\circ$), with a
consistency of $\pm 0.03$ between the different sets of $^{13}\text{C}$ nuclei
in reasonable agreement with previous values, but slightly
lower. A full determination of the tensors from solid state
work will yeild precise values of $S$ and molecular conformation
parameters and such work is under way in our laboratory.

4. In the nematic phase, cross-polarization between the
$^1\text{H}$ and $^{13}\text{C}$ spins is efficient and most of the spectra were
obtained using this technique. Unlike the case of solids, this
probably proceeds by an intramolecular transfer since transla­
tional diffusion is rapid. The advantage of this approach
cver normal Fourier-transform nmr are enhanced signal/noise
and the possibility of studying order fluctuations through
$^{13}\text{C}-^1\text{H}$ cross-polarization dynamics.

This work shows that high resolution nmr in liquid crystals
is indeed possible and that a great deal of information is
available from our approach. Further details of those experi­
ments and results on other nematic and smectic systems will be
reported elsewhere.

The experiments were performed on a homebuilt double
resonance spectrometer operating at 26.7 MHz for $^{13}\text{C}$. Proton
decoupling fields were provided by a tuned amplifier delivering
several hundred watts of rf power into a double coil probe in
the bore of a superconducting magnet. The probe was tuned with
high voltage capacitors of polished copper tubes with teflon
dielectric. Temperature was controlled with a stream of dry Nitrogen gas passing through a dry-ice acetone heat exchanger and then through a heated copper column. Further experimental details will be published separately.

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References

1. Some recent reviews describing the application of nmr and other techniques to liquid crystals are:
8. This temperature shows that our sample is not absolutely pure, but this has been found to have no significant effect.


Figure Captions

Figure 1 Carbon-13 Fourier transform nmr spectra of p-methoxy benzylidene p-n-butylaniline (MBBA). All spectra except (b) are proton spin decoupled. Spectrum (e) was obtained rapidly by proton-enhanced nuclear induction spectroscopy. The low field group of lines is from the aromatic carbon nuclei, the lower ones on the para axes and the higher ones from the ortho positions. The line at 75 ppm is from the methoxy group and the high field lines are from the n-butyl chain. The effect of molecular ordering in the isotropic-nematic transition is a discontinuous change in frequencies, and spectrum (c) shows lines characteristic of both the nematic and isotropic phases. A discontinuous change in linewidth occurs in the nematic-solid transition and hysteresis is observed in this region (e) - (g).

Figure 2 Dependence of $^{13}$C line positions in MBBA on temperature. The points below 18°C were taken with temperature decreasing from the nematic phase, since the lines are broad in the solid.
Fig. 1
Fig. 2

-100 -80 -60 -40 -20 0 20 40 60 80
T (°C)

σ (ppm from benzene)

Solid Nematic Nematic Isotropic

XBL 743-5843
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