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Authors

Pines, A.
Chang, J.J.

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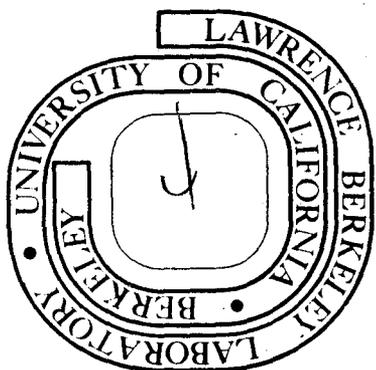
A. Pines and J. J. Chang

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THE EFFECT OF PHASE TRANSITIONS ON ^{13}C NMR SPECTRA
IN P-AZOXYDIANISOLE, A NEMATIC LIQUID CRYSTAL

A. Pines and J. J. Chang

Department of Chemistry, University of California
and Inorganic Materials Research Division, Lawrence Berkeley Laboratory
Berkeley, California 94720

ABSTRACT

High resolution ^{13}C nmr spectra obtained by high power spin decoupling are reported for p-azoxydianisole (PAA). In the isotropic-nematic transition the aromatic ^{13}C lines shift discontinuously downfield while the methoxy ^{13}C line remains relatively unaffected. In the nematic-solid transition the lines broaden, leaving the methoxy ^{13}C chemical shielding elements as the only discernible features and yielding an anisotropy $\Delta\sigma = 62 \pm 6$ ppm for this tensor. There is evidence that the benzene rings rotate rapidly in agreement with conclusions from proton nmr. It is concluded that the principle axis of σ for the methoxy ^{13}C makes an angle of $\sim 55^\circ$ relative to the benzene para axes. Relative values of the order parameter describing the molecular ordering in the nematic phase are reported from the temperature dependence of the chemical shifts.

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The Effect of Phase Transitions on ^{13}C NMR Spectra
in p-Azoxydianisole, A Nematic Liquid Crystal

Sir:

Liquid crystals are comprised of long, rod-like molecules. (1)
At high temperatures, they form normal liquid phases in which the molecules tumble isotropically. As the temperature is lowered, a transition occurs into a liquid crystal phase characterized by long range orientational order of the molecules. The study of these phases is of extreme interest because of their importance in several areas, including their role as model systems for biological membranes, the study of phase transitions and critical phenomena, their use as orienting solvents, etc. In this regard, nuclear magnetic resonance (nmr) has formed a valuable tool. (2) However, the use of nmr has been restricted by the near impossibility of obtaining tractable high resolution spectra of the liquid crystal molecules. This is because the magnetic dipole-dipole couplings between nuclear spins are not averaged to zero as in liquids, and the abundant protons produce a large number of overlapping lines rendering the spectra broad and intractable except in special cases such as partially deuterated materials. (3.4)

The development of techniques to obtain routinely simple, high resolution nmr spectra would clearly be quite valuable. An especially appealing possibility is that ^{13}C nmr, since:

- (a) if the ^1H spins are decoupled, the spectra should be simple and tractable due to the absence of ^{13}C - ^{13}C couplings,

- (b) the chemical shielding anisotropy for ^{13}C is large, thus making the nmr sensitive to orientational effects and molecular ordering
- (c) spin relaxation of ^{13}C is dominated primarily by intramolecular magnetic couplings.

The only problems with this approach have been the traditional ones of sensitivity and resolution and the requirements of high power spin decoupling.

We have overcome the requisite technical problems and recently reported the observation of high resolution ^{13}C nmr spectra in the nematic phase of p-methoxybenzylidene p^l-n-butylaniline (MBBA),⁽⁵⁾ exhibiting the effects of phase transitions, molecular ordering, conformation and motion. This has opened the way for the application of nmr to detailed microscopic studies of structure and dynamics in liquid crystals. In this communication, we report preliminary results of work on p-azoxydianisole (PAA), one of the simplest compounds exhibiting a nematic phase. Figure 1 shows ^{13}C nmr spectra obtained in the isotropic, nematic and solid phases of PAA. In the isotropic phase, the chemical shifts σ_i are given by:

$$\sigma_i = \frac{1}{3} \text{Tr } \sigma \quad (1)$$

where σ are the chemical shielding tensors. In the nematic phase, rapid rotation about the long molecular axis yields an averaged tensor $\bar{\sigma}$ with elements $\bar{\sigma}_{\parallel}$ and $\bar{\sigma}_{\perp}$ along and perpendicular to the long axis and the shifts σ are given by:

$$\sigma = \sigma_i + \frac{2}{3} s(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp}) \quad (2)$$

where S is the order parameter, ⁽⁶⁾

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (3)$$

and θ is the angle between the long molecular axis and the external magnetic field.

For aromatic nuclei, the general features of σ have been characterized in single crystal studies. ⁽⁷⁾ The least shielded element of σ is normally in the aromatic plane pointing radially out from the ring, and the most shielded element is perpendicular to the plane. Thus $\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp} < 0$ and we expect a downfield shift in the isotropic-nematic transition exactly as observed. The lines remain sharp and no additional splittings occur indicating rapid motion of the benzene rings about the para axes in agreement with the conclusion of Rowell et al ⁽³⁾ and our results on MBBA. ⁽⁵⁾

The methoxy ^{13}C line remains sharp and does not shift appreciably in the isotropic-nematic transition. This indicates that the angle between the axis corresponding to $\bar{\sigma}_{\parallel}$ and the para axis of the ring is close to 55° , the magic angle. This is similar to the behavior we have observed in higher homologs of the azoxybenzenes (p-dipentyloxy and p-diheptyloxyazoxybenzene.) ⁽⁸⁾

In the nematic-solid transition, the lines broaden due to chemical shielding anisotropy and the only tractable feature is assigned to the methoxy group, with a theoretical line inserted in figure 1(d) corresponding to a tensor σ with elements:

$$\sigma_{11} = 49 \pm 3, \quad \sigma_{22} = 55 \pm 3, \quad \sigma_{33} = 114 \pm 3 \quad (4)$$

in ppm relative to liquid benzene. The anisotropy is $\Delta\sigma = 62 \pm 6$ ppm which is similar to the value reported for methanol.⁽⁹⁾

Relative values of the order parameter are plotted vs. temperature in figure 2. These were obtained from the shifts of the aromatic lines and equation (2). Values of $\bar{\sigma}_{||}$ and $\bar{\sigma}_{\perp}$ were calculated by taking average σ tensors for aromatic ^{13}C nuclei from solid state work⁽⁹⁾ and averaging about the long molecular axis which was taken as 10° from the para axes. These values of S are good to within a normalization factor, since neither the exact tensors σ nor the exact molecular conformation are known for this system. The overall behavior is similar to that reported previously. A determination of the full ^{13}C σ tensors from single crystal work should permit a detailed determination of molecular ordering, conformation and motion in the liquid crystal phase; and such work is currently under way in our laboratory. Measurements of ^{13}C spin relaxation, recently initiated by Wang, Grant and coworkers,⁽¹⁰⁾ should prove extremely useful in this regard.

The experiments were performed on a homebuilt double resonance spectrometer described briefly elsewhere.⁽¹¹⁾ We are grateful to Dr. S. Meiboom and Dr. M. P. Kellin for helpful discussions and to T. W. Shattuck and D. N. Shirley for assistance with the experiments.

A. Pines,* J. J. Chang

Department of Chemistry, University of California
and Inorganic Materials Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

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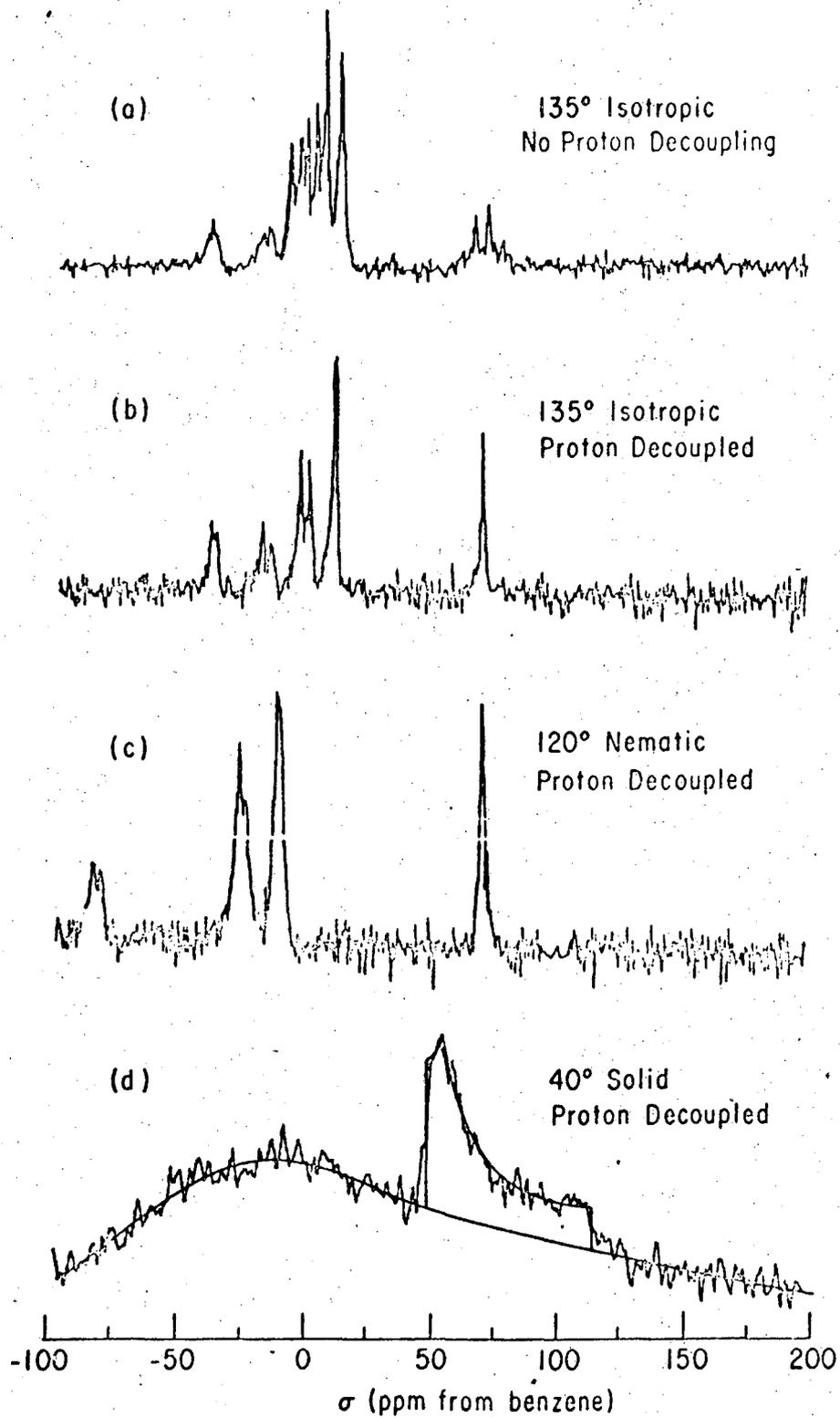
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Figure Captions

Figure 1: Fourier transform ^{13}C nmr spectra in PAA. (a) and (b) are in the isotropic phase. The undecoupled spectrum (a) aids in line assignment. (c) was taken in the nematic phase. Without proton decoupling in this phase a broad structureless resonance is obtained. The aromatic lines shift discontinuously downfield in the isotropic-nematic transition and the lines from ^{13}C bound to nitrogen disappear due to severe broadening. (d) was obtained by proton-enhanced nmr in the solid phase.

Figure 2: Temperature dependence of the relative order parameter in the nematic phase of PAA. These values were obtained by measuring the temperature dependence of σ for the intense aromatic lines and using average shielding tensors from model solids. The clearing point for this sample is $T_c = 133^\circ\text{C}$.



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Fig. 1

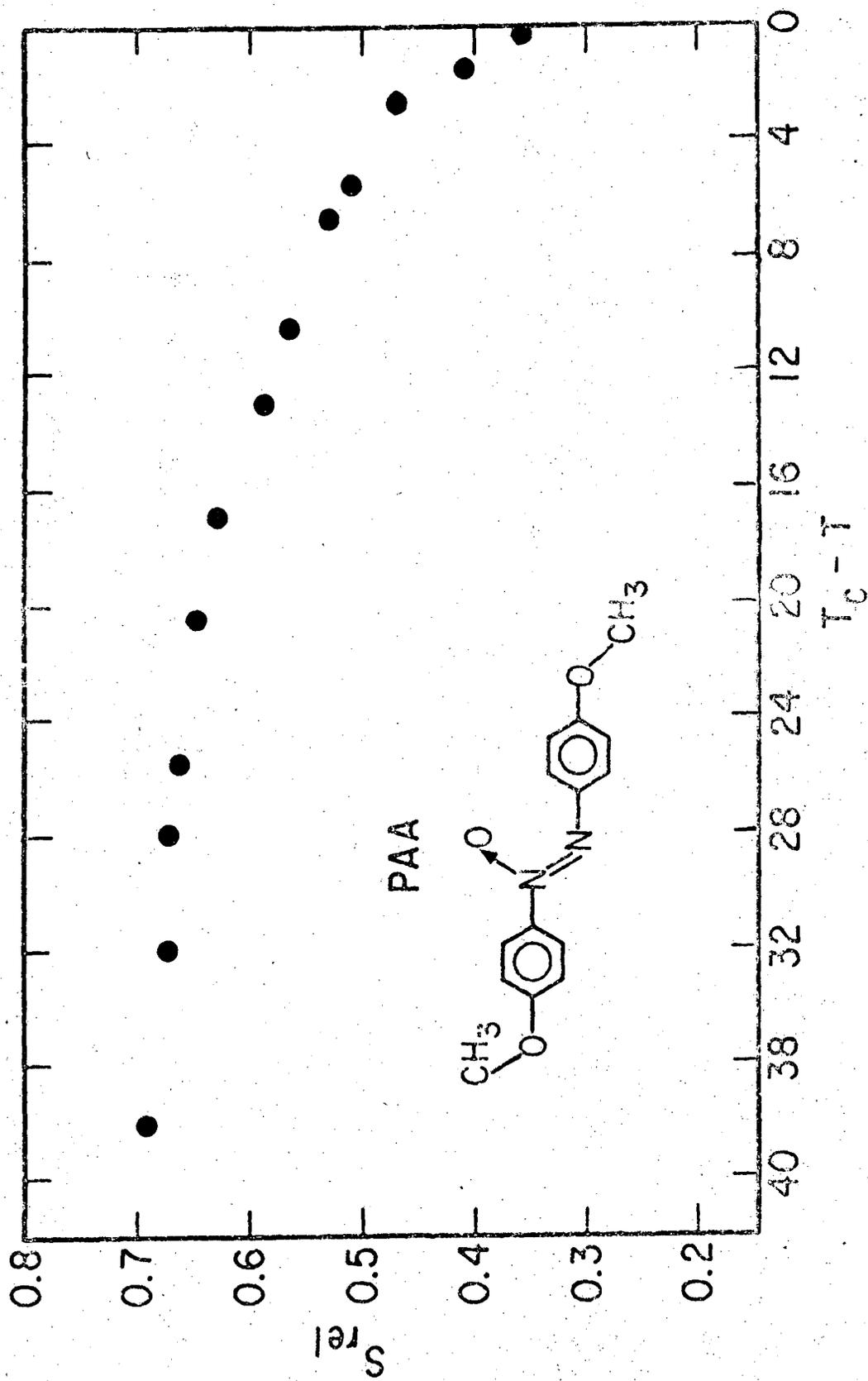


FIG. 2

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