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SHORT COMMUNICATION

^{1}H Multiple-Pulse Solid-State NMR Investigations of Electrically Oriented Liquid Crystals

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For the discussion of orientional states in liquid crystals, quadrupolar (^{2}H NMR) and dipolar (^{1}H NMR) interactions have mainly been exploited. There have also been attempts to describe the individual (regarding different positions in a molecule) orientation and order by means of chemical shift information (^{13}C NMR). Owing to the large chemical shift range of carbons, ^{13}C NMR spectroscopy is suitable for providing resolved spectra of highly ordered systems such as low molecular mass liquid crystals. In the case of ^{1}H NMR, the chemical shift range is much smaller than the dominating dipolar interactions. An attempt to use multiple-pulse techniques to extract chemical shift information for static samples is presented. The tensor character of the chemical shift is reflected in the orientational dependence of the line position. The orientation of the liquid crystals can be manipulated by the *in situ* application of electric fields. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Among the NMR techniques exploiting chemical shifts, proton resonance in the solid state is commonly obtained using multiple-pulse experiments. In the usual single-pulse experiments there still remain contributions from dipolar interactions, even if high-speed magic angle spinning (MAS) techniques are applied. For static samples, as in our investigation, dipolar interactions completely cover the chemical shift range (expected to be of the order of 5–10 ppm). Owing to the anisotropy of the chemical shift in powder samples, the additional use of low-speed MAS[1–4] (about 1 kHz) or synchronized high-speed MAS[5] may be necessary to extract valuable information. Linewidth reduction factors regarding the homonuclear dipolar interaction of the order of 500 can be achieved by the use of multiple pulse irradiation. As known from investigations on single crystals, where there is no need for additional low-speed MAS, the spectral resolution of different chemical shift positions can be high enough to provide isolated resonance lines. In static samples, such as single crystals or ordered liquid crystalline systems, the resonance position depends on the orientation of the tensor in the laboratory frame. For single crystals, or other systems such as oriented polymers, access to the different tensor values is in principle possible by rotation around defined axes. Attempts have been made also to exploit the fluorine chemical shift tensor information to describe orientations in fluorine polymers by applying the MREV-8 pulse group to static samples,[6,7] using changes of the angular position of the sample relative to the magnetic field B_0. In the case of self-orienting nematic liquid crystals, the situation is more complicated because of the fact that the director of the nematic phase immediately follows the magnetic field. Additionally, the resolution will be reduced by the presence of distributions of molecular orientations in the sample. We assume a transverse isotropy, because of fast orientations around the molecular axes, and an axially symmetric distribution of the directors of nematic domains around a preferred axis in the sample (e.g. induced by the magnetic field B_0). The orientation of many liquid crystalline systems can be influenced by electric fields. We combined multiple-pulse NMR techniques and electrical excitations to access relatively defined orientational states. Early attempts at the application of multiple-pulse methods in the investigation of electrically induced orientation effects in electrets have been presented,[8] with discussion of the effect of orientation on the relaxation time T_{2e}.

EXPERIMENTAL

For test purposes, the well researched nematic liquid crystal *p*-pentyl-*p*′-cyanobiphenyl (5CB) (Merck) was

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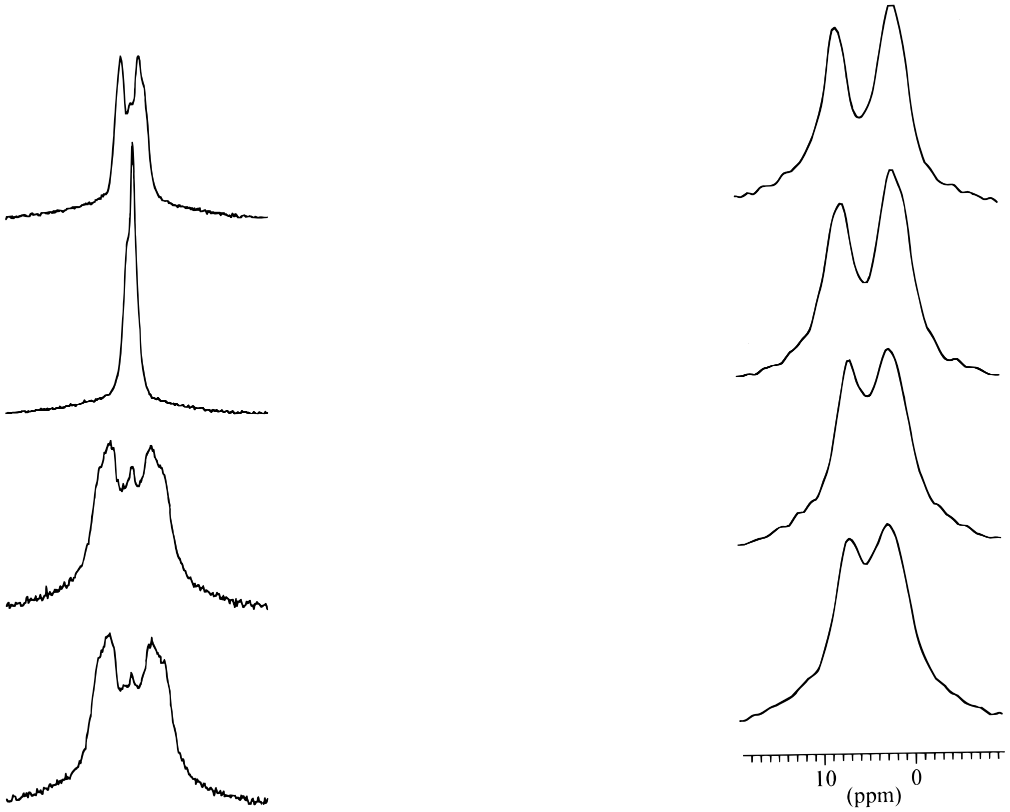


(a) (b)

Figure 1. Demonstration of the influence of electric fields on a capacitor sample of 5CB (thickness 200 µm) on (a) dipolar effects and (b) chemical shift information. The ^{1}H NMR spectrum acquired after a single 90° pulse shows the typical pattern of oriented liquid crystals. The spectrum is dominated by dipolar interactions. Multiple-pulse operation leads to drastically narrowed spectra, revealing the chemical shift information. (a) Stack plot of selected single-pulse spectra in dependence on the applied voltage (spectral width 80 kHz). (b) Analogous plot showing the multiple-pulse spectra acquired under identical electric conditions (MREV8). Voltages (from bottom): 0, 85, 120, 140 V.

investigated. This substance exists in the nematic phase between 22.5 and 35 °C. The NMR experiments were carried out using a 100 MHz (proton resonance frequency) spectrometer (Bruker MSL100). A probe with an extremely short ring-down time, operating only at proton frequencies, with improved background conditions (Bruker HP FF 100WB 1H sol5) was used. The resonance frequency of 100 MHz is a compromise regarding the NMR sensitivity, the rising influence of the chemical shift at higher magnetic fields on the dipolar-dominated spectra and the ratio of the anisotropies of the permittivity and the diamagnetic susceptibility.

For recording the chemical shift spectra the sequence MREV8[9] $(\tau, -x, \tau, y, 2\tau, -y, \tau, x, 2\tau, x, \tau, y, 2\tau, -y, \tau, -x, \tau)$ was applied. A 90° pulse duration of 1.5 µs was used. The spacing in the MREV8 sequence was 3 µs; 256 data points taken in the last large window of a group of eight pulses were acquired stroboscobically. Since the experiments were carried out on static highly oriented systems, isotropic chemical shifts were not known *a priori*. Therefore, scaling experiments were performed. The chemical shifts are given in relation to the position of the methylene resonance of poly(dimethylsiloxane). In contrast to the capacitor design of the nematic film, a spherical sample of PDMS was used.

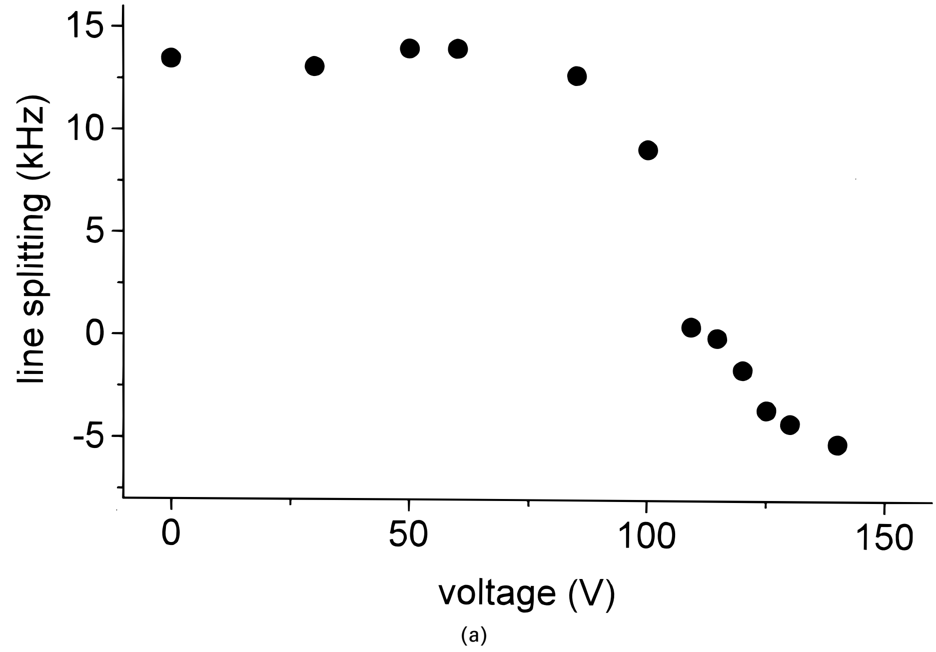
Laboratory-made equipment for realizing a special high-voltage design was constructed for the experiments. The broadline spectra and the multiple-pulse spectra were recorded under identical conditions for electric excitation. Using known electric parameters from preliminary experiments, the field was applied for only a short period before the first 90° pulse, until the orientation achieved an equilibrium state (of the order of 10 ms) and during the data acquisition (1 ms FID, 10 ms multiple pulse) in order to avoid degradation and any turbulence effects. The normal to the capacitor surface (electric field direction) was placed at an angle of about 90° relative to the magnetic field because of the positive values of the anisotropy of the permittivity and of the susceptibility.

The preparation of the sample has been described elsewhere.[10]

In contrast to ^{13}C NMR experiments, the disadvantage of the time-consuming tuning procedure for proton multiple-pulse experiments is mitigated by the sensitivity of the proton resonance. Investigations of effects in relatively thin films (≥ 10 µm, which means amounts of ≥ 0.5 mg) of liquid crystal material under the influence of electric fields are also possible using multiple-pulse experiments.

RESULTS AND DISCUSSION

In order to discuss the orientational state of the material, the dipolar-dominated lineshape of the sample



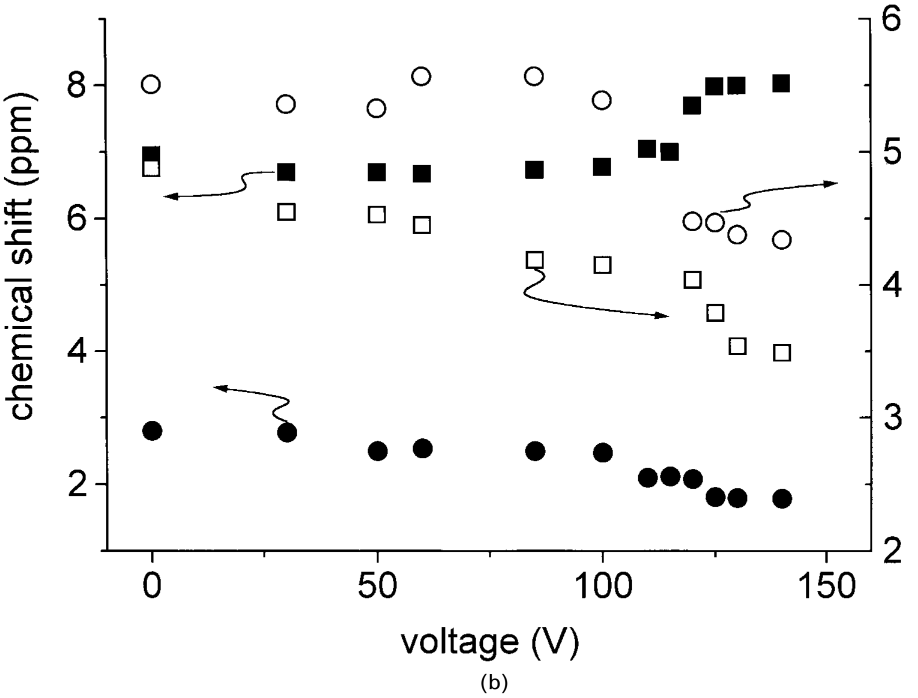


Figure 2. (a) Dependence of ^{1}H NMR line splitting on the applied voltage. (b) Electric field effects on the chemical shift: dependence of resonance position on the voltage (full symbols) and narrowing of the linewidth of the individual resonances under the influence of the electric field (open symbols); circles denote the aliphatic resonance line and squares the phenylene resonance.

has been investigated with regard to its dependence on the voltage. The orientational state of a nematic liquid crystal is reflected in the angular dependence on the lineshape. There is almost no indication of the chemical shift influence on the broadline spectrum. The line-splitting data can be used for correlation with the analogous information obtained by means of the multiple-pulse experiments. Known functionalities between dipolar splitting and orientational angle[10] were used. The line splitting depends on the position of the director resulting from the equilibrium of the magnetic and electric field torques. An isotropic distribution and molecular motion around the macroscopic alignment were assumed for the investigated nematic liquid crystal 5CB.

The chemical shift part of the spectrum is revealed after the manipulation of the spin system using the MREV8 sequence. The residual linewidth in the multiple-pulse spectra arises mainly from to orientational distributions in the sample, from imperfections due to deviations of the sample form, from the theoretically predicted ideal shape and from the multiple-pulse technique itself. The influence of the applied voltage on the broadline spectra and on the higher resolution spectra is shown in Fig. 1. The angular dependence on the alignment angle relative to the magnetic fields can be derived from the line splitting in the broadline spectra. For lower voltages, the occurrence of the effect of the Freedericksz transition[11] from homogeneous to homeotropic orientation can be discussed qualitatively in the same way by means of both broadline and chemical shift spectra. A threshold voltage of about 50 V was found with both methods.

We expect two effects on individual resonance lines in the chemical shift spectrum. First, the line position represents the tensor character of the anisotropic chemical shift interaction. Second, an influence of the strength of the applied fields on the molecular order could be reflected in a changed linewidth. As demonstrated in Fig. 2(a), both effects are observed. The spectra show two clearly resolved peaks arising from the aliphatic and the phenylene protons. The chemical shift positions of the aliphatic and phenylene parts of the molecule depend on the applied voltage. The broad line and the multiple-pulse spectra were acquired under identical electrical conditions. The difference between the lines starts from about 4 ppm and increases under the influence of the electric fields up to 6 ppm. The values are comparable to those reported in the literature regarding chemical shift anisotropies of small molecules such as benzene.[12] The observed chemical shift can be used in a similar way to the dipolar splitting to describe the orientational state. In order to extract linewidth information, all spectra were deconvoluted using a two-component Lorentzian fit [Fig. 2(b)]. The use of an electric field allows the investigation of field-strength effects. The increase in the orientational order is reflected in the linewidth of both lines after the deconvolution in the same way. No differentiation can be observed in the behaviour of the aliphatic and phenylene parts.

The extraction of orientational parameters from the chemical shift spectra alone is complicated by the superposition of different effects. The influence of the residual linewidth in the application of multiple-pulse narrowing techniques has to be considered.

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REFERENCES

1. U. Haeberlen and S. Waugh, *Phys. Rev.* **175**, 453 (1968).
2. J. S. Waugh, L. M. Huber and U. Haeberlen, *Phys. Rev. Lett.* **20**, 180 (1968).
3. G. Scheler, U. Haubenreisser and H. Rosenberger, *J. Magn. Reson.* **44**, 134 (1981).
4. P. Jackson and R. K. Harris, *Magn. Reson. Chem.* **36**, 1003 (1988).
5. S. Hafner and H. W. Spiess, *J. Magn. Reson. A* **121**, 160 (1996).
6. J. Brandolini, M. D. Alvey and C. Dybowski, *J. Appl. Polym. Sci., Polym. Phys. Ed.* **21**, 2524 (1983).
7. J. Brandolini, K. J. Rocco and C. Dybowski, *Macromolecules* **17**, 1455 (1984).
8. D. Geschke, P. Holstein and M. Mendler, *Acta Polym.* **39**, 206 (1988).
9. W. K. Rhim, D. D. Ellemann and R. W. Vaughan, *J. Chem. Phys.* **59**, 3740 (1973).
10. M. Winkler, D. Geschke and P. Holstein, *Liq. Cryst.* **17**, 283 (1994).
11. P. G. deGennes and J. Prost, *The Physics of Liquid Crystals*. Clarendon Press, Oxford (1993).
12. P. Diehl and C. L. Khetrapal, *J. Magn. Reson.* **1**, 524 (1969).