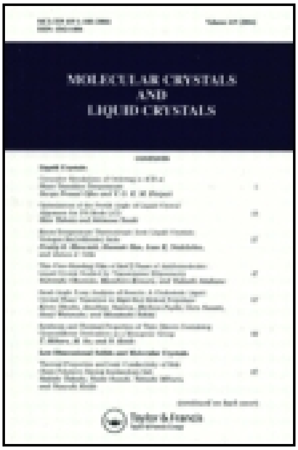

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Behaviour of Alkyloxybenzylidenealkylanilines in the Smectic G Phase

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The liquid crystalline smectic G phases of two alkyloxybenzylidenealkylanilines (nO.m) were studied by means of ^{13}C-NMR. The spectral patterns provide information about order and orientation of the sample. The asymmetry parameter η of 50.6 was found to be very small, $\eta < 0.02$; for all chemical shift tensors of the aromatic core, the shielding tensors are averaged by fast molecular motions practically to rotational symmetry. The principal axis z of the time averaged interaction is unchanged at the S_F-S_G transition. In contrast, the spectra of 70.4 show that the orientation of the z-axes tilts with respect to their original orientation c at the S_C-S_G transition. From the angular dependence of the spectra in the S_G-phase, we conclude that the molecular rotation is strongly hindered; the η values are increased by at least one order of magnitude. The local order parameter of the benzene rings was found to be $S = 0.90$ in the S_G phase of both substances. The results are compared with ^{2}H-investigations.

INTRODUCTION

The liquid crystalline smectic G phase belongs to the low temperature smectic phases of three-dimensional order with a *c*-face centered monoclinic lattice. The molecules are ordered pseudohexagonally within the layers with tilt angles ranging from 25 to 35° for different compounds.[1] The low symmetry causes optical biaxiality in the S_G phase. It is therefore interesting to measure the asymmetry of other properties.[2,3] ^{13}C-NMR measures the time averaged chemical shift. Nearly all positions of the carbon skeleton of the molecule are resolved and can be observed separately. The spectra provide information about the order parameters and the orientational behaviour of the samples. Whereas in smectic C samples, NMR-measurements of biaxiality are difficult because of the reorientation of the directors in the external magnetic field,[4] in the smectic G phase the director distribution is 'frozen' and interpretation of the spectra is unambiguous.

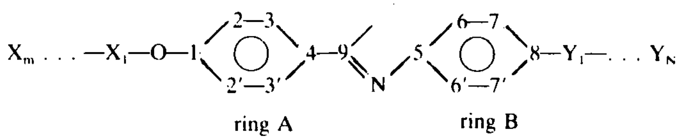
In this paper we report the results of ^{13}C-investigations of two homologues of the benzylideneaniline series. Both substances show qualitatively different behaviour in the smectic G phase. Compound 50.6 (4*n*-pentyloxybenzylidene-4'*n*-hexylaniline) possesses a S_F-S_G transition while 70.4 (4*n*-heptyloxybenzylidene-4'*n*-butylaniline) shows a S_C-S_G transition.[5] In both cases, the transition into the smectic G phase is first order and is accompanied by a discontinuous change in the tilt angle. The transition enthalpy of 70.4 is larger than that of 50.6. The lattice parameters of both compounds are very similar with monoclinic tilt angles of 115.5° and 116.7° respectively.[5] Table I lists the transition temperature and enthalpies. Furthermore, it gives the chemical structure of the carbon skeleton and denotes the carbon sites for the assignment of the NMR-lines. We have mainly confined our investigations to the carbons of the aromatic core of the molecules, since the chemical shifts of the aliphatic chain carbons are less anisotropic and hence less suited for interpretation.

TABLE I

Transition temperatures and enthalpies for 50.6 and 70.4[5]

70.4						
T(°C)	76.5	74.5	65.2	63.9	32.6	
	iso	nem	S_A	S_C	S_G	cryst
H(kJ/mole)	1.33	2.15		3.69	31.8	
50.6						
T(°C)	73.0	61.2	52.8	51.3	43.0	
	iso	nem	S_A	S_C	S_B	S_F-
H(kJ/mole)	1.17	0.97		2.15	0.21	
T(°C)	40.2	35.2				
	S_F	S_G	cryst			
H(kJ/mole)	0.09	25.7				

Carbon positions in the investigated compounds
70.4 $m = 7$ $n = 4$ 50.6 $m = 5$ $n = 6$



EXPERIMENTAL

The ^{13}C-spectra were recorded with a homebuilt, solid state high resolution spectrometer at $\nu_0 = 22.638$ MHz carbon resonance frequency (2.114 T). Proton decoupling was performed by a 1 mT rf-pulse of 35 ms length at the proton resonance frequency. The remaining linewidth is of the order of 1 to 2 ppm and results mainly from magnetic field inhomogeneity. We have used a cross polarization pulse experiment except for the powder spectra, which were recorded with a simple $\pi/2$ pulse technique. The length of the mixing pulse in the CP experiment was 3 ms. The applied rf-power increases the sample temperature by about 2K with respect to the temperature controlling air flow. This contribution was found to be stationary during the acquisition time. Even in the nematic phase, near the clearing point, where the measured chemical shifts are strongly temperature dependent, we obtained sharp spectral lines which indicate a temperature stability and homogeneity within the sample better than 0.5 K. The absolute temperature scale was gauged at the N-I and S_A-N transitions which can be detected by the ^{1}H- and ^{13}C-NMR signals.

The sample tubes had an inner diameter of 5 mm. Surface effects can therefore be neglected and the behaviour of the sample bulk is observed. The numerical calculations of the ^{13}C-spectra were performed with a MC 80 microcomputer.

THEORETICAL

The proton decoupled ^{13}C-spectra are governed by the tensor properties of the chemical shift. For any carbon position i the components of the shielding tensor in its principal axes system are σ^i_{11}, σ^i_{22}, σ^i_{33}. Their values strongly depend on the chemical bonds. The isotropic shielding values $\sigma^i_{iso} = \frac{1}{3}(\sigma^i_{11} + \sigma^i_{22} + \sigma^i_{33})$ are different for all carbons of the rings and most of the chain carbons (Figure 2). Hence the tensor components of the individual positions also differ, but little is known about their values and the directions of the principal axes. From single crystal investigations of substituted benzenes,[13] it was found that σ_{33} was always perpendicular to the ring plane and σ_{11} was located in the direction of the external bond. The tensor values vary strongly for different substituents.[9] The tensor components in our substances should be similar to those of the corresponding carbons in diethoxybenzene for position 2, while for position 1 we expect small deviations. The assignation of σ_{11} parallel to the bond directions is an approximation. It is justified by our measured $\sigma_{\zeta\zeta}$ values. However it should be noted that this assumption is not important for the conclusions drawn from our experiments. Table II gives the tensor components found by Höhener.[9]

These tensor components are connected with the experimentally observed frequency shifts by the orientational order matrix $S^{ab}_{\alpha\beta}$. Since we are analysing the behaviour of the central part of the molecules only, we introduce the local order matrix $S^{ab}_{\alpha\beta,A}$ of the benzylidene ring and use the symbol $\tilde{\sigma}_{\alpha\beta} = \sigma_{\alpha\beta} - \sigma_{iso}$ for the anisotropic shielding tensor part. In the following we omit the index A, but keep in mind that the order parameter values refer to the ring A.

We choose the axes ζ parallel to the *para*-axis and η perpendicular to the ring plane. Then we find the time averaged components in the director system (x, y, z)

$$\tilde{\sigma}^{i}_{ab} = \tfrac{2}{3} S^{ab}_{\alpha\beta}\, \tilde{\sigma}^{i}_{\alpha\beta}\ (a, b \mathrel{\hat{=}} x, y, z;\ \alpha, \beta \mathrel{\hat{=}} \xi, \eta, \zeta) \tag{1}$$

The director system is a principal axes system for the time averaged interactions. It is axially symmetric in the nematic phase ($\tilde{\sigma}^{i}_{zz} = -2\tilde{\sigma}^{i}_{xx} = -2\tilde{\sigma}^{i}_{yy}$). In the S_G phase the tensor $\overset{\leftrightarrow}{\tilde{\sigma}}$ should deviate from rotational symmetry,

$$(\eta^{i} = (\tilde{\sigma}^{i}_{xx} - \tilde{\sigma}^{i}_{yy})/\tilde{\sigma}^{i}_{zz} \neq 0)$$

The equivalence of the positions 2, 3, 6, 7 with their primed counterparts in all experimental spectra, despite their different shielding tensors,[9] indicates the existence of fast jumps, at least 180°-flips, of

TABLE II

Components of the anisotropic part of the shielding tensor relative to benzene

	δ_{11}	δ_{22}	δ_{33}	δ_{iso}		η^{i}_{M}
pos. 1	−79	−5	+84	−26 ppm	/9/	1.1
pos. 2	−80.6	−18.1	+98.7	−12.9 ppm	/9/	

	$\delta_{\zeta\zeta}$	$\delta_{\eta\eta}$	$\delta_{\xi\xi}$	δ_{iso}		η^{i}_{M}
pos. 1	−84.5				/7/	
pos. 2	−33.7	−65	+98.7	−12.9 ppm	/7/	4.8
averaged (flips)						

the rings about their *para*-axes. Therefore the (ξ, η, ζ)-system is a principal axes system for the shielding tensors of the ring.

Thus equation (1) gives the $\bar{\sigma}^i_{zz}$

$$\bar{\sigma}^i_{zz} = S^{zz}_{\zeta\zeta}\bar{\sigma}^i_{\zeta\zeta} + \tfrac{1}{3}(S^{zz}_{\xi\xi} - S^{zz}_{\eta\eta})(\bar{\sigma}^i_{\xi\xi} - \bar{\sigma}^i_{\eta\eta}) \tag{2}$$

The order parameters can be expressed as a function of the Eulerian angles φ, θ, ψ of the ξ, η, ζ-system in the director system: $S = S^{zz}_{\zeta\zeta} = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$ and $S^{zz}_{\xi\xi} - S^{zz}_{\eta\eta} = D = \frac{3}{2}\langle \sin^2\theta \cos 2\psi\rangle$. The brackets denote time averaging.

Similar expressions can be written for the $\bar{\sigma}_{xx}$ and $\bar{\sigma}_{yy}$ components and we find $\bar{\sigma}^i_{xx} - \bar{\sigma}^i_{yy} = (S^{xx}_{\zeta\zeta} - S^{yy}_{\zeta\zeta})\bar{\sigma}^i_{\zeta\zeta} + (S^{xx\prime}_{\xi\xi} - S^{yy}_{\xi\xi} - S^{xx}_{\eta\eta} + S^{yy}_{\eta\eta})(\sigma^i_{\xi\xi} - \sigma^i_{\eta\eta})^3$

$$\eta^i = [\langle \tfrac{3}{2}\sin^2\theta \cos 2\varphi\rangle + \tfrac{1}{3}\langle \tfrac{3}{2}(\cos^2\theta + 1)\cos 2\varphi \cos 2\psi$$
$$- 3\cos\theta \sin 2\varphi \sin 2\psi\rangle\, \eta^i_M]\sigma^i_{\zeta\zeta}/\sigma^i_{zz}$$

with

$$\eta^i_M = (\sigma^i_{\xi\xi} - \sigma^i_{\eta\eta})/\bar{\sigma}^i_{\zeta\zeta} \tag{3}$$

The measured chemical shift of one single carbon position *i* for a fixed direction of the magnetic field with respect to the director system is given by

$$\nu^i = \nu^i_a\left[\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) + \frac{\eta^i}{2}\sin^2\theta \cos 2\phi\right] + \nu^i_{iso} \tag{4}$$

where θ and ϕ are polar and azimuthal angles of $\vec{B}_0$ according to Figure 1, ν^i_{iso} is the isotropic resonance frequency, and $\nu^i_a = -\nu_0 \cdot \bar{\sigma}^i_{zz}$.

For the interpretation of the ^{13}C-spectra a successive separate determination of the unknown parameters

$$\nu^i_a(T),\ \eta^i(T),\ \theta,\ \phi,\ \nu^i_{iso}$$

of Eq. (4) in a set of independent experiments is necessary. This is shown in the results section. A completely oriented sample yields sharp resonance at ν^i (T, θ, ϕ). In general, because the macroscopic samples are not monocrystalline, but represent polydomain systems, the spectra are more complex. A computer simulation of the lineshape is necessary and a comparison with the experimental spectra yields the required quantities.

For a description of the director system distribution we introduce the density function $n'(\theta, \phi)$, which describes the relative number of director systems in a defined spatial orientation with respect to the external magnetic field. The lineshape function in such systems is calculated by

$$I(\nu^*) \frac{\mathrm{d}N}{\mathrm{d}\nu}\bigg|_{\nu=\nu^*} = \int_{\nu=\nu^*} \frac{n'(\theta, \phi)\, \mathrm{d}l}{|\mathrm{grad}\ \nu|} \tag{5}$$

where

$$\mathrm{d}l = \sqrt{1 + \frac{1}{\sin^2\theta}\left(\frac{\partial\theta}{\partial\phi}\right)_{\nu\ =\ \mathrm{const}}}\ \mathrm{d}\phi\ \sin\theta;$$

$$\mathrm{grad}\ \nu = \frac{\partial\nu}{\partial\phi} \cdot \frac{\vec{e}_\phi}{\sin\theta} + \frac{\partial\nu}{\partial\theta}\vec{e}_{\theta 2}$$

and N is the total number of director systems ('domains') in the sample.

For uniaxial phases ($\eta' = 0$), we introduce the function $n(\theta) = \int n'(\theta, \phi) \sin\theta\, \mathrm{d}\phi = \sin\theta \cdot n'(\theta, \phi) \cdot 2\pi$ and Eq. (5) reduces to

$$I(\nu^*) = \frac{\partial N}{\partial\theta}\frac{\partial\theta}{\partial\nu}\bigg|_{\nu=\nu^*} \propto \frac{n(\theta)}{\sin 2\theta}\bigg|_{\theta(\nu^*)} \tag{6}$$

The experimental lineshape is found by convoluting $I(\nu)$ with the spectrometer function.

Since the samples were oriented in the nematic phase by the spectrometer field $B > 2T$, the field direction in the nematic phase defines the preferred orientation axis which will subsequently be denoted by c. The orientation system a, b, c (see Figure 1) is used to describe the director orientation in the smectic phase where the z-axes may deviate from their original orientation c, especially in tilted phases. The system a, b, c is fixed relative to the sample tube. The a and b axes are chosen such that, under rotation of the sample tube, the field direction remains in the ac-plane; the angle between B-direction and c-axis is denoted by θ_h.

The orientation of the director system x, y, z in the a, b, c-system

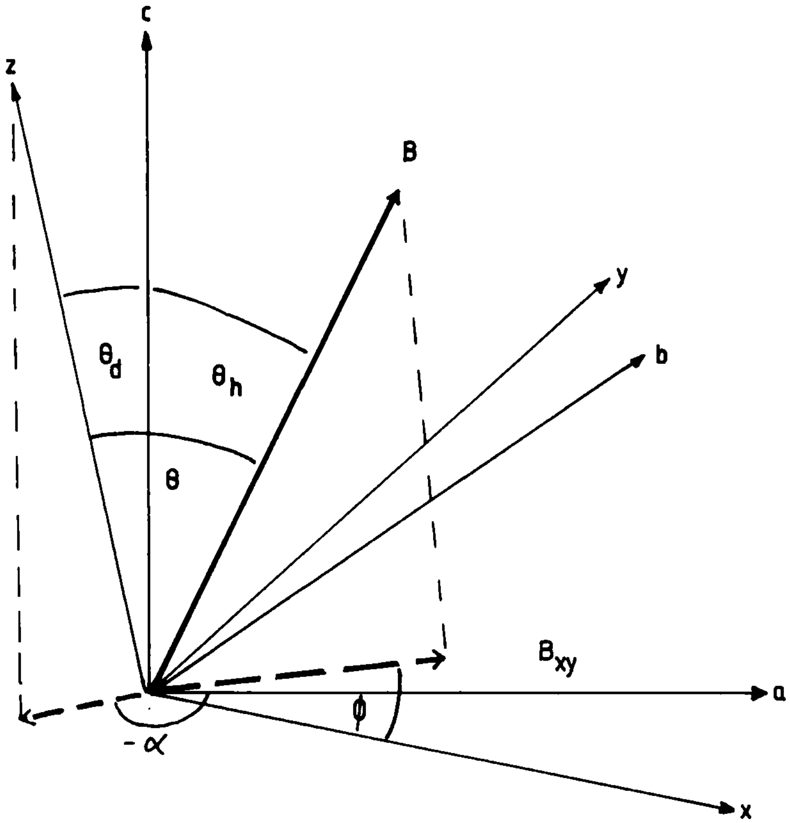


FIGURE 1 Relations between the orientation frame *a*, *b*, *c* (fixed to the sample tube), the principal axes *x*, *y*, *z* of the time averaged chemical shielding tensors (director system) and the magnetic field direction B. ϕ is the azimuthal angle of B in the director system. α, θ_d, β are Eulerian angles of *xyz* in the *abc*-system.

is described by the Eulerian angles α(between the *a*-axis and the projection of *z* onto the *ab*-plane), θ_d (polar angle), and β. From the symmetry of the aligning magnetic field we can conclude that the macroscopic symmetry of the sample is uniaxial (randomly distributed angles α). The angle θ between the *B*-direction and *z* is calculated by

$$\cos\theta = \cos\theta_d \cos\theta_h - \sin\theta_d \sin\theta_h \cos\alpha \qquad (7)$$

Further we suppose that the *cz*-plane in the tilted S_G phase is a mirror plane and defines the symmetry in the orientation of the director systems, $\sin 2\beta = 0$.

Then the calculation of the expression $\sin^2\theta \cos 2\phi$ in Eq. (4) gives

$$\sin^2\theta \cos 2\phi = [(\cos\theta_h \sin\theta_d + \sin\theta_h \cos\theta_d \cos\alpha)^2 - \sin^2\theta_h \sin^2\alpha]$$

With these assumptions the computation of the spectral patterns for different orientations of the smectic G sample in the magnetic field was performed.

RESULTS

The isotropic chemical shifts of both substances were determined for the isotropic liquid phase. The identification of the individual carbon positions was taken from ref. 7. It coincides with that of other authors for similar compounds.[10] Figure 2 shows the isotropic ^{13}C-spectrum of 50.6 and the assignment of the carbons. All aromatic carbons have different shift values in the isotropic phase.

In the nematic phase the directors align with the magnetic field. The lines in the aromatic part of the spectrum are shifted to higher frequencies with decreasing temperature due to the increasing order. The temperature dependences are given for the carbon lines 1 to 9 in the $\theta_h = 0$ spectra in Figures 3 and 4. Position 5 is strongly broadened by the non-decoupled ^{13}C-^{14}N- interactions in the liquid crystalline phases; it is hence not observable. All other lines have linewidths in the oriented liquid crystalline 0°-spectra which are equal to the widths of the isotropic lines, except for the OCH$_2$-group X$_1$ (where proton decoupling is not completely obtained with the low rf-power), and the smectic G phase of 70:4, which is discussed separately. The line intensities are equally enhanced for all positions in the CP-spectra.

For compound 50.6, the resonance lines remain narrow in all phases when the oriented sample is cooled from the nematic to the smectic G phase and the phase transitions are passed sufficiently slow. The frequency shift is more strongly temperature dependent for the *para*-positions 1,4 and 8 than for the *ortho*- and *meta*-positions 2, 3, 6 and 7. The line of position 9 is more weakly temperature dependent and intersects the positions of line 8 and 4. All positions of the aromatic core are resolved. The ν_a^i can be calculated from the line shifts with respect to the resonances ν_{iso}^i in the isotropic spectrum.

The experimentally determined values of the ratio ν_a^i/ν_a^j for different carbon sites i and j are nearly temperature independent (Figure 5). This is explicable only if both terms of Eq. (2) have the same

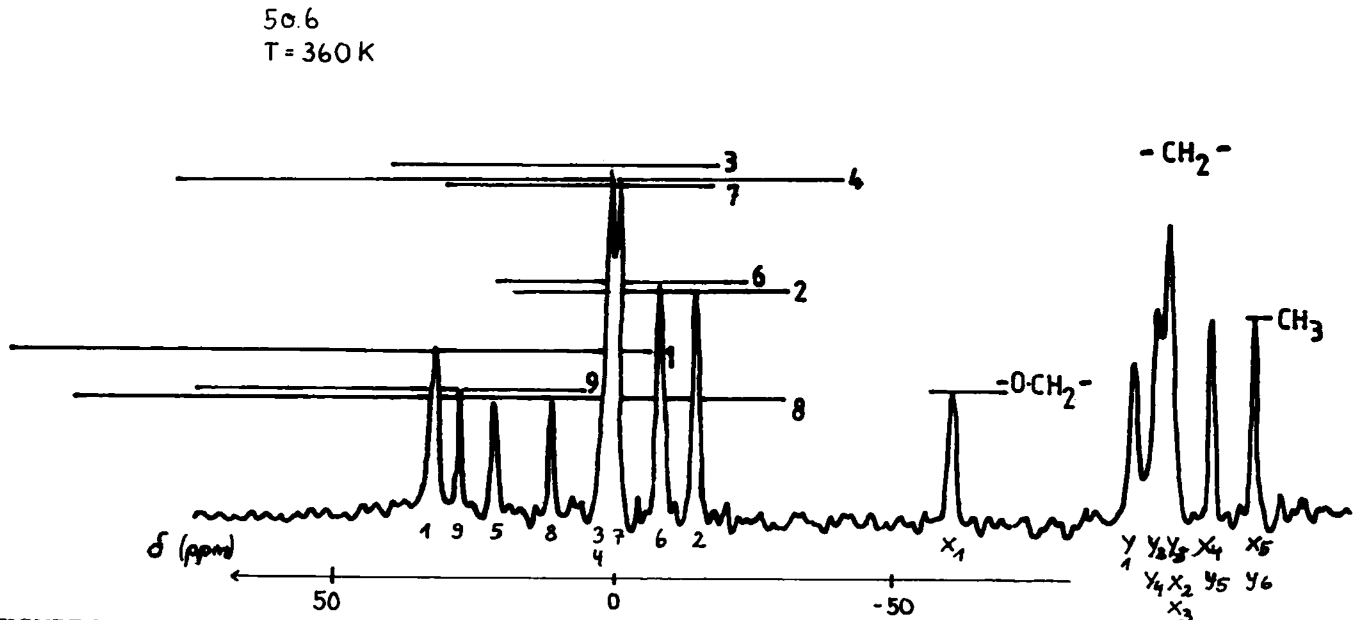


FIGURE 2 Isotropic ^{13}C-spectrum of 50.6 at 360 K in the liquid phase. The horizontal lines indicate the region of chemical shift anisotropy (between $\nu_{\parallel}^{i}$ and $\nu_{\perp}^{i} = \nu^{i}(\theta = 90°)$) at T = 300 K in the S_G phase. The numbers correspond to the notation in Table I. δ is the chemical shift with respect to benzene.

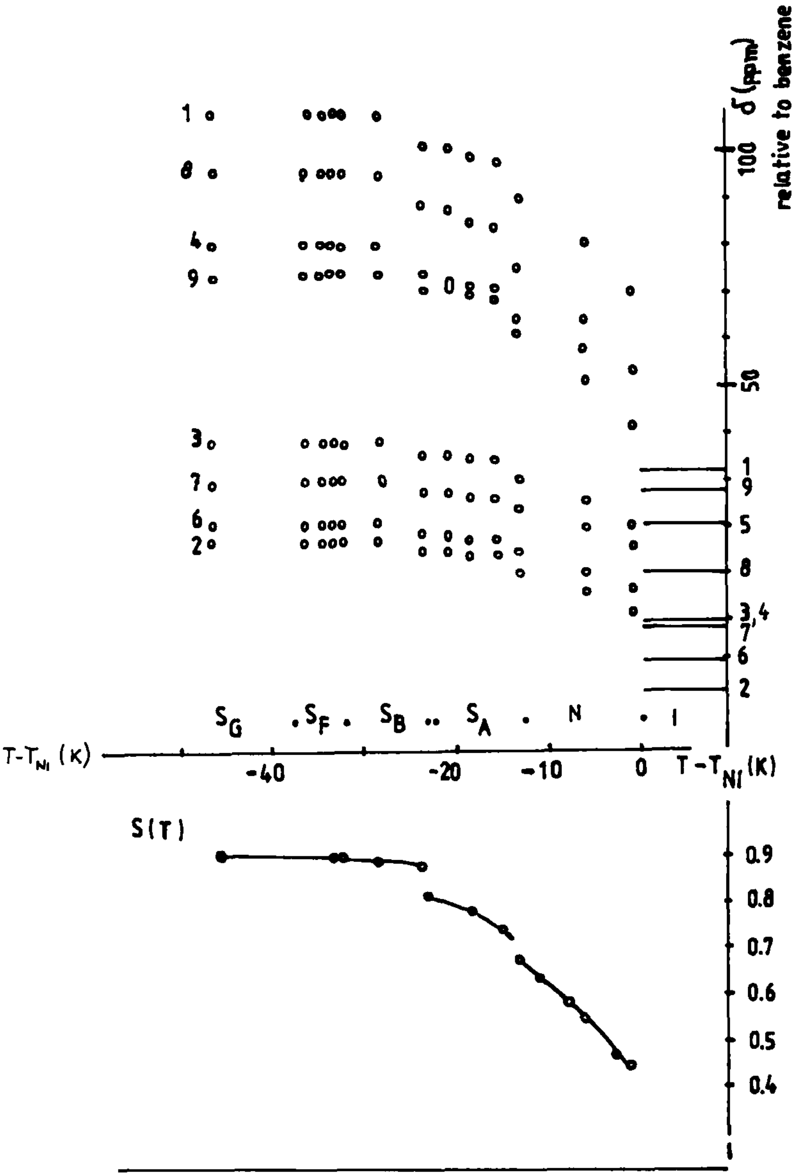


FIGURE 3 Temperature dependence of the $\nu_{\parallel}^{i}$ in 50.6 (aromatic carbons). The lower curve gives the calculated $S(T)$ for ring A (benzylidene-ring), assuming $\sigma^{1}_{\zeta\zeta} = -84.5$ ppm. The same temperature dependence is found for ring B (aniline-ring).

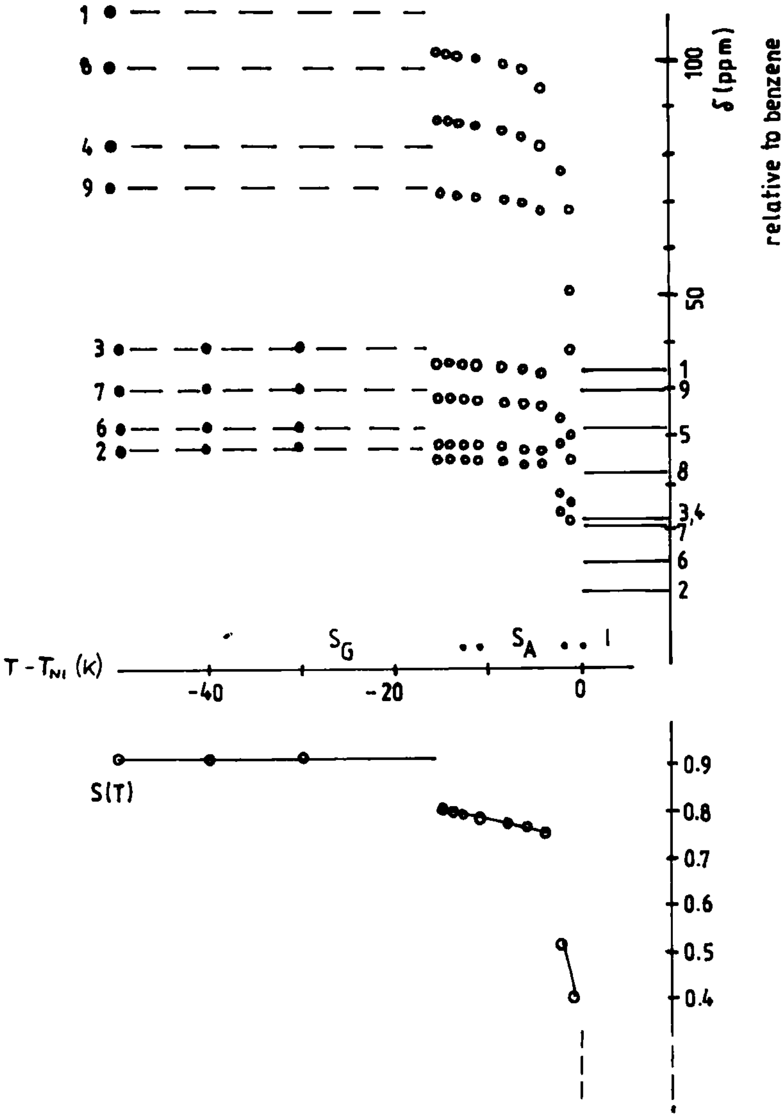


FIGURE 4 Temperature dependence of $\nu_{\parallel}^{i}$ of the aromatic carbons of 70.4. The $S(T)$ curve is shown below as in Figure 3. The full circles represent the positions measured in the 20°-spectra for S_G.

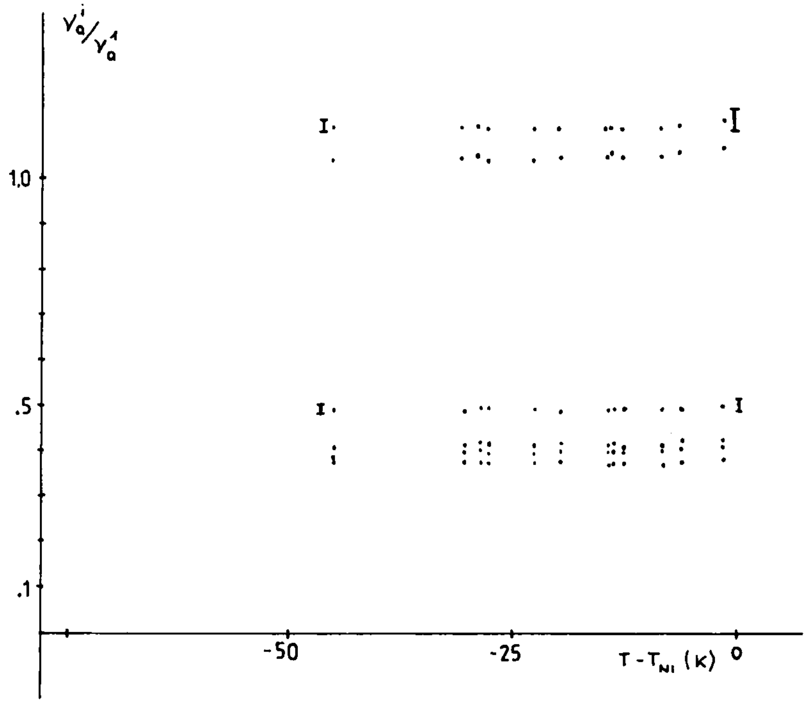


FIGURE 5 Temperature dependence of the ratios ν_a^i/ν_a^1 for 50.6.

temperature dependence or if the second term is negligible. The temperature dependences of S and D should be totally different, even possibly of opposite sign, hence we conclude that D is very small and can be neglected while S varies from the nematic phase to S_G by roughly a factor of 2. The absolute quantity of S is found by scaling the $\nu_a^i(T)$ curve. From proton NMR measurements, the $S(T)$-curves of homologous substances were determined (The doublet splitting of the *ortho*-protons gives the order parameter for the axis ζ, since the dipolar interaction is rotationally symmetric around the *para*-axis), and the temperature dependence of the ^{13}C-resonance of position 1 was fitted. The obtained scaling value is $\bar{\sigma}_{\zeta\zeta}^i = -84.5$ ppm (Table II).[7,8] Since the ratios are constant, we could have used any other carbon position for the determination of $S(T)$, with the same results. Differences of the order parameters of both rings are not detectable by ^{1}H-NMR; the observed value is an average of both rings.

The order parameter S increases with decreasing temperature up to a value $S = 0.90$ in the S_G phase. At the transition T_{BC} from the S_C to the S_B phase, it jumps by $\Delta S_{CB} = 0.07$ and at T_{AN} by $\Delta S_{AN} =$

0.05. In the smectic G phase, the order parameter remains nearly unchanged.

From the sharp lines in the 0°-spectra of 50.6, we conclude that the orientation of the directors is preserved in all smectic phases, except for a slight broadening of the distribution $n(\theta_d)$ around the *c*-axis. The distribution function n' retains its maximum at $\theta_d = 0$.

Turning the field into the direction *a*, we expect a splitting of the lines according to Eq. (4), as $\cos 2\phi = \cos 2\alpha$ for $\theta_d = 0$ and $\theta_h = 90°$ (Eq. (7, 8)) and the angles α are randomly distributed. Such a splitting was not observed in 50.6; the lines remain sharp at $\theta_h = 90°$. Hence $\nu^i_a \eta^i$ must be smaller than the natural linewidth of ~ 2 ppm; that is $\eta < 0.02$ for all positions (Figure 6). A value of $\eta^i = 0.015$ seems to be indicated by a small broadening at least for the positions 1 and 4.

The completely recorded angular dependence of the spectra in the smectic phases (θ_h varied in 10°-steps from 0 to 90°) shows, that the line maxima shift with

$$\nu^i_{max} = \nu^i_a\left(\frac{3}{2}\cos^2\theta_h - \frac{1}{2}\right) + \nu^i_{iso}$$

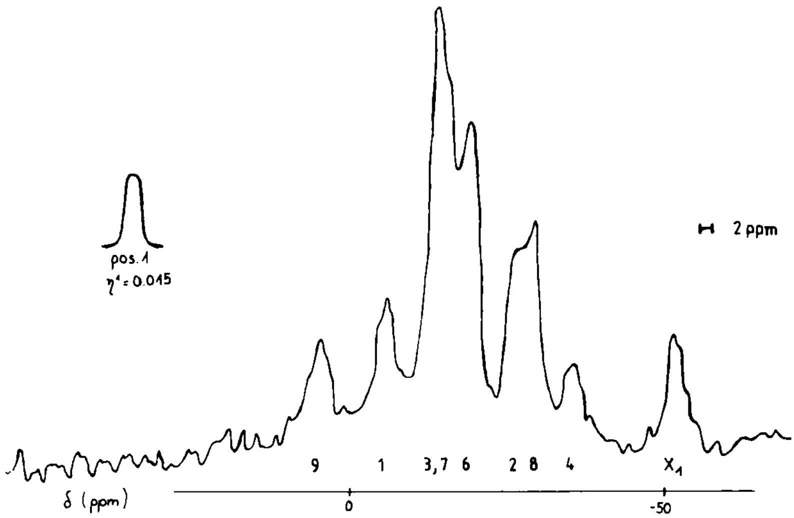


FIGURE 6 Spectrum of the aromatic carbons of 50.6 in the S_G phase at 300 K for $\theta_h = 90°$. For comparison the calculated lineshape for position 1 with $\eta = 0.015$ is shown above. The spectral pattern and the line positions are unchanged throughout the S_G phase down to the transition from supercooled S_G to the crystalline phase at −10°C.

in accordance with Eq. (4), with $\theta = \theta_h$. As the z-axes are not perfectly aligned to the axis c, the lines are broadened due to the director distribution. The quality of the alignment of the directors is characterized by the half width $\theta_{1/2}$ of $n(\theta_d)$. The distribution is narrow; hence the actual shape is of minor importance. For the numerical calculations we assumed a Boltzmann distribution

$$n(\theta_d) \propto \sin\theta_d \exp\,(A \cdot \cos^2\theta_d)$$

with the half width $\theta_{1/2} = \arccos\,((\ln 2/A)^{1/2})$ (about 50% of the director total forms angles $\theta_d < \theta_{1/2}$ with the c-axis).

For small $\theta_{1/2}$ we find $\theta \sim \theta_h$ from Eq. (7). The linewidth $\Delta\nu$ varies with approximately

$$\Delta\nu = \frac{\partial\nu}{\partial\theta}\Delta\theta + L = \tfrac{3}{2}\sin 2\theta_h \cdot \Delta\theta\nu_a^i + L$$

(with L being the natural linewidth). The broadening due to the director distribution is maximal at $\theta_h = 45°$ and negligible for $\theta_h = 0$ and $\theta_h = 90°$. Thus the distribution was extracted by comparing the experimental spectra for $\theta_h = 45°$ with the simulated spectra in the S_A, S_B and S_G phases respectively (Figure 7). For the non-tilted phases S_A and S_B, distribution half widths smaller than 1° were found. This points at an excellent orientation of the sample. Actually the quality of the alignment depends on the investigated compound and somewhat on the cooling conditions. Particularly, the phase transitions have to be scanned slowly to obtain a perfectly oriented smectic sample.

In the smectic G phase, the distribution broadens to about 3.5°, but still the distribution n' is most dense in the c-direction ($\theta_d = 0$).

The tilt angle in the S_G phase is about 25°. Hence the transition into the low temperature phases of 50.6 is accompanied by a deformation of the smectic layers. They are tilted with respect to the c-axis while the preferred orientation of the ζ-axes remains c. The broadening of the distribution $n(\theta_d)$ can be explained by the appearance of local defects in the distorted layer structure.

For the compound 70.4, the order parameter was calculated in a similar way to that for 50.6 for the S_A, S_C and nematic phases. The positions of the sharp line maxima are shown in Figure 4. The order parameter jumps to the relatively high value of $S = 0.73$ at the transition from the nematic to the S_A phase. High order parameters

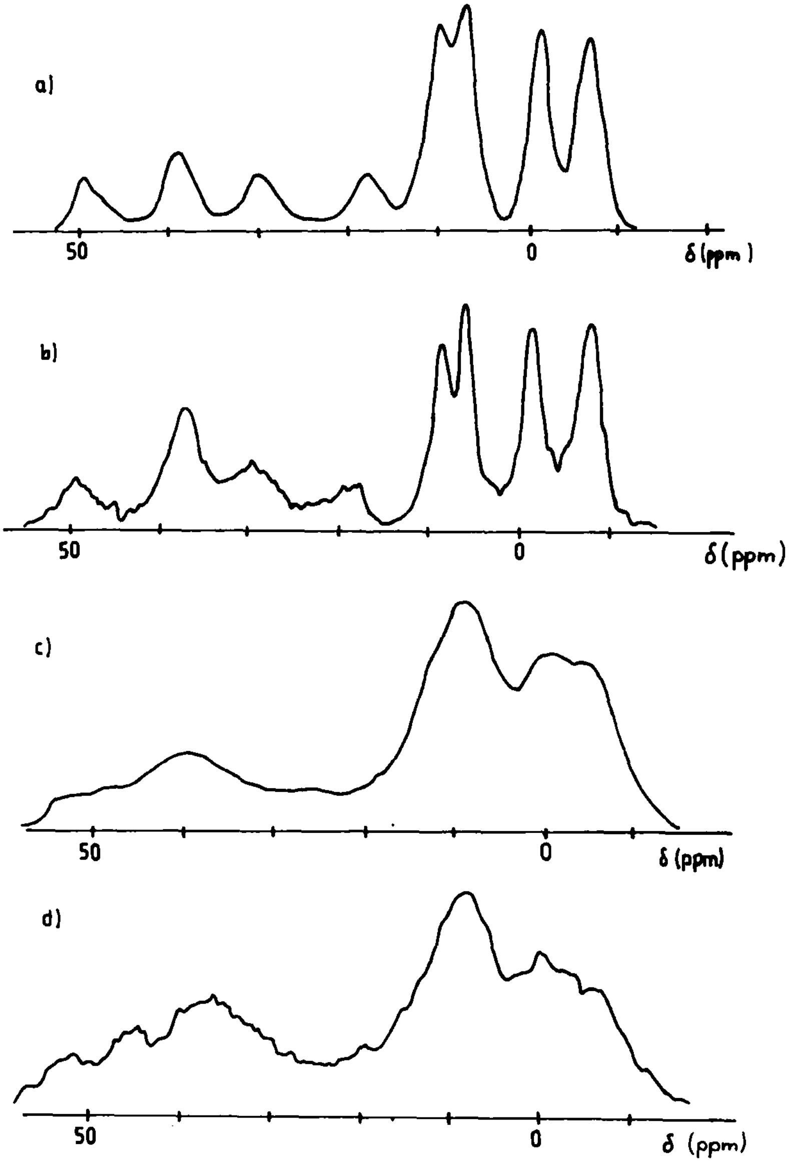


FIGURE 7 Spectrum of the aromatic carbons of 50.6 for $\theta_h = 45°$

a) simulated with a Boltzmann director distribution of half width 0.7° and the ν_a' values of $T = 328$ K

b) corresponding experimental spectrum for the S_A phase at 328 K; in the S_B phase the lines are only slightly broader.

c) simulated with the ν_a' for $T = 300$ K and with a distribution of $\theta_{1/2} = 3.5°$.

d) corresponding experimental spectrum for the S_G phase at 300 K are common to smectic A phases which are preceded by only small nematic ranges.

In the smectic G phase, the lines become very broad in the 0°-spectra and the maxima are shifted towards the ν^i_{iso} positions. A decrease of the ν^i_a can be excluded; hence the director distribution must have shifted to angles $\theta_d > 0$. The 0°-spectra are therefore inappropriate for the determination of the ν^i_a. The frequency peaks at $\nu^i_\parallel = \nu^i_a + \nu^i_{iso}$ can be found, however, if the sample is turned to an angle $\theta_h = 20°$.

It is seen from Eq. (6) that the denominator of the lineshape function is zero at $\theta = 0$. Hence the frequency peaks at $\nu^i_\parallel$ appear when the distribution $n(\theta)$ is not zero at $\theta = 0$. This applies also to Eq. (5), because for small θ the asymmetry term in Eq. (4) can be neglected. Therefore, we can state that the z-axes are tilted with respect to the c-direction by about 20° when the oriented smectic C sample is cooled to S_G. The azimuthal distribution of the tilt is uniform (angles α). At $\theta_h = 20°$, the magnetic field direction intersects this cone of the z-axes distribution, yielding $\theta = 0$ for $\alpha = 0$, and a certain portion of the directors is aligned with the field direction (Figure 8). From the peak positions in the 20°-spectra, the ν^i_a were calculated (indicated in Figure 4 by closed circles), and a constant order parameter $S = 0.9$ in the S_G phase was found as for 50.6. The ratios ν^i_a/ν^j_a are found to be constant in the whole temperature range as for the 50.6 sample.

With the known ν^i_a values, we have simulated the lineshape of the 0°-spectrum (Figure 8). The best correspondence of experimental and calculated spectra was found with the distribution depicted in Figure 8d, which has its maximum in the vicinity of $\theta_h = 20°$ as already suggested. For comparison, we show the simulated spectrum with an only slightly altered distribution function in Figure 8e to prove the sensibility of the simulated spectral pattern.

For angles $\theta < 20°$, the term $\sin^2\theta \cos 2\phi$ in Eq. (4) is small compared with $(3 \cos^2\theta - 1)/2$; hence an asymmetry of the interaction tensors does not influence the spectrum.

As the director axes z are tilted to the c-axis by an angle which is comparable with the tilt angle, the experiment strongly supports the suggestion that the layer normals retain their orientation at the S_C-S_G transition.

With the known z-axes distribution we were able to calculate the spectra for arbitrary angles θ_h. The 90°-spectrum is shown in Figure 9. It is clearly seen that the assumption of $\eta^i = 0$ gives a very poor correspondence of the simulated with the experimental lineshape. Since the ν^i_a, ν^i_{iso} and θ values are fixed, there is only the parameter

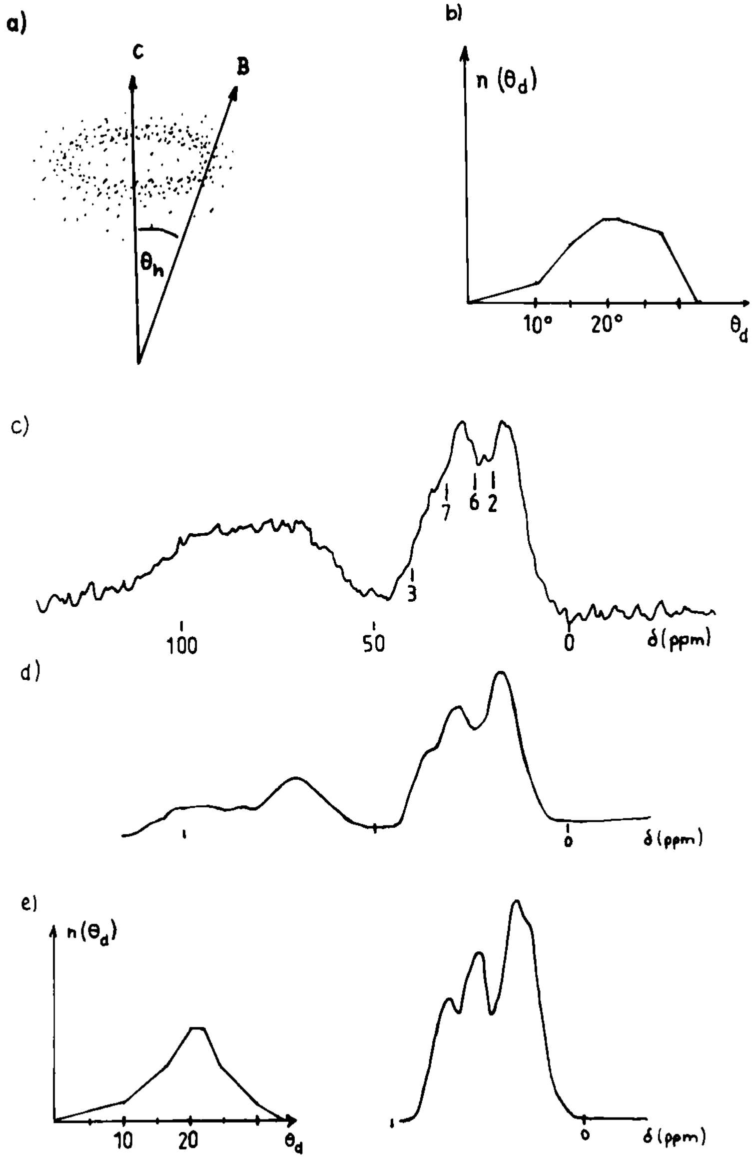


FIGURE 8 a) Schematic drawing of the distribution of the z-axes for the S_G phase of 70.4 after cooling an oriented S_C sample. The dots represent the density of $n'(\theta_d, \alpha)$ on a unit sphere.

b) distribution function for the simulated spectrum in Figure 8d

c) experimental spectrum of the aromatic carbons of 70.4 at $T = 300$ K for the S_G phase ($\theta_h = 0$). The $\nu_{\|}^{i}$ frequencies for the *ortho*- and *meta*-positions are labeled.

d) best fitted calculated spectrum.

e) calculated spectrum with a slightly changed director distribution to show the dependence of the lineshape on $n(\theta_d)$

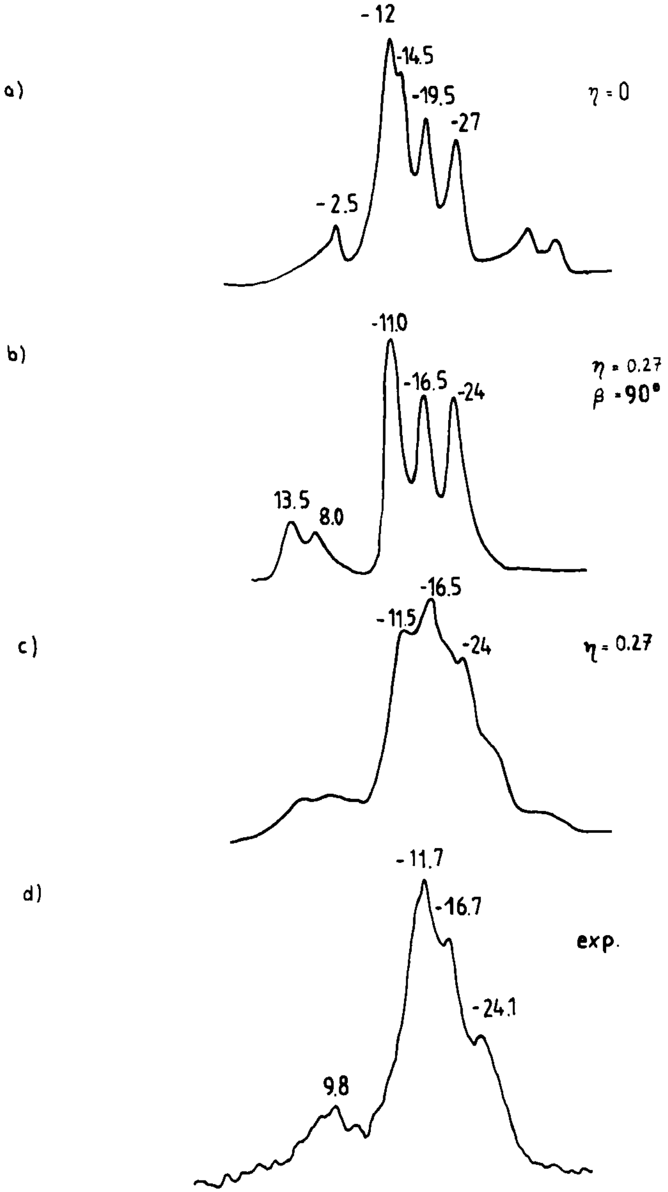


FIGURE 9 90°-spectra of 70.4 in the smectic G phase at $T = 300$ K (aromatic carbon section); the peak frequencies are given (in ppm).
a) simulated with $\eta = 0$ and the distribution $n(\theta_d)$ of Figure 8b
b) simulated with $\eta = 0.27$ and $\beta = 90°$. The peak frequencies are in good agreement with the experiment.
c) simulated with $\eta = 0.27$ and a random distribution of the angles β
d) experimental spectrum.

η^i left to be varied to refine the correspondence to the experimental spectrum. The pattern of Figure 9b was calculated with a value $\eta = 0.27$ for all carbons. This is clearly a very rough approximation, since the η^i should depend strongly on the position i.

Yet the *para*-carbons are practically not observable, because each position is occupied by only one carbon in the molecule in contrast to two carbons in each *meta*- and *ortho*-position (i, i'), and the intensities are smeared out due to the director distribution over a much greater anisotropy range. Hence the intensities of the positions 2, 3, 6, 7 are larger by a factor ~5. The determined value of η^i is thus valid for the latter carbon sites only. All *meta*- and *ortho*-carbon shielding tensors have similar molecular anisotropies $\eta^i_M = (\sigma_{\xi\xi} - \sigma_{\eta\eta})/\bar{\sigma}_{\zeta\zeta}$; hence similar η^i can be expected. A value of $\beta \simeq 90°$ was used for the calculation of 9b. There is a good coincidence of the peak positions which should appear at the frequencies

$$\nu = -\tfrac{1}{2}\nu^i_a + \eta^i/2 \cdot \nu^i_2 + \nu^i_{iso}.$$

In spectrum 9d we have additionally introduced a random distribution of the angles β. This distribution does not alter the positions of the peaks, but broadens the peaks at the low frequency edge. The actual distribution of the angles β should lie between both extremes. We have not determined its exact shape because of the mathematical expense, though we consider it to be possible with refined methods.

Furthermore, we have tried to measure the biaxiality from the comparison of experimental and simulated 'powder' spectra. If the sample is cooled from the isotropic phase to S_G in the absence of the orienting magnetic field, the distribution of the director systems is isotropic, $n'(\theta, \phi) = \sin\theta$ and the determination of the η^i is straightforward since we have not to take into consideration distributions of the angles β.

Figure 10 shows the experimental and simulated line patterns. The calculated spectra are in good agreement with the experimental spectra with the same η^i value as the oriented 90°-spectrum.

The same procedure was applied to the sample 5O.6. As is seen from Figure 11, the powder spectrum for the S_A phase is in good agreement with the calculated lineshape for $\eta = 0$, while for the smectic G phase the measured spectrum differs remarkably from the calculated spectrum, even with a small η value. The powder distribution of the director systems is proved by the fact that the lineshape is constant if the sample is turned through an arbitrary angle θ_h. Experiments to clarify the reason for this deviation are under way.

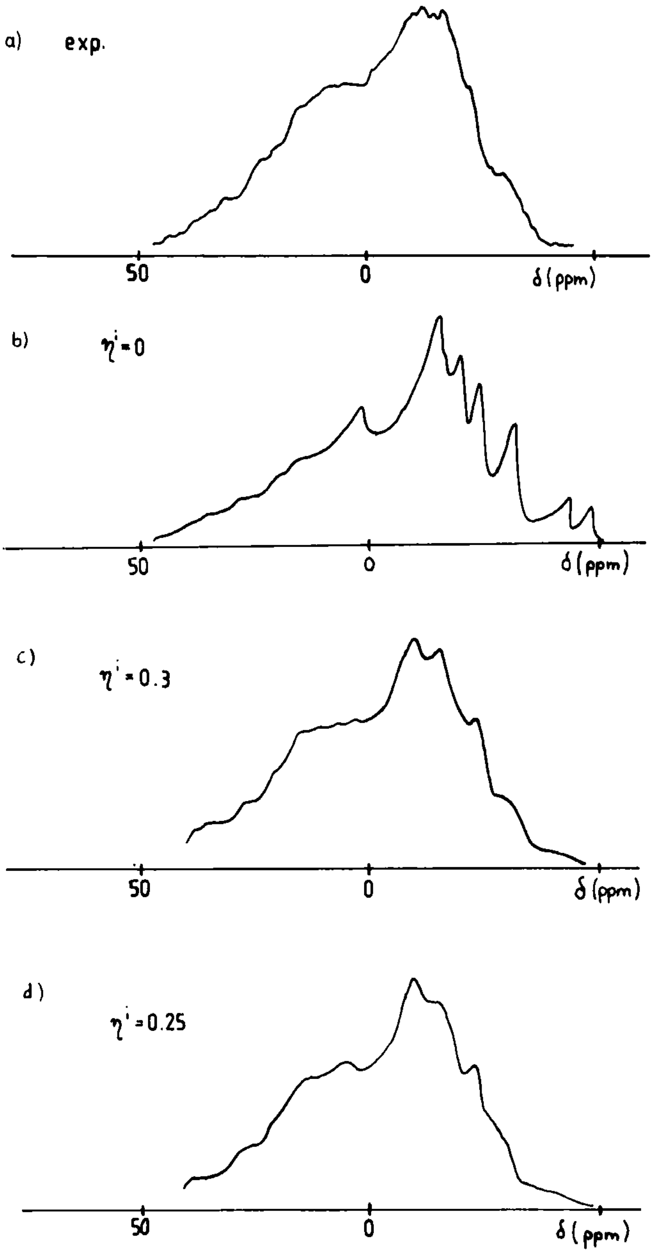


FIGURE 10 'Powder' spectra for 70.4 (aromatic part), T = 300 K.
a) experimental
b) simulated with η = 0 for all positions
c) simulated with η = 0.3 for all positions
d) simulated with η = 0.25 for all positions.

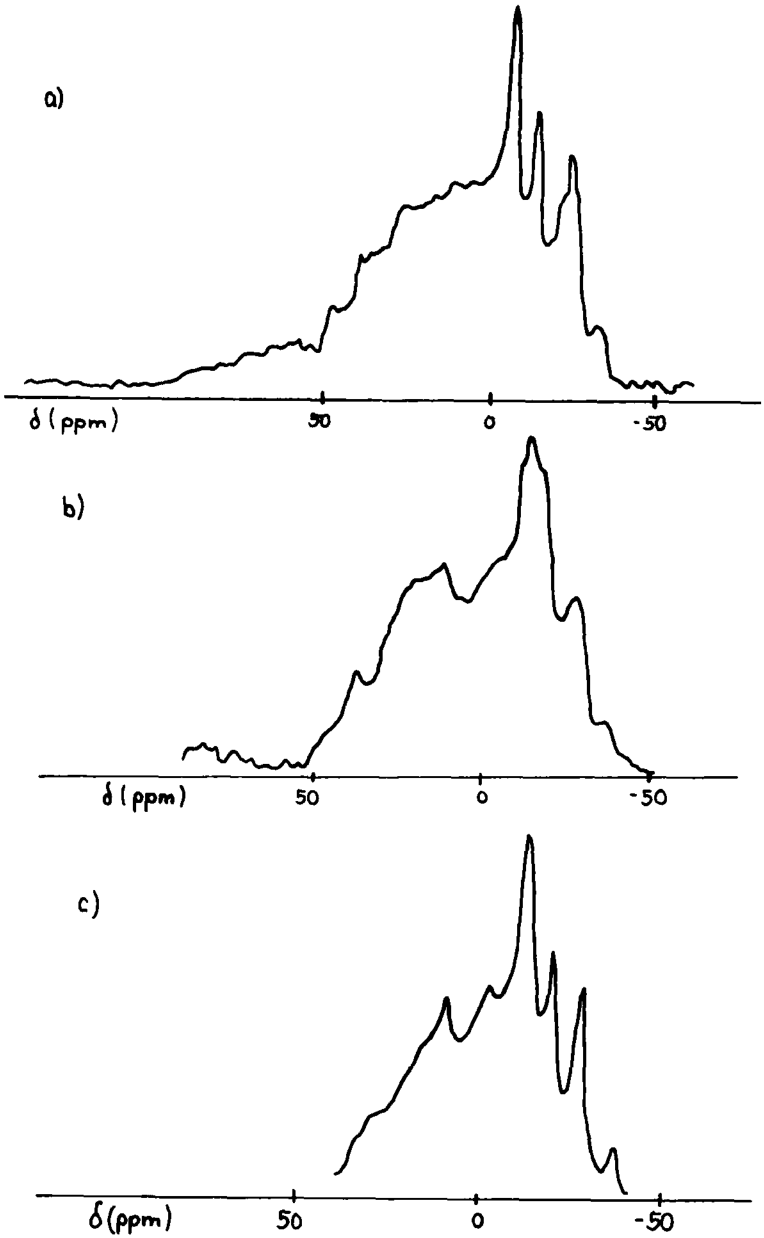


FIGURE 11 'Powder' spectra for 50.6 (aromatic part). The powders were prepared by cooling the sample from the liquid phase to the S_A phase in the absence of the external field.

a) experimental spectrum for S_A at 328 K

b) experimental spectrum for S_G at 300 K

c) simulated with $n'(\theta, \phi)$ = const., $\eta' = 0.015$ and the ν'_a for T = 300 K.

SUMMARY

No asymmetry of the time averaged interaction tensors of the aromatic molecular core has been found for the oriented 50.6 sample in the S_G phase. Both asymmetrical long axes fluctuations and deviations of the fast molecular rotations from rotational symmetry are small ($\eta^i < 0.02$). Since the first term in Eq. (3) (asymmetrical fluctuations of ζ) is position independent and the second term depends on the tensor property η^i_M of the individual position, both do not compensate. We can state that

$$\langle \tfrac{3}{2}\sin^2\theta \cos 2\varphi \rangle < 0.018$$

and

$$\eta^i_M \langle \tfrac{3}{2}(\cos^2\theta + 1) \cos 2\varphi \cos 2\psi - 3 \cos\theta \sin 2\varphi \sin 2\psi \rangle < 0.054$$

The molecular core can be considered rod-like; if a herringbone-like structure in S_G exists, it manifests itself on a much shorter timescale than that of ^{13}C-NMR or is connected with the orientation of the alkyl chains only.

For the compound 70.4, we found a completely different behaviour. At the transition from S_C to S_G, the z-axes are shifted from their aligned orientation. We found an asymmetry of the shift tensors for the *ortho-* and *meta-*ring carbons $\eta = 0.27$ which is one order of magnitude larger than that for 50.6.

For comparison we refer to ^{2}H-measurements of Dong *et al.*[2] They detected an asymmetry parameter $\eta = 0.2$ for the quadrupole interaction of the *ortho* ring ^{2}H-positions, but no shift of the z-axes for 50.7. This substance is similar to 50.6, with the same polymorphism, similar transition temperatures, and similar enthalpies (except for the missing S_F phase). Furthermore, they stated a shift of the director system but no asymmetry for a mixture of 90.4 with 24.7 wt% of 50.6.

A shift of the director systems at the S_C to S_G transition is also pointed out for terephthalylidene-*bis*-propylaniline, by results of ^{1}H[12] and ^{13}C-NMR.[11]

It should be mentioned that in all investigated substances the original orientation of the directors is re-established if the sample is reheated into the smectic A phase again (though the lineshape is slightly broadened because of local defects in the layer structure which arise at the transitions from the non-tilted to the tilted phases).

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