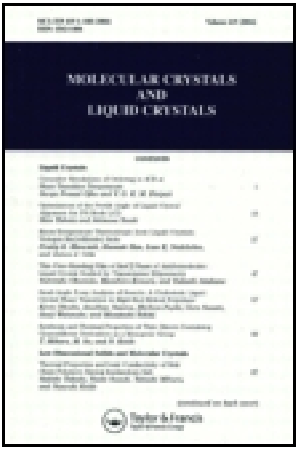


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular Motions and Mesophases in Anhydrous Thallium (I) Soaps Studied by ^{1}H- and ^{205}TL-NMR. The ^{205}TL Chemical Shift Tensor

G. Klose [a], F. Volke [a], M. Hentschel [a] & A. Möps [a]

[a] Department of Physics, Karl Marx University Leipzig, DDR-7010, Leipzig, Linnestr. 5, G.D.R.

Version of record first published: 20 Apr 2011.

To cite this article: G. Klose , F. Volke , M. Hentschel & A. Möps (1983): Molecular Motions and Mesophases in Anhydrous Thallium (I) Soaps Studied by ^{1}H- and ^{205}TL-NMR. The ^{205}TL Chemical Shift Tensor, Molecular Crystals and Liquid Crystals, 90:3-4, 245-254

To link to this article: http://dx.doi.org/10.1080/00268948308072453

Mol. Cryst. Liq. Cryst., 1983, Vol. 90, pp. 245–254
0026-8941/83/9004-0245$18.50/0

Printed in the United States of America

Molecular Motions and Mesophases in Anhydrous Thallium (I) Soaps Studied by ^{1}H- and ^{205}TL-NMR. The ^{205}TL Chemical Shift Tensor.

G. KLOSE, F. VOLKE, M. HENTSCHEL and A. MÖPS

Department of Physics, Karl Marx University Leipzig, DDR-7010 Leipzig, Linnestr. 5, G.D.R.

(*Received May 12, 1982*)

The thermotropic phases of fatty acid (C_{12}, C_{14}, C_{22}) thallium (I) salts were studied by the spin-1/2-pair dipolar echo ^{1}H-NMR method and by ^{205}Tl-NMR in the temperature range from 230 K to 480 K. For the first time the ^{205}Tl chemical shift tensor in such soaps in the crystalline state was shown to be axially symmetric and to exhibit an anisotropy of -780 ± 8 ppm. Also for the first time, a detailed characterization of the dynamical properties of the liquid crystalline mesophases was performed; this allows some conclusions to be reached about the structure of the mesophases present in the C_{12} and C_{14} soaps below their isotropic states. The phases of the various soaps studied were unambiguously assigned.

INTRODUCTION

While the liquid crystalline phase behavior of anhydrous sodium, potassium and calcium soaps has been extensively studied by different methods, little is known about that of thallium (I) soaps[1] (and references cited therein). Meisel *et al.*[2] started a study of the thermal behavior of some thallium (I) soaps and this was systematically extended to a complete homologous series of soaps by Lindau *et al.*[3] employing also polarizing microscopy and X-ray diffraction. The characterization of the different phases observed in the various soaps leaves many questions open for discussion, and almost nothing is known about the dynamical properties of the thermotropic phases.

The NMR of the thallium nucleus in combination with proton NMR provide powerful methods to obtain information about the structure and the dynamical properties of the phases of thallium (I) soaps. We have studied three aliphatic thallium (I) soaps with chain lengths of 12, 14 (short chains) and 22 (long chain) carbon atoms by the spin-1/2-pair-dipolar echo ^{1}H-NMR method and by ^{205}Tl-NMR. For the first time, detailed dynamical properties of the molecules in the liquid crystalline mesophases could be deduced by these methods. Also some indications relating to structural features were obtained. An unambiguous assignment of these phases was made which can be generalized to other soaps studied in Ref. 3.

Finally, we have determined for the first time the solid state thallium-205 screening tensor for thallium (I) soaps.

METHODS AND MATERIALS

The ^{1}H- as well as the ^{205}Tl-NMR measurements were performed at 32 MHz (Bruker, BKR 322 s spectrometer).

The proton interpair moments M_2 (interpair) were determined using the spin-1/2-pair-dipolar echo (SPDE) method.[4-6] According to this method two 90°-phase shifted 90° pulses were applied; the time distance τ of these was varied from 5 to 300 μs (pulse width 1.5 μs). The maximum echo amplitude appearing after the second pulse was measured as a function of τ. From the initial decay of the maximum echo amplitude, the average M_2 (interpair) can be determined. The moments obtained are considered to be accurate to within $\pm 10\%$.

The ^{205}Tl-NMR spectra were obtained by the Fourier technique. The following experimental conditions were used: pulse width about 4 μs, spectrum points 4 k, spectrum width 250 KHz, delay time 0.5 . . . 2 s; up to 4 k scans were collected in the case of the solid state spectra, otherwise less. The line shape calculations from the ^{205}Tl-NMR spectra were performed with a computer program in an analog manner as in Ref. 17.

The sample temperature was controlled with an accuracy of ± 1 K. The three thallium (I) soaps of the corresponding aliphatic fatty acids with $n = 12$, 14 and 22 carbon atoms (denoted below as TlC_{12}, TlC_{14}, TlC_{22}) were kindly supplied by Dr. Lindau, Chemical Department, Martin Luther University, Halle.

RESULTS AND DISCUSSION

In Figure 1, the values of M_2 (interpair) are shown as a function of temperature. In the low temperature region, denoted by C in Figure 1, M_2 (interpair) in the three soap systems is between 7 and $8 \cdot 10^{-8}T^2$. Such values are characteristic of solid, crystalline systems with an all-trans chain conformation.[5] In TlC_{12} at 253 K, a moment of $9.2 \cdot 10^{-8}T^2$ was measured (not indicated in Figure 1). With increasing temperature, M_2 (interpair) decreases drastically at definite temperatures and levels out at about $3 \cdot 10^{-8}T^2$ for all soaps. The transition region coincides quite well with the phase transition temperature obtained by means of DSC, polarizing microscopy, and X-ray scattering.[3] The decrease of M_2 (interpair) to values of about $3 \cdot 10^{-8}T^2$ is very similar to the behavior of the aliphatic chains in synthetic phospholipids in the gel state. There are thermally activated, restricted rotational oscillations of the chain segments which average the interpair dipolar interactions to some extent. Obviously, the chains in TlC_{22} exhibit a somewhat higher mobility at the high temperature end of phase II with respect to those in TlC_{12} and TlC_{14} at their high temperature ends of this phase (see Figure 1). This can be explained by two or three trans-gauche isomerizations within one chain[5,6] which occur preferably at the chain ends. Apparently the long chain TlC_{22} differs from the short chain soaps TlC_{12} and TlC_{14} which are in phase II in the all-trans state. For TlC_{22} an increasing number of trans-gauche defects with increasing temperature will reduce the value of M_2 (interpair).[5]

In TlC_{12} and TlC_{14}, a further M_2 (interpair)-plateau (denoted by I in Figure 1) with a value of about $1.3 \cdot 10^{-8}T^2$ is observed which does not occur in TlC_{22}. This is caused by a higher degree of segmental motions. The value of the moment in phase I is comparable with that at the high temperature end of the pretransition region of dipalmitoylglycerophosphatidylcholine (307–315 K).[5] In TlC_{12} and TlC_{14} at temperatures higher than 400 K (up to the transition into the isotropic state), no well-resolved solid echos could be detected. From the shape of the transient signal observed we conclude that the intrapair dipolar interactions are no longer stronger than the interpair interactions, a condition which must be fulfilled for the SPDE method.

The reduction of the intrapair interaction can be explained by less restricted segmental motions of the chains with respect to real lamellar systems. Moreover, since ^{205}Tl-NMR still indicates a strongly motional-restricted head group of the soap (COOTl segment), the presence of non-lamellar structures is likely (see below). Maybe the ribbon struc-

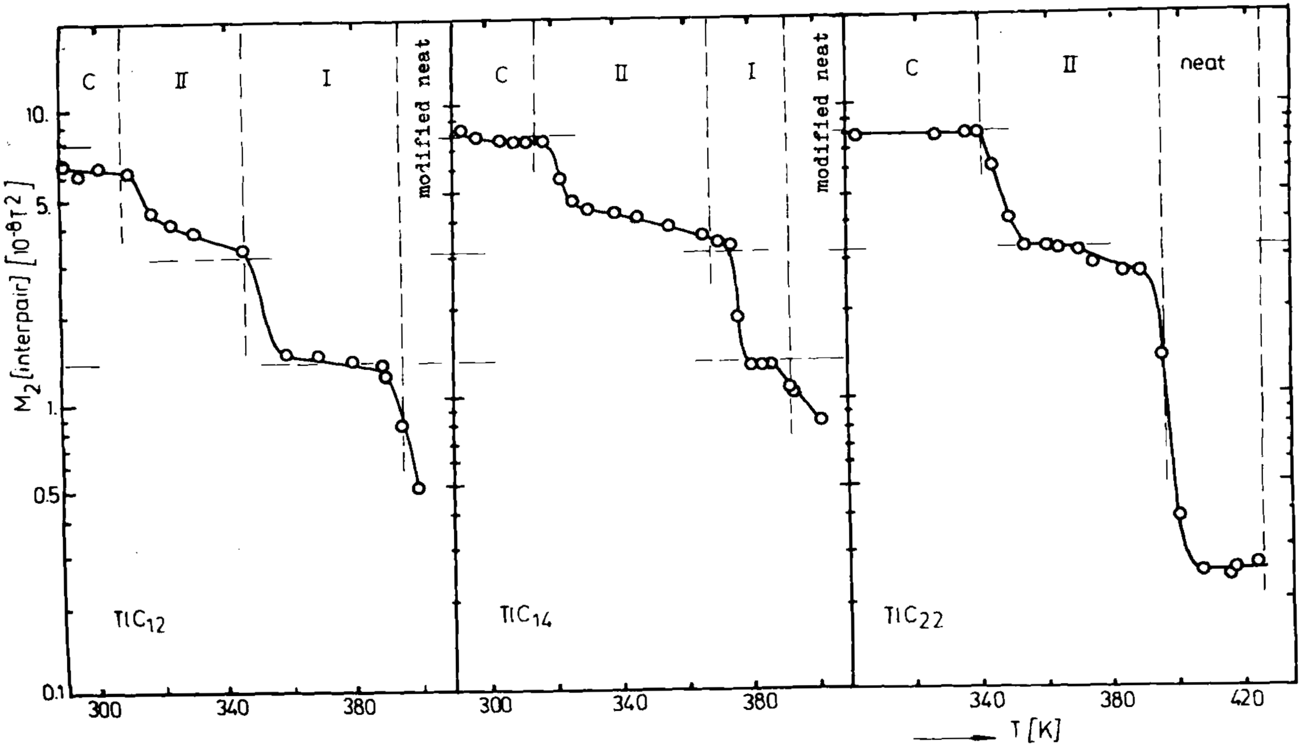


FIGURE 1 M_2 (interpair) as a function of temperature. The dashed lines are for visual help in comparing the three soaps and show approximately the phase transition temperatures.

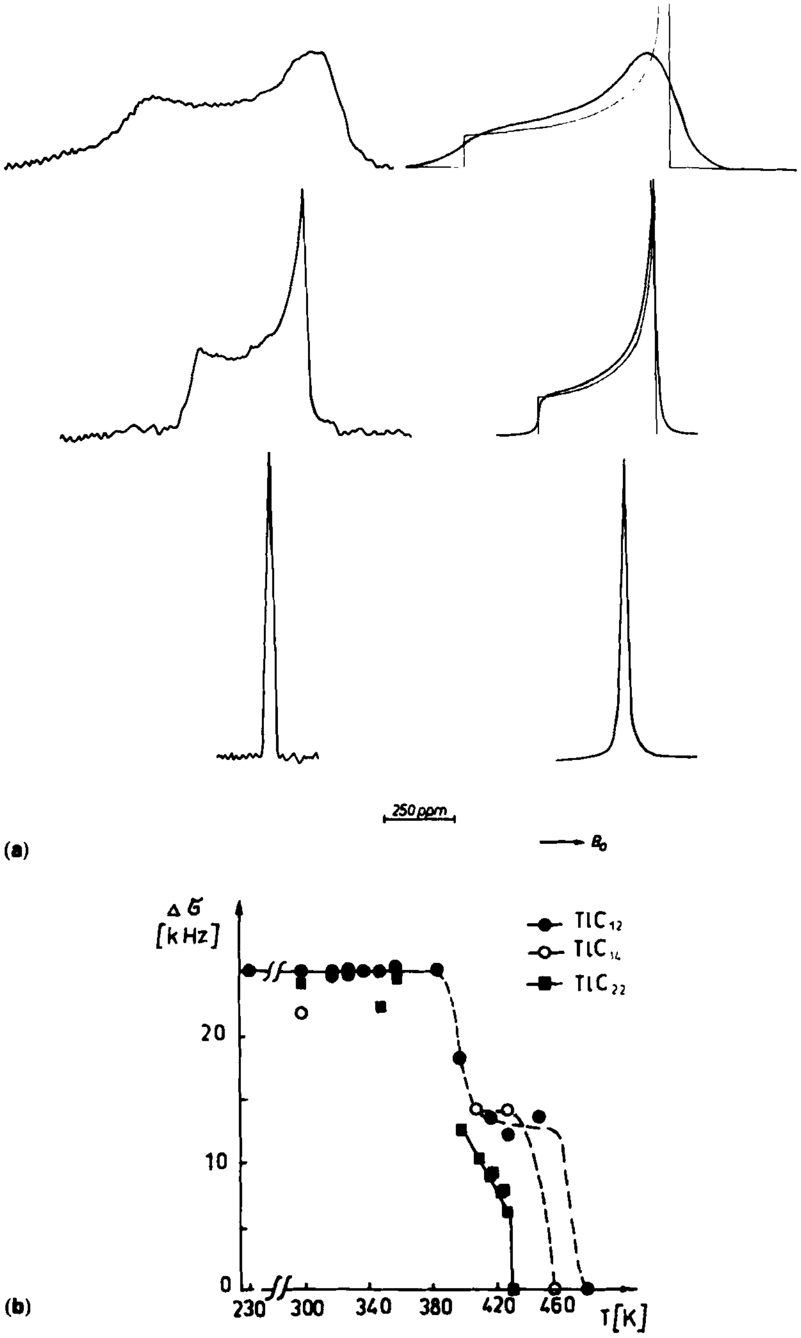
ture is preserved or other smaller units (discs) are formed.[1] This can be understood if we assume that in short chain soaps the Coulomb interactions between the head groups are the determining intermolecular interactions. From the larger Tl chemical shift anisotropy with respect to that in TlC_{22} in the high temperature phase (see below), we can infer that the head groups in TlC_{12} and TlC_{14} are more closely packed than the head groups in TlC_{22}.

The high temperature phase of TlC_{22} exhibits a structure[3] and dynamical properties characteristic of the neat phase.[1] The dynamical properties of TlC_{12} and TlC_{14} in the high temperature phase are considerably different from the properties of TlC_{22} in the neat phase. We term this phase "modified neat" phase, to differentiate it from the neat phase in TlC_{22} and for reasons discussed in connection with the Tl-NMR spectra in these phases. On the other hand Lindau *et al.*[3] termed the "modified neat" phase as a neat state. The term "modified" takes into account the observed dynamical difference between these neat phases in the three soaps. Obviously phase C is the crystalline phase. In TlC_{22}, the phase I is not realized because of the stronger van der Waals interactions between the chains in comparison with those in the short chain soaps. These interactions force TlC_{22} to transform directly from phase II to the lamellar state (neat phase) on raising the temperature.

The SPDE method yields a well-resolved echo in the neat phase of TlC_{22}. The analysis gives M_2 (interpair) $= 0.25 \cdot 10^{-8} T^2$ which is characteristic of the fluid lamellar state.[5] The average order parameter of the chains is 0.17 and can be explained by 5 to 7 trans-gauche defects per chain and effective rotational symmetry of the molecules about the long axis. Furthermore, a fast lateral diffusion of the molecules averages out all intermolecular dipolar interactions.

The ^{205}Tl-NMR spectra typical of the thallium soaps are shown in Figure 2a. The line shape as well as the line width of the individual lines does not change in the low temperature phases C, II and I measured down to 230 K. Together with our knowledge from ^{1}H-NMR, this is evidence that we are observing solid state ^{205}Tl-NMR powder spectra and that the phase transitions between the low temperature phases cannot be connected with significant structural and/or dynamical changes of the head group segment, but with changes in the mobility of the hydrocarbon chains. Apparently the head groups form very rigid units in the low temperature phases (ribbons or discs[1,7]) because of their strong Coulomb interactions.

Surprisingly, the ^{205}Tl-NMR screening tensor is axially symmetric within the limits of the accuracy of the measurements; this is also the


250 ppm
→ B_0
(a)
Δσ [kHz]
20
10
0
230
300
340
380
420
460
T [K]
TlC₁₂
TlC₁₄
TlC₂₂
(b)

case in the low temperature phases. Computer simulations of the thallium-anisotropy of chemical shift spectra were made and showed that even a small deviation from the axially symmetric tensor would be detected if the difference of two tensor components is about 1 KHz. Similar results for an axially symmetric screening tensor for the solid state of a lyotropic liquid crystal were published by Söderman *et al.*[18] for the fluor-counterion.

The analysis of the spectra yields the solid state chemical shift anisotropy

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = -780 \pm 8 \text{ ppm}.$$

The position of the screening tensor in the head group can be experimentally be determined using single crystals. Unfortunately such crystals of thallium soaps were not available. However, we can find out its position taking advantage of the effective chemical shift anisotropy $\Delta\sigma_{\text{eff}}$ measured for TlC_{22} in the neat phase (Figure 2b).

The head group atoms span a plane (Figure 3) and the oxygen atoms are chemically equivalent.[8,9] This was proved for the TlC_{22} soap by IR-spectroscopy, using a Perkin-Elmer 621 spectrophotometer.[19] It is reasonable to assume that the thallium atom lies in this plane and on the symmetry axis of the head group A defined by the C_1—C_2 bond direction.

We need only consider two possibilities for the position of the symmetry axis A^{CSA} of the thallium solid state screening tensor: (1) A^{CSA} parallel to A and (2) A^{CSA} perpendicular to A (in or perpendicular to the plane).

In the neat phase of TlC_{22} we take into account a fast rotation of the head group around its symmetry axis A and a fast symmetrical motion around the director D of the lamellae (see Figure 3)—(motional model of Petersen and Chan[10]). The same motional model was employed to explain for example the ^{31}P-NMR spectra in liquid crystalline lipid-water dispersions (see e.g. Ref. 11). In case (1) the rotation around A does not influence the screening tensor. However, the motion around

FIGURE 2 (a) ^{205}Tl-NMR spectra of anhydrous thallium (I) soaps recorded at a frequency of 32 MHz. Experimental spectra are shown on the left. The calculated spectra (solid lines) were broadened by Gaussian lines (for solid state spectra) or Lorentzian lines (for all remaining cases). At the top, the spectrum for the C, II and I phases is given. In the middle, the spectrum of the neat and/or "modified" neat phase is shown, and at the bottom, the spectrum is for the isotropic phase of the three thallium soaps.

(b) Thallium-205 chemical shift anisotropy as a function of temperature for the three soaps investigated. The solid lines are only to aid visual clarity.

D reduces the chemical shift anisotropy according to

$$\Delta\sigma_{\mathrm{eff}} = S\Delta\sigma$$

where $S = \frac{1}{2}\,\overline{(3\cos^2\theta - 1)}$ is the order parameter.[16] The bar denotes the time average. Using $\Delta\sigma_{\mathrm{eff}} = -406$ ppm measured for the neat phase (Figure 2b), we obtain $S = 0.52$. Assuming $\theta = \theta_0 =$ constant, we have $\theta_0 = 34°$. Or, if we assume motions in a cone with half cone angle θ_0^{cone}, and a constant distribution in the cone, $S = \frac{1}{2}\cos\theta_0^{\mathrm{cone}}(1 + \cos\theta_0^{\mathrm{cone}})$ and we obtain $\theta_0^{\mathrm{cone}} = 50°$.[10]

In both models the C_1—C_2 bonds are oriented preferably parallel to D in the neat phase, which is likely. In the frame of the motional model assumed, case (2) leads to contradictions and is therefore unlikely. The orientation of A^{CSA} parallel to A found by these considerations is in agreement with the rule that the largest screening value is oriented along the axis of the largest electron density.[12,15] In TlC_{22}, $\Delta\sigma_{\mathrm{eff}}$ decreases in the neat phase if the temperature is raised (Figure 2b). This is explainable by increasing fluctuations of A with respect to D (increasing chain mobility) which should cause a decrease of the layer thickness. In TlC_{12} and TlC_{14} in the modified neat phase, the temperature influence on $\Delta\sigma_{\mathrm{eff}}$ is smaller (Figure 2b). These findings are in agreement with the observations made by means of X-ray scattering that in long chain thallium soaps the layer thickness decreases more strongly than in short chain thallium soaps.[3]

$\Delta\sigma_{\mathrm{eff}}$ in TlC_{12} and TlC_{14} in the modified neat phase is somewhat larger than $\Delta\sigma_{\mathrm{eff}}$ in TlC_{22} in the neat phase. This indicates that the head group motions in the former soaps are more restricted than in the latter.

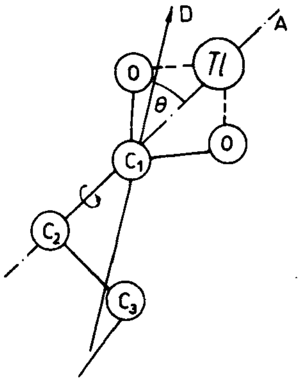


FIGURE 3 The model assumed for thallium soap head group motions.

All results obtained for thallium (I) soaps agree with the concept[7] that in soaps having a small organic part, the ionic directional forces will dominate, while if the organic part is large, its space requirements will govern the structure and the dynamical properties.

At the transition to the isotropic state, $\Delta\sigma_{eff}$ drops to zero as expected. The intensity distribution of the thallium NMR line shapes observed for the neat and modified neat phases is strange. One explanation would be a non-statistical distribution of the directors of the lamellar or other structural units.[13,14] However, a change of the sample orientation in the magnetic field does not influence the line shape. That means that a partial orientation in the sample must rapidly (some minutes) follow the magnetic field or there is another reason for the strange line shape. A medium fast motion, e.g., trans-gauche transitions involving the C_2C_1OOTl segment as a whole unit (rotation around the C_2—C_3 bond) can also yield the line shapes observed for the neat phase.[15]

CONCLUSION

1. The low temperature phases below neat and modified neat for thallium (I) soaps differ in the dynamical properties of the hydrocarbon chains, but not in those of the head groups.
2. The assignment of the phases in the different soaps is unambiguous using proton interpair moments.
3. A neat phase is observed for TlC_{22} at high temperature, while in the short chain soaps TlC_{12} and TlC_{14}, a modified neat phase is formed below the isotropic phase. The chains are more ordered in the neat phase than in the modified neat phase, while the head groups are less closely packed in the neat phase than in the modified neat phase.
4. The tensor of the thallium chemical screening is axially symmetric in crystalline thallium (I) soaps and exhibits an anisotropy of $\Delta\sigma = -780 \pm 8$ ppm.

Acknowledgments

The authors thank Dr. Lindau (MLU, Halle) for supplying the soaps and are also grateful to him and Dr. Förster (MLU, Halle) for many helpful discussions. We are indebted to Mr. B. Hillner for excellent NMR service. We thank Dr. M. Ackermann (KMU, Leipzig) for running the IR-spectra and the interpretation of the results.

References

1. G. J. T. Tiddy, *Phys. Rep.*, **57**, 1 (1980).
2. T. Meisel, K. Seybold, Z. Halmos, J. Roth and C. Melykuti, *J. Thermal Analysis*, **10**, 419 (1976).
3. J. Lindau, S. Diele, H. Krüger and H.-D-Dörfler, *Z. Phys. Chemie*, **262**, 775 (1981).
4. N. Boden and Y. K. Levine, *J. Magn. Reson.*, **30**, 327 (1980).
5. F. Volke, PhD Thesis, Karl Marx University, Leipzig (1981).
6. F. Volke, K. Arnold and K. Gawrisch, *Chem. Phys. Lipids* (1982) in press.
7. K. Fontell in "Thermodynamic and Transport Properties of Organic Salts", Ed., P. Franzosini and M. Sanesi, Pergamon Press, 1982.
8. R. H. Pearson and I. Pascher, *Nature*, **281**, 499 (1979).
9. M. Sundaralingam, *Ann. N.Y. Acad. Sci.*, **195**, 325 (1972).
10. N. O. Petersen and S. I. Chan, *Biochemistry*, **16**, 2657 (1977).
11. K. Arnold, E. Löbel, F. Volke and K. Gawrisch, *Studia Biophys.*, **82**, 207 (1981).
12. T. Weller, U. Franck, G. Klose and R. Lochmann, *Z. Phys. Chem.*, **22**, 62 (1981).
13. R. Hentschel, J. Schlitter, H. Sillescu and H. W. Spiess, *J. Chem. Phys.*, **68**, 56 (1978).
14. H. W. Spiess in "NMR-Basic Principles and Progress", Vol. 15 (1978) Springer Verlag.
15. M. Mehring in "NMR-Basic Principles and Progress", Vol. 11 (1976) Springer Verlag.
16. R. F. Campell, E. Meirovitch and J. H. Freed, *J. Phys. Chem.*, **83**, 525 (1979).
17. N. Bloembergen and T. J. Rowland, *Phys. Rev.*, **97**, 1679 (1955).
18. O. Söderman, A. Khan and G. Lindblom, *J. Magn. Reson.*, **36**, 141 (1979).
19. M. Ackermann, unpublished results.