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Dispersion of proton spin-lattice relaxation in a cholesteric liquid crystal

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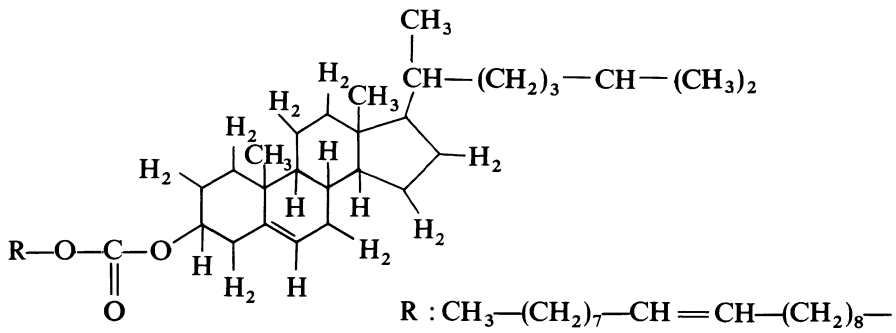
Résumé. — La dépendance en fréquence et en température de T_1 et $T_{1\rho}$ en phase cholestérique et isotrope du COC a été déterminée, de même que la dépendance en température du coefficient d'auto-diffusion D en phase isotrope. Dans le domaine du MHz la relaxation est dominée par l'auto-diffusion moléculaire — avec D de l'ordre de 10^{-12} m^2/s — et par les rotations moléculaires locales avec $\tau_c \approx 2 \times 10^{-10}$ s à $T = 24$ °C. Par contre, dans le domaine du kHz, les fluctuations du directeur contrôlent la relaxation de façon prépondérante. L'influence sur $T_{1\rho}$ de la rotation des molécules due à la diffusion le long de l'hélice, spécifique des structures hélicoïdales, n'a pas été observée dans le COC en raison d'un temps de corrélation rotationnel trop long.

Abstract. — The frequency and temperature dependence of T_1 and $T_{1\rho}$ in the cholesteric and isotropic phases of cholesteryl-oleyl-carbonate (COC) have been determined together with the temperature dependence of the self-diffusion constant D in the isotropic phase. In the MHz region the relaxation is dominated by molecular self-diffusion — with D being of the order 10^{-12} m^2/s — and by local molecular rotations with $\tau_c \approx 2 \times 10^{-10}$ s at $T = 24$ °C. In the kHz region, on the other hand, order director fluctuations predominantly influence the relaxation. The influence upon $T_{1\rho}$ of the rotation of the molecules caused by their diffusion along the helix, an effect occurring only for twisted structures, was not observed in COC in view of too long a rotational correlation time.

Whereas proton spin-lattice relaxation in nematic liquid crystals seems to be well understood by now [1, 2] relatively little is known about the nature of the spin-lattice relaxation processes in the liquid crystals where a helical twist of the molecular director takes place. Helical distortion of the structure has been observed in pure cholesteric liquid crystals, and in ordinary nematic liquid crystals if an optically active and structurally similar compound has been added [3]. The studies of the relaxation rate in twisted nematic liquid crystals performed so far [4, 5] have shown that the relaxation mechanisms remain the same in the twisted as in the pure nematic compound, i.e. order director fluctuations predominantly relax the protons in both cases. This conclusion has been obtained for mixtures where only about 1 percent of the chiral compound has been added to produce the twist. The measurements of T_1 in cholesteryl-esters [6] showed a non-exponential decay of the magnetization in the cholesteric phase, but no analysis of the relaxation mechanisms has been made so far.

In this paper we report the first study of a dispersion of the proton spin-lattice relaxation in a cholesteric mesophase. In order to get a comprehensive view of the relaxation mechanisms involved, the temperature dependences — in addition to the frequency dependences — of the relaxation times in the laboratory (T_1) and in the rotating frame ($T_{1\rho}$) have been determined as well as the diffusion constant. T_1 and $T_{1\rho}$ data have been obtained using the standard 90°-τ-90° pulse sequence and the « spin-locking » method, respectively. The experimental error is estimated to be less than 5 % for T_1 and less than 8 % for $T_{1\rho}$ measurements. The pulsed magnetic field gradient spin-echo method enabled the direct determination of the diffusion constant in the isotropic phase above the cholesteric to isotropic transition. Additionally, proton T_2 has been measured in the isotropic phase by the Carr-Purcell pulse sequence, and in the cholesteric phase from the free induction decay (FID) signal.

The substance under study was cholesteryl-oleyl-carbonate



(COC) which is widely used in mixtures suitable for liquid crystalline temperature controllers. On cooling our sample exhibited a transition from the isotropic to the cholesteric phase at $T = 32.5$ °C. There is also an intermediate narrow « blue » phase which was not investigated in this study. The cholesteric phase then extends down to 17 °C where a transition to the smectic phase takes place.

The cholesteric phase of COC tends to align with the axes of the helices parallel to the magnetic field. However, very strong magnetic fields are required in order to overcome the elastic forces and those related to the textural defects of the mesophase. Luz *et al.* [7] observed for a derivative of cholesterol that it was not completely oriented even on cooling in a magnetic field of 6 T while the degree of orientation was only ~ 25 % on heating the sample. The shape of the proton free induction decay in the cholesteric phase of COC observed in this work was structureless in comparison with the nematic signal, and the same either on cooling or on heating the sample. This suggests that the effect of the external magnetic fields used in our experiments (up to 2 T) was not large enough to orient the axes of the helices uniformly throughout the sample. In spite of this the recovery of the longitudinal magnetization, yielding the relaxation times, was observed to be monoexponential to a good approximation.

The experimental results are presented in figure 1 and 2. The transition from the isotropic to the cholesteric phase is characterized by an abrupt decrease in T_2 from ~ 10 ms in the isotropic phase to only ~ 100 μs in the cholesteric and smectic phase as shown in figure 1. T_1 and $T_{1\rho}$ measured at $\nu_L = 58$ MHz exhibit completely different temperature dependences. T_1 undergoes a minimum in the isotropic phase at $T = 50$ °C to increase steadily in the cholesteric phase on cooling. $T_{1\rho}$, on the other hand, decreases in the isotropic phase on approaching the transition, and falls abruptly to a value of only about 4 ms in the ordered phase. Figure 2 shows that T_1 exhibits definitely a dependence on the Larmor frequency in the MHz region both in the cholesteric phase and in the isotropic phase. The relaxation rate at 12 MHz is a factor of 5 times larger than at 90 MHz. $T_{1\rho}$ in the cholesteric phase smoothly changes with

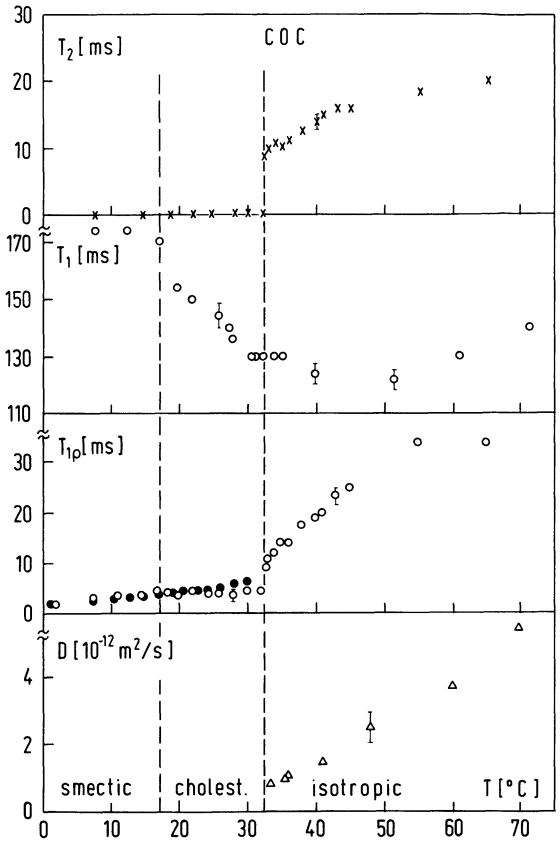


Fig. 1. — Temperature dependences of T_2, T_1, $T_{1\rho}$ and D in COC at $\nu_L = 58$ MHz. Circles represent $T_{1\rho}$ data at $H_1 = 3.7$ G and full dots at $H_1 = 10.4$ G.

the magnitude of the rotating magnetic field H_1 for $H_1 > 3$ G.

In order to understand the relaxation mechanism in the cholesteric phase of COC one has to take into account (in analogy with nematic liquid crystals) [1, 2, 8] at least two different relaxation mechanisms which may be responsible for the peculiar T_1 dispersion in the cholesteric phase : order director fluctuations caused by elastic deformations of the liquid crystal or the modulation of the intermolecular dipolar interactions due to slow molecular self-diffusion.

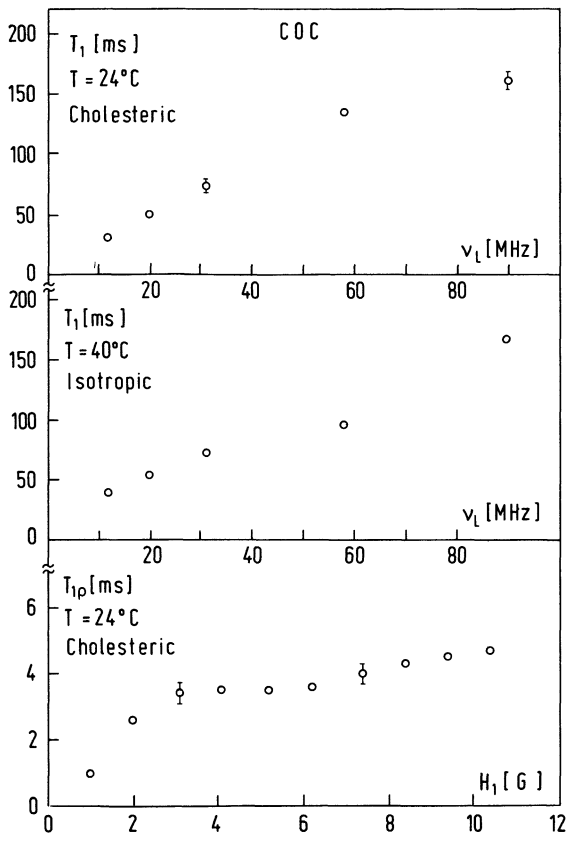


Fig. 2. — Frequency dependences of T_1 in the cholesteric (T = 24 °C) and isotropic (T = 40 °C) phase of COC, and of $T_{1\rho}$ in the cholesteric phase (T = 24 °C).

For a nuclear probe consisting of two protons with a fixed separation distance r, the dipole-dipole interactions of which are modulated by fluctuations in the orientation of the internuclear vector **r** with respect to the external magnetic field **H** due to nematic order director fluctuations, the spin-lattice relaxation rate is [8]

$$(T_1^{-1})_{\mathrm{ODF}} = \frac{C}{\sqrt{\omega}}\left[f_1(\Delta)\, g(u) + \frac{1}{\sqrt{2}} f_2(\Delta)\, g(\sqrt{2}\, u)\right], \tag{1a}$$

and in the rotating frame

$$(T_{1\rho}^{-1})_{\mathrm{ODF}} = C\left[\frac{1}{4} f_0(\Delta) \frac{1}{\sqrt{2\,\omega_1}} g(\sqrt{2}\, u_1) + \frac{5}{2} f_1(\Delta) \frac{1}{\sqrt{\omega}} g(u) + \frac{1}{4} f_2(\Delta) \frac{1}{\sqrt{2\,\omega}} g(\sqrt{2}\, u)\right] \tag{1b}$$

where C is a constant independent of the Larmor frequency ω and of ω_1 ; $f_0(\Delta)$, $f_1(\Delta)$ and $f_2(\Delta)$ are functions of the angle Δ between the molecular director and magnetic field,

$$g(u) = \pi - \frac{1}{2} \ln \frac{u^2 + \sqrt{2}\, u + 1}{u^2 - \sqrt{2}\, u + 1} - \mathrm{arctg}\,(\sqrt{2}\, u + 1) - \mathrm{arctg}\,(\sqrt{2}\, u - 1), \tag{1c}$$

and

$$u_1 = (\omega_1/\omega_c)^{1/2}, \qquad u = (\omega/\omega_c)^{1/2} \tag{1d}$$

with the cut-off frequency ω_c being given by

$$\omega_c = K q_c^2/\eta, \tag{1e}$$

where $q_c \simeq \frac{\pi}{l}$ and l is a distance of the order of the molecular length, K elastic constant and η the viscosity. For $\omega \ll \omega_c$, $g(u)$ is constant and $(T_1^{-1})_{\mathrm{ODF}}$ proportional to $\omega^{-1/2}$.

In cholesteric liquid crystals the elastic deformations which have wavelengths larger than the pitch of the helix ($p \approx 3\,000$ Å) and which can be observed by light scattering, include the effects of the twisted structure [9]. On the other hand, the orientational fluctuations with wavelength smaller than the pitch which contribute the most to the spin-lattice relaxation rate in the MHz region, can be to a good approximation described as nematic fluctuations, and their contribution to the relaxation rate, $(T_1^{-1})_{\mathrm{ODF}}$, is given by equations 1.

The relaxation rate due to spin-relaxation caused by the modulation of the intermolecular dipolar interactions by self-diffusion $(T_1^{-1})_{\mathrm{SD}}$, has been derived by Torrey [10] for viscous isotropic liquids. It has been later shown by Žumer and Vilfan [11] that Torrey's expression can be used for anisotropic, nematic liquid crystals as well, if a diminution factor of 1.4 is taken into account. We believe that in view of the range of dipolar interactions, which extend to the near neighbours, the same expression can be used for the cholesteric phase as well :

$$(T_1^{-1})_{\mathrm{SD}} = \frac{3}{5} \frac{\gamma^4 \hbar^2 \pi n}{a^3\, \omega} [f(\alpha, x) + 2 f(\alpha, \sqrt{2}\, x)]. \tag{2a}$$

Here n is the number of spins per unit volume, a is the distance of closest approach of two spins on neighbouring molecules,

$$\alpha = \frac{\langle r^2 \rangle}{12\, a^2} \tag{2b}$$

with $\langle r^2 \rangle$ being the mean square flight distance for the diffusion process,

$$x = \left(\frac{\omega a^2}{D}\right)^{1/2} \tag{2c}$$

where D is the self-diffusion constant, and $f(\alpha, x)$ an analytical function given in reference 10.

The experimental results for COC at $T = 24\ ^{o}C$ (Fig. 2) are compared with the predicted frequency dependence of T_1^{-1} for the order director fluctuation mechanism (Eqs. 1) and for the self-diffusion intermolecular mechanism (Eqs. 2).

As can be seen from figure 3 the measured relaxation rate T_1^{-1} in the MHz region can be explained by a superposition of two contributions : $(T_1^{-1})_{SD}$ caused by molecular self-diffusion, which is responsible for the dispersion of T_1^{-1}, and a nearly frequency independent term in the range investigated, called $(T_1^{-1})_R$. This last term can be most probably ascribed to fast local molecular rotations. Using Torrey's equations 2 divided by the factor 1.4, with $n = 0.09\ \text{Å}^{-3}$ (calculated from the density $\rho = 1.3 \times 10^3\ \text{kg/m}^3$) and $\langle r^2 \rangle / a^2 \approx 1$, one can fit the adjustable parameters to the experimental data with

$$a = 3.1\ \text{Å}, \qquad D = 2.2 \times 10^{-12}\ \text{m}^2/\text{s},$$
$$(T_1^{-1})_R = 5\ \text{s}^{-1}.$$

It should be mentioned that a good fit can be also obtained by taking a larger value for the diffusion constant ($D \approx 5 \times 10^{-12}\ \text{m}^2/\text{s}$) if the root mean square jump length is increased by a factor of 2, and approximately equals the diameter of the molecule. The fitted value of D obtained from the T_1^{-1} data in the cholesteric phase of COC is unexpectedly low (of the order $10^{-12}\ \text{m}^2/\text{s}$) being 100 times smaller than D in nematic PAA [12]. However, this low value is supported by direct NMR measurements of D in the isotropic phase by means of the pulsed gradient spin-echo method. This method (which unfortunately could not be applied to the cholesteric phase) yielded in the isotropic phase of COC a diffusion constant ranging from $9.5 \times 10^{-12}\ \text{m}^2/\text{s}$ at $T = 80\ ^{o}\text{C}$ to $0.8 \times 10^{-12}\ \text{m}^2/\text{s}$ just above the transition into the cholesteric phase at $T = 35\ ^{o}\text{C}$ (Fig. 1). The activation energy determined is $\simeq 49$ kJ/mole. Taking into account that at the transition into the liquid crystalline phase the ordering of the molecules usually makes the diffusion anisotropic but does not affect its average magnitude [12], the agreement between the measured D in the isotropic phase and that extracted from T_1 in the cholesteric phase seems to be reasonable.

The contribution $(T_1^{-1})_R$, which is frequency independent up to $\nu_L = 90$ MHz and equals $5\ \text{s}^{-1}$, can be ascribed to the fast ($\omega\tau_c \ll 1$) local reorientations of the molecule as a whole or to the motion of separate molecular segments. The lack of the change in T_1 at the transition from the isotropic to the cholesteric phase measured at $\nu_L = 58$ MHz (Fig. 1), where $(T_1^{-1})_R$ contributes about 60 % to the total relaxation rate, indicates that this motion is not affected very much by the onset of molecular ordering. A rough estimate of its correlation time τ_c can be obtained by using the well known formula [13] :

$$(T_1^{-1})_R = \frac{3}{2}\gamma^4 \hbar^2 r^{-6} \tau_c, \qquad (3)$$

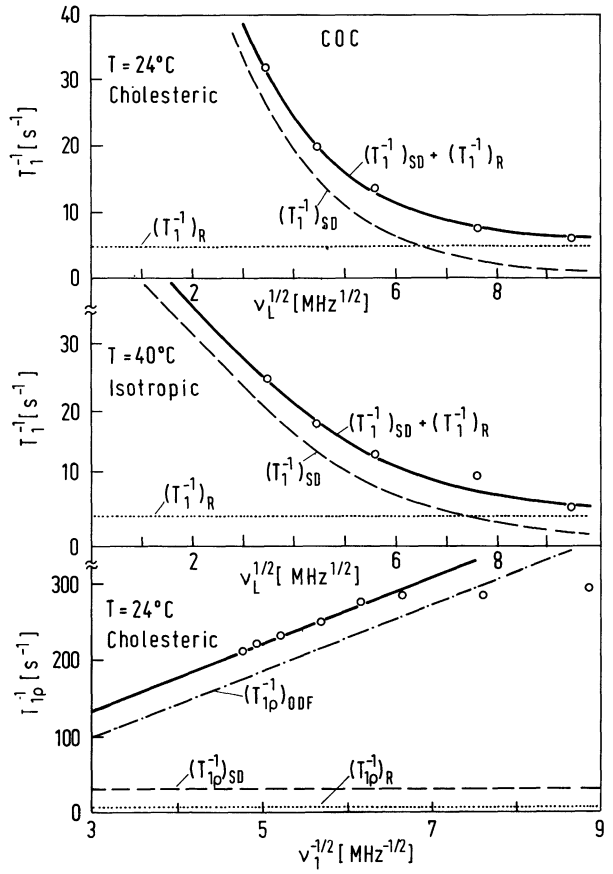


Fig. 3. — Contributions of various relaxation mechanisms to T_1^{-1} and $T_{1\rho}^{-1}$ in COC. T_1^{-1} is explained by a superposition of a molecular self-diffusion relaxation mechanism, $(T_1^{-1})_{SD}$, and local molecular reorientations, $(T_1^{-1})_R$, whereas $T_{1\rho}^{-1}$ is governed predominantly by order director fluctuations.

which gives the relaxation rate due to isotropic rotation of spin pairs in the fast motion limit with r standing for the intramolecular interproton distance. Taking $r = 1.78$ Å which is the interproton distance in CH_2 and CH_3 groups (they include about two thirds of all protons in the COC molecule) the value obtained for the correlation time is $\tau_c = 1.9 \times 10^{-10}$ s at $T = 24\ ^{o}C$.

It should be mentioned that the frequency dependence of the experimental T_1^{-1} data (taken by itself) could be also explained by the order director fluctuations relaxation (Eqs. 1) with a « cut-off » frequency $\nu_c = 40$ MHz. This explanation is, however, inconsistent with the temperature dependence of T_1 at $\nu_L = 58$ MHz (Fig. 1) for the following reasons :

i) Order director fluctuations undergo a drastic change at the transition from the isotropic into the cholesteric phase, which should be reflected as a discontinuity in the relaxation rate [2]. This is not what is observed.

(ii) The relaxation induced by order director fluctuations in the ordered phase is usually characterized

by a T_1 which slightly decreases with decreasing temperature [2]. This is exactly opposite to the temperature dependence of the T_1 observed in COC which increases with decreasing temperature in the cholesteric phase. On the other hand, this increase is exactly what is expected if the self-diffusion and local molecular reorientations are the main relaxation mechanisms. $(T_1)_{SD}$ namely increases with decreasing temperature if the average time between jumps τ_D is slow enough to give $\omega\tau_D > 1$. In COC the evaluated values $D = 2.2 \times 10^{-12}$ m^2/s and $\langle r^2 \rangle \approx a^2 = 3.1^2$ Å^2 yield according to the relation

$$\tau_D = \langle r^2 \rangle/(6\,D)$$

approximately $\tau_D = 7.3 \times 10^{-9}$ s at 24 °C and $\omega\tau_D = 2.6$. Though at 58 MHz the contribution of $(T_1^{-1})_{SD}$ to the total relaxation rate is only about 40 %, it can dominate the temperature dependence as the activation energy of the diffusion process, 49 kJ/mole, is supposed to be considerably greater than the activation energy for local molecular reorientations.

iii) The dispersion of T_1^{-1} in the isotropic phase at $T = 40$ °C implies essentially the same relaxation mechanisms as in the cholesteric phase (Fig. 3) but yields for $\langle r^2 \rangle/a^2 \approx 1$ the diffusion constant $D = 5.5 \times 10^{-12}$ m^2/s, $a = 3.5$ Å, and $(T_1^{-1})_R = 4.4\ s^{-1}$. The corresponding τ_D is 3.7×10^{-9} s at $T = 40$ °C. $(T_1)_{SD}$ should exhibit a minimum with respect to the temperature at $\omega\tau_D \simeq 0.8$. By taking into account the values of τ_D at $T = 24$ °C and at $T = 40$ °C, and the activation energy $E_a = 49$ kJ/mole, the expected T_1 minimum should occur close to 50 °C. A minimum, though shallow, is observed exactly at this temperature.

We conclude that the proton spin-lattice relaxation in the MHz region of the cholesteric COC is governed by molecular self-diffusion modulating intermolecular proton interactions and by fast local molecular rotations.

An insight into the kHz region, on the other hand, is accessible by studying the relaxation rate in the rotating frame. The $T_{1\rho}$ data for COC (Figs. 1, 2 and 3, lower parts) exhibit a completely different frequency and temperature behaviour from T_1. There is indeed a factor about 30 between T_1 and $T_{1\rho}$ at $\nu_L = 58$ MHz in the cholesteric phase of COC, whereas in the nematic phase of PAP [14], for example, $T_{1\rho}$ is only 4 times smaller than T_1. This difference certainly indicates the onset of an additional relaxation mechanism in COC at low frequencies not present in the MHz region.

The investigation of $T_{1\rho}$ in the cholesteric is particularly interesting because a relaxation mechanism which is specific for the twisted structure and which can be detected only at low frequencies, was proposed independently by Žumer, Vilfan and Blinc [15] and by Andreev [16] a few months ago. Diffusion along the helix in twisted structure modulates not only the inter-molecular dipolar interactions (as in nematic systems) but also the intra-molecular dipolar coupling as the molecule slowly rotates when moving in the direction of the helix. The relaxation rate $(T_1^{-1})_{DR}$ due to this process (« diffusion induced rotation », DR) has been calculated [15] to be

$$(T_1^{-1})_{DR} = \frac{9}{8}\frac{\gamma^4\hbar^2}{r^6}\frac{2\,\tau_{DR}}{1 + 4\,\omega^2\,\tau_{DR}^2} \tag{4}$$

for the oriented sample with all axes of the helices parallel to the magnetic field, and with the molecules lying in the planes perpendicular to the helix axis. All interactions between proton pairs (with proton separation distance r) on one molecule have been here assumed to lie in the direction of the long molecular axis due to fast molecular rotation around it. It should be noted that equation 4 predicts a non-zero relaxation rate due to « diffusion induced rotation » for the case when all the helix axes are parallel to the external magnetic field **H** as not only the change of the polar angle between interproton vector **r** and **H** but also the change of azimuthal angle ϕ, determining the position of **r** by its rotation around **H**, yields $J_2(\omega)$ different from zero [17, 18]. In evaluating equation 4 perfect local orientational order of molecules has been assumed. In a more realistic model with $S \neq 1$, $(T_1^{-1})_{DR}$ would be diminished but the predicted frequency behaviour would not be changed. τ_{DR} in equation 4 is the characteristic decay time of the autocorrelation function for diffusion induced rotation and represents in fact the time required for one molecule to change its orientation by about $1/\sqrt{2}$ radian. It is given by

$$\tau_{DR} = \frac{p^2}{16\,\pi^2\,D_h} \tag{5}$$

where p denotes the length of the pitch and D_h the component of diffusion along the helix axis. It should be stressed that τ_{DR} is much longer than the time τ_D required for the molecule to make a single jump to the nearest neighbouring site. Therefore diffusion induced rotation is expected to influence in particular $T_{1\rho}$, i.e. relaxation at considerably lower frequencies than the intermolecular diffusion relaxation mechanism.

If the angle between the axis of the helix and magnetic field assumes a value Δ' different from zero $(T_1^{-1})_{DR}$ becomes

$$(T_1^{-1})_{DR} = \frac{9}{8}\frac{\gamma^4\hbar^2}{r^6}\frac{\tau_{DR}}{4} \times \left[\frac{(2\sin^2\Delta' - \sin^4\Delta')}{1 + \omega^2\,\tau_{DR}^2} + \frac{(8 - 8\sin^2\Delta' + \sin^4\Delta')}{1 + 4\,\omega^2\,\tau_{DR}^2}\right] \tag{6}$$

(the result differs from that obtained by Andreev [16] in the factor determining the angular dependence of

the spectral density at 2ω, as equation 14 of reference 16 contains in our opinion a misprint).

The relaxation rate in the rotating frame is found to be

$$(T_{1\rho}^{-1})_{DR} = \frac{9}{8}\frac{\gamma^4\hbar^2}{r^6}\frac{\tau_{DR}}{8} \times \left[\frac{9}{2}\frac{\sin^4 \Delta'}{1 + 4\omega_1^2\tau_{DR}^2} + 5\frac{(2\sin^2\Delta' - \sin^4\Delta')}{1 + \omega^2\tau_{DR}^2} + \frac{1}{2}\frac{(8 - 8\sin^2\Delta' + \sin^4\Delta')}{1 + 4\omega^2\tau_{DR}^2}\right]. \quad (7)$$

In the case of cholesteric COC at $T = 24$ °C the correlation time for « rotational » relaxation due to molecular diffusion along the helix, τ_{DR}, is calculated by means of equation 5 to be 2.6×10^{-4} s. Here we assumed that the length of the pitch is about 3 000 Å whereas D was taken from the T_1 data. By putting this value of τ_{DR} into equation 7 an estimate of $(T_{1\rho}^{-1})_{DR}$ can be obtained. For a « polycrystalline » unoriented sample and an effective average distance between protons of 1.78 Å a rough estimate for $(T_{1\rho}^{-1})_{DR}$ at $H_1 = 10$ G came out to be 80 s^{-1}. This is an upper limit to this contribution as the diminishing of dipolar interactions due to fast molecular rotation around its long axis, resulting in a larger effective interproton distance, has not been taken into account. Even the upper limit 80 s^{-1} is much smaller than the measured value $T_{1\rho}^{-1} \approx 220$ s^{-1} at $T = 24$ °C and $H_1 = 10$ G. In addition, the dependence of $T_{1\rho}^{-1}$ on H_1 is not of the BPP type as predicted by equation 7 and it depends only smoothly on temperature. Therefore we conclude that the intra-molecular contribution of diffusion to relaxation, which is specific for twisted structures, has not been observed in COC.

The contribution to $T_{1\rho}^{-1}$ from self-diffusion affecting the inter-molecular dipolar coupling is only 31 s^{-1} (with parameters used in the fit of T_1^{-1}), and the contribution from local molecular reorientations only 5 s^{-1}. A large contribution to $T_{1\rho}^{-1}$ is thus still missing. As will be shown below the mechanism which dominates the spin-lattice relaxation in the rotating frame in the cholesteric phase are order director fluctuations. This mechanism, strongly reduced at high frequencies because of the « cut-off » obviously becomes important in the kHz region. Its onset is supported by the temperature and frequency dependences of $T_{1\rho}^{-1}$. Above 20 kHz (Fig. 3) $T_{1\rho}^{-1}$ shows a characteristic linear dependence on $\nu_1^{-1/2}$. The full line in figure 3 represents the calculated $T_{1\rho}^{-1}$ by means of equation 1*b* with $C = 8.3 \times 10^4$ $s^{-3/2}$ and $\nu_c = 2.5$ MHz together with the contributions $(T_{1\rho}^{-1})_{SD}$ and $(T_{1\rho}^{-1})_R$. The deviation from the calculated curve occurs for $\nu_1 < 20$ kHz where the transition from the rotating frame into the dipolar reservoir starts to occur. The temperature dependence of $T_{1\rho}$, which shows a marked decrease already in the isotropic phase on approaching the transition into the cholesteric phase, then an abrupt decrease at the transition, and a smooth decrease in the cholesteric phase with decreasing temperature, is characteristic of the ODF relaxation mechanism. The decrease in the isotropic phase is due to pretransition effects, i.e. the formation of cholesteric clusters in the isotropic liquid, which have been observed by light scattering as well [19].

A similar difference between the dominating relaxation mechanisms in the MHz and in the kHz region as in cholesteric COC has been previously observed in nematic MBBA [8, 20].

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