Study of the isotropic-nematic-solid transitions in a liquid crystal by carbon-13–proton double resonance*

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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 were 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. Employing average values from studies of ^{13}C chemical shielding tensors in model aromatic solids, absolute values of the order parameter S are estimated and normalized values are compared with previous results. The nematic-solid transition is accompanied by sudden and severe line broadening due to anisotropic chemical shielding.

INTRODUCTION

Although nuclear magnetic resonance (NMR) has featured prominently in the study of liquid crystals,[1] its application has not been straightforward. The reason for this is readily appreciated: The molecules comprising liquid-crystal systems are normally long and rodlike in character.[2] In the 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,[3] wide-line spin relaxation times and second moments,[4] partial deuteration,[5] etc., and no general useful approach has been available.

In this paper we report the observation of ^{13}C NMR spectra in the isotropic, nematic, and solid phases of p-methoxy benzylidene p'-n-butylaniline (MBBA), Fig. 1. 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 owing to its low natural isotopic abundance (~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.

RESULTS AND DISCUSSION

Figure 2 shows Fourier transform ^{13}C NMR spectra of neat MBBA under different conditions. At high temperature (46 °C), the system exhibits normal isotropic liquid behavior and spectra are shown for experiments with and without proton spin decoupling.[6] 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 σ_i correspond to an isotropic average over the chemical shielding tensors $\bar{\sigma}$,

$$\sigma_i = \tfrac{1}{3}\mathrm{tr}\bar{\sigma}. \tag{1}$$

In the nematic phase, the molecules are aligned preferentially with the long axis (the molecular director D in Fig. 1) along H, 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.[7] *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°)[8] 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-de-
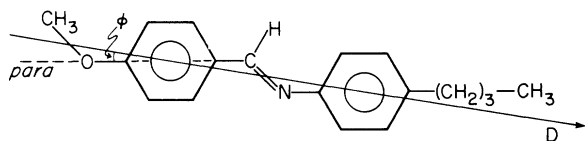
FIG. 1. Structure of the p-methoxy benzylidene p'-n-butylaniline (MBBA) molecule. The molecular director is denoted by D, and ϕ is the angle between D and the benzene para axis.

coupled ^{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.[9] We observe no hysteresis in the nematic-isotropic transition, in agreement with the low free-energy barrier found by light scattering.[10]

Figure 3 depicts the ^{13}C line positions over a wide temperature range in MBBA. The six sets of points below 18 °C 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:

(i) In the nematic phase only one line is observed from each pair of orthocarbon positions. This demonstrates unequivocally that the benzene rings reorient rapidly about their para axes.

(ii) 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 average 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 observed similar behavior and have found $\sigma_\parallel - \sigma_\perp \sim 60$ ppm for the O-CH$_3$ group in the solid.[11]

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

$$\bar{\sigma}_\parallel^{(p)} = \cos^2\phi\,\sigma_{11} + \sin^2\phi\,\sigma_{22}, \tag{2}$$

$$\bar{\sigma}_\perp^{(p)} = \tfrac{1}{2}[\sin^2\phi\,\sigma_{11} + \cos^2\phi\,\sigma_{22} + \sigma_{33}],$$

for the aromatic ^{13}C nuclei on the para axis, and

$$\bar{\sigma}_\parallel^{(o)} = \tfrac{1}{4}(1 + 2\sin^2\phi)\sigma_{11} + \tfrac{1}{4}(1 + 2\cos^2\phi)\sigma_{22},$$

$$\bar{\sigma}_\perp^{(o)} = \tfrac{1}{2}[\tfrac{1}{4}(1 + 2\cos^2\phi)\sigma_{11} + \tfrac{1}{4}(1 + 2\sin^2\phi)\sigma_{22} + \sigma_{33}], \tag{3}$$

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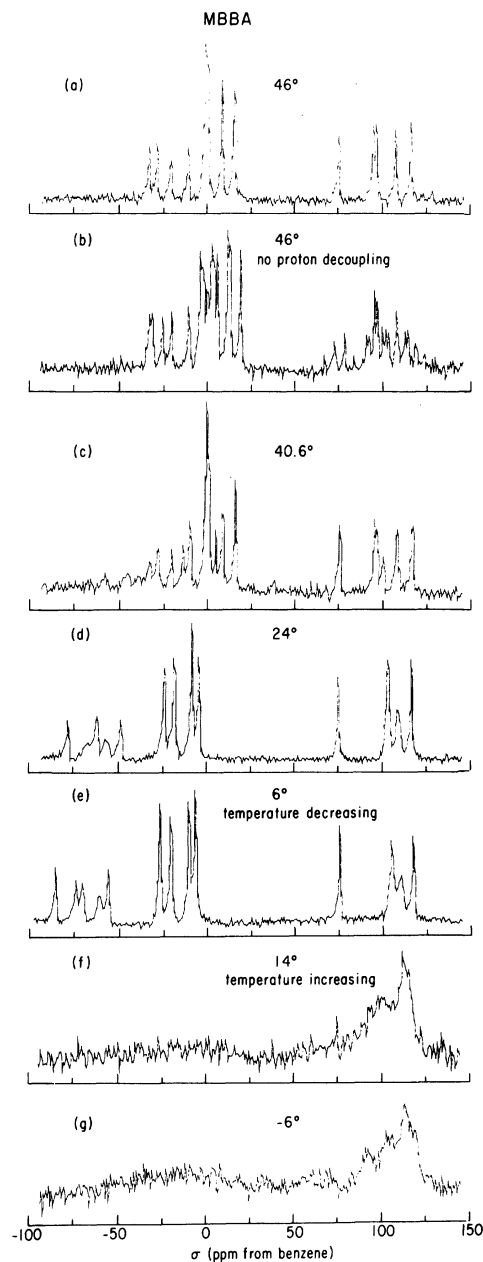

FIG. 2. Carbon-13 Fourier transform NMR spectra of p-methoxy benzylidene p'-n-butylaniline (MBBA). All spectra except (b) are proton-spin decoupled. Spectrum (e) was obtained rapidly by proton-enhanced nuclear induction spectroscopy. The low-field group of lines is from the aromatic carbon nuclei, the 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).
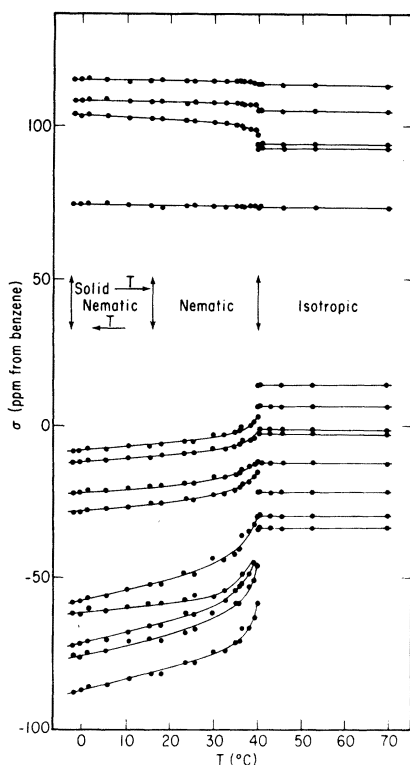
FIG. 3. Dependence of ^{13}C line positions in MBBA on temperature. The points below 18 °C were taken with temperature decreasing from the nematic phase, since the lines are broad in the solid.

$$\Delta\sigma = \tfrac{2}{3}S(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp}), \qquad (4)$$

where S is the order parameter. We have used average data for $\bar{\sigma}$ 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 Fig. 3 and Eqs. (1)–(4) with $\phi = 9°$. We estimate, for example, $S = 0.58$ at 10 °C in the nematic phase and $S = 0.29$ just below the clearing point (40.6 °C), with a consistency of ±0.03 between the different sets of ^{13}C nuclei. To compare our results with previous work, Fig. 4 shows relative values of S calculated from the ^{13}C shifts and normalized (N) to the value at $T_c - T = 2°$.[12] A full determination of the tensors $\bar{\sigma}$ from solid-state work will yield precise values of S and molecular conformation parameters and such work is under way in our laboratory.

(iv) In the nematic phase, cross polarization between the ^{1}H and ^{13}C spins[13] is efficient and most of the spectra were obtained using this technique.
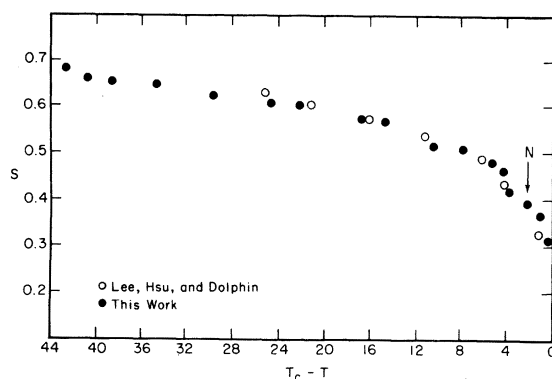

FIG. 4. Order parameter for MBBA calculated from ^{13}C chemical shifts in Fig. 3 and normalized (N) to 0.39 (Lee, Hsu, and Dolphin, cited in Ref. 12) at $T_c - T = 2°$.

Unlike the case of solids, this probably proceeds by an intramolecular transfer since translational diffusion is rapid.[14] The advantages of this approach over normal Fourier-transform NMR are enhanced signal-to-noise ratio and the possibility of studying order fluctuations through ^{13}C-^{1}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 experiments and results on other nematic and smectic systems will be reported elsewhere.

The experiments were performed on a "home-built" double-resonance spectrometer operating at 26.7 MHz for ^{13}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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