Proton NMR Studies of the Smectic-G Phase of Terephthalylidene-Bis-4-n-propylaniline (TBPrA)

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Z. Naturforsch. **39 a**, 651–657 (1984); received March 19, 1984

Proton NMR studies and lineshape simulations of the smectic-G phase of TBPrA are presented. From them a model for the layer arrangement in smectic-G is suggested. It postulates a freezing-in of the layer structure at the smectic-C–G phase transition. The layer normals are inclined at a fixed angle to the polarizing magnetic field corresponding to the tilt angle at the end of the C phase. The tilt of the molecular directors in the G phase is much greater (because of a relatively large negative jump in the layer thickness at the C–G-transition) and grows with decreasing temperature. Moreover a distribution of the molecular directors on the fictive tilt cone (in smectic-G there is no possibility for the directors to reorient about the layer normal as in smectic-C) has to be employed to get a good fit to the experimental data.

1. Introduction

In a recent paper [1] we have presented a proton NMR investigation of three alkyloxybenzylidene-alkylanilines (nO.m's) in their mesophases. It could be shown that even in the smectic-G phases the molecular directors, once aligned by a strong magnetic field (≈ 0.75 T) in the smectic-A phase, remain aligned parallel to the direction of the original polarizing field, i.e. as fixed in smectic-A.

The proton NMR spectra of these compounds didn't change significantly from nematic to smectic-G, and the angular dependences in all smectic phases were very similar (except, of course, smectic-C). In the present substance TBPrA the spectral lineshape changes with temperature from nematic to smectic-H markedly, as discussed already before [2]. In this paper we shall be mainly concerned with the transition from smectic-C to smectic-G and the latter phase itself. The substance investigated here seems very interesting also from the fact that there is a relatively large "jump" in the layer thickness (and hence the tilt angle) at the smectic-C to smectic-G transition in contrast to TBBA where only a very small discontinuity can be observed [3]. We shall interpret the proton NMR data by suggesting a model for the structural organization within this phase which differs from that of the smectic-G phase of the nO.m's.

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2. Results

In Fig. 1 typical proton NMR spectra of nematic, smectic-A, smectic-C, and some characteristic spectra of he C–G transition region and the G phase are shown. (All spectra have been recorded at 32 MHz corresponding to magnetic fields of about 0.75 T.) The temperature dependence of the splittings of the main doublet peaks $\Delta\nu$ (which is a good measure for the orientational order, cf., e.g. [4]) and of the square roots of the second moments $\sqrt{M_2'}$ (that should be proportional to $\Delta\nu$ as long as there are no conformational changes of the molecule and the fluctuations remain fast on NMR time scale, see also [1, 4]) are given in Figure 2. Quite conspicuous are the considerable amount of orientational order even already at the end of the C phase where $\Delta\nu \approx 25$ kHz, corresponding to an order parameter S of nearly one under the usual assumptions [5, 6], and the sudden drop of both $\Delta\nu$ and $\sqrt{M_2}$ at the C–G transition below which obviously the proportionality between $\Delta\nu$ and $\sqrt{M_2}$ is lost, too. In the smectic-H phase the second moment again increases a little, however, there can be observed no splitting because of the broad structureless spectrum.

At a first sight one could be tempted to explain the dramatic decrease of the second moment and doublet splitting by an irreversible loss of alignment by a formation of more or less orientationally disordered "crystallites". However, we observed a perfect preservation of the alignment once obtained in the A phase after re-heating from the G or H phase, with some loss of order even from the crystalline

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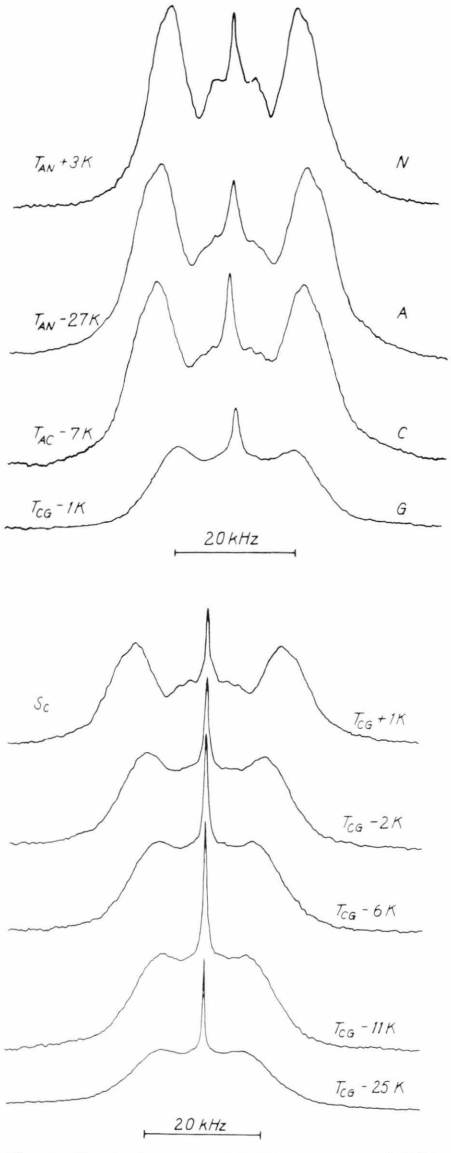

Fig. 1. Typical proton NMR spectra of TBPrA; a) in the nematic, smectic-A, -C, and -G phase; b) near the smectic-C- smectic-G transition in the C phase and in the G phase.

state (cf. [7]), at any angle between the original direction of polarizing field and the instantaneous magnetic field direction; i.e. after polarization in the nematic/smectic-A phase the sample could be rotated, e.g., in smectic-C or smectic-G in any angle (e.g. $\Phi = 50°$), further cooled down to smectic-G or H, and then be re-heated in smectic-A. Then the angular dependence of the spectra could be compared to that obtained after the original polarization process. No significant differences, especially with regard to the linewidth at magic angle orientation (which is very sensitive to changes in the overall alignment of the sample), were observed. These findings clearly show that the changes occuring at the C−G transition are reversible in nature.

Nevertheless, the lineshape alterations must be caused by a redistribution of the molecular directors about the direction of the original polarization (z-axis of the laboratory frame) since a reduction of the magnitude of the orientational order parameter in the smectic-G phase appears improbable as comparison with the NMR results of, e.g., the nO.m's demonstrate [1].

The angular dependences of the second moments in the smectic-G phase (see Fig. 3) differe distinctly from that to be expected for samples where the molecules or the molecular directors (≙ the mean orientation of the long molecular long axes) remain parallel to the direction of alignment fixed in the smectic-A phase, as it was observed for the nO.m's [1]. With decreasing temperature the ratio of the second moments $M_2(0)$ and $M_2^{\perp}(0)$ ($M_2(0)$ is M_2 for $\Phi = 0$, Φ is the angle between the laboratory frame z-axis, i.e. the direction of the originally polarizing magnetic field, and the Z-axis of a sample system, defined by the direction of the layer normals in smectic-A; $M_2^{\perp}(0)$ is the maximum second moment for $S = 1$, which should correspond approximately to the second moment for $\Phi = 0$ at

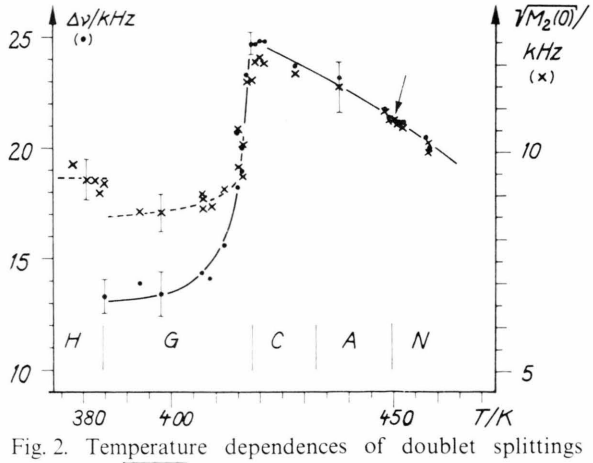

Fig. 2. Temperature dependences of doublet splittings $\Delta\nu(0)$ and $\sqrt{M_2(0)}$.

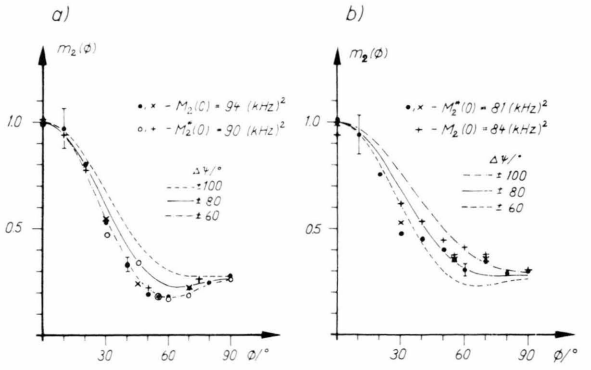

Fig. 3. Angular dependences of the reduced second moments $m_2(\Phi)$ in the smectic-G phase for a) $T_{CG} - 3$ K (corresponding to $\delta_G = 33°$ [3]), and b) $T_{CG} - 11$ K ($\delta_G = 36°$ [3]). The theoretical curves have been calculated according to the CFL model for a) $\delta_G = 33°$, and b) $\delta_G = 36°$ ($\Delta\psi$ as indicated in the figure).

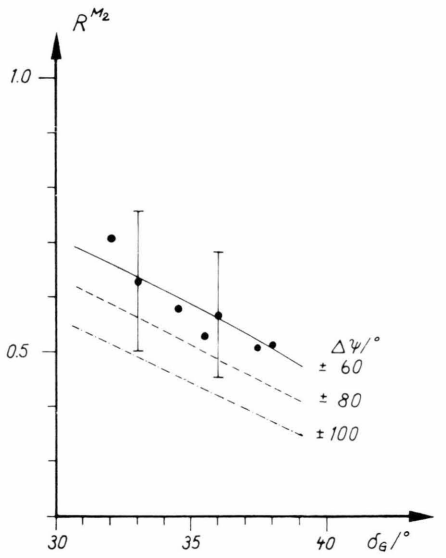

Fig. 4. Ratio R^{M_2} of the second moments of the smectic-G phase spectra at $\Phi = 0$ $M_2(0)$ to the maximum second moment (corresponding to $S = 1$) $M_2^1(0)$ at the end of the C phase ($M_2^1(0) \approx 145$ (kHz)^2) versus the tilt angle δ_G of the G phase (as derived from the X-ray data of Kumar [3]). The theoretical curves apply to the CFL model ($\Delta\psi$ as indicated in the figure).

the end of the C phase since we can derive an order parameter $S = 1$ to a good approximation from our NMR results) is decreasing from 0.7 at 2 K below the transition to about 0.5 at 20 K below (see Figure 4). Likewise, the ratio of the doublet splittings $\Delta\nu(0)$ ($\Phi = 0$) in smectic-G and $\Delta\nu^1(0)$ ($\Phi = 0$) at the end of the C-phase (≈ 25 kHz) diminishes with falling temperature (see Figure 5). In Figs. 4 and 5 the ratios have been plotted versus the tilt angle calculated from the high-resolution x-ray data of TBPrA obtained by Kumar [3].

From this x-ray analysis tilt angles of 33° and 36°, resp., could be derived for the temperatures 3 K and 11 K, resp., below the C–G transition, for which the angular dependences of $m_2 = M_2(\Phi)/M_2(0)$ are exhibited in Figure 3. Obviously, the magnitude of the "misalignment" along the preferred sample (Z-)axis becomes larger with decreasing temperature. We now checked three models to explain the NMR data.

In all three models it is assumed that the molecules are inclined by a certain (temperature dependent) tilt angle δ_G to their layer normals, which are azimuthally uniformly distributed about the sample Z-axis, as it has been normally accepted for smectic-C phases [8, 9]. However, because of its "crystalline" character the freedom of the molecular directors to reorient on the "tilt cone" has vanished, i.e. the molecular directors are rigidly fixed with respect to their layer normals.

I) The layer normals are at any temperature in the G phase distributed as they were in the smectic-C phase with the same tilt angle (i.e. inclined by δ_G to

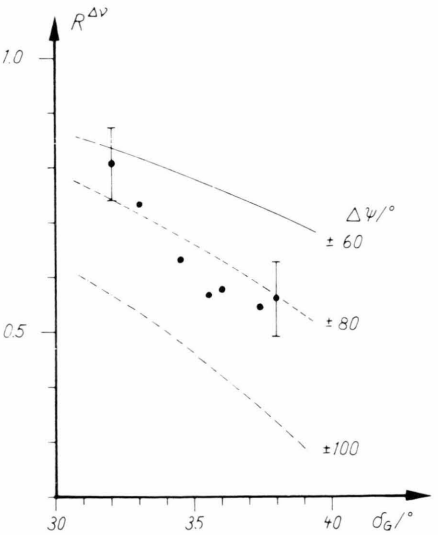

Fig. 5. Ratio $R^{\Delta\nu}$ of the doublet splittings $\Delta\nu(0)$ of the smectic-G phase spectra at $\Phi = 0$ to the maximum splitting $\Delta\nu^1(0)$ for $S = 1$ (≈ 25 kHz) at the end of the C phase versus δ_G. Theoretical curves according to the CFL model.

the preferred direction and azimuthally equally distributed about it). Moreover, there is now an additional distribution of molecular directors on the mantle of the fictive tilt cone characterized by an azimuthal angle ψ with $\psi = 0$ corresponding to the energetically most favourable orientation (at $\Phi = 0$) parallel to the preferred direction (Z-axis). The width of the distribution is $\pm \Delta\psi$, within which limits all values of ψ are assumed to be equally probable for simplicity (C-like distribution, CLD model). It means that the angle between the layer normals and the Z-axis jumps from 16.7° at the end of the C phase to 30° in the G phase at the transition point.

II) It could be supposed that because of it crystalline nature the G phase is fairly rigid so that temperature dependent layer inclinations in the G phase should be strongly confined. So, we assume that the layer distribution is "frozen in" at the end of the C phase (corresponding to a tilt angle $\delta_C = 16.7°$), i.e. the layer normals remain inclined permanently at an angle of $\delta_C = 16.7°$ to the Z-axis throughout the whole G phase whereas the tilt angle is allowed to vary with temperature as suggested by the layer thickness. Again an additional distribution on the tilt cone ($\pm \Delta\psi$) is taken into account (C-fixed layers, CFL model).

III) A synthesis of I) and II). As in the CLD model the angle between preferred axis and layer normals "jumps" from 16.7° (at the end of the C phase) to 30° (beginning G phase). Then the layer arrangement is fixed as in the CFL model and only the layer thickness (and with it the tilt angle) is allowed to vary with temperature (G-fixed layers, GFL model).

The three models are drawn in Figure 6.

In Fig. 7 the theoretical dependences of $m_2(\Phi)$ for different distribution widths $\Delta\psi$ according to the CLD (a) and the GFL models (b) have been plotted for a tilt angle $\delta_G = 36°$, whereas the corresponding theoretical curves for the CFL model are given in Figure 3b). As can be readily learnt from the graphics a satisfactory fit is possible in the CLD model only for $|\Delta\psi|$ clearly greater than 80°, for the GFL model if $|\Delta\psi|$ is greater than 90°, and for the CFL model for $|\Delta\psi| \approx 60° \ldots 80°$. The reduction ratios R^{M_2} and $R^{\Delta\nu}$, resp., for these parameters are less than 0.56 (R^{M_2}) and 0.27 ($R^{\Delta\nu}$), resp., for the CLD model, and less than 0.51 (R^{M_2}) and 0.22 ($R^{\Delta\nu}$!) for the GFL model. From this GFL and CLD model seem to reflect the actual data poorly before all because of their totally wrong values for $R^{\Delta\nu}$ (which reflect the dramatic deviation from the experimental lineshape of the simulated spectra using the above-mentioned parameters, cf. Figure 8).

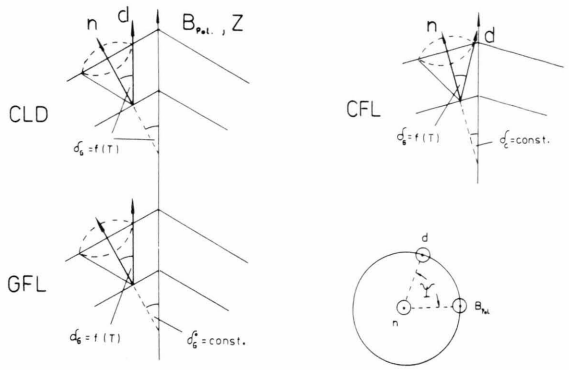

Fig. 6. Schematic sketch of the models of the smectic-G phase at the transition point smectic-C–G as described in Section 2. d is the molecular director, n the layer normal (the normals are equally distributed around the Z-axis).

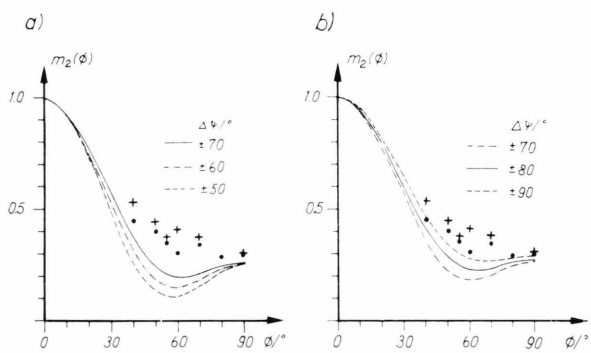

Fig. 7. Theoretical angular dependences of the reduced second moment $m_2(\Phi)$ according to a) the CLD model, b) the GFL model for different distribution widths $\Delta\psi$ as indicated in the figures. For comparison there are also displayed some of the experimental values of Fig. 3b for rotation angles $\Phi \geqq 40°$ which are especially illustrative.

Only the CFL model yields fairly good agreement between experimental and theoretical values as to the ratios $R^{\Delta\nu}$ and R^{M_2} (cf. Figs. 4 and 5) as to the angular dependences of the reduced second moments $m_2(\Phi)$ (cf. Fig. 3) for *all* temperatures (and, hence, tilt angles) using distributions $\Delta\psi = \pm 60 \ldots \pm 80°$ and keeping in mind the experimental errors, especially for M_2. For smaller tilt

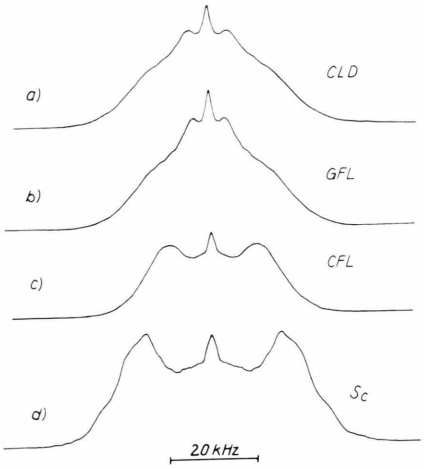

Fig. 8. Comparison of the simulated spectra according to a) the CLD model with $\Delta\psi = \pm 80°$, b) the GFL model with $\Delta\psi = \pm 90°$, c) the CFL model with $\Delta\psi = \pm 80°$, for a tilt angle $\delta_G = 36°$ in the G phase. d) Stimulated spectrum of the smectic-C phase used as the basis for the computation of the G phase spectra (cf. [2]).

angles the differences in the models are not so drastic but still evident. In Fig. 1 typical spectra of the phase transition region and the smectic-G phase have been displayed.

For comparison there are shown in Figure 8 computed spectra using the procedure described elsewhere [4, 9] to produce the spectrum giving best fit to a typical C phase ^{1}H-NMR spectrum. The relevant parameters as well as information with regard to the molecular conformation entering the procedure can be taken from [2]. Together with the simulated spectrum of the C phase there are drawn the spectra of the G phase for a tilt angle $\delta_G = 36°$ according to the different models.

Obviously the fairly intensive central peak in smectic-G is not reproduced so well in the calculated spectra. That should at least in part be due to the lack of the intensive central spike already in the simulated C phase spectra.

The $\Delta\psi$-values have been chosen so as it would seem reasonable by comparison with the $m_2(\Phi)$ dependences, i.e. $\Delta\psi = \pm 80°$ for both CLD and CFL models, and $\Delta\psi = \pm 90°$ for the GFL model. Clearly only the CFL-model yields a fairly satisfactory agreement. This is confirmed by comparing the whole angular dependences of the lineshapes for $\delta_G = 33°$ (corresponding to $T_{CG} - T = 3$ K) and $\delta_G = 36°$ ($T_{CG} - T = 11$ K), what has been performed in Figs. 9 and 10, where the theoretical spectra have been calculated applying the CFL model. Generally the agreement between experimental and theoretical lineshapes is fairly good. Simulations applying the other models yield satis-

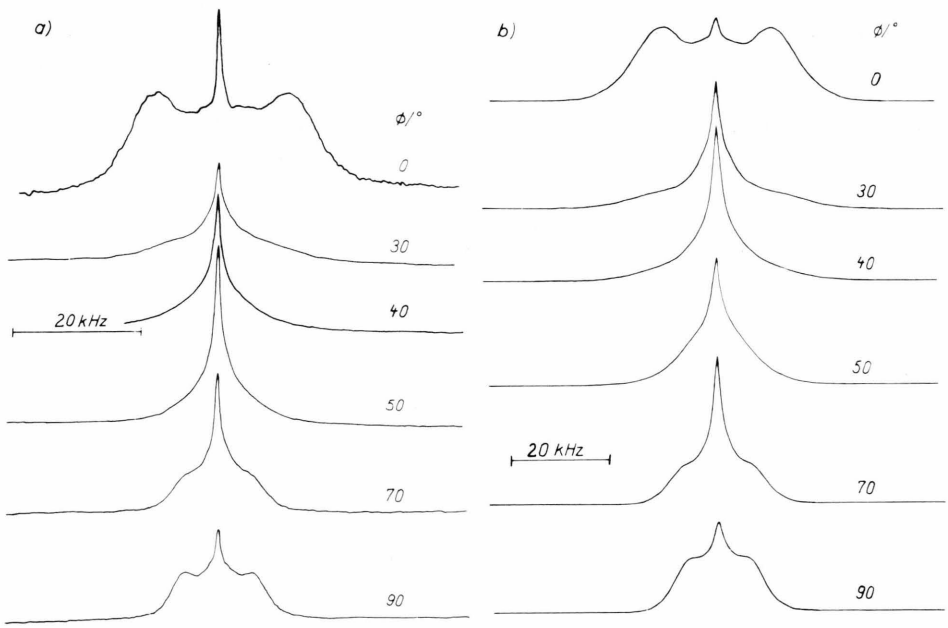

Fig. 9. Comparison of a) experimental (at $T_{CG} - 3$ K) and b) theoretical spectra calculated according to the CFL model ($\Delta\psi = \pm 80°$) for $\delta_G = 33°$.

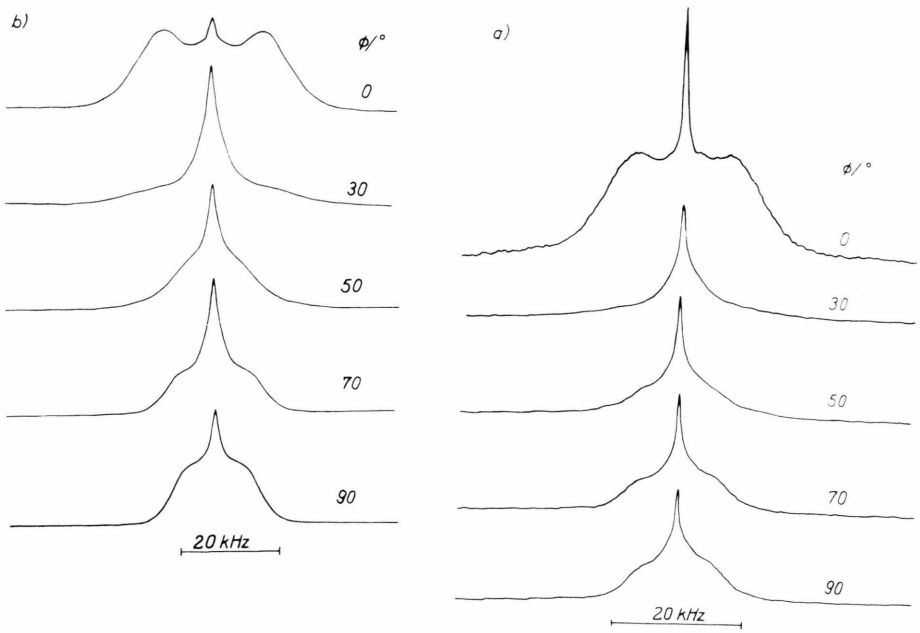

Fig. 10. The same as in Fig. 9 for a temperature $T_{CG} - 11$ K (experimental, a)) corresponding to $\delta_G = 36°$. Theoretical angular dependence computed according to the CFL model for $\delta_G = 36°$ with $\Delta\psi = \pm 80°$.

factory results only for $\delta_G = 33°$, whereas for $\delta_G = 36°$ theoretical spectra severely deviate from the experimental ones.

3. Discussion

As it was shown before the proton NMR lineshape, its angular dependence upon rotation in a magnetic field as well as the second moment angular dependence can be interpreted quite satisfactorily assuming that both molecular conformation and intramolecular mobility and/or order do not change significantly (on NMR time scale) on going from the smectic-C to the smectic-G phase since the theoretical spectra can be fitted well to the experimental ones using the spectrum matching the smectic-C phase best as a starting point.

Tentatively we have varied the values of the conformational parameters S_j from 0.31 for the methin proton (as used for the smectic-C and G spectra of Fig. 8) to 0.5 and greater and those of other protons, too. In all cases the overall fit was deteriorated thereby.

Additionally a specific distribution of the molecular directors has to be employed where the layer arrangement is "frozen in" at the end of the C-phase, i.e. it corresponds to a smectic-C layer distribution with a tilt angle of 16.7° whereas the actual tilt angle jumps at the transition into the smectic-G phase to about 30° and then varies with temperature with the layer arrangement being fixed as described above (CFL model). The distribution of the molecular directors on the mantle of the (fictive) tilt cone, characterized by the distribution parameter $\Delta\psi$, does not mean that within one domain there should occur different tilt directions but rather different domains should have different values of ψ.

There arises, however, some problem concerning the postulated "rigid" layer structure in the smectic-G phase. If the layer thickness is varying whereas the layer orientation remains fixed the layers have to be rearranged in such a manner that there are no "holes" left over because of the "shrinking" of the domains in the direction of the layer normals.

Obviously the mean orientational distribution cannot be changed too much with decreasing layer thickness since from the lineshape simulation as well as the second moment considerations one has to conclude that the distribution width varies only weakly (at measuring field of 0.75 T from about $\Delta\psi = \pm 60°$ for $\delta_G = 33°$ to about $\Delta\psi = \pm 80°$ for $\delta_G = 36°$) with tilt angle.

Acknowledgements

Thanks are due to Prof. Dr. D. Demus (Sektion Chemie der Martin-Luther-Universität Halle) and his group for kindly supplying the substance. Very fruitful and stimulating discussions with Dr. H. Schmiedel, Dr. K. Eidner, R. Stannarius, and B. Hillner are gratefully acknowledged.

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