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Proton NMR studies of smectic phases of three N-(4-n-alkyloxybenzylidene)-4'-n-alkylanilines (n0.m's)

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Résumé. — On présente quelques résultats de recherche sur les cristaux liquides 50,6, 70,5 et 70,6. Dans toutes les phases mésomorphes, on observe une remarquable proportionnalité entre les « splittings » dipolaires du profil de la raie de RMN des protons et le deuxième moment correspondant, indiquant que les mouvements qui contrôlent les profils de raie observés restent rapides à l'échelle des temps observables par RMN, même dans les phases bien ordonnées smectiques G, et qu'il n'y a pas de changements de conformation essentiels. On peut conclure des dépendances angulaires des profils de raie et des deuxième moments que la direction préférentielle du spécimen, une fois aligné par un champ magnétique fort en phase smectique A, est préservée à travers toutes les phases smectiques, malgré les transitions des phases inclinées (avec « tilt ») aux phases normales (sans « tilt »). Des mesures de largeur de raie à l'« angle magique » permettent de déterminer l'énergie d'activation du mouvement moléculaire dans les phases smectiques à basse température (B, F, G). Cette énergie d'activation est différente pour B et F/G. Des simulations de spectres de protons confirment la rotation du cycle d'aniline contre le plan renfermant le cycle benzaldéhyde et le groupe d'azométhine suggérée par des calculs quantiques et des études aux rayons X de substances semblables. En outre, il faut supposer un mouvement additionnel qui diminue l'interaction dipolaire entre le proton du groupe d'azométhine et les protons voisins des cycles aromatiques.

Abstract. — Proton NMR studies of the liquid crystals 50.6, 70.5, and 70.6 are presented. In all mesophases there is a clear proportionality between dipolar doublet splittings of the proton NMR spectra and the corresponding second moments indicating that the motions giving rise to the observed lineshapes remain fast on the NMR timescale even in the highly-ordered smectic-G phases and that no essential conformational changes occur. From the angular dependences of the lineshapes and second moments it could be concluded that the preferred direction of the sample, once aligned by the strong magnetic field in smectic-A, is preserved through all smectic phases though there are several changes from untilted to tilted phases. From linewidth measurements at the magic-angle orientation, activation energies for a thermally activated motional process could be derived in the low-temperature smectic phases (B, F, G) which differ for B- and F/G- phases, respectively. Simulations of the proton NMR lineshape confirm the existence of a twist of the aniline ring against the benzaldehyde — azomethine group plane as suggested by quantum-chemical considerations and X-ray investigations of related compounds. Besides one has to assume an additional motion decoupling the dipolar interaction between the azomethine proton and the protons of the neighbouring ring.

1. Introduction.

In this paper we present the results of the investigations of three N-(4-n-alkyloxybenzylidene)-4'-n-alkylanilines (n0.m's), namely 50.6, 70.5, and 70.6. We aimed especially at the study of the so-called « low-temperature » smectic phases (by this term we denote here all smectic phases with positional order within the layers).

These compounds had been chosen for their rich smectic polymorphism and their relatively low transition temperatures. Their phase sequences and tran-

sition temperatures are given in table I. Besides this class of substances has been studied by other methods, including for example ^{13}C NMR [1], X-ray [2, 3], and dielectric relaxation [4].

Our aim was to examine by comparison of the experimental and calculated proton NMR spectra, if changes in intramolecular mobility (especially of the aliphatic chains) and conformation occur on passing from the nematic or smectic-A phase, respectively, to smectic-G and if it is possible to detect alterations in the molecular arrangement and the overall molecular motions by means of proton NMR.

Table I. — Phase sequences and transition temperatures of 50.6, 70.5, and 70.6 [29]. All temperatures are given in degrees centigrade (°C).

50.6 : Cr-34.5...35.0-S _G -37.3...37.5-S _F -40.0...40.2-S _B -50.5-S _C -51.5-S _A -60.4-N-72.8-isotropic
70.5 : Cr-25.2-S _G -56.4-S _B -64.0-S _C -68.2-S _A -79.6-N-83.2-isotropic
70.6 : Cr-38.5-S _G -57.7-S _B -66.0-S _C -69.4-S _A -80.6-isotropic

2. Temperature dependence of the proton NMR spectra.

All samples studied were first heated up into their isotropic phases (about 5 K above the clearpoint) and kept there for about 20 min in presence of a magnetic field of 1.4 T. Afterwards they were slowly cooled down (at rates of 1 K/5 min) into the nematic phases in the magnetic field. Near the phase transition points the cooling rates were reduced to 1 K/10 min. Generally the samples were studied down to room temperature (≈ 298 K) without any rotation of the samples during the whole measuring cycle.

Figure 1 shows typical proton NMR spectra (taken at measuring frequency of $\nu_0 = 60$ MHz) for all the mesophases of 50.6 (for 70.5 and 70.6 the spectra show a similar appearance and the same qualitative features in their temperature dependences). There are only small changes in the overall lineshape (going from the nematic to the smectic-G phases) taking into account the influence of the increasing orientational order parameter S

$$S = 1/2 \langle 3 \cos^2 \theta - 1 \rangle$$

(θ : angle between the preferred direction of the sample (director) and the long molecular axis of a

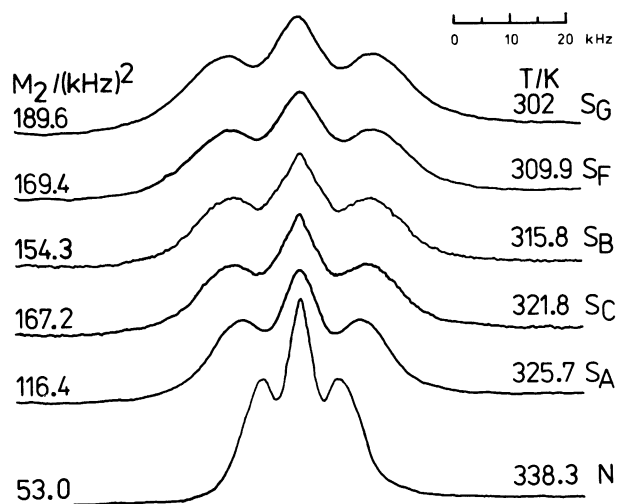


Fig. 1. — Characteristic proton NMR spectra of the different mesophases of 50.6 along with their corresponding second moments M_2 .

molecule, bracket indicates averaging), which gives rise to a scaling of the frequency spectrum in the case of fast reorienting motions (cf. [5]). There is only a slight decrease in the ratio of the heights of central peak and outer doublet peaks (from 1.65 in the nematic phase to about 1.54 in the smectic-G phase) and possibly a weak « smearing out » of the structure.

In figure 2 the temperature variation of the doublet peak splittings of 50.6, 70.5, and 70.6 are displayed together with the square root of the proton NMR second moment. $\sqrt{M_2}$ should be proportional to S provided that the molecules undergo rapid (on NMR time scale, i.e. compared to T_2) reorientations (cf. [5, 6]), and the same should be valid for $\Delta\nu$ — this means that $\Delta\nu \sim \sqrt{M_2}$.

As can be seen from figure 2 the proportionality between $\Delta\nu$ and $\sqrt{M_2}$ is maintained throughout the whole mesophase range for all three compounds indicating fast reorientational motions even in the smectic-G phases (and no essential conformational changes). The orientational order parameter S (neglecting all other possible order parameters which, in principle, could be introduced, cf. for example [5, 7, 8], because of their minor influence on proton NMR spectrum) could be derived from the dipolar doublet splitting in a simple manner with great accuracy if the dipolar splitting for $S = 1$ (perfect ordering) were known, or, alternatively, if one could determine the exact ortho proton distances at the phenyl rings which to a first approximation are responsible for the doublet peaks. Otherwise one can only estimate S with limited accuracy assuming (as is often done) an ortho proton distance of about 2.45 Å yielding a maximum splitting $\Delta\nu_{\max} = 24.5$ kHz (neglecting the small angle between the phenyl ring para-axis and molecular director). For a more detailed discussion see [6, 9].

In the smectic-G phases $\Delta\nu$ reaches remarkably high values of about 25 kHz (50.6, 70.6) and even 28 kHz for 70.5. Since S cannot be greater than 1 this can only mean that either the proton distance is distinctly less than 2.45 Å (cf. also [9]) or that other interactions of near-neighbouring protons superimpose on the ortho-proton doublet. This could be, for example, the interaction between the bridge methine proton and the inner ortho-proton of the aniline ring (Fig. 7). This will be discussed in section 5.

Schulz has derived from ^{13}C NMR spectra of 50.6 order parameters S of about 0.9 in the smectic-G phase [1].

Generally from figure 2 only the transition C-B can be determined reasonably well indicating a distinct jump of the order parameter S at this phase transition.

3. Angular dependences of the second moments.

To obtain the angular dependences of the proton NMR spectra the samples were aligned by a magnetic field of 1.4 T by cooling them down from the isotropic

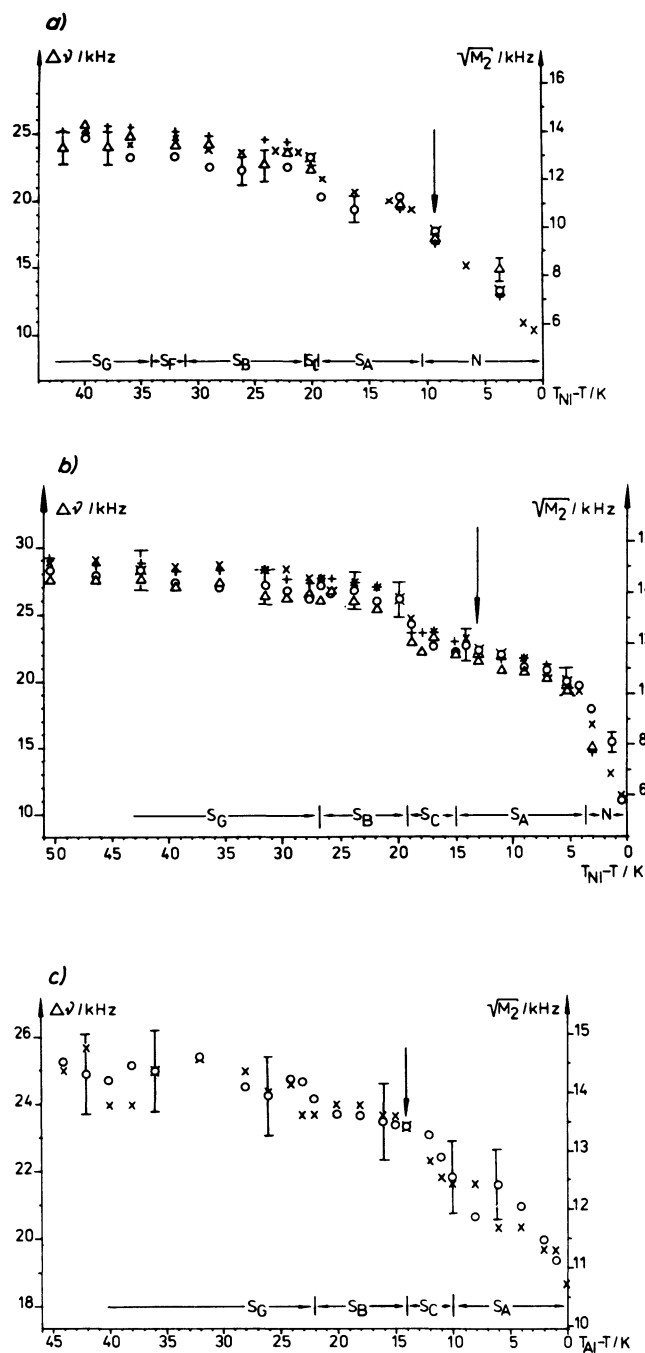


Fig. 2. — Temperature dependence of dipolar doublet splittings $\Delta\nu$ and the square roots of the second moments $\sqrt{M_2}$ for :

- a) 50.6 ($\times$, $+$ $\triangleq$ doublet splittings from two measuring cycles; O , Δ $\triangleq$ the corresponding values of $\sqrt{M_2}$);
 b) 70.5, and
 c) 70.6 (symbols like a)). The arrows mark the fitting point of the $\sqrt{M_2}$ curve to the $\Delta\nu$ curve. T_{NI} is the clearpoint temperature.

phase to the temperature at which the angular dependence should be recorded in the manner described in the preceding section. Then the samples were rotated about an axis perpendicular to the direction of the magnetic field by angles Φ between 0° and 180° .

For the smectic-B phase of 50.6 some spectra at different rotation angles are shown in figure 3.

The dependences of the second moments are given in figures 4 and 5, where the reduced moments

$$m_2(\Phi) = M_2(\Phi)/M_2^*(0)$$

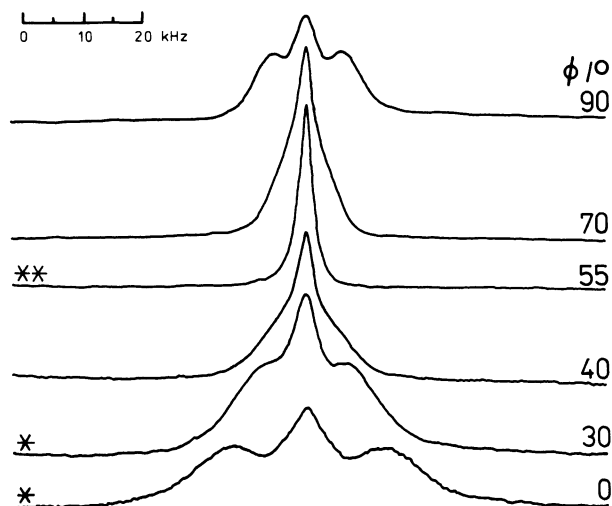


Fig. 3. — Dependence of the proton NMR spectra of 50.6 on the rotation angle Φ between the layer normals and the magnetic field direction at $T = 312.9$ K (smectic-B phase). * denotes a factor 0.5 in the vertical display scale, ** a factor 2 compared to the unmarked spectra.

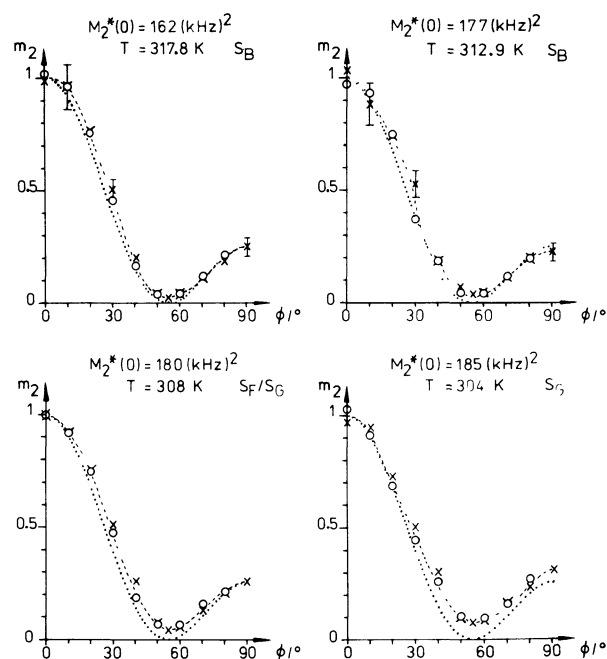


Fig. 4. — Typical angle dependences of the reduced second moments of the proton NMR spectra for the different smectic phases of 50.6. Dashed lines are merely aids to the eye joining the experimental points, dotted lines correspond to a $(1/2(3 \cos^2 \Phi - 1))^2$ -curve ($\times$: values for $\Phi = 0 \dots 90^\circ$, O for $\Phi > 90^\circ \dots 180^\circ$).

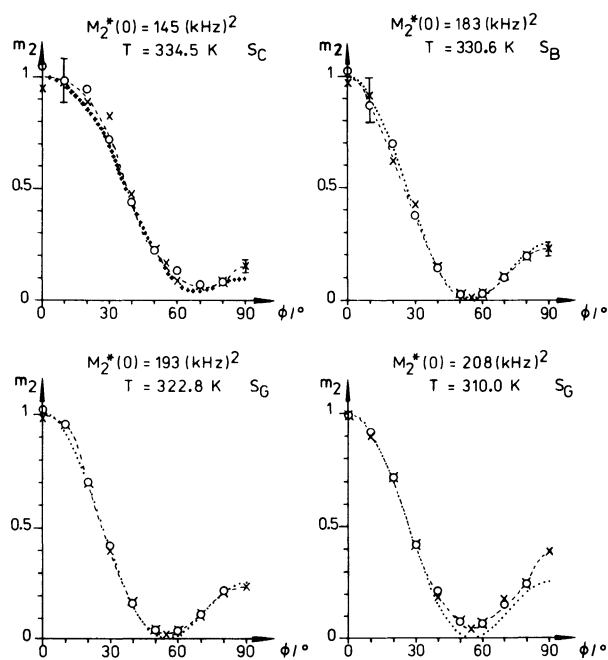


Fig. 5. — The same as in figure 4 for 70.5. The crosses (+) in the smectic-C plot correspond to the theoretical dependence according to the Luz-Meiboom/Wise-Smith-Doane model [11, 12] calculated as specified in [10] for a tilt angle $\delta = 12.5^\circ$.

have been plotted, with

$$M_2^*(0) = 1/2.(M_2(0) + M_2(180^\circ)).$$

The $m_2(\Phi)$ for $\Phi > 90^\circ$ have been mirrored into the $0 \dots 90^\circ$ range what additionally serves to illustrate the symmetry of the spectra (and second moment values) around $\Phi = 90^\circ$.

The smectic-C phases of 50.6 is so narrow that no angular dependences could be taken. For 70.6, however, an angular dependence at the end of the smectic-C phase has been recorded, yielding by comparison with theoretical angular dependences (detailed description in [10]) a tilt angle of about 12° (assuming the validity of the Luz-Meiboom/Wise-Smith-Doane model [11, 12]).

It is remarkable that all the angular dependences in the other phases — whether they are tilted phases or not — exhibit a clear minimum of the residual second moment at the « magic angle » ($\Phi = 55^\circ$), i.e. the angular dependences can be described approximately by a $(P_2(\cos \Phi))^2$ -function (as is well-known for the smectic-A phase) with the value of $M_2(55^\circ)$ increasing with decreasing temperature from smectic-B to smectic-G (cf. also the following section).

This means that the alignment of the molecular directors (originally along the direction of the polarizing magnetic field) is preserved through *all* smectic phases from smectic-A to smectic-G though there are transitions untilted (A)-tilted (C)-untilted (B)-tilted (F or G), i.e. the layer normals are (for $\Phi = 0$)

tilted with respect to the magnetic field in the tilted phases and « jump » back to their parallel orientation in the untilted phases (for example, at the C-B transition).

If the orientation is fixed, for example in the smectic-A phases, the sample can be rotated in any angle to the magnetic field and cooled down into any other phase at this angle. Afterwards a full angular dependence can be obtained which does not differ from those recorded after cooling down from the isotropic phase at $\Phi = 0$, i.e. there is a « memory » for the direction of the original alignment forcing the molecular directors (in B, F, G) to remain aligned along the original direction of polarization. Though one could argue that the alignment would be perturbed if the sample is, for example at $\Phi = 40^\circ$, cooled from the smectic-C phase to smectic-B, however, the angular dependence is in smectic-B after this the same as that following the usual preparations described above.

In contrast to this, for the propyl member of the TBBA homologous series we observed a distinct change in the proton NMR lineshape at the C-G transition at $\Phi = 0$ [13]. This is due to the fact that the molecular directors do not remain aligned to the original polarizing direction because there is a jump of the tilt angle at this transition of about 14° [14] not accompanied by a corresponding change in the inclination of the layers. Obviously the viscosity in smectic-G is too high in this substance to admit alterations in the layer distribution [13].

4. Linewidth at Magic Angle Orientation (MAO).

If all molecules of the sample perform rapid reorientations (on the NMR timescale) about their average directions (molecular directors) and there is no director distribution as is the case, for example, in a well-aligned smectic-A sample (provided that there are no intermolecular dipolar interactions which are removed by fast translational diffusion and molecular rotations) the angular dependence of the second moments on rotation in the magnetic field is described by

$$\begin{aligned} M_2(\Phi) &= M_2^0.(P_2(\cos \Phi))^2 \\ &= M_2^0.(1/2(3.\cos^2 \Phi - 1))^2, \end{aligned}$$

Φ being the rotation angle between the magnetic field direction and the molecular director and M_2^0 the second moment for parallel orientation of the director to the magnetic field. At the magic angle orientation (MAO), where

$$\begin{aligned} P_2(\cos \Phi) &= 0 \\ \text{i.e. for } \Phi &= 54.74^\circ, \end{aligned}$$

the line should consequently collapse to a single, very narrow line (second moment theoretically zero) as is indeed approximately observed for well-aligned

smectic-A phases. However, when the molecular motions which gave rise to the averaging-out of the intermolecular interactions are slowed down with decreasing temperature, the influence of intermolecular dipolar interactions can manifest itself in a growing linewidth at MAO.

Here we applied two different experimental procedures to obtain the temperature dependent MAO spectra :

1) The sample was aligned as described above in smectic-A phase and then rotated in MAO with the sample remaining in this position throughout the whole measuring cycle, i.e. during the whole temperature dependence.

2) The sample was again aligned in smectic-A, then brought to the measuring temperature ($\Phi = 0$) and only then rotated to MAO with the sample rotating back to $\Phi = 0$ after completing the accumulation of FID's. Hereafter the next temperature was chosen and the procedure repeated.

The different procedures are marked in figure 6 by crosses (process (1)) and circles (process (2)). Obviously there are no significant differences leading us to the conclusion that there are no remarkable disturbances in the alignment of the samples for process (1) as reported in [18].

As shown in figure 6 the linewidth at half height $\Delta\nu_{1/2}$ at MAO obeys an Arrhenius law, i.e. the linewidth broadening should be caused by a thermally activated process. With τ_c denoting the correlation time of the corresponding motion the temperature dependence of $\Delta\nu_{1/2}$ can be expressed by

$$\Delta\omega_{1/2} = 2\pi \cdot \Delta\nu_{1/2} = \Delta M_2 \cdot \tau_c(T),$$

where ΔM_2 is the contribution to the second moment of the rigid sample which is diminished by the corresponding motional process (cf. [15]). The temperature dependence of the correlation time τ_c is, as usually, assumed to be Arrhenius-like :

$$\tau_c(T) = \tau_{c\infty} e^{E_A/RT}$$

with $\tau_{c\infty}$: correlation time at infinite temperature, E_A : activation energy, R : universal gas constant.

From figure 6 several phase transitions can be clearly determined, which cannot be seen from the temperature dependence of the spectra at $\Phi = 0$ (cf. Fig. 2). Distinct jumps are discernible at the transitions smectic-A-smectic-C (since the linewidth minimum in smectic-C is shifted towards greater rotation angles because of the possibility of nearly free rotation of the molecular directors on the tilt cone, cf. [10-12]), smectic-C-smectic-B, and smectic-B-smectic-G. Whereas in smectic-A the MAO-linewidth seems to be temperature independent ($\Delta\nu_{1/2} \approx 1.4$ kHz for 50.6 and ≈ 1.0 kHz for 70.5), it clearly grows with falling tem-

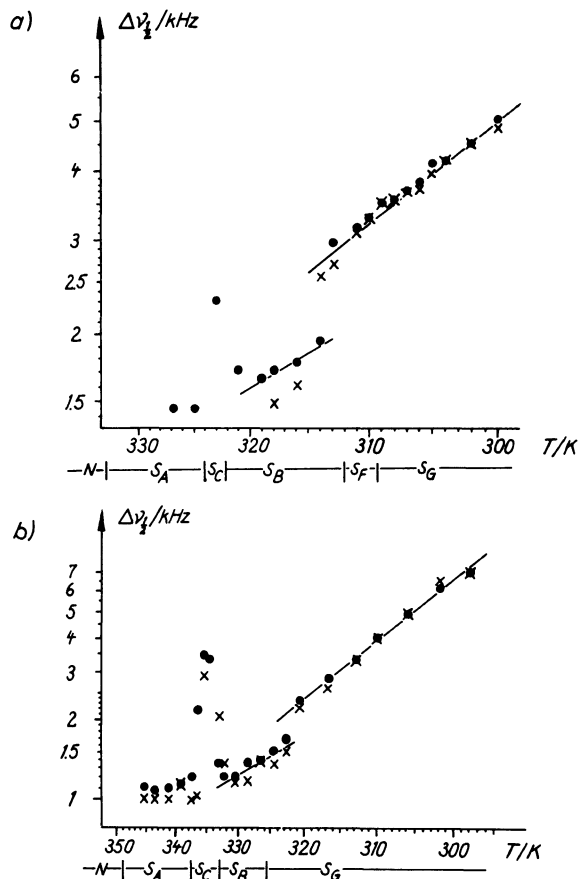


Fig. 6. — Temperature dependences of the linewidth at the magic angle orientation (MAO) for :

a) 50.6, and b) 70.5.

($\times \triangleq$ process (1) ; $\bullet \triangleq$ process 2 : for details see section 4).

perature in smectic-B and smectic-G (probably also in the smectic-F phase of 70.5, however, because of the narrow temperature range of 2.5 K reliable assertions are somewhat difficult to make). In both cases the activation energies in the B-phase ($E_A \approx 24$ kJ.mol $^{-1}$ for 50.6 and 28 kJ.mol $^{-1}$ for 70.5) are lower than in the G- (and F-) phase ($E_A \approx 34$ kJ.mol $^{-1}$ for 50.6 and 41 kJ.mol $^{-1}$ for 70.5). Schmiedel and Eser [18] obtained by the same procedure an activation energy of about 24 kJ.mol $^{-1}$ for the smectic-G phase of TBBA.

The kind of motion responsible for the line broadening could be translational diffusion. From NMR studies of TBBA [16] it is known that the translational self-diffusion coefficient is diminished drastically at the C-G transition (from 9×10^{-11} in the C phase to 1.4×10^{-13} m 2 s $^{-1}$ in the G phase) with $E_A = 100$ kJ.mol $^{-1}$ for smectic-G.

Besides, a slowing down of the fluctuations of the long molecular axes about their mean directions could also be considered. Dielectric measurements of Kresse *et al.* [4] suggest also a reorientational motion of the long molecular axes around the short axes which are

strongly hindered ($E_A \approx 94 \text{ kJ} \cdot \text{mol}^{-1}$ in smectic-G, $E_A \approx 82 \text{ kJ} \cdot \text{mol}^{-1}$ in smectic-B/F), however the activation energies measured by this method are distinctly greater than those determined here by NMR. Likewise, the correlation times τ_c for this process from the dielectric relaxation of up to $> 10^{-4} \text{ s}$ in the smectic-G phase (though τ_c determined from dielectric measurements are systematically greater than NMR correlation times by a factor 3 from methodical reasons [18]) are already nearly « static » for NMR and would cause a superposition of spectra coming from a « static » distribution of molecular directors oriented at different angles with respect to the magnetic field. This should result in a remarkable smearing-out of the proton NMR spectra in the smectic-G phase compared to the, for example, A phase, which, however, was not observed (cf. Fig. 1).

5. Simulation of the proton NMR lineshapes for 50.6.

The details of the computation of the theoretical proton NMR spectra have already been described elsewhere [5, 6, 9, 20]. As discussed in [6, 9] the use of standard bond lengths (which give rise to a ortho proton distance $r = 2.47 \text{ \AA}$) generally leads to splitting (and accordingly second moments) clearly too small compared to the experimental values. If, however, atom positions from an X-ray crystallographic analysis are available even the quantitative agreement between computed and experimental spectra is quite good (cf. [13, 18-20]). In the present case we cannot expect a very good quantitative agreement because of the use of standard data rather than X-ray results. So we mainly try to fit the theoretical spectra qualitatively to the experimental data.

As in former studies we start with a planar all-trans conformation, i.e. all carbon atoms are co-planar. The conformational parameters S_j ascribed to each proton (with S_j, S_k characterizing the degree of the reduction of the dipolar interaction between the proton j and k compared to the totally rigid case where $S_j = S_k = 1$, cf. [5, 6, 19]) are then varied systematically. Different

sets of S_j were tested beginning with large S_j of the ring-neighbourd methylene protons (for example 0.9 for the alkoxy chain, 0.95 for the alkyl chain) and then varying the rate of the falling of the S_j values along the aliphatic chains towards the terminal methyl groups (for example between about 0.7 and 0.2 for S_{methyl}). Then another value for the S_j of the ring-neighbourd methylene protons was chosen and the procedure repeated, and so on.

It turned out, however, that it was impossible to fit the experimental lineshape even only approximately by a planar conformation. This was expected, since from quantum chemical considerations of Perrin and Berges of the benzylidene aniline molecule [21] and TBBA [22] as well as from several X-ray investigations (for example, for benzylidene aniline, p-methylbenzylidene-nitroaniline, benzylidene aniline-p-carboxylic acid by Bürgi and Dunitz [23], for n-(p-methylbenzylidene)-p-methylaniline by Bar and Bernstein [24], and other related benzylidene aniline derivatives [25, 26] it becomes clear that the benzylidene ring and the azomethine group planes are nearly co-planar (dihedral angle $0 \dots 14^\circ$) whereas the aniline ring is twisted with respect to the azomethine group plane by an angle of about 30° to 55° .

Therefore we chose a conformation with aldehyde ring and azomethine group planes being co-planar and aniline ring and azomethine group planes forming an angle of 45° (see Fig. 7), the planes of alkoxy and alkyl chains, resp., remaining parallel at first. Though the agreement with experimental spectra now could be improved, the side wings are still too broad and the central peak is too high. The best fit is obtained if additionally the chain planes are twisted by 90° to the aldehyde and aniline ring planes as it has been suggested from quantum chemical studies of the TBBA molecule [22] and X-ray investigations of TBBA [27]. For the set of S_j giving the best fit simulated proton NMR lineshapes for the three conformations described above can be compared in figure 8. Clearly the agreement with experimental spectra (cf. Fig. 1) is best for the last conformation (Fig. 8c).

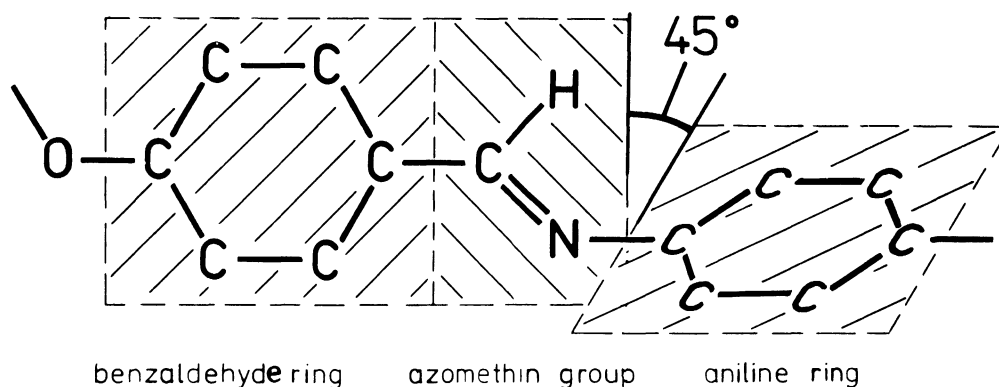


Fig. 7. — Schematic representation of the conformation of the central part of the 50.6 molecule.

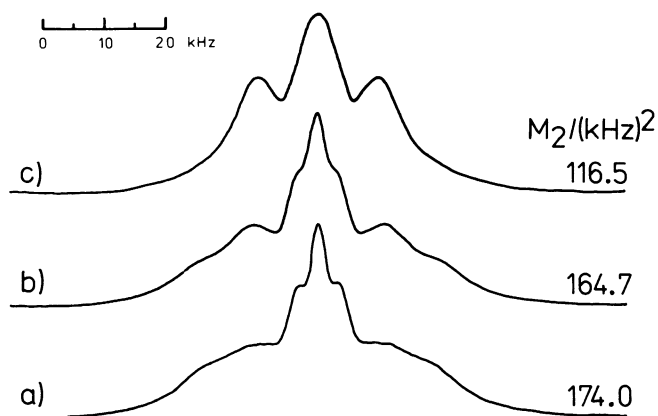


Fig. 8. — Simulated proton NMR spectra using standard bond lengths and angles of 50.6 for :

- a) planar all-trans conformation :
- b) dihedral angle of 45° between aniline ring and azomethin group planes, chain planes co-planar with corresponding ring planes :
- c) as in b), but additionally alkoxy and alkyl chain planes, respectively perpendicular to the aldehyde and aniline ring planes, resp. Conformational parameters S_j are given in section 5.

In figure 9 the influence of the dihedral angle between azomethin group and aniline ring planes is documented. In figures 8 and 9 the S_j yielding the best fit have been used for all spectra. Beginning with the ring-neighbouring methylene group (α -CH₂) and running to the terminal methyl group these S_j are :

a) alkoxy chain : 0.9 (α), 0.85 (β), 0.8 (γ), 0.75 (δ), 0.4 (CH₃);

b) alkyl chain : 0.95 (α), 0.9 (β), 0.85 (γ), 0.8 (δ), 0.75 (ϵ), 0.4 (CH₃).

The S_j of the ring protons equal 1 because of the relative internal rigidity of the phenyl rings. Besides,

180° -flips about their para-axes and CH₃-group rotations (threefold jumps) have been assumed. It is remarkable that a good fit of spectra could be attained only when the S_j of the azomethin proton was clearly less than 1, otherwise the embayments between central peak and the doublet peaks cannot be reproduced. The same phenomenon was observed by Schmiedel *et al.* for the computation of the proton NMR spectra of TBBA [18] as well as for the propyl member of the TBBA series (TBPrA) [13]. This means that the interaction between azomethin proton and protons of the neighbouring rings (esp. aniline ring) is still reduced further than can be achieved by the simple 180° jumping motion of the rings about their para-axes. This additional decoupling can be explained by assuming a greater twist angle than that used in our computations (45°). Since the most important interactions of the methin proton are those with the inner protons of the aniline ring the methin S_j hence will reflect mainly the reduction of the dipolar interaction between methin and inner aniline ring protons to a good approximation. In our case this interaction would be diminished by a factor of 0.3 if the dihedral angle is increased to about 57° , i.e. using a methin S_j of 0.3 which gave the best fit in the simulations with the above-described conformation (dihedral angle between azomethin group and aniline ring planes) would mean that the actual dihedral angle should amount to about 57° , as simple calculations show [30]. Moreover, this reduction could also be (at least partly) due to motional decoupling (cf. also [13]). The ratio of the heights of central and doublet peaks can be adjusted by a proper choice of the S_j of the methyl protons within certain limits. This is demonstrated in figure 10. The lower the value of S_{methyl} the more intense is the central peak in comparison to the doublet peaks (the ratio of the peak heights varies from 2.33 for $S_{\text{methyl}} = 0.2$ to 1.27 for $S_{\text{methyl}} = 0.6$ with a best fit for $S_{\text{methyl}} = 0.4$ giving a height ratio of 1.54 in good agreement with experimental data, cf. section 2).

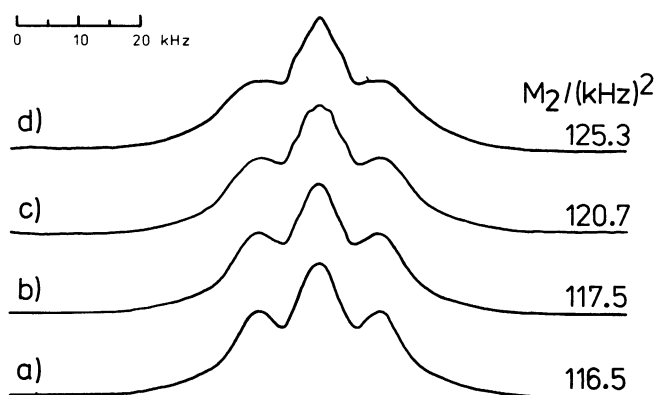


Fig. 9. — Influence of varying the dihedral angle between the azomethine group and aniline ring planes on the simulated proton NMR spectra for a) 45° ; b) 35° ; c) 25° ; d) 15° . Other parameters as in figure 8.

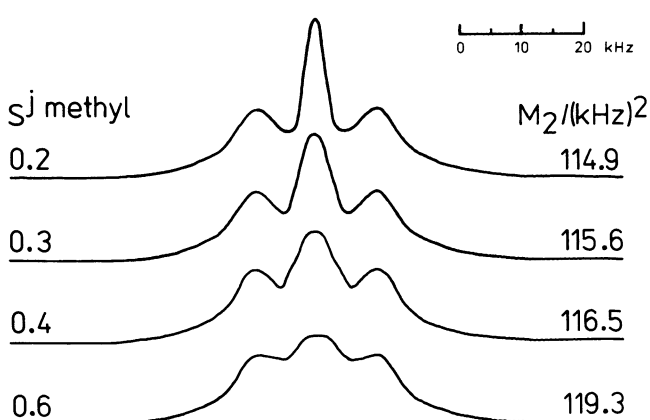


Fig. 10. — Influence of different values of the methyl proton conformational parameter S_j on the simulated proton NMR spectra. Other parameters as in figure 8.

Otherwise, the small decrease in the height ratio which is accompanied by a slight « smearing out » of the line structure could also, at least at part, be attributed to the increasing influence of intermolecular dipolar interactions which give rise to the broader lines at MAO (cf. Fig. 6). In the simulated spectra this can be taken into account by a broader width of the Lorentzian line by which the stick spectrum of δ -lines (that is originally produced in the computation procedure) is convoluted. Figure 11 demonstrates the effect of increasing convolution linewidth $\delta\nu$ on the calculated spectrum. Again there is a slight decrease in the height ratio with growing $\delta\nu$, altogether, however, one has to state that the spectra of all phases can be fitted quite satisfactory by only little variations in $\delta\nu$. In the spectra of figures 8 to 10 a value of $\delta\nu \approx 0.93$ kHz generally has been applied.

For the smectic-G phase a $\delta\nu$ of about 1.55 kHz appeared to be favourable, even this is still clearly less than the linewidth at MAO (cf. Fig. 6).

6. Discussion and summary.

As mentioned in section 2 we find for all three substances very high values of the doublet splitting $\Delta\nu$ which would yield orientational order parameters greater than 1 on the basis of ortho proton distances frequently used in the determination of S by proton NMR. So one can suppose that the ortho proton distances are clearly less than 2.45 Å which indeed is justified by evaluation of the X-ray data yielding about 2.39 Å as a reasonable average (cf. discussion in [9]) where, admittedly, the accuracy of the measurements concerning protons naturally is not very high. Moreover, to explain splittings of 28 kHz (70.5) unreasonably small distances would have to be assumed. Hence, the splittings should additionally be enlarged by interactions between near-neighbouring protons other than the ortho phenyl protons. A possible candidate would be the interaction between the methin group and the inner protons of the aniline ring. Since, however, the S_j of the methin group is very small to fit the lineshape satisfactorily it can be concluded that this interaction is reduced too much to broaden the splitting. This is emphasized by the fact that even a small dihedral angle between azomethine group and aniline ring planes (which brings the protons in question fairly close together) does not change the splitting significantly.

A greater influence could be expected by the interaction of the outer phenyl protons with the α -CH₂ protons (especially of the alkyl chain). In a co-planar conformation of ring and chain planes the splitting therefore is distinctly larger than in the perpendicular ones. Perhaps a less drastic twist ($\geq 45^\circ$) of the alkyl chain out of the aniline ring plane would already increase the splitting without deteriorating the overall fit too much.

An important result of our investigations is the proportionality of $\Delta\nu$ and $\sqrt{M_2}$ throughout the whole

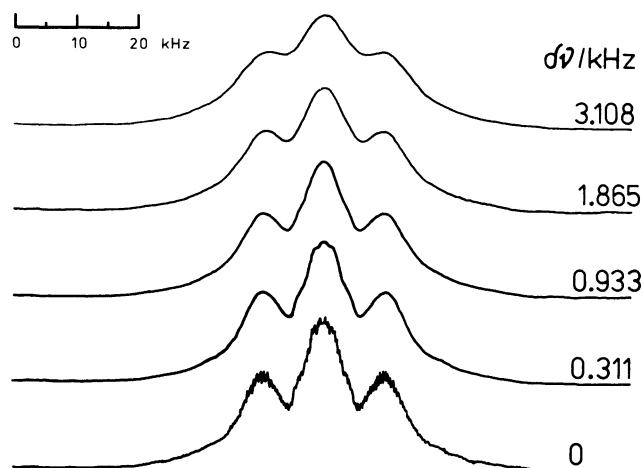


Fig. 11. — Effect of the convolution linewidth $\delta\nu$ on the simulated proton NMR spectra. Parameters as in figure 8.

temperature range, i.e. from the nematic down to the end of the smectic-G phase. This means (as is also suggested by the only small changes of the lineshape) that the molecular motions, for example rotation about the long molecular axis, causing the lineshape (which differs greatly from that to be expected by a crystalline solid) remain fast on the NMR time scale even in the smectic-G phase (the corresponding correlation times should be $\lesssim 10^{-5}$ s) and there occur *no essential changes* in the molecular conformation. Otherwise the intermolecular interactions should increase (probable by slowing down of translational self diffusion) and/or the rate of the long axis fluctuations should be diminished, respectively, as indicated by thermally activated linewidth broadening at MAO in smectic-B [F] G phases with decreasing temperature (see section 4). As, for example, the deuterium NMR results of Barbara and Dailey [32] and Yaniv *et al.* [33] have shown the smectic-G phase should be biaxial. The magnitude of the biaxiality is described by an « asymmetry parameter » η which depicts the anisotropy of the fluctuations of the long molecular axis along the mantle of the (fictive) tilt cone and perpendicular to this direction, respectively (cf. [10]). One now could be tempted to ascribe the line broadening, at least in smectic-G, to an increase in η . Simple calculations (using the general expression for the second moment derived in [10]), however, show that for a very well-aligned sample (as in our case) the effect of η in MAO is fairly small. There the residual second moment due to the biaxiality is $m_2(54.74^\circ) = \eta^2/18$, i.e. even for $\eta = 0.5$ (which seems already to be fairly large in view of the value of 0.3 determined by deuterium NMR [32, 33]) m_2 would only amount to 0.014 whereas the experimental data for 50.6 (Fig. 4) yield already about 0.08 in S_G , for 70.5 (Fig. 5) ≈ 0.05 in the middle of the G phase. Thus the strong thermal activation of the line broadening with decreasing temperature at MAO, together with the minor

influence of η , in our opinion, renders the above-discussed explanations more likely. These observations make clear that there are from the point of view of proton NMR (as well as from ^{13}C NMR [1]) the differences between high-temperature (A, C) and low-temperature phases (B, F, G) discussed here are not as striking as perhaps in X-ray investigations (see for example, Doucet and Levelut [3] and [28]). Especially, there is no hint to the «crystalline» character of the smectic-B and -G phases which certainly will not be surprising since NMR is not sensitive to positional ordering (at least as long as intermolecular interactions play no important rôle).

The angular dependences of the second moments (section 3) obey in the smectic phases (except smectic-C) a $(P_2(\cos \Phi))^2$ law which means that the alignment of the molecular directors once produced in smectic-A is preserved also in the smectic-G phase without redistribution of the molecules though alternating tilted and untilted phases.

From the lineshape simulations one has to conclude that a twist occurs of the aniline ring against the aldehyde ring-azomethin group plane of about 55° to 60° . The small value of the conformational parameter $S_j = 0.3$ of the methin protons suggests an additional rotation of the aniline ring by about 12° against the azomethin group plane compared to the conformation used in the computation (dihedral angle of 45°). The chain planes should be rotated with respect to the ring planes, however, not necessarily by 90° , as assumed in our calculations.

The mobility of the chain protons decreases from the rings ($\alpha\text{-CH}_2$) towards the terminal CH_3 -groups

as expected. The spectra of all phases can be fitted by nearly the same conformational parameters S_j with only slight modifications. This indicates no significant changes in intramolecular mobility and conformation (on the NMR time scale) between nematic and smectic-G phase which differs somewhat from the behaviour found for TBBA [19] and TBPrA [13].

Though our results agree qualitatively with the findings of Hsi, Zimmermann, and Luz [31] from deuterium NMR as to the chain ordering, a quantitative comparison seems fairly difficult since by ^2H -NMR indeed an individual methylene deuteron pair can be observed *via* the corresponding quadrupolar line splitting whose magnitude is determined directly by its motional state and/or relative order, respectively. In our simulations, however, a certain S_j ascribed to a given methylene proton pair influences the dipolar interaction with *all* other protons (where, of course, intrapair interactions and those with the protons of the neighbouring methylene groups dominate by far). Nevertheless, a direct quantitative comparison seems not generally feasible, especially for long chains as has been discussed already formerly (cf. [6]).

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