

pathway. We are reluctant at present to accept this facile explanation, since its application to the [1,7] pathway in **1** is by no means clear. Since [1,7] pathways in both **1** and **2** have the same activation energy ($\Delta G^\ddagger \approx 19 \text{ kcal mol}^{-1}$), a similar rationale might be expected for both octahedral and tetrahedral metal centers.

We are continuing our efforts to establish an understanding of the fluxional behavior of compounds of this class.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Professor R. E. D. McClung for valuable discussions of the spin saturation transfer experiments.

Registry No. **2**, 80387-87-7; $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]$, 42802-20-0.

Deuteron NMR Study of Molecular Order and Motion in a Liquid Crystalline Polymer

H. Geib,[†] B. Hisgen,[‡] U. Pschorn,[†] H. Ringsdorf,[‡] and H. W. Spiess*[†]

*Institut für Organische Chemie
and Institut für Physikalische Chemie
Johannes Gutenberg Universität, D-6500 Mainz, Germany*

Received September 28, 1981

A variety of liquid crystalline polymers has systematically been synthesized recently, following the model^{1,2} of decoupling the molecular motions of the mesogenic side groups and the main chain by inserting a flexible spacer. Nematic, smectic, and even cholesteric phases have been obtained.^{3,4} In certain cases, both nematic and smectic phases could be generated simply by varying the length of the spacer. An example of this behavior is provided by the systems depicted schematically in Figure 1, involving phenyl benzoates as mesogenic groups. These materials show properties of polymers, e.g., a glass transition where molecular motions are frozen in. Their glass transition temperature T_g is influenced by the length of the spacer (Figure 1) and the mesogenic group. As to be expected, T_g also depends on the nature of the main chain.⁴ In addition and as already described, these polymers also show properties of liquid crystals at temperatures above T_g , e.g., they can be oriented in electric^{5,6} and magnetic fields. In contrast to low molecular weight liquid crystals, these polymeric systems do not crystallize when cooled below T_g . Thus the liquid crystalline structure can be frozen in, allowing the investigation of glassy liquid crystalline systems. Unknown so far are any details about the influence of the spacer on the behavior of the mesogenic groups; especially there is no information about possible motions and the molecular order of the mesogenic units below T_g . The question to what extent the side group is decoupled from the main chain can be tackled, in principle, by a variety of techniques which can be employed to study liquid crystalline systems.⁹ In this com-

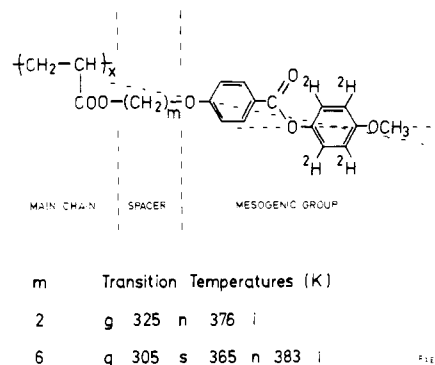


Figure 1. Structure and phase transitions of selectively deuterated liquid crystalline polymers. The molecular axis (---) of the mesogenic group as revealed by ^2H NMR line-shape analysis as well as the local C_2 axis (---) of the phenyl ring are shown. g denotes glass transition; s, n, i = transition to liquid crystalline smectic or nematic phase or to isotropic melt (determined by DSC).

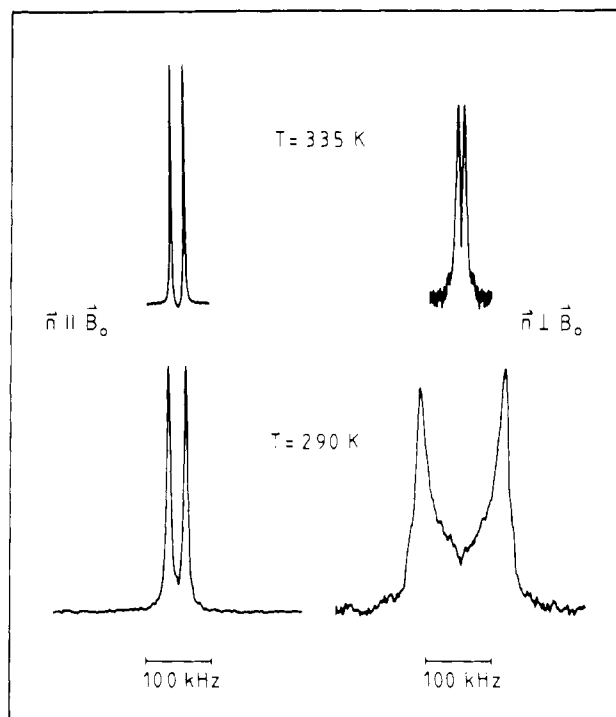


Figure 2. ^2H NMR spectra of the smectic liquid crystalline polymer (Figure 1), oriented in its nematic phase by the magnetic field (8.5T) of the NMR spectrometer, at 335 (above T_g) and 290 K (below T_g) with director \mathbf{n} parallel (left) and perpendicular (right) to the magnetic field.

munication we wish to give a preliminary report of a detailed study of molecular order and motion using ^2H NMR spectroscopy, concentrating on the system with a spacer length of $m = 6$, which shows both nematic and smectic phases. Deuteron NMR spectroscopy is especially appealing since it allows direct observation of the mesogenic group.¹⁰⁻¹⁵ Moreover, substantial changes are expected to show up in the ^2H spectra at T_g . While in the liquid crystalline phase the quadrupole coupling experienced by the ^2H nucleus is partially averaged due to molecular motion,^{9,10-15} leading

[†] Institut für Physikalische Chemie.

[‡] Institut für Organische Chemie.

(1) Finkelmann, H.; Ringsdorf, H.; Wendorff, J. H. *Makromol. Chem.* **1978**, *179*, 273-276.

(2) Shibaev, V. P.; Platě, N. A.; Freidzon, Y. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1655-1684.

(3) Finkelmann, H.; Portugall, M.; Ringsdorf, H. *Makromol. Chem.* **1978**, *179*, 2541-2544.

(4) Ringsdorf, H.; Schneller, A. *Br. Polym. J.* **1981**, *13*, 43-46.

(5) Ringsdorf, H.; Zentel, R. *Makromol. Chem.*, in press.

(6) Finkelmann, H.; Naegle, D.; Ringsdorf, H. *Makromol. Chem.* **1979**, *180*, 803-806.

(7) Finkelmann, H.; Day, D. *Makromol. Chem.* **1979**, *180*, 2269-2274.

(8) Kothe, G.; Ohmes, E.; Portugall, M.; Ringsdorf, H.; Wassmer, K. H., to be published.

(9) Luckhurst, G. R.; Gray, G. W. "The Molecular Physics of Liquid Crystals"; Academic Press: New York, 1979.

(10) Rowell, J. C.; Phillips, W. D.; Melby, L. R.; Panar, M. *J. Chem. Phys.* **1965**, *43*, 3442-3454.

(11) Luz, Z.; Hewitt, R. C.; Meiboom, S. *J. Chem. Phys.* **1974**, *61*, 1758-1765.

(12) Diehl, P.; Tracey, A. S.; *Mol. Phys.* **1975**, *30*, 1917-1920.

(13) Dong, R. Y.; Tomchuk, E.; Wade, C. G.; Visintainer, J. J.; Bock, E.; *J. Chem. Phys.* **1977**, *66*, 4121-4125; **1981**, *74*, 633-636.

(14) Emsley, J. W.; Khoo, S. K.; Luckhurst, G. R. *Mol. Phys.* **1979**, *37*, 959-972.

(15) Samulski, E. T.; Luz, Z. *J. Chem. Phys.* **1980**, *73*, 142-147; **1981**, *74*, 5825-5837.

to relatively narrow spectra, broad solid-state spectra are expected if the molecular motion of the mesogenic group is frozen in at T_g .

The selectively deuterated acrylate monomers were synthesized in analogy to the corresponding methacrylates^{1,16} by standard methods using 4-methoxyphenol- d_4 . This in turn was prepared from hydroquinone- d_4 (deuterated by exchange,¹⁷ 98.5% ^2H in the ring). The monomers were radically polymerized in solution, leading to heterotactic polymers with high contents of syndiotactic sequences; for details see ref 18. Phase transitions were determined by DSC (Perkin Elmer DSC 2c). ^2H spectra were obtained at 55 MHz by using the solid echo technique with quadrature phase detection described elsewhere.¹⁹ Typically 250–500 signals were accumulated with a repetition time of 0.5 s and a pulse delay of $\tau = 50 \mu\text{s}$. In Figure 2 ^2H NMR spectra at temperatures above and below T_g are shown for the smectic system ($m = 6$) with director \mathbf{n} parallel and perpendicular, respectively, to the magnetic field \mathbf{B}_0 . Above T_g , at 335 K the rotational motion of the phenyl ring about the direction of order is rapid enough to cause partial averaging of the quadrupole coupling. The angular dependence of the quadrupole splitting $\Delta\nu_Q$ on β_0 , the angle between \mathbf{n} and \mathbf{B}_0 , was observed to be in accord with

$$\Delta\nu_Q = \frac{3}{8}(e^2qQ/h)S_2(3 \cos^2 \theta - 1)(3 \cos^2 \beta_0 - 1) \quad (1)$$

which is characteristic for a smectic A system.^{9,11} Here e^2qQ/h is the quadrupole coupling constant of the deuteron, S_2 is the order parameter, and θ is the angle between the C– ^2H bond direction and the molecular axis of the mesogenic group (see below). The nomenclature is in accord with ref 20–22, where details are given. The values of the quadrupole splittings (7–13.6 kHz in the nematic, 16.4–27.7 kHz in the smectic phase with $\mathbf{n} \parallel \mathbf{B}_0$), and their temperature dependence are similar to those observed for deuterons in phenyl rings of low molecular weight liquid crystals,^{10–14} details will be given at a later date.²³

Below T_g , at 290 K a considerable increase in spectral width is observed with director $\mathbf{n} \perp \mathbf{B}_0$. In fact, a solid-state type spectrum is observed, covering a total width of more than 100 kHz. This immediately proves that the molecular motion of the mesogenic group changes appreciably at T_g . Of course, the dynamic glass transition temperature²⁴ as detected through a change in the ^2H spectrum is approximately 10 K higher than T_g as measured by DSC. Even at 335 K the motional averaging for $\mathbf{n} \perp \mathbf{B}_0$ is not yet complete; the doublet sharpens considerably at higher temperatures. For $\mathbf{n} \parallel \mathbf{B}_0$, however, a single quadrupole splitting is observed below T_g , although the phenyl ring contains two inequivalent deuterons in the rigid case. This is a first indication that restricted molecular motion of the mesogenic group might be present in the glassy state.

Both nature and timescale of that motion can be clarified by taking a rotation pattern for different orientations of \mathbf{n} with respect to \mathbf{B}_0 . The corresponding spectra as shown in Figure 3 never extend over the full spectral range of 250 kHz observed for rigid deuterons,^{19,21,22} proving that residual motions must be present. Considerable details can, in fact, be obtained from a line-shape analysis^{22,25} of the spectra observed (Figure 3), where calculated spectra are plotted at the right. The fit to the experimental ones yields three distinct pieces of information.

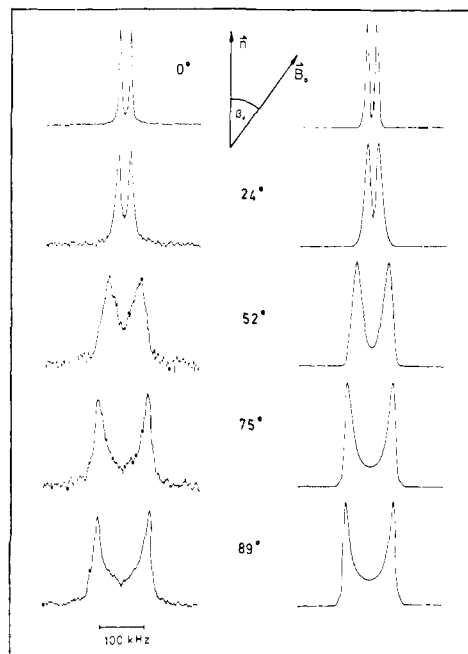


Figure 3. Observed and calculated ^2H spectra of the smectic liquid crystalline polymer (Figure 1) in its glassy state ($T = 290 \text{ K}$) for various angles β_0 between the director \mathbf{n} and the field \mathbf{B}_0 . For the deuteron the rotational motion generates an exchange between two sites, and the spectra were calculated as described elsewhere,^{25,26} taking into account the distortions of the experimental line shapes introduced by the solid echo techniques.²⁷ The line-shape function $S(\nu)$ was expanded in terms of planar distributions^{21,22} and the orientational distribution function $P(\beta)$ was expanded as suggested by a molecular field theory of liquid crystals:²⁸ $P(\beta) = \exp[\sum A_l P_l(\cos \beta)] / \exp[\sum A_l]$, $l = 0, 2, 4, \dots$, where β is the angle between the director and the molecular axis of the mesogenic group.^{20–22} The fitted values are $A_2 = 4$, $A_4 = 1$, $A_6 = 0.5$; $A_l = 0$ otherwise.

(i) The *type of motion* consisting of 180° rotational jumps of the phenyl rings about the molecular axis of the mesogenic group as indicated in Figure 1: It is the only type of motion consistent with the spectra observed. The molecular axis, about which the rotation occurs, and the local C_2 axis of the phenyl ring form an angle of $10 \pm 1^\circ$. This angle can directly be calculated from the ratio of the quadrupole splittings for $\beta_0 = 0$ and 90° , respectively.

(ii) The *correlation time* of the motion, $\tau_c = (3 \pm 1) \times 10^{-7}$ s at 290 K, a value at least two orders of magnitude longer than usually observed in liquid crystalline phases of low viscosity: It thus corresponds to a relatively slow motion observed even in crystalline solids.^{25,26}

(iii) The *degree of order*, which must be high as indicated by the marked angular dependence of the spectra: In fact, the complete orientational distribution function^{9,20–22} $P(\beta)$ of the molecular axes can be determined. It is found to closely resemble a Gaussian with width at half-height of $\pm 14^\circ$, corresponding to an order parameter $S_2 = 0.85 \pm 0.05$, in good agreement with the results of the ESR investigation of the same polymer.⁸

The high value of the order parameter observed in the glassy state, at least as high as found in low molecular weight smectic A systems,⁹ shows that the molecular order can fully be maintained when cooling a liquid crystalline polymer below the glass transition. Our ^2H investigation presented here proves, however, that the decoupling of the mesogenic group from the main chain while effective is not complete, as originally discussed^{1,3} and already contradicted by Magagnini,²⁹ because the molecular motion of the side groups changes appreciably at the glass transition of the

(16) Finkelmann, H.; Ringsdorf, H.; Siol, W.; Wendorff, J. H. *ACS Symp. Ser.* **1978**, No. 74, 22–32.

(17) Charney, E.; Becker, E. D. *J. Chem. Phys.* **1965**, *42*, 910–913.

(18) Hisgen, B. Master Thesis, University Mainz, 1980. Portugall, M. Ph.D. Thesis, University Mainz, 1981.

(19) Hentschel, R.; Spiess, H. W. *J. Magn. Reson.* **1979**, *35*, 157–162.

(20) Hentschel, R.; Schlitter, J.; Sillescu, H.; Spiess, H. W. *J. Chem. Phys.* **1978**, *68*, 56–66.

(21) Hentschel, R.; Sillescu, H.; Spiess, H. W. *Polymer*, in press.

(22) Spiess, H. W. In "Developments in Oriented Polymers"; Ward, I. M., Ed.; Applied Science Publishers London, 1981.

(23) Hisgen, B.; Pschorn, U.; Ringsdorf, H.; Spiess, H. W., to be published.

(24) Elias, H. G. "Macromolecules"; Wiley: London, 1977.

(25) Spiess, H. W. In *NMR, Basic Princ. Prog.* Diehl, P., Fluck, E., Kosfeld, R., Eds.; **1978**, *15*, 55–214.

(26) Pschorn, U.; Spiess, H. W. *J. Magn. Reson.* **1980**, *39*, 217–228.

(27) Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* **1981**, *42*, 381–389.

(28) Humphries, R. L.; James, P. G.; Luckhurst, G. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1031–1044.

(29) Bresci, B.; Frosini, V.; Lupinacci, D.; Magagnini, P. L. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 183–186.

polymer. The rotation about the molecular axis is severely restricted in the glassy state, where only solid-state-type rotational jumps by 180° are observed. This behavior is not unique to the systems studied here, e.g., the analogous liquid crystalline polymer with a spacer length of $m = 2$ (Figure 1) shows²³ a similar restricted motion below T_g . Rotational jumps of phenyl rings by 180° have also been proposed to exist in low molecular weight liquid crystalline systems and have recently been observed, e.g., for side groups in the crystalline pentapeptide enkephalin³⁰ and amorphous polystyrene³¹ below T_g .

Acknowledgment. We would like to thank H. Zimmermann (Max-Planck-Institut f. med. Forschung, Heidelberg) for helpful discussions concerning ^2H labeling. Financial support by the Deutsche Forschungsgemeinschaft (SFB 41) is gratefully acknowledged.

Registry No. Deuterated acrylate monomer ($n = 2$), 80434-50-0; deuterated acrylate monomer ($n = 6$), 80434-51-1; deuterated acrylate polymer ($n = 2$), 80434-75-9; deuterated acrylate polymer ($n = 6$), 80434-76-0.

(30) Rice, D. M.; Wittebort, R. J.; Griffin, R. G.; Meirovitch, E.; Stimson, E. R.; Melnwald, Y. C.; Freed, J. H.; Scheraga, H. A. *J. Am. Chem. Soc.* **1981**, in press.

(31) Pschorn, U.; Wehrle, M.; Sillescu, H.; Spiess, H. W. to be published.

High-Resolution NMR Spectroscopy of Quadrupolar Nuclei in Solids: Sodium Salts

Eric Oldfield,*† Suzanne Schramm, Michael D. Meadows, Karen Ann Smith, Robert A. Kinsey, and Jerome Ackerman†

School of Chemical Sciences
University of Illinois at Urbana
Urbana, Illinois 61801

Received September 4, 1981

Most elements that have a nuclear spin are quadrupolar, and it is generally accepted that high-resolution solid-state NMR studies of these systems using magic-angle sample spinning will be very difficult for nuclei having quadrupole coupling constants ≥ 100 kHz, due to technical limitations on rotor stability, and the presence of second-order quadrupolar broadening.¹⁻⁵ This view is of course correct for integral spins $I = 1, 2, 3$, etc., but about two out of three elements that possess nuclear spin have nonintegral spins $I = 3/2, 5/2, 7/2$, or $9/2$. The central $(1/2, -1/2)$ spin transition is only broadened by dipolar, chemical shift (or Knight shift) anisotropy and second-order quadrupolar broadening, and thus these $(1/2, -1/2)$ line widths are generally $\ll e^2qQ/h$. We show in this communication that high-resolution solid-state spectra may be easily obtained for ^{23}Na nuclei having e^2qQ/h values of up to 2-3 MHz, by monitoring the $(1/2, -1/2)$ spin transition selectively under conditions of rapid sample rotation, and note that these values may be increased to ~ 10 -15 MHz for other nuclei at higher magnetic field strengths, using high-field high-speed sample spinning techniques.

We show in Figure 1 ^{23}Na Fourier transform NMR spectra of a variety of ^{23}Na -containing solids, in which e^2qQ/h values vary from ~ 0 to ~ 2.6 MHz.⁶⁻¹⁰ Figure 1A shows static and mag-

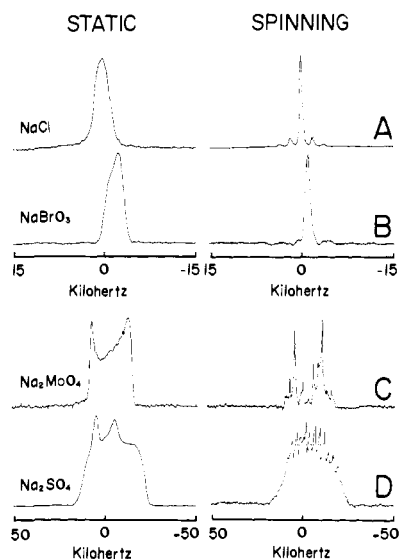


Figure 1. 40-MHz ^{23}Na Fourier transform NMR spectra of various ^{23}Na salts, with and without magic-angle ($\theta = 54.7^\circ$) sample spinning. (A) NaCl ($e^2qQ/h \sim 0$); (B) NaBrO₃ ($e^2qQ/h \sim 860$ kHz, $\eta \sim 0$); (C) Na₂MoO₄ (anhydrous, $e^2qQ/h \sim 2.6$ MHz, $\eta \sim 0$); (D) Na₂SO₄ ($e^2qQ/h \sim 2.6$ MHz, $\eta \sim 0.6$). Samples were spun at ~ 2 -3 kHz; sample size was ~ 0.5 cm³. The number of scans varied but was typically in the range 100-200. Chemicals were reagent grade and were checked by microanalysis. Spectra were recorded on a home-built instrument operating with a 3.5-T, 4.0-in. bore, superconducting solenoid.

ic-angle spinning spectra of $^{23}\text{NaCl}$, a cubic structure having $e^2qQ/h \sim 0$. As reported previously by others^{1,10} there is considerable line narrowing upon rotation at a rate of ~ 2 kHz, the static breadth. Similar results are, however, also obtained when investigating $^{23}\text{NaBrO}_3$ (Figure 1B) where e^2qQ/h values of 0.864 (± 0.008) MHz with $\eta \sim 0$ have been reported previously.^{8,9} The explanation, as suggested above, is that we are observing only the $(1/2, -1/2)$ spin transition and that the second-order broadening in this system is small (1-2 kHz^{11,12}) and, moreover, is substantially averaged upon magic-angle rotation, as seen more clearly below. Partial averaging of second-order quadrupolar broadening by spinning at 90° to the applied field has been noted previously by Nolle¹³ in which Mo(CO)₆ ($e^2qQ/h \sim 21$ kHz, $W_{1/2}^{(2)} \lesssim 100$ Hz) was rotated at speeds of up to 80 Hz¹³ and was first investigated theoretically by Andrew.¹⁴

For larger values of e^2qQ/h , for example, in the cubic spinel $^{23}\text{Na}_2\text{MoO}_4$ ($e^2qQ/h \sim 2.6$ MHz, $\eta = 0 \pm 0.1$ ref 6) or in $^{23}\text{Na}_2\text{SO}_4$ ($e^2qQ/h \sim 2.6$ MHz, $\eta \sim 0.6 \pm 0.1$, ref 7), residual second-order breadths are much larger, since the broadening is $\propto (e^2qQ/h)^2$. Residual breadths of ≈ 20 -30 kHz are thus observed (at 3.5 T), with the result that numerous spinning sidebands or rotational echoes are obtained in the spinning experiment^{15,16} (Figure 1C,D).

The results of Figure 1C,D indicate the need for (a) much higher field operation and (b) much higher spinning speeds, if such spinning experiments are to be of general utility, since the second-order broadenings are $\propto H_0^{-1}$. In addition, we have found that, as expected,^{3,17} magic angles other than 54.7° are more

*USPHS Research Career Development Awardee, 1979-1984.

†Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

(1) A. C. Cunningham and S. M. Day, *Phys. Rev.*, **152**, 287 (1966).
(2) A. Tzalmona and E. R. Andrew, *Magn. Reson. Relat. Phenom., Proc. Congr. Ampere*, **18th**, 241 (1974).

(3) M. M. Maricq and J. S. Waugh, *J. Chem. Phys.*, **70**, 3300 (1979).
(4) J. L. Ackerman, R. Eckman, and A. Pines, *Chem. Phys.*, **42**, 423 (1979).

(5) R. Eckman, M. Alla, and A. Pines, *J. Magn. Reson.*, **41**, 440 (1980).
(6) G. F. Lynch and S. L. Segel, *Can. J. Phys.*, **50**, 567 (1972).

(7) W. Gauss, S. Günther, A. R. Haase, M. Kerber, D. Kessler, J. Kronenbitter, H. Krüger, O. Lutz, A. Nolle, P. Schrader, M. Schüle, and G. E. Sieglösch, *Z. Naturforsch. A*, **33**, 934 (1978).

(8) H. S. Gutowsky and G. A. Williams, *Phys. Rev.*, **105**, 464 (1957).

(9) S. L. Segel and R. B. Creel, *Can. J. Phys.*, **48**, 2673 (1970).

(10) E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature (London)*, **183**, 1802 (1959).

(11) A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford, 1961, p. 233.

(12) M. D. Meadows, K. A. Smith, R. A. Kinsey, T. M. Rothgeb, R. P. Skarjune, and E. Oldfield, *Proc. Natl. Acad. Sci. U.S.A.*, in press.

(13) A. Nolle, *Z. Phys. A*, **280**, 231 (1977).

(14) E. R. Andrew, *Arch. Sci.*, **12**, 103 (1959).

(15) E. Lippmaa, M. Alla, and T. Tuherm, *Magn. Reson. Relat. Phenom. Proc. Congr. Ampere*, **19th**, 113 (1976).

(16) E. O. Stejskal, J. Schaefer, and R. A. McKay, *J. Magn. Reson.*, **25**, 569 (1977).