NMR Investigations of the Pitch Dependence of Self-diffusion in Cholesteric Liquid Crystals

S. Oehler, R. Stannarius, and H. Schmiedel
Sektion Physik der Karl-Marx-Universität, Leipzig, DDR

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Self-diffusion in the isotropic and twisted nematic phases of mesogenic substances has been studied by means of ^{1}H- and ^{13}C-NMR.

From the line shape analysis of the recorded ^{13}C-NMR spectra we obtained the diffussion coefficient $D_\perp$ along the helical pitch.

Various concentrations of a chiral additive changed the pitch P_0 of a nematic mixture of phenylbenzoates from 4.7 µm to 7.8 µm. The measured values of $D_\perp$ were in the range from $2.4 \cdot 10^{-12}\,\mathrm{m^2\,s^{-1}}$ to $1.9 \cdot 10^{-11}\,\mathrm{m^2\,s^{-1}}$. We found an Arrhenius behaviour with an activation energy of about 55 kJ/mole nearly independent of the pitch. The obtained data for $D_\perp$ seem to have a lower than quadratic dependence on P_0.

Introduction

NMR investigations of the structure and dynamics of liquid crystalline (LC) phases have been practised for several years. Measurements of the self-diffusion coefficient are of basic significance. Many experiments have been performed in the nematic phase where a homogeneous orientation of the sample in the direction of the magnetic field can easily be attained. In cholesteric phases, at low magnetic fields (below the critical field), the helical structure is preserved and a parallel alignment of the molecules to the external field is inpossible. For a positive anisotropy $\Delta\chi$ of the nematic compound, the helical axes of the corresponding twisted sample N^* are oriented perpendicular to the external NMR field $\boldsymbol{B}_0 = B_0\,\boldsymbol{e}_x$. The director orientation $\boldsymbol{n}$ can be described by a chiral twist

$$\boldsymbol{n} = \boldsymbol{e}_z \cos\theta + \boldsymbol{e}_y \sin\theta,$$

where $\theta = 2\pi x / P_0$. P_0 is the pitch length, and $\boldsymbol{e}_{x,y,z}$ are the unit vectors of an orthogonal laboratory coordinate frame.

The NMR spectra of the cholesteric sample are sensitive to self-diffusion of the molecules along the helical axis [1–4], since such a translational diffusion enforces a change of the average orientation of the molecular long axis with respect to the external field.

In this paper we describe the dependence of self-diffusion upon temperature and pitch length for an undistored helix. For the measurement of $D_\perp$ (the component of the diffusion tensor in direction of the helix), we use ^{13}C NMR and a theoretical model for ^{13}C NMR line shape simulation. The investigated substances have pitch lengths between 4.7 and 7.8 µm. For a B_0 field of 1.46 T the distortion of the helices can be neglected, as will be demonstrated by our investigations. The diffusion coefficients in the isotropic phase have been determined with pulsed field gradient (PFG) NMR.

Experimental

A) Substances

The nematic material was a mixture of four disubstituted phenylbenzoates; it was twisted by addition of chiral cholesteryl-undecylcarbonate (ChUC). Figure 1 shows the structure of the liquid crystal and the denotation of the carbon positions in the spectrum; the composition of the mixture is given in Table 1. Since the mixture consists of molecules of different chain lengths we have to take into account

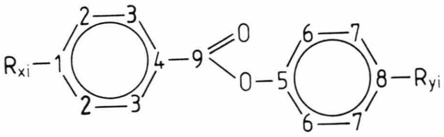

Fig. 1. Structure of the nematic compounds and denotation of the ^{13}C positions.

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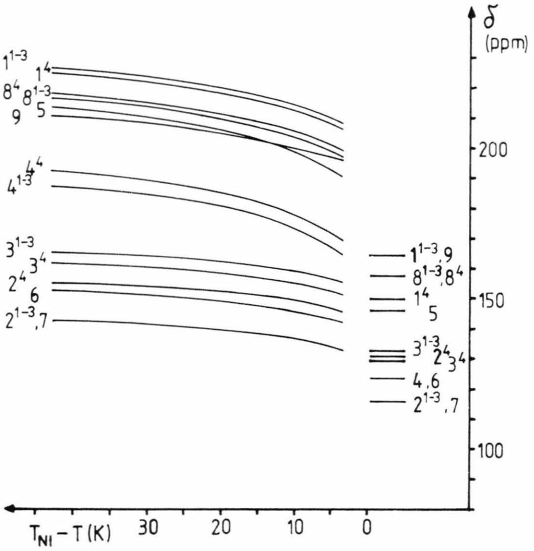

Fig. 2. Temperature dependence of chemical shift (with respect to TMS) for the aromatic carbon sites (the indices 1, 2, 3, 4 at the individual lines denote the number of the component in the mixture).

Table 1. Composition of the nematic mixtures.

Compound	R_x	R_y	Portion (wt%)
1	$X_1 - 0$	$0 - Y_1 \dots Y_6$	22.0
2	$X_5 \dots X_1 - 0$	$0 - Y_1 \dots Y_8$	30.3
3	$X_6 \dots X_1 - 0$	$0 - Y_1 \dots Y_7$	13.3
4	$X_6 \dots X_1$	$0 - Y_1 \dots Y_4$	34.4

Sample	ChUC (wt%)	P_0 (μm)
1	2.0	9.6
2	2.5	7.8
3	3.0	6.45
4	3.5	5.5
5	4.0	4.75

Table 2. Composition of the cholesteric mixtures.

that we can extract only an average diffusion coefficient. Considering the differences of the molecular masses [5], the ratio of the maximum and minimum diffusion coefficients for the individual compounds should not exceed 1.12.

Since the aromatic parts of the four nematic components are identical, troublesome multiplication of the number of lines in the spectrum (see Fig. 2) does not occur. The relatively large temperature range of the nematic phase (3.5 °C to 70 °C) of this mixture represents an essential advantage.

We have prepared several cholesteric mixtures with different concentrations of ChUC (see Table 2). The pitch lengths were determined optically from the fingerprint texture in specially prepared sandwich cells. The temperature dependence of the pitch length P_0 is very weak. The experimental error for the determination of P_0 was ± 10%.

B) ^{13}C NMR Measurements

Proton decoupled ^{13}C spectra were recorded at a frequency of 15.68 MHz ($B_0 = 1.46$ T) by means of the CP method of Pines, Gibby and Waugh [6]. The mixing pulse length was 2 ms and the observation time, i.e. the length of the decoupling pulse, was 40 ms. Its magnetic field strength of $B_1 = 1.0$ mT ensures a complete decoupling of the proton – carbon dipolar interactions. The field inhomogeneity was 1.5 ppm.

The isotropic chemical shifts relative to TMS and their anisotropy in the pure nematic mixture have been measured in the isotropic and nematic phases, respectively. The ^{13}C positions 1 to 9 of the aromatic core display a large anisotropy of chemical shift. They are, in contrast to the chain sites, individually well resolved in the spectrum. Figure 2, shows the temperature dependence of the chemical shift in the nematic phase for the aromatic ^{13}C positions.

For small amounts of cholesteric added to the nematic mixture the order parameter as well as the chemical shielding tensors are assumed to remain constant.

The cholesteric spectrum differs from the nematic one in two ways:

a) the distribution of the molecular orientations ('cylindrical' powder spectrum) results in a distribution of the shielding tensor orientations with respect to $\boldsymbol{B}_0$.
b) diffusion in the helix direction influences the average orientation of the molecules during the time of measurement.

Both effects are accounted for in a line shape simulation program [4] which was applied for the determination of the diffusion coefficient.

C) ^1H NMR Field Gradient Measurements

The determination of the diffusion constant in the isotropic phase was performed using the well-known ^{1}H NMR spin echo PFG method [7] on a Bruker

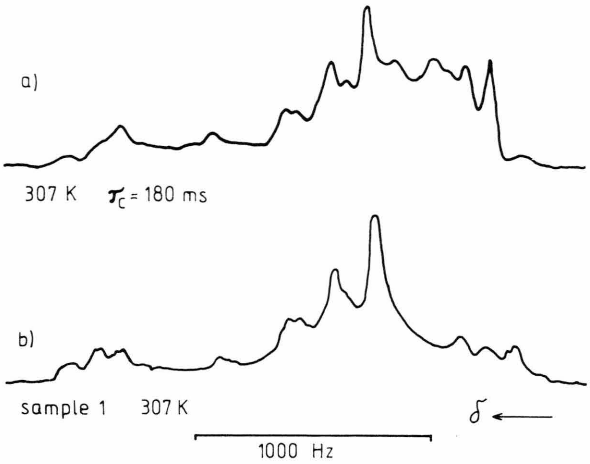

Fig. 3. Experimental (b) and fitted (a) spectrum for $T = 307$ K and $P_0 = 9.6$ µm. The loss in the intensity of the experimental spectrum in the region with low δ-values indicates the unwinding of the helical structure.

BKR 322 s spectrometer at 32 MHz with home built gradient coils. The fiels gradient could be varied up to 1.70 T/m, its pulse length was $\delta = 2.5$ ms, and the spacing Δ of the field gradients ran from 6 ms to 14 ms. Temperature stability and homogeneity in the sample were in all experiments better then 1 K.

D) Influence of B_0 on the Pitch in the Cholesteric Phase

For a positive local diamagnetic susceptibility anisotropy $\Delta\chi > 0$, a magnetic field applied perpendicular to the pitch axes supports an unwinding of the structure [8]. The effect increases with increasing temperatures and larger pitch lengths [2]. It is observed in ^{13}C spectra by an intensity loss of the lines corresponding to the position with $\boldsymbol{n} \perp \boldsymbol{B}$ ($\theta \sim 90°$). For a field strength $B = 1.46$ T, we detect an obvious distortion of the helix (Fig. 3) for long pitch values. Figure 3 b shows the experimental spectrum at $T = 307$ K, Fig. 3 a displays the simulated spectrum for the same temperature. For pitch lengths $P_0 < 8$ µm, we can neglect distortions of the helices throughout the investigated temperature range in the cholesteric phase. The recorded spectra for concentrations $c > 2.5$ wt% of ChUC are typical for a homogeneous distribution of orientations along the pitch. This result is in accordance with the statements on the magnetic field dependence of the cholesteric helices published by Yaniv [9].

Theory

The model that describes the influence of self-diffusion along the pitch on the spectral line shape in ^{13}C NMR is discussed in detail in [4]. In the following, we outline the basic background.

Assuming the local symmetry of the cholesteric phase to be uniaxial (the asymmetry parameter η was below the level of detection in the experiments), we find a resonance frequency of the i-th carbon site of

$$\nu^i = \nu^i_a \cdot (3\cos 2\theta + 1)/4 + \nu^i_{\text{iso}} .$$

$\nu^i_a = \nu_0\, \tilde{\sigma}^i_{zz}$ is the chemical shift anisotropy with $\tilde{\sigma}^i_{zz}$ the time averaged component of the chemical shielding tensor in direction of $\boldsymbol{B}_0$ in the nematic phase. The time average involves any kind of fast molecular motions (compared to the experimental time scale) which are both present in the nematic and cholesteric phases.

$$\nu_0 = \left|\frac{\gamma}{2\pi}\boldsymbol{B}_0\right|, \text{ and } \nu_{\text{iso}} = \nu_{\text{reference}} - \nu_0\,\sigma_{\text{iso}} .$$

θ is the angle between the external field direction and the local director. ν^i_{iso} is determined from spectra in the isotropic phase; it is temperature-independent. ν_a is obtained from spectra in the nematic phase, it depends upon temperature via the order parameter S.

With the assumption of a Markovian diffusion process with correlation time $\tau_c = P_0^2/16\pi D_\perp$, the model gives an FID for the sample in the cholesteric phase

$$G(t) = \sum_i n_i J_0\left(\frac{3\pi}{2}\nu^i_a \tau\right) \exp(-\Delta^2_{\text{min}} - t/T_2),$$

where J_0 is the Bessel function of order zero.

$\tau = \tau_c(1 - \exp(-t/\tau_c))$ and T_2 is the transverse relaxation time that is determined from the line widths in the nematic phase. The function Δ_{min} depends on τ_c and accounts for phase distributions of the spins, and n_i is the number of equivalent carbon sites. The only parameter for the fitting of simulated spectra to experimental ones is the correlation time τ_c. We simulate only the aromatic part of the spectrum since it is clearly separated from the chain carbon lines.

The latter are poorly resolved. The line width, caused by T_2 relaxation and the limited decoupling time of 40 ms, is of the same order as ν^i_a. Thus, the chain sites are not suited for a determination of τ_c from line shape fitting. The determination of $D_\perp$ by means of fitting the line shape of the aromatic part has an accuracy of approximately 10%.

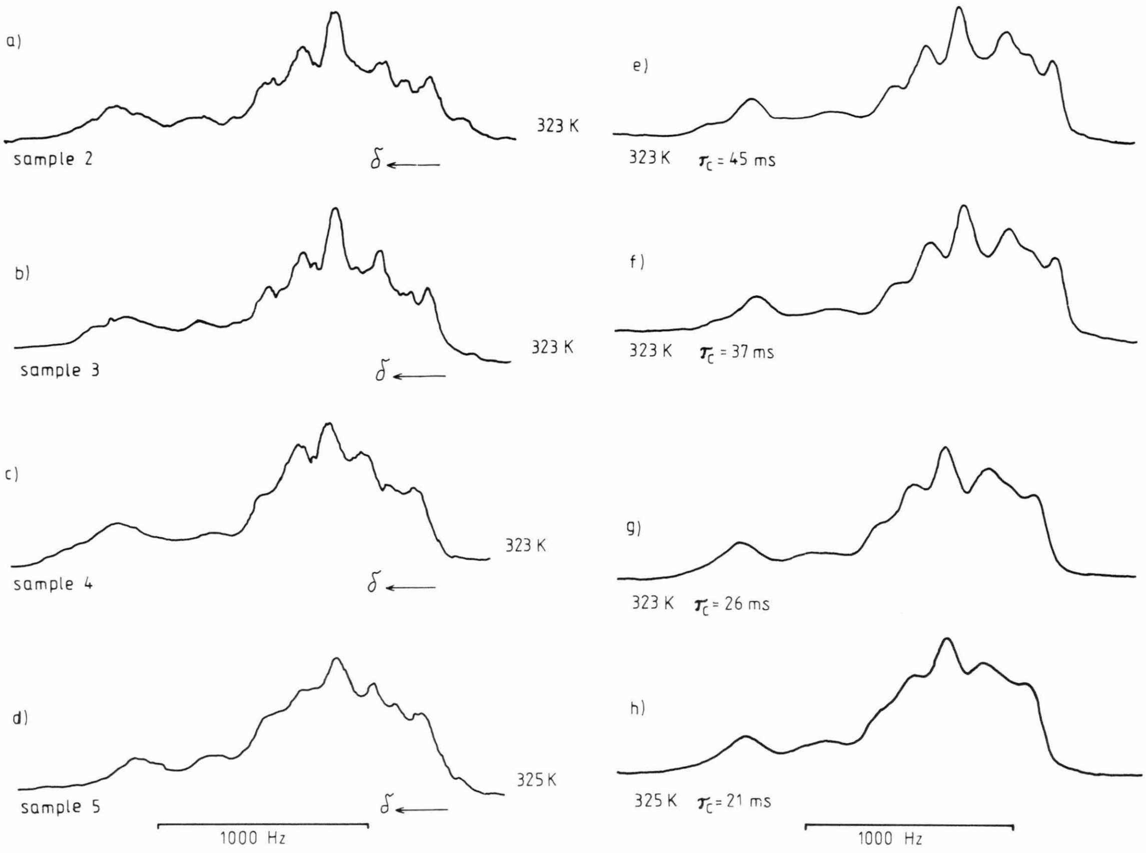

Fig. 4. Experimental (a–d) and corresponding computed (e–h) spectra for different pitch lengths.

Results and Discussion

The simulated ^{13}C spectra are based on the ν_a^i and ν_{iso}^i values from the nematic and isotropic phases, respectively. We have taken into account 13 distinct carbon lines (see Figure 2). The splittings of the lines of the N* spectra range from 400 to 900 Hz. Hence the time scale of the measurement is ≤ 1 ms. Thus we measure only the short time behaviour of $D_\perp$, other than in the ^{1}H PFG experiments of Blinc et al [10]. With an improved spectral resolution one could determine D simultaneously for longer time scales if the Y_1-, X_1-methyloxy-carbons could be included into the simulation. Those have ν_a splittings of about one order of magnitude lower than the ring carbons and hence a time scale being extended by a factor of about 10.

In Fig. 4 some experimental and corresponding computed spectra for different pitch lengths are represented. For the pitch length 9.6 µm (sample 1) no satisfactory fit was possible; the distortion of the helix by the B_0-field gives rise to a very low intensity of the 90°-peaks, and the mismatching fitting yields irregularly high τ_c values with large error. The values of the self-diffusion coefficients determined in the cholesteric phase for samples 2 to 5 are given in Table 3.

With the field gradient method we have measured the diffusion coefficients of the pure nematic mixture and samples 1.5 in the isotropic phase. As expected, no dependence of the isotropic diffusion coefficient D_i on the amount of added ChUC was found within the experimental error. D_i was measured for different temperatures. The values of D_i at the phase transition temperature T_NI are higher than in the cholesteric

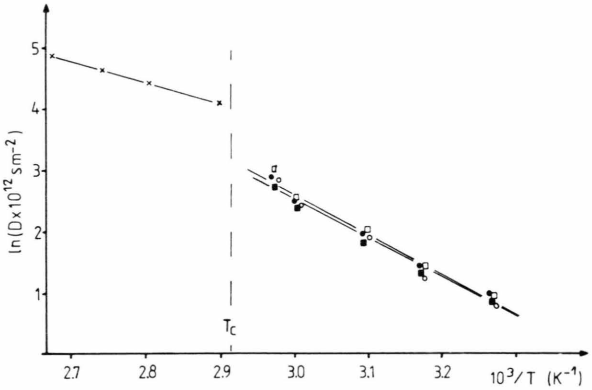

Fig. 5. Arrhenius plot of the diffusion coefficient (■-sample 5, □-sample 4, ●-sample 3, ○-sample 2).

Table 3. Temperature dependence of the self-diffusion coefficient for samples with different pitch lengths.

Sample 2 $D_\perp$ [m²/s]	$P_0 = 7.8$ μm T [K]	Sample 3 $D_\perp$ [m²/s]	$P_0 = 6.45$ μm T [K]
$2.9 \cdot 10^{-12}$	306	$2.6 \cdot 10^{-12}$	306
$4.5 \cdot 10^{-12}$	315	$4.1 \cdot 10^{-12}$	315
$8.6 \cdot 10^{-12}$	323	$7.1 \cdot 10^{-12}$	323
$1.28 \cdot 10^{-11}$	332	$1.20 \cdot 10^{-11}$	332
$1.93 \cdot 10^{-11}$	336	$1.78 \cdot 10^{-11}$	336
Sample 4 $D_\perp$ [m²/s]	$P_0 = 5.5$ μm T [K]	Sample 5 $D_\perp$ [m²/s]	$P_0 = 4.75$ μm T [K]
$2.4 \cdot 10^{-12}$	306	$2.4 \cdot 10^{-12}$	307
$4.0 \cdot 10^{-12}$	315	$3.6 \cdot 10^{-12}$	316
$7.1 \cdot 10^{-12}$	323	$6.9 \cdot 10^{-12}$	325
$1.20 \cdot 10^{-11}$	332	$1.02 \cdot 10^{-11}$	333
$1.72 \cdot 10^{-11}$	336	$1.87 \cdot 10^{-11}$	338

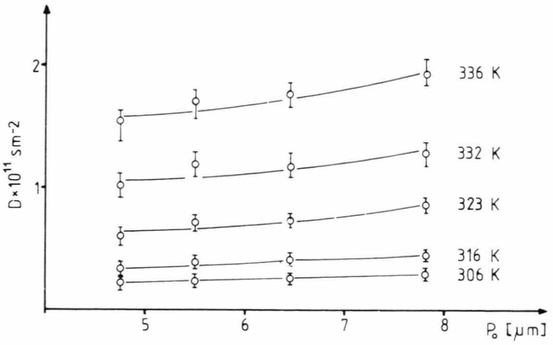

Fig. 6. Diffusion coefficient versus pitch length P_0.

Table 4. Self-diffusion coefficient D_i in the isotropic phases of purely nematic mixture, and samples 1 and 5.

Pure nematic D_i [m²/s]	Sample 1 D_i [m²/s]	Sample 5 D_i [m²/s]	T [K]
$5.6 \cdot 10^{-11}$	$6.4 \cdot 10^{-11}$	$6.2 \cdot 10^{-11}$	345
$7.6 \cdot 10^{-11}$	$8.3 \cdot 10^{-11}$	$7.8 \cdot 10^{-11}$	355
$1.0 \cdot 10^{-10}$	$1.1 \cdot 10^{-10}$	$1.1 \cdot 10^{-10}$	365
$1.3 \cdot 10^{-10}$	$1.3 \cdot 10^{-10}$	$1.3 \cdot 10^{-10}$	375

phase. This result is not in contradiction with the paper of Noack [11], as stated below. The D_i are collected in Table 4; the experimental error was 15%.

In Fig. 5, the Arrhenius plot of the diffusion coefficient is depicted for the isotropic and cholesteric phases. We have found activation energies of approximately 55 kJ/Mole for samples 2 to 5.

In the isotropic phase, the activation energy amounts to $E_a = (28 \pm 4)$ kJ/Mole. Figure 6 shows the self-diffusion coefficient in dependence on the pitch length for different temperatures.

We find an increase of diffusion with the pitch length. The quantity D/P_0^2 was stated in [12] and [13] to be constant. In our measurements, the value of $D_\perp/P_0^2$ fluctuates much more at temperatures in the vicinity of T_{NI} than at low temperatures. The data for $D_\perp$ seem to have a lower than quadratic dependence on P_0. For a more exact determination we have to investigate a larger range of concentrations.

The same substances as in this work have been used in an optical mass transport (OMT) measurement [14]. The principles of the OMT technique are given, e.g., in [15]. This method measures the diffusion of the cholesteric compound ChUC in the nematic/cholesteric mixture, in particular the diffusion averaged over all directions perpendicular to the pitch axis.

Similar to our results, the corresponding diffusion coefficient decreases with higher concentrations of ChUC. It was found to be, e.g., $8.0 \cdot 10^{-12}$ m²/s and $7.1 \cdot 10^{-12}$ m²/s at $c = 3\%$ and $c = 4\%$, respectively, at a temperature of 298 K.

The activation energies for the diffusion process of the nematic molecules along the pitch obtained in this work are slightly higher than the usual values in the nematic phase (~40 kJ/Mole) [16]. Diffusion coefficients are generally lower than those for nematics [11, 16]. To be sure, the isotropic values of the diffusion coefficient are higher than in the cholesteric phase. If, however, the values are extrapolated, with the respective activation energies, to temperatures above 100 °C, we can confirm the results of Noack [11]. He found for nematics of the PAA homologuous series larger diffusion coefficients in the nematic than in the isotropic phase at T_{IN}, which is well above 100 °C for these substances.

Acknowledgements

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