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^{13}C N.M.R. and ^{14}N N.Q.R. in ferroelectric liquid crystals Polar versus quadrupolar ordering

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Invited Article

^{13}C N.M.R. and ^{14}N N.Q.R. in ferroelectric liquid crystals

Polar versus quadrupolar ordering

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^{13}C nuclear magnetic resonance and ^{14}N nuclear quadrupole resonance spectra of ferroelectric smectic C* liquid crystals and their non-chiral analogues allow for a microscopic determination of the polar and quadrupolar (or bipolar) biasing of rotation around the long molecular axis as well as for a determination of the anisotropy in the fluctuations of this axis. The results show that the microscopic origin of the biquadratic coupling between the polarization and the tilt, which has been recently introduced into the extended Landau model of the S_A–S_C^* transition, is the quadrupolar (or bipolar) rotational bias induced by the anisotropy in the fluctuations of the long molecular axis. The tilt induced anisotropy in the fluctuations is practically identical in chiral and non-chiral smectic C phases.

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1. Introduction

Ferroelectric smectic C* liquid crystals [1, 2] are orientationally ordered liquids with a one dimensional density modulation. The periodicity of the helicoidal orientational ordering is incommensurate to the periodicity of the one-dimensional density modulation. The smectic C phase is ferroelectric if the molecules are chiral and have a permanent dipole moment transverse to their molecular axis. In the high temperature smectic A phase the molecules rotate freely around their long axes which are on the average oriented perpendicular to the smectic layers ($n_z = 1$, $n_x = n_y = 0$). The point symmetry of each layer corresponds to the group D_∞.

The transition to the ferroelectric smectic C* phase is induced [2] by the two dimensional representation E_1 and the point symmetry of the layers is reduced to C_2. The order parameters of the transition are the molecular tilt, i.e. the quadratic combinations

$$\xi_1 = n_z n_x \quad \text{and} \quad \xi_2 = n_z n_y \tag{1 a}$$

and the components

$$P_x, P_y \tag{1 b}$$

of the in-plane spontaneous polarization. It is generally accepted that the tilt of the long molecular axes with respect to the layer normals, which exists also in the non-chiral smectic C phase where the point group symmetry is C_{2h}, is the primary and the spontaneous polarization the secondary order parameter. Ferroelectric liquid crystals are thus improper ferroelectrics [3].

It is generally assumed that the tilt induces a biasing of the rotation around the long molecular axis. The biasing is quadrupolar in achiral systems and assumed to be polar in chiral systems. The exact relation of these two effects is still unknown and is the subject of this paper.

2. Theoretical models

In chiral smectic C* systems the molecular tilt as well as the in-plane polarization slowly rotate on going from one smectic plane to the other, resulting in a helical structure. The pitch of the helix is of the order of 10^3 interlayer distances and is, in general, incommensurate with the one dimensional translational periodicity of the smectic density modulation. In achiral S_C system the tilt is constant, i.e. the pitch is infinite.

In contrast to achiral systems, symmetry allows in chiral S_C^* systems for two types of bilinear coupling between the molecular tilt and the molecular polarization; namely

$$P_x\xi_2 - P_y\xi_1 \tag{2a}$$

and

$$P_x\frac{\partial\xi_1}{\partial z} - P_y\frac{\partial\xi_2}{\partial z}\,. \tag{2b}$$

Both of these couplings result in a proportionality between the tilt, θ, and the in-plane polarization, P, so that

$$P/\theta = \text{const} \neq f(T). \tag{3}$$

Early measurements seemed to support this proportionality [4] and led to a Landau type theory of ferroelectric liquid crystals based on a free energy density of the form [5, 6]

$$g(z) = \tfrac{1}{2}a\theta^2 + \tfrac{1}{4}b\theta^4 - \Lambda\theta^2 q + \tfrac{1}{2}K_{33}\theta^2 q^2 + \frac{1}{2\varepsilon} - P^2 - \mu P\theta q + CP\theta,$$

where we have used

$$\xi_1 = \theta\cos\phi, \qquad \xi_2 = \theta\sin\phi, \tag{5a}$$

$$P_x = -P\sin\phi, \quad P_y = P\cos\phi, \tag{5b}$$

$$\phi = \mathbf{q}\cdot\mathbf{z}. \tag{5c}$$

Here $\mathbf{q}$ is the wavevector of the S_C^* helix, $a = \alpha(T - T_0)$, Λ is the coefficient of the Lifshitz-invariant term, whereas μ and C are the coefficients of the two bilinear coupling terms between the tilt and the polarization. The Lifshitz term, $\Lambda\theta^2 q$ and the flexoelectric term $\mu P\theta q$, which are both of chiral origin, are responsible for the modulated structure and the finite pitch.

While the free energy density equation (4) describes some basic features of ferroelectric liquid crystals, it also leads to some serious disagreements with recent experimental data [7]; for example

(*a*) The pitch of the helix is generally temperature dependent and not temperature independent, as predicted by expression (4).

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(*b*) The ratio between the polarization and the tilt θ is temperature dependent

$$P/\theta = f(T) \tag{6}$$

and not constant.

(*c*) The spontaneous polarization shows [8] an *S*-shaped temperature dependence, in contrast to the classical square root type behaviour.

To correct for these discrepancies, a generalized Landau model has been developed [8, 9] where a biquadratic non-chiral coupling term

$$\Delta g = -\Omega P^2\theta^2 \tag{7 a}$$

is added to expression (4). Far below the S_A–S_C^* transition temperature, this term, which induces a quadrupolar ordering of the transverse molecular axes, is large compared to the chiral bilinear coupling terms

$$-CP\theta \tag{7 b}$$

and

$$-\mu P\theta q, \tag{7 c}$$

which induce a polar ordering of the transverse axes. Thus a cross-over takes place from the regime close to T_c (where because of the smallness of θ only the bilinear term is important) to the regime far below T_c where θ is large and the biquadratic term dominates. The main open problem is the question why is the non-chiral biquadratic term $\Omega P^2\theta^2$ large as compared to the chiral bilinear one, $CP\theta + \mu P\theta q$. If the $P^2\theta^2$ term would be just the square of the $P\theta$ term this could obviously never be the case.

We have recently proposed [10] that the origin of this effect is the biaxiality of the tilted smectic phases which is present both in the non-chiral S_C phase as well as in the chiral S_C^* phase. It leads to a quadrupolar ordering of the transverse molecular axes, i.e. to a bipolar biasing of the rotation around the long molecular axis:

$$\bar{\eta}_{bp} \propto (3/2)\sin^2\theta\,\langle\cos 2\varphi\rangle \tag{8 a}$$

which is non-zero even in non-chiral tilted S_C phases. Here θ is the molecular tilt angle whereas $\varphi(t)$ designates the orientation of the short molecular axis as the molecule rotates around its long axis. $\langle\cos 2\varphi\rangle$ obviously measures the degree of bipolar (i.e. quadrupolar) ordering which is proportional to the square of the tilt. For small tilt angles this leads to a biquadratic coupling between the square of the tilt and the anti-polarization, i.e. to a term

$$-\theta^2P^2. \tag{8 b}$$

Expression (8 *b*) has the form of expression (7 *a*). The brackets $\langle\ \rangle$ in (8 *a*) designates the time average.

In chiral systems we have an additional contribution, i.e. the polar biasing of the rotation around the long axis

$$\tilde{\eta}_p \propto \sin 2\theta\,\langle\cos\varphi\rangle \tag{8 c}$$

which represents just the bilinar coupling

$$-\theta P \tag{8 d}$$

between the tilt and the polarization. The microscopic origin of the bilinear coupling between the tilt and the polarization, $P\theta$, is thus the η_p and the $\langle\cos\varphi\rangle$ term, whereas

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the microscopic origin of the biquadratic, $P^2\theta^2$, coupling is assumed to be η_{bp} and the $\langle\cos 2\varphi\rangle$ term. N.M.R. and N.Q.R. allow for a determination of the magnitude of these two terms on a microscopic level.

3. Experimental

The ^{14}N nuclear quadrupole resonance (N.Q.R.) spectra of mixtures of achiral terephthalylidene-bis-(4-*n*-butylaniline) (TBBA) and chiral TBACA were measured with the help of high resolution proton–nitrogen nuclear double resonance in the laboratory frame [11] involving magnetic field cycling. The spectra of pure TBBA and pure TBACA [11] were also remeasured to increase the experimental resolution so as to allow for a definite determination of the order parameters.

The proton decoupled ^{13}C N.M.R. spectra of MORA-8, DOBAMBC and HOBACPC were measured with the Pines–Gibby–Waugh proton enhanced nuclear induction [12] technique at 6·3 T. Racemic DOBAMBC was studied as well.

The detailed analysis of the experimental data will be presented elsewhere. Here we wish to concentrate on the order parameter determination and particularly on the question of polar versus quadrupolar ordering in the S_C phase.

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4. ^{14}N nuclear quadrupole resonance in achiral and chiral tilted smectic phases

The two questions we wish to answer by ^{14}N nuclear quadrupole resonance in smectic phases are:

(i) Is there an ordering of the transverse molecular axes in the S_C and other tilted smectic phases?

(ii) What is the nature of this ordering of the short molecular axes, if it exists at all? How large is the bipolar and how large the polar ordering?

The possible biasing of the rotation of the outboard transverse molecular dipoles (i.e. the C–N=CH–C groups) around the long molecular axis in achiral TBBA and chiral TBACA has been studied by [11] via a determination of the asymmetry parameter

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}. \tag{9}$$

of the electric field gradient (EFG) tensor at the ^{14}N sites. Four free rotation around the long molecular axis the largest principal component, V_{ZZ}, will point along the long molecular axis and the EFG tensor will be axially symmetric;

$$V_{XX} = V_{YY}, \quad \eta = 0. \tag{10}$$

Here $|V_{ZZ}| \geqslant |V_{YY}| \geqslant |V_{XX}|$ represent the principal components of the EFG tensor. Any anisotropy or biasing of the rotation will destroy the axial symmetry so that $\eta \neq 0$. This leads to the appearance of three ^{14}N N.Q.R. lines

$$\nu_{1,2} = (3/4)(eQV_{zz}/h)(1 \pm \eta/3), \tag{11 a}$$

$$\nu_3 = \nu_2 - \nu_1 \tag{11 b}$$

instead of a single line, $\nu_1 - \nu_2$, $\nu_3 = 0$. The biasing of the rotation can therefore be expressed in frequency units.

If the five independent EFG tensor components in the molecular frame x_0, y_0, z_0 are known we can calculate all the components of the time averaged EFG tensor for

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a given model of molecular motion and compare the resulting values for the effective quadrupole coupling constant and asymmetry parameter with the experiment. From that the order parameters can be determined. Transforming from the molecular frame x_0, y_0, z_0 into a frame $x \perp y \perp z \parallel z_0$, where $z \parallel z_0$ is the axis of rotation. $\varphi = \varphi(t)$ is the angle between x and x_0 and x points along the direction of polar or bipolar ordering, we find the instantaneous ^{14}N EFG tensor as:

$$V_{xx} = -\tfrac{1}{2}V_{z_0z_0} + \tfrac{1}{2}(V_{x_0x_0} - V_{y_0y_0})\cos 2\varphi - V_{x_0y_0}\sin 2\varphi, \tag{12a}$$

$$V_{xy} = \tfrac{1}{2}(V_{x_0x_0} - V_{y_0y_0})\sin 2\varphi + V_{x_0y_0}\cos 2\varphi, \tag{12b}$$

$$V_{xz} = V_{x_0z_0}\cos\varphi - V_{y_0z_0}\sin\varphi, \tag{12c}$$

$$V_{yy} = -\tfrac{1}{2}V_{z_0z_0} - \tfrac{1}{2}(V_{x_0x_0} - V_{y_0y_0})\cos 2\varphi + V_{x_0y_0}\sin 2\varphi, \tag{12d}$$

$$V_{yz} = V_{x_0z_0}\sin\varphi + V_{y_0z_0}\cos\varphi, \tag{12e}$$

$$V_{zz} = V_{z_0z_0}. \tag{12f}$$

Since the correlation frequency of the rotational motion is much larger than the ^{14}N N.Q.R. frequencies, the nucleus experiences only the time averaged EFG tensor which is obtained by averaging $\cos\varphi$, $\sin\varphi$, $\cos 2\varphi$ and $\sin 2\varphi$ in expressions (12*a–f*). The mean values of $\langle\cos 2\varphi\rangle$, $\langle\cos\varphi\rangle$, etc., play the role of order parameters which are characteristic for a given type of orientational ordering. For free rotation the time averaged EFG tensor is of course axially symmetric as $\langle V_{zz}\rangle = V_{z_0z_0}$, $\langle V_{xx}\rangle = \langle V_{yy}\rangle$ and all the off-diagonal tensor elements vanish, $\langle V_{ij}\rangle = 0$ for $i \neq j$. The rigid lattice ^{14}N EFG tensor V_{ij} of the C–N=CH–C group in TBBA expressed in the x_0, y_0, z_0 molecular frame [10] is

$$V_{ij}/\mathrm{MHz} = \begin{array}{|ccc|} \multicolumn{1}{c}{x_0} & y_0 & \multicolumn{1}{c}{z_0} \\ -3{\cdot}15 & \pm 0{\cdot}15 & \pm 2{\cdot}41 \\ \pm 0{\cdot}15 & 1{\cdot}95 & \pm 0{\cdot}40 \\ \pm 2{\cdot}41 & \pm 0{\cdot}40 & +1{\cdot}20 \end{array}\,. \tag{13}$$

Here z_0 is the long molecular axis, y_0 is normal to the C–N=CH–C plane and x_0 is perpendicular to z_0 and y_0.

The ^{14}N data [11] in the low temperature part of the smectic VI phase of TBBA are compatible with 180° orientational jumps around the long molecular axis. For this motion $\langle\cos\varphi\rangle = \langle\sin\varphi\rangle = \langle\sin 2\varphi\rangle = 0$ and $\langle\cos 2\varphi\rangle = 1$. Thus all off-diagonal elements of $\langle V_{ij}\rangle$ vanish except $\langle V_{xy}\rangle = V_{x_0y_0}$, $\langle\cos 2\varphi\rangle$ changes from 1 at 70°C to about 0·85 at 82·5°C. The rigid body of the TBBA molecules is now reorienting in a six-fold potential well around the long molecular axis. Two equilibrium sites separated by 180° have a lower energy and an occupation probability p_1 whereas the four orientations with a higher energy have an occupation p_2. The bipolar order parameter is here given by

$$\langle\cos 2\varphi\rangle = 2(p_1 - p_2) \tag{14a}$$

and

$$2p_1 + 4p_2 = 1. \tag{14b}$$

At the low temperature end of the S_H phase of TBBA $\langle\cos 2\varphi\rangle = 0{\cdot}15$ so that $p_2 = 0{\cdot}14$ and $p_1 = 0{\cdot}22$. With increasing temperature $\langle\cos 2\varphi\rangle$ decreases and reaches about 0·09 at the high temperature end.

For bipolar ordering $\langle\cos 2\varphi\rangle \neq 0$, $\langle\cos\varphi\rangle = \langle\sin\varphi\rangle = \langle\sin 2\varphi\rangle = 0$ the effective ^{14}N quadrupole coupling e^2qQ and asymmetry parameter η are obtained as

$$e^2qQ = V_{z_0z_0}eQ, \tag{15a}$$

$$\eta = \frac{2}{V_{z_0z_0}}[V_{x_0y_0}^2 + \tfrac{1}{4}(V_{x_0x_0} - V_{y_0y_0})^2]^{1/2}\langle\cos 2\varphi\rangle. \tag{15b}$$

The temperature dependence of the ^{14}N asymmetry parameter η therefore measures directly the degree of bipolar orientational ordering. The quadrupole coupling constant, on the other hand, is *not* effected by the degree of bipolar ordering and so should be temperature independent, in fair agreement with the experimental data in the S_H of TBBA [11].

For pure polar ordering $\langle\cos\varphi\rangle \neq 0$, $\langle\cos 2\varphi\rangle = \langle\sin\varphi\rangle = \langle\sin 2\varphi\rangle = 0$ the situation is radically different. Here

$$e^2qQ = eQV_{z_0z_0}(1 + \eta) \tag{16a}$$

and

$$\eta = \frac{2}{3}\frac{V_{x_0z_0}^2 + V_{y_0z_0}^2}{V_{z_0z_0}^2}\langle\cos\varphi\rangle^2, \tag{16b}$$

so that both e^2qQ and η are temperature dependent and the temperature variation of η reflects the changes of the *square* of the polar order parameter $\langle\cos\varphi\rangle$.

In the S_H phase of chiral TBACA both e^2qQ and η vary with temperature in a way compatible with this model. Here $\langle\cos\varphi\rangle$ varies from $\langle\cos\varphi\rangle = 0{\cdot}006$ at 147°C to $\langle\cos\varphi\rangle = 0{\cdot}107$ at 132°C. A physical model describing this situation could be given by a rotatable dipole with six equilibrium orientations interacting with a local field. The occupation probabilities p_i of the six dipolar orientations are now given by

$$p_i = C_i \exp[\mu_i E_i \cos\varphi_i/kT]; \quad i = 1\text{–}6, \tag{17}$$

where μ_i is the electric dipole moment and E_i the local electric field.

In contrast to the S_H phase, where there is a large difference between chiral TBACA and non-chiral TBBA, the ^{14}N N.Q.R. spectra are not basically different for TBBA and TBACA in the S_C phases [11]. The same is true for mixtures of achiral TBBA and chiral TBACA. It should be stressed that here the degree of polar or bipolar biasing of the rotation around the long molecular axis is much smaller than in the S_H phase.

The temperature variation of $\eta(\equiv(V_{XX} - V_{YY})/V_{ZZ})$ is determined mainly by anisotropic fluctuations of the long molecular axis which are a consequence of the molecular tilt and essentially the same in chiral and achiral S_C phases. To take into account anisotropic fluctuations of the long molecular axis, we make another transformation of the EFG tensor from the x, y, z frame (cf. equations (12*a*–*f*) to a frame $\xi, \hat{\eta}, \zeta$, where ζ is normal to the smectic planes, ξ is the direction of the projection of the long molecular axis on the smectic plane and $\hat{\eta}$ is perpendicular to ξ and ζ. Designating by $\tilde{\theta}$ $(\equiv \theta + \delta\theta(t))$ the instantaneous value of the tilt angle between angle between the long molecular axis and the normal to the smectic planes, i.e. the ζ axis, and with ϕ $(\equiv \phi(t))$ the angle between the projections of the instantaneous and

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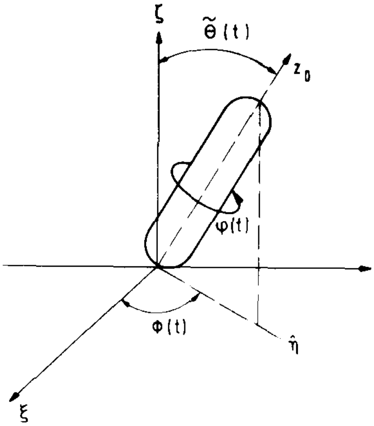

Figure 1. Relation between the molecular frame x_0, y_0, z_0 and the time independent ξ, $\hat{\eta}$, ζ frame, where ζ is normal to the smectic plane. $\tilde{\theta}(t)$ and $\phi(t)$ designate the instantaneous direction of the long molecular axis, $\varphi(t)$ denotes the orientation of the short molecular axes during the molecular rotation around its long axis.

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average directions of the long molecular axis on the smectic plane (see figure 1), we find the time averaged value of the ^{14}N EFG tensor in the S_C phase as

$$\begin{aligned} \langle V_{\xi\xi}\rangle &= \langle (V_{zz} - V_{xx})\sin^2\tilde{\theta}\cos^2\phi\rangle + \langle V_{xx}\cos^2\phi\rangle + \langle V_{yy}\sin^2\phi\rangle \\ &\quad + \langle V_{xz}\sin 2\phi\cos^2\phi\rangle, && (18\,a) \\ \langle V_{\xi\hat{\eta}}\rangle &= \langle V_{xy}\cos\tilde{\theta}\cos 2\phi\rangle + \langle V_{yz}\sin\tilde{\theta}\cos 2\phi\rangle, && (18\,b) \\ \langle V_{\xi\zeta}\rangle &= \langle (V_{zz} - V_{xx})\sin\tilde{\theta}\cos\tilde{\theta}\cos\phi\rangle + V_{xz}\cos 2\tilde{\theta}\cos\phi\rangle, && (18\,c) \\ \langle V_{\hat{\eta}\hat{\eta}}\rangle &= \langle (V_{zz} - V_{xx})\sin^2\tilde{\theta}\sin^2\phi\rangle + \langle V_{xx}\sin^2\phi\rangle + \langle V_{yy}\cos^2\phi\rangle \\ &\quad + \langle V_{xz}\sin 2\tilde{\theta}\sin^2\phi\rangle, && (18\,d) \\ \langle V_{\hat{\eta}\zeta}\rangle &= \langle V_{xy}\sin\tilde{\theta}\cos\phi\rangle + \langle V_{yz}\cos\tilde{\theta}\cos\phi\rangle, && (18\,e) \\ \langle V_{zz}\rangle &= \langle (V_{zz} - V_{xx})\sin^2\tilde{\theta}\rangle + \langle V_{zz}\rangle - \langle V_{xz}\sin 2\tilde{\theta}\rangle. && (18\,f) \end{aligned}$$

The anisotropic fluctuations destroy the axial symmetry of the ^{14}N EFG tensor even in the absence of any rotational bias. For $\langle\cos\varphi\rangle = \langle\cos 2\varphi\rangle = \langle\sin\varphi\rangle = \sin 2\varphi\rangle = 0$ the asymmetry parameter η is now different from zero;

$$\eta_a = (3/2)\tilde{\theta}^2\,[\langle\cos\phi\rangle^2 - \langle\cos 2\phi\rangle] - (3/2)\langle\delta\theta^2\rangle\langle\cos 2\phi\rangle. \qquad (19\,a)$$

The term $(3/2)\langle\delta\theta^2\rangle\langle\cos 2\phi\rangle$ is responsible for the maximum in η in the middle of the S_C phase. The maximum is due to the opposite temperature dependences, of $\langle\delta\theta^2\rangle$ and $\langle\cos 2\phi\rangle$. $\langle\delta\theta^2\rangle$ increases whereas $\langle\cos 2\phi\rangle$ decreases with increasing temperature. At low temperatures $\langle\cos 2\phi\rangle \approx 1$ and η increases with increasing temperature due to the increase in $\langle\delta\theta^2\rangle$. At higher temperatures η decreases as $\langle\cos 2\phi\rangle \to 0$ at the $S_C - S_A$ transition. Such behaviour has indeed been observed both in TBBA and in TBACA (figure 2). The same is true for their mixtures.

If, in addition to anisotropic fluctuations, bipolar ordering is present, we have

$$\eta_b \approx \eta_a - \frac{V_{x_0x_0} - V_{y_0y_0}}{V_{z_0z_0}}\langle\cos 2\phi\rangle\langle\cos 2\varphi\rangle. \qquad (19\,b)$$

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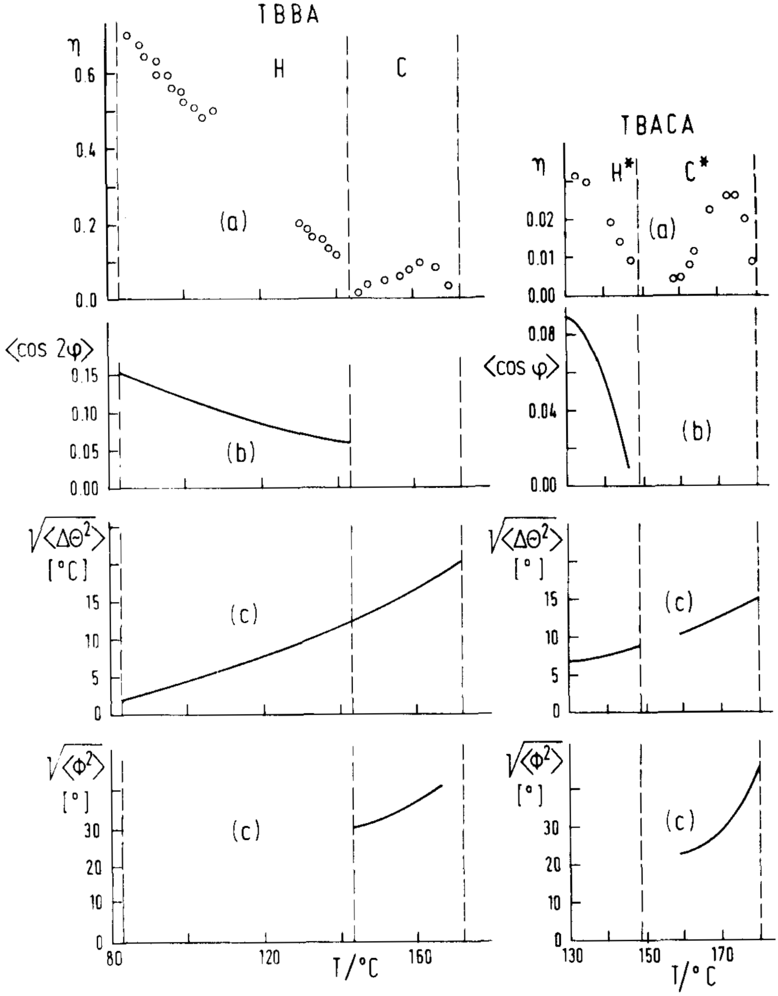

Figure 2. (*a*) Temperature dependence [11] of the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ of the ^{14}N electric field gradient tensor in achiral TBBA and chiral TBACA. (*b*) Temperature dependence of the bipolar order parameter $\langle\cos 2\varphi\rangle$ in TBBA and the polar order parameter $\langle\cos\varphi\rangle$ in TBACA. (*c*) Temperature dependence of the anisotropy in the fluctuations of the long molecular axis in the S_C phases of achiral TBBA and chiral TBACA.

The maximum value of $\langle\cos 2\varphi\rangle$ in the S_C phase of TBBA is only about 5×10^{-3}. This value is found just above the $S_H - S_C$ transition. If on the other hand polar biasing is present, in addition to anisotropic fluctuations as in TBACA, we find

$$\eta_p \approx \eta_a + \frac{V_{x_0z_0}}{V_{z_0z_0}}\,\theta\,\langle\cos\varphi\rangle(1 - \langle\cos 2\phi\rangle). \tag{19c}$$

Here we obtain the maximum value of $\langle\cos\varphi\rangle$ as less than 2×10^{-3}.

In the smectic *A* phase the asymmetry parameter of the ^{14}N EFG tensor vanishes, $\eta = 0$. There is no biasing of rotation around the long molecular axis, $\langle\cos 2\varphi\rangle = \langle\cos\varphi\rangle = \langle\sin\varphi\rangle = \langle\sin 2\varphi\rangle = 0$, and the fluctuations of the long molecular axis are isotropically distributed around the smectic planes, i.e. with respect to the nematic-like director.

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5. ^{13}C N.M.R. and molecular order in the S_C^* phase

A major advantage of ^{13}C N.M.R. [12] over ^{14}N N.Q.R. [11] is the possibility to determine the order parameters at each carbon site in the molecule and not only at one site as for ^{14}N N.Q.R. If the ^{13}C chemical shift tensor in the molecular frame is known for a given site, all the components of the time averaged ^{13}C tensor can be calculated for a given model of molecular motion, and the resulting values of the chemical shift compared with experiment.

In view of the fast random translational and rotational motion we observe, in the isotropic phase, only the isotropic part of the ^{13}C chemical shift tensor $\boldsymbol{\sigma}$

$$\sigma_i = (1/3)\operatorname{Tr}\boldsymbol{\sigma}, \tag{20a}$$

since the anisotropic part is averaged to zero. In the S_A phase the chemical shift tensor is no longer isotropic. The relevant molecular motions, which average the ^{13}C chemical shift tensor are: fast molecular rotations around the long molecular axes, and fluctuations of the long molecular axis around the molecular director **N** which is parallel to **H** and also to the normals to the smectic layers. The component of the chemical shift tensor in the direction of the external magnetic field is

$$\sigma = \sigma_i + (2/3)S(\sigma_{\parallel} - \sigma_{\perp}), \tag{20b}$$

where $\sigma_{\parallel} = \sigma_{z_0 z_0}$ is the chemical shift tensor component along the direction of the long molecular axis ($\parallel z_0$) and $\sigma_{\perp} = (1/2)(\sigma_{x_0 x_0} + \sigma_{y_0 y_0})$ is the average component in the $x_0\, y_0$ plane. Here

$$S = S_{z_0 z_0} = \langle (3/2)\cos^2\beta - 1/2 \rangle, \tag{20c}$$

measures the amount of nematic-like ordering of the long molecular axis with respect to the molecular director **N**. The angle $\beta(t) = \sphericalangle(z_0, z')$ corresponds to $\delta\theta(t)$ in the N.Q.R. §4 and x', y', $z' \parallel \mathbf{N}$ designate the average director frame.

In the non-chiral S_C phase the long molecular axes remain parallel to **H**, whereas the normals to the planes are tilted with respect to **H**. On the other hand, in the chiral S_C^* phase at 6·3 T the helicoidal axis and the normals to the smectic layers are parallel to the direction of the external magnetic field, whereas the director **N**, that is the average direction of the long molecular axes, is tilted by an angle θ with respect to the field direction [12] in all chiral compounds investigated so far. The chemical shift in the S_C^* phase is given by

$$\sigma - \sigma_i = \tfrac{2}{3}S(\sigma_{\parallel} - \sigma_{\perp})(\tfrac{3}{2}\cos^2\theta - 1/2) + \Delta_a + \Delta_p + \Delta_{bp}. \tag{21}$$

The first term on the right hand side of expression (21) takes into account the fact that the long molecular axes are now tilted away from the direction of the external magnetic field whereas Δ_a, Δ_p and Δ_{bp} stand for the contributions due to anisotropic fluctuations, polar, and bipolar biasing respectively. The contribution due to the anisotropy in the fluctuations with respect to the molecular director **N** is given by

$$\Delta_a = (1/2)(\sigma_{\parallel} - \sigma_{\perp})\sin^2\theta\,\langle \sin^2\beta\cos 2\phi \rangle. \tag{22a}$$

Here $\langle \sin^2\beta\cos 2\phi \rangle = \tilde{\eta}_a = S_{xx} - S_{yy}$ is a measure of the biaxiality of the S_C phase. The contribution due to the polar biasing is obtained as:

$$\Delta_p = 2\sigma_{x_0 z_0}\sin(2\theta)\langle \cos\varphi \rangle \tag{22b}$$

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and is proportional to $\tilde{\eta}_p$ (cf. equation 8 *c*), whereas the contribution due to bipolar biasing is

$$\Delta_{bp} = (\sigma_{x_0x_0} - \sigma_{y_0y_0})\sin^2\theta\,\langle\cos 2\varphi\rangle \qquad (22\,c)$$

and is proportional to $\tilde{\eta}_{bp}$ (cf. equation 8*a*).

In the absence of anisotropic fluctuations and polar or bipolar biasing, i.e. where $\Delta = \Delta_a + \Delta_p + \Delta_{bp} = 0$, the temperature dependence of $(\sigma - \sigma_i)/((3/2)\cos^2\theta - 1/2)$ would be proportional to S which is known to increase monotonically with decreasing temperature. This is indeed true for most aliphatic carbons, e.g. C(18) in DOBAMBC and HOBACPC. It can even be used to determine the temperature dependence of the tilt angle, θ, along the molecule. There are however deviations [12] from this relation for aromatic carbons and carbons in the neighbourhood of the chiral group. For DOBAMBC [12] at $T = T_{S_C^*S_A} - 20\,\mathrm{K}$, $\Delta = 10$ p.p.m. for the carbonyl carbon (i.e. the C=O group), 3 p.p.m. for the aromatic carbons at the ortho- and $\Delta = 1{\cdot}5$ p.p.m. for the aromatic carbons at the para-sites (see figure 3).

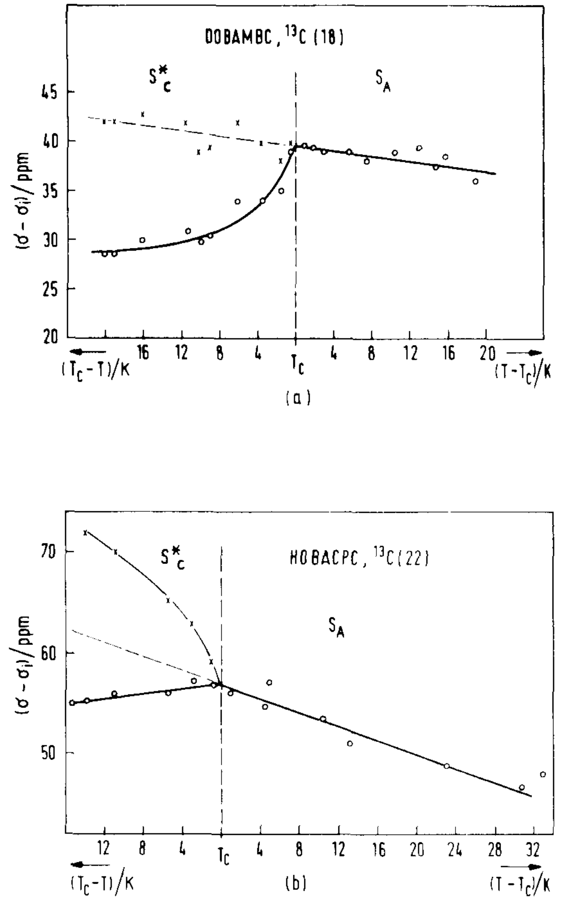

Figure 3. Temperature dependence [12] of the ^{13}C chemical shift $\sigma - \sigma_i$ (circles) near the $S_C^* - S_A$ transition in (*a*) DOBAMBC for the aliphatic carbon C(18) and (*b*) HOBACPC for the carbonyl carbon C(22). The crosses show the calculated temperature dependence of $(\sigma - \sigma_i)/((3/2)\cos^2\theta - 1/2)$ whereas the dotted line shows the temperature dependence of $(2/3)S(\sigma_\parallel - \sigma_\perp)$ obtained by a linear extrapolation of S from the S_A into the S_C^* phase.

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The deviations of the $(\sigma - \sigma_i)/((3/2)\cos^2\theta - 1/2)$ versus temperature plot from a straight line (see figure 3) for aromatic carbons in DOBAMBC and HOBACPC in the S_C^* phase can be explained by Δ_a, i.e. by anisotropic fluctuations of the long molecular axis about **N**. This agrees with ^{14}N N.Q.R. results in TBBA and TBACA for the S_C phase. For aromatic carbons in the ortho-position, $\sigma_{\parallel} - \sigma_{\perp} = 52$ p.p.m. whereas $\sigma_{\parallel} - \sigma_{\perp} = 142$ p.p.m. for aromatic carbons in the para-positions. The observed S values at the aromatic sites [12] are $S \approx 0{\cdot}8$ at the $S_C^* - S_A$ transition, whereas the S value at the C=O bond in DOBAMBC is only about 0·6.

Anisotropic fluctuations are however not capable of explaining the observed value of Δ for the C=O group. Here [12] $\Delta_p = 320\theta \langle\cos\varphi\rangle$ p.p.m. whereas $\Delta_{bp} = 40\theta^2 \langle\cos 2\varphi\rangle$ so that $\Delta_{bp} \ll \Delta_p$ though $\langle\cos\varphi\rangle$ and $\langle\cos 2\varphi\rangle$ would be comparable. At $T = T_{S_C^*S_A} - 20\,\mathrm{K}$ we find $\langle\cos\varphi\rangle = 5 \times 10^{-2}$ whereas we obtain $\langle\cos\varphi\rangle \sim 4 \times 10^{-2}$ from macroscopic measurements of the spontaneous polarization. The agreement between the microscopic and the macroscopic results is therefore rather good.

For aromatic carbons in the ortho-positions $\sigma_{x_0z_0} = 100$ p.p.m. From the measured value of $\Delta \approx 2$ p.p.m. we obtain upper limit for $\langle\cos\varphi\rangle_{\max}$ of 8×10^{-3}. This demonstrates that the rotation of the central part of the DOBAMBC molecule in the S_C^* phase is nearly free, in good agreement with the ^{14}N data. The DOBAMBC molecule is thus far from a rigid body and a proper theory of ferroelectric liquid crystals should take into account the variation of the order along the molecule.

6. Conclusions

The analysis of the ^{14}N N.Q.R. [11] and ^{13}C N.M.R. [12] spectra of ferroelectric liquid crystals and their non-chiral analogues in the tilted smectic phases show that:

(i) The molecular tilt induces in the smectic C and C* phases an anisotropy in the fluctuations of the long molecular axis which is practically the same for chiral and non-chiral molecules. It is responsible for the temperature variation of the ^{14}N asymmetry parameter η in the smectic C and C* phases, i.e. for the apparent quadrupolar ordering of the transverse molecular axes. Polar or bipolar orientatial ordering is here negligible for the central part of the molecule.

(ii) In the low temperature tilted smectic phases like the S_H and the S_{VI} phases with a two dimensional translational ordering of the molecules, non-chiral molecules show a pronounced bipolar, and chiral molecules a pronounced polar orientational ordering. Fluctuations of the long molecular axes are unimportant at least for the central part of the molecules where the ^{14}N nuclei in TBBA or TBACA are located.

(iii) Polar orientational ordering of the transverse outboard molecular dipoles close to the chiral group, like the C=O group in DOBAMBC and HOBACPC, can be clearly observed by ^{13}C N.M.R. The polar orientational biasing of the rotation around the long molecular axis is rather small (see figure 4) thus accounting for the small value of the spontaneous polarization in the S_C^* phase of ferroelectric liquid crystals. The chiral polar ordering coexists with the non-chiral quadrupolar one produced by the biaxiality of the S_C^* phase, i.e. tilt-induced anisotropy in the fluctuations of the long molecular axis.

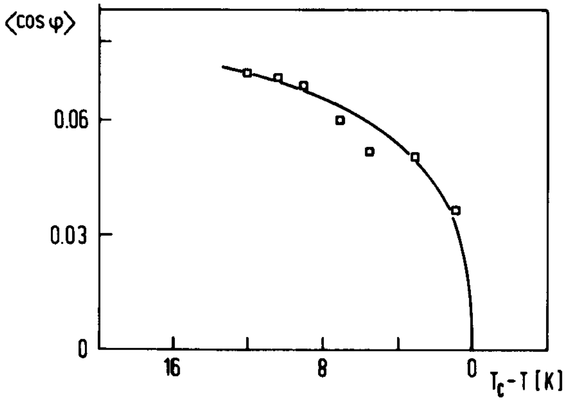

Figure 4. Temperature dependence of the polar order parameter $\langle \cos \varphi \rangle$ of the $C=O$ group in HOBACPC.

(iv) The anomalously large value of the biquadratic coupling between the polarization and the tilt (cf. expression (7 *a*)) is to a large extent the result of the non-chiral quadrupolar ordering induced by the biaxiality of the S_C^* phase and not just a higher power of the chiral bilinear coupling between the polarization and the tilt. To see this we have to express the free energy density in terms of all scalar invariants of θ, $P \propto \langle \cos \varphi \rangle$, $\langle \cos 2\varphi \rangle$ and $\langle \sin^2 \beta \cos 2\phi \rangle$ and, by minimization, eliminate the $\langle \cos 2\varphi \rangle$ and $\langle \sin^2 \beta \cos 2\phi \rangle$ variables. The ^{13}C N.M.R. and ^{14}N N.Q.R. results allow for a microscopic estimate of the relative importance of these terms and thus provide a microscopic basis for the extended Landau model of ferroelectric liquid crystals [8, 9].

(v) It should be stressed that although the extended Landau model [8, 9] is capable of describing nearly all thermodynamic properties of S_C^* ferroelectric liquid crystals, it still has only limited validity as it assumes that the molecule can be described as a rigid body with a unique set of order parameters. N.M.R. data clearly show that the molecule is far from being rigid and that the order parameters differ in different parts of the molecule.

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