An examination of the literature reveals that many of the spectra described above have been previously observed by more sophisticated techniques.[14] However, it is apparent that the use of the present technique offers distinct advantages for optical studies of free radicals because they are present in a host medium of high optical transparency in the uv and visible regions and can be *positively* identified by epr spectroscopy. Preliminary experiments indicate that most of the radicals which have been studied by epr using this method[4,5,7,9,15] also exhibit strong optical spectra. These results will be described in subsequent publications from these laboratories.

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(15) For further examples, see D. E. Wood, R. V. Lloyd, and W. A. Lathan, *J. Amer. Chem. Soc.*, **93**, 4145 (1971); D. E. Wood, C. A. Wood, and W. A. Lathan, *ibid.*, **94**, 9278 (1972); L. F. Williams, M. B. Yim, and D. E. Wood, *ibid.*, **95**, 6475 (1973); D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *ibid.*, **95**, 7978 (1973).

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Effect of Phase Transitions on Carbon-13 Nuclear Magnetic Resonance 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

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

(2) Some recent reviews describing the application of nmr to liquid crystals are: (a) S. Chandrasekhar and N. V. Madhusadana, *Appl. Spectrosc. Rev.*, **6**, 189 (1973); (b) A. Saupe, *Annu. Rev. Phys. Chem.*, **24**, 441 (1973); (c) G. H. Brown, J. W. Doane, and V. D. Neff, "A Re-

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 ^{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'*-*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

$$\sigma_i = \frac{1}{3} Tr\acute{\sigma} \tag{1}$$

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

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

where S is the order parameter[6]

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

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

For aromatic nuclei, the general features of $\acute{\sigma}$ have been characterized in single-crystal studies.[7] The

view of the Structure and Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971; (d) S. Meiboom and L. C. Snyder, *Accounts Chem. Res.*, **4**, 81 (1971).

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

(4) Y. S. Lee, Y. Y. Hsu, and D. Dolphin, presented at the American Chemical Society Symposium on Ordered Fluids and Liquid Crystals, Chicago, Ill., 1973.

(5) A. Pines, presented at the 15th Experimental Nuclear Magnetic Resonance Conference, Raleigh, N. C., 1974; A. Pines and J. J. Chang, *Phys. Rev. A*, in press.

(6) A. Saupe, *Z. Naturforsch. A*, **19**, 161 (1964).

(7) S. Pausak, A. Pines, and J. S. Waugh, *J. Chem. Phys.*, **59**, 591 (1973).
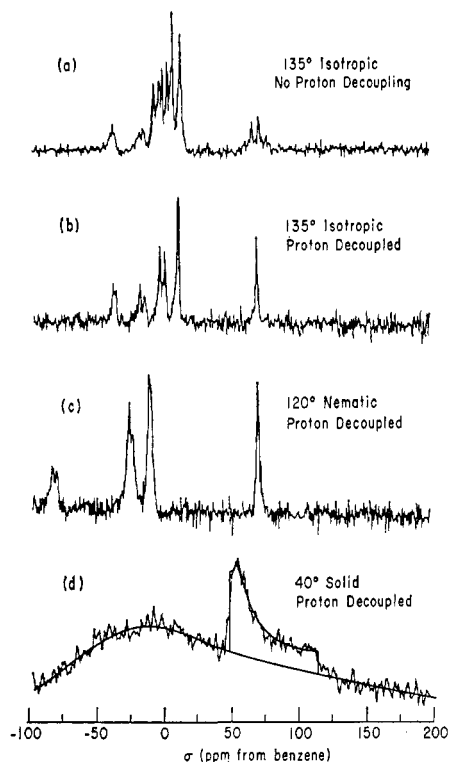
Figure 1. Fourier transform ^{13}C nmr spectra in PAA. (a) and (b) are in the isotropic phase. The undecoupled spectrum (a) aids in line assignment. (c) was taken in the nematic phase. Without proton decoupling in this phase a broad structureless resonance is obtained. The aromatic lines shift discontinuously downfield in the isotropic–nematic transitions 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 $T_c = 133°$.

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 $\bar{\sigma}_{||} - \sigma_{\perp} < 0$, 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]
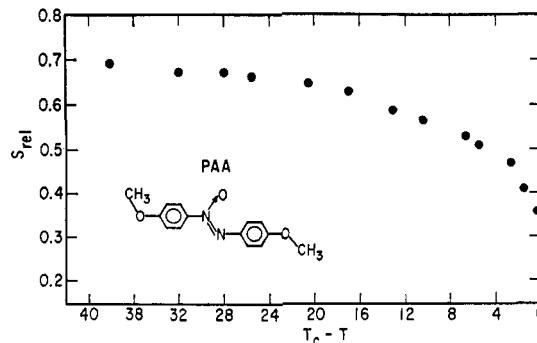
The methoxy ^{13}C line remains sharp and does not shift appreciably in the isotropic–nematic transition. This indicates that the angle between the axis corresponding to $\sigma_{||}$ and the para axis of the ring is close to 55°, the magic angle. This is similar to the behavior we have observed in higher homologs of the azoxybenzenes.[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 1d corresponding to a tensor σ with elements: $\sigma_{11} = 49 \pm 3$, $\sigma_{22} = 55 \pm 3$, $\sigma_{33} = 114 \pm 3$, in parts per million 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 eq 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. Klein for helpful discussions and to T. W. Shattuck and D. N. Shirley for assistance with the experiments.

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(9) A. Pines, M. G. Gibby, and J. S. Waugh, *Chem. Phys. Lett.*, **15**, 373 (1972).

(10) M. Schwartz, P. E. Fagerness, C. H. Wang, and D. M. Grant, *J. Chem. Phys.*, in press. This describes the measurement of ^{13}C spin-lattice relaxation times in PAA. We are grateful to Professor Wang for sending us a preprint of this work.
(11) A. Pines, J. J. Chang, and R. G. Griffin, *J. Chem. Phys.*, in press.

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Radical Generation from Polymolecular Reactions of Closed Shell Molecules. Molecule-Assisted Homolysis (MAH). Hydrogen Atom Transfer from a Diels–Alder Adduct to an Alkene

Sir:

There are three types of polymolecular processes by which radicals can be produced from the interaction of closed shell molecules. They are: molecule-assisted homolysis (MAH), in which acceleration of a