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Determination of Pitch in a Cholesteric DSCG-Water Lyomesophase by NMR Techniques

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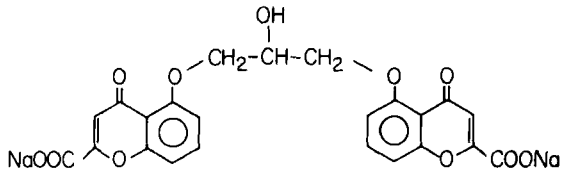
Nuclear Magnetic Resonance (NMR) techniques are used to determine the pitch in a cholesteric lyomesophase prepared by adding of *l*-alanine to a solution of disodiumcromoglycate (DSCG) in water. The method, which is particularly suitable for the study of bulk samples, consists of a combination of two independent types of measurements: (i) The effective reorientational correlation time of the director, due to molecular translational diffusion, is determined by a lineshape analysis of the deuterium resonances of the solvent D_2O and/or deuterated *l*-alanine. (ii) The translational self-diffusion coefficients of both these constitutents is determined by a pulsed field-gradient spin-echo experiment. From the results of these measurements, the pitch and its dependence on the chiral dopant concentration is determined.

I. INTRODUCTION

Solutions of disodiumcromoglycate (DSCG) in water form several



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different types of lyomesophases, depending on the concentration and temperature of the sample.[1-4] In the concentration range 5–15 wt.% DSCG and above −4°C, a type II ($\Delta\chi < 0$) nematic phase is formed. When this mesophase is doped with chiral compounds, a cholesteric mesophase, also of type II, is obtained. The dependence of the pitch, P, on the concentration of added chiral dopants (in particular amino acids) was recently studied by Lee and Labes[3] using optical microscopy on aligned "fingerprint" textures. The results indicated a very strong dependence of P on the dopant concentration. For example in the range 0.5 to 1 molal *l*-alanine at 20°C, the pitch changed from 60μ to 20μ. Moreover, a very unusual effect of magnetic field on pitch was observed: when a cholesteric DSCG-water sample was allowed to stay in a magnetic field for several hours, the pitch shortened with time until it reached a steady state value of about $\frac{1}{3}$ of its original value.

Since thin capillaries were used in the optical microscopy study, and relatively long pitches were observed, in particular at low dopant concentration, it is possible that, at certain orientations of the magnetic field, wall effects might influence the behavior of the cholesteric mesophase. We have therefore undertaken a similar study of the pitch and its dependence on dopant concentration in the cholesteric DSCG-Water system, using a magnetic resonance method which is suitable for large bulk samples. This method consists of a combination of two types of measurements. One involves dynamic lineshape analysis and provides information on the effective reorientation rate of the director due to translational diffusion of the constituent molecules.[5-8] The second consists of direct determination of molecular translational diffusion.[9] The principle of the method is based on the fact that translational diffusion of molecules along the cholesteric axis is effectively, as far as the NMR lineshape is concerned equivalent to director reorientation. The correlation time for this reorientation, $1/\tau_R$, depends on both the translational diffusion constant, D_T, of the corresponding species and on the pitch, P. Thus if both τ_R and D_T are known for the same constituent species, P can readily be determined. The two types of experiments were performed on both the solvent water, and on the dopant (alanine) which was added to induce twist. For the determination of τ_R, the NMR lineshape of deuterium of the solvent D_2O and of the CD_3 signal in deuterated alanine were used. These results are described in section III A. The translational diffusion constant D_T was determined (section III B) using the proton resonance signals of the same constituents. Finally in section III C, the results of the pitch determinations are presented and discussed.

II. EXPERIMENTAL

A. Materials and sample preparation

DSCG was kindly provided by the Pharmaceutical Division of Fison Ltd. (Loughborough, U.K.) as a crystalline solid hydrate. Normal *l*-alanine and racemic *d, l*-alanine were purchased from Sigma Chemical Co., while the deuterated compounds *l*-alanine-3,3,3-d_3 and *d,l*-alanine-3,3,3-d_3 (98 at.% D) were obtained from Merck Sharp and Dohme (Canada). The D_2O (97 at.%) was from Merck. For the solutions in normal water we used doubly distilled H_2O.

The cholesteric lyomesophases were prepared by adding weighed amounts of DSCG, *l*-alanine and (racemic) *d,l*-alanine to D_2O or H_2O. The mixture was kept at 40–50°C for about 30 minutes with occasional mixing until all the solid material dissolved. In all solutions (except one) the concentration of DSCG and the total concentration of alanine (*l* + racemic) were kept as nearly constant as possible (~14.4 wt.% and ~10.0 wt.% respectively) in order to maintain constant viscosity. In one case, a higher concentration of *l*-alanine (13.3 wt.%) was used and *d*-lysine was also added in order to obtain a shorter pitch and thus extended the range of the diffusion studies. The composition of all solutions investigated are shown in Table I. Note that "net *l*-alanine" corresponds to the extra optically active dopant in excess of the amount included in the column "*d,l*-alanine."

TABLE I

The composition of the solution used for the lineshape and diffusion measurements in the present work.

Solution No.	wt.% DSCG	wt.% *d,l*-alanine	wt.% net *l*-alanine	remarks
1	14.1	10.1	0.0	a
2	14.5	7.8	2.5	a
3	14.3	6.0	4.0	a
4	14.3	5.0	5.0	a
5	15.0	5.0	5.0	b
6	14.5	4.0	6.1	a
7	14.1	1.1	8.8	a
8	13.9	—	9.9	a
9	15.0	—	9.9	b
10	14.8	—	10.1	a
11	15.0	—	13.3	c

[a] Solutions of isotopically normal alanine in 97 at.% D_2O.
[b] Solutions of alanine-d_3 in H_2O.
[c] This solution contains, in addition to the excess *l*-alanine, 4.9 wt.% *d*-lysine.

Unless specifically indicated, all experiments were done in 5 mm o.d. NMR tubes. The tubes were sealed immediately after adding the mesophase constituents, yielding sample holders with a total length of about 4 cm. These samples were inserted into 10 mm o.d. tubes for the NMR measurements. To check possible wall effects on the results, some experiments were done using rectangular capillaries of inner dimensions 20 × 3 × 0.3 mm and 20 × 2 × 0.2 mm (Vitro Dynamics, Inc.). The capillaries were filled by inserting them into the desired mesophase solution, and were then sealed with rapid Araldite Epoxy. To increase the signal to noise ratio from these samples, several capillaries (four for the thicker ones, and ten for the thinner) were stacked together and glued in parallel to a 0.7 mm wide microscope slide. The whole assembly was then placed in 10 mm o.d. tubes for the NMR measurements.

B. NMR measurements

Both the deuterium lineshape and the diffusion measurements were performed on a Bruker WH-90 spectrometer. The lineshape studies were done on deuterium at 13.8 MHz using a standard variable frequency probe, while the self-diffusion measurements were done on protons, using a modified fixed-frequency probe at 90 MHz with an external ^{2}D lock. A detailed description of the modifications made for performing these experiments will be given elsewhere.[9] Basically it allows producing pulses of field gradients of up to 8.8 Gauss per cm along and perpendicular to the main field direction, using a quadrupole coil arrangement (ten turns of 34 AWG magnet wire per quadrant on a mylar form around the glass insert of the ^{1}H probe) matched to a homemade transistor switch circuit and digitally controlled from the Nicolet 1180 software. The pulse sequence[10] for the spin-echo experiment is schematically given in Figure 1. In practice the intervals between the r.f. pulses and the pulse-gradient spacing, τ and Δ, were held constant at 35.9 ms and δ, the variable pulse-gradient duration, was varied from 1 to 27 ms. The second half of the FID spin echo signal was Fourier transformed and the water and alanine signal intensities recorded for different values of the interval δ. The intensities of the signals are given[10] by

$$I = I_0 \exp[-K D_T \delta^2(\Delta - \delta/3)] \qquad (1)$$

where K is a gradient constant. This constant was calibrated using cyclohexane as a standard taking[11] D_T(cyclohexane at 25°C) = 1.475 × 10^{-9} m^2 sec^{-1}.

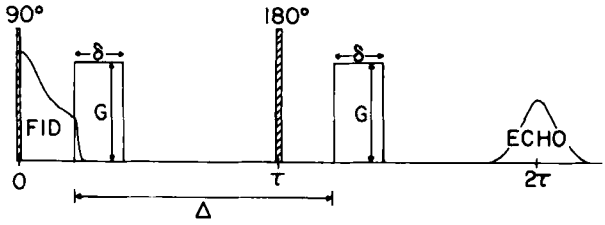

FIGURE 1 The pulse sequence for the determination of self-diffusion by the pulsed-gradient spin-echo technique used in the present work. A magnetic field gradient pulse of strength G and duration δ is applied between the 90° and 180° rf pulses. After a time Δ from the onset of the first gradient pulse, a second gradient pulse, identical to the first, is applied. Echo signals are recorded as function of the gradient pulse duration, δ.

The temperature of both the diffusion and lineshape experiments was controlled with a Bruker BST 100/700 unit, and its absolute value was calibrated with a Fluke 2190 digital thermometer. The temperature accuracy is estimated at ±1°C.

III. RESULTS AND DISCUSSION

In this section we present the results obtained from the two types of NMR measurements described above. We first discuss the lineshape analysis and then proceed to describe the measurements of the self-diffusion coefficients. Finally we combine the two sets of data and compute the pitch of the cholesteric.

A. NMR lineshape measurements—the correlation time for the effective reorientation of the director

As indicated in the introduction, when chiral dopants are added to the nematic lyomesophase of DSCG a cholesteric phase is obtained. This phase is of type II, as are the other lyomesophases of DSCG, and thus it tends to align in a magnetic field with its director perpendicular to the field. Accordingly, upon slow cooling from the isotropic liquid to the cholesteric phase, an aligned mesophase with a domain structure in which all helix axes, **P** are parallel to the external field, is formed. This structure will persist even after reorienting the sample in a magnetic field provided there is strong anchoring at the walls and that the viscosity of the sample is high. In Figure 2 are shown examples of the ^2D spectra of D_2O in solution No. 10 of Table I. In each series of spectra in this figure, the bottom trace was obtained after aligning the sample in the magnetic field and cooling it to the designated temperature. These

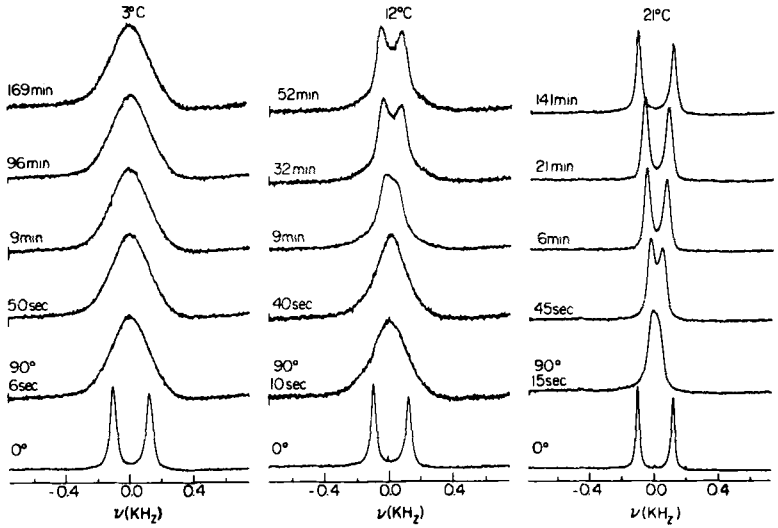

FIGURE 2 Deuterium NMR spectra of D_2O in alanine doped (10.1 wt.%) DSCG-Water (14.8 wt.%) lyomesophase (solution No. 10 of Table I). The spectra show the effect of realignment of the cholesteric pitch following rotation of the sample with respect to the magnetic field at different temperatures. The bottom traces were obtained from aligned samples in 5 mm o.d. tubes at the temperatures indicated in the figure. All other traces were obtained after rotating the sample by 90° about an axis perpendicular to the magnetic field, and recording the spectra at successive intervals as indicated.

spectra therefore correspond to a structure in which **P** is parallel to the field, and the observed doublet splittings correspond to the average quadrupole interaction, ν_Q, with the director **n** perpendicular to the field direction. The other traces in each series of experiments were recorded after rotating the sample by 90° at successive intervals as indicated in the figure. Clearly, immediately after the sample was rotated **P** is perpendicular to H and **n** is distributed in a plane parallel to the field. There is, therefore, a planar (two-dimensional) distribution of **n** making angles between zero and π with H. If there is no strong anchoring, **P** will reorient until it is again parallel to the field. It may be seen from the traces in Figure 2 that at 21°C, reorientation of **P** occurs within about two hours while at 3°C the spectrum remains essentially unchanged for a period of at least 3 hours. The observed traces in the latter series are typical of planar distribution of directors[6] with the magnetic field parallel to the plane of the distribution and with a certain degree of motional averaging. Thus, in order to obtain the desired dynamic lineshape with a well-defined distribution, it is necessary to per-

form the experiments at or below 3°C in order to avoid helix reorientation. This statement, of course, applies to 14 wt.% DSCG + 10 wt.% alanine solutions at a magnetic field of 21 KGauss. At higher fields, helix reorientation may occur even below 3°C.

It was shown previously[4] that around −4°C the DSCG-Water mesophase transforms to a new phase, which was called phase III. This low temperature phase, which is smectic-like and has apparently a considerably different structure than the high temperature DSCG-Water mesophases, also manifests itself in chirally doped DSCG-Water solutions. In this phase, one observes a discontinuous change in the quadrupole splittings of the constituent species. Thus, e.g. in solution No. 10 we found at the transition point to phase III (~ −4°C) a change of $\nu_Q(D_2O)$ from 265 Hz to 381 Hz and at the same time for solution No. 9 $\nu_Q(CD_3\text{-alanine})$ changed from 271 Hz to 221 Hz. We have chosen to perform our measurements at 2 to 3°C for two reasons: (i) in order to minimize the helix reorientation problem, and (ii) to be sufficiently far from the transition to the phase III region, thus avoiding possible pretransitional effects on the pitch. It should be noted that in samples with longer pitch, the reorientation was slightly faster.

Two types of samples were studied: (a) samples prepared as described above, in which **P** was first aligned parallel to H and subsequently rotated so that it became perpendicular to H. (b) Powder samples prepared by allowing the solution to cool from the isotropic to the cholesteric phase outside the magnetic field, with occasional shaking. The sample was then cooled to ~2°C and placed in the NMR probehead which was precooled to 2°C. The resulting cholesteric phase consisted of a mixture of domains with a random distribution of **P**.

To understand the effect of translational diffusion on director reorientation, consider[6] a single cholesteric domain with **P** at an angle α to the external field (Figure 3). Molecular translational diffusion along this axis is effectively equivalent to reorientation of the director in a plane perpendicular to **P**. If this reorientation affects the relative direction of the director with respect to the magnetic field, modulation of the quadrupole interaction will occur. Clearly if $\alpha = 0$, all directors are perpendicular to H and no modulation of the quadrupole splitting takes place. However if $\alpha \neq 0$ and in particular for $\alpha = \pi/2$, the translational diffusion is associated with effective reorientation of the director with respect to H, and accordingly the NMR lineshape should be affected by the motion. The effective reorientation of the director by this mechanism can be characterized by a (planar) reorientation corre-

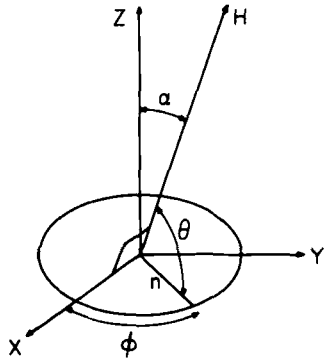

FIGURE 3 The coordinate system used to calculate the dynamic lineshape of the cholesteric system. The cholesteric axis is parallel to Z, and the magnetic field is inclined at an angle α to this axis.

lation time, τ_R, which is related to the molecular translational diffusion constant, D_T, and to P, by[6]:

$$\frac{1}{\tau_R} = \frac{2D_T}{(P/2\pi)^2} \tag{2}$$

Thus by determining τ_R and D_T for the same mesophase constituents, P can be determined. In practice, the dynamic lineshape measurements are most sensitive to the rate when $\nu_Q \tau_R \sim 1$, i.e. $P^2 \nu_Q \sim 8\pi^2 D_T$.

We have determined τ_R for both D_2O and alanine-d_3 from their deuterium NMR signals in the solutions listed in Table I. The determination of τ_R was done by comparing the experimental spectra with simulated traces, using the same simulation procedure as described in detail in Ref. 6. In the simulation of the spectra of the type (a) samples we found it necessary to assume a certain degree of distribution of the helix axis. This was done by introducing a Gaussian distribution in the angle α about $\alpha = \pi/2$, i.e.:

$$f(\alpha) \propto \exp\left[-\frac{1}{2}\left(\frac{\alpha - \pi/2}{\sigma}\right)^2\right] \sin(\alpha - \pi/2) \tag{3}$$

where the variance, σ^2, was taken as a free parameter. For the powder samples (b) a spherical distribution of P was taken:

$$f(\alpha) \propto \sin \alpha \tag{4}$$

In Figure 4 are shown examples of experimental and simulated deuterium spectra of *l*-alanine-d_3 in solutions 9 and 5 of Table I. The bottom spectra correspond to samples of type (a), with $\alpha = 0$, while

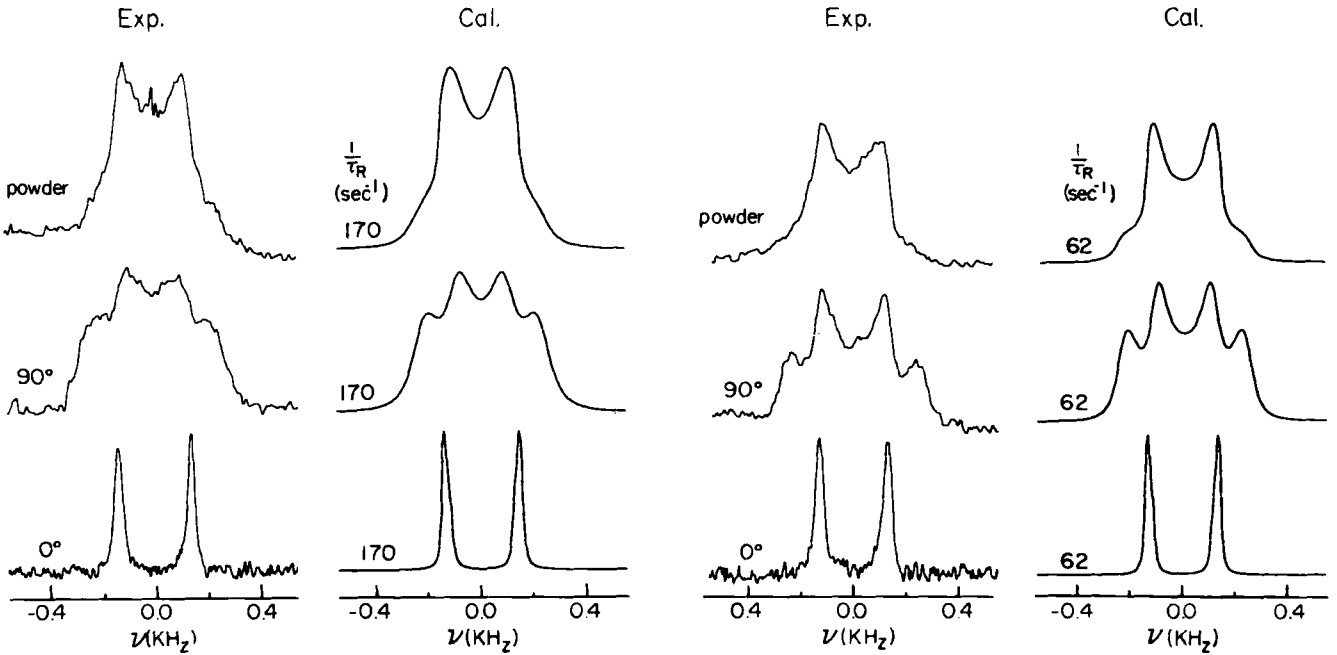

FIGURE 4 Experimental and simulated deuterium NMR spectra of alanine-d_3 in the cholesteric phase of DSCG-Water (15 wt.%). The experimental spectra on the left correspond to a solution containing 1.07 molal net *l*-alanine (solution 9 of Table I) and those on the right to 0.54 molal (solution 5). For each series of spectra the bottom traces were obtained after aligning the sample in the magnetic field and reducing the temperature to 2°C. The middle traces were recorded after rotating the sample by 90°. The upper traces correspond to a powder sample. The calculated spectra were simulated as explained in the text using the parameters given in Table II. A distribution parameter $\sigma = 4°$, was used for the middle traces and a natural linewidth $1/T_2^\circ = 7$ Hz for all spectra.

the middle spectra were obtained after rotating the samples by $\pi/2$. The upper traces correspond to powder samples (type b). Two series of experimental spectra are shown, both correspond to 15 wt.% DSCG but with different concentrations of net *l*-alanine (10 wt.% on the left and 5 wt.% on the right). For each series of experimental spectra, a corresponding set of simulated spectra are also shown. The parameters used in the simulation are indicated in the figure and its caption.

A similar set of experimental and simulated spectra are shown in Figure 5 for the D_2O resonance of solutions 1, 4, 10 and 11. Here the spectra on the left correspond to samples of type (b), and those on the right to samples of type (a). (The parameters used in the simulation are indicated in the caption to the figure.) Note that both in this figure and in Figure 4 the same τ_R values are used to simulate the spectra of samples (a) and (b) for corresponding solutions. This fact and the good overall correspondence of the simulation procedure lends confidence to the procedure used in determining τ_R. On the other hand, it may be seen in both Figures 4 and 5 that the correspondence is somewhat better for the samples with higher chiral dopant concentration than for those with lower *l*-alanine content. As indicated above, anchoring seems to be better in the short pitch samples and it is possible that some helix reorientation occurred in the samples with low *l*-alanine content during the experiments, thus spoiling the correspondence. The results for the whole list of solutions studied are summarized in Table II. Also given in the table are the quadrupole interactions, ν_Q, as measured in the samples of type (a) at $\alpha = 0$. These values are essentially independent of the ratio [*d*-alanine]/[*l*-alanine], indicating that there is no change in the water ordering on going from the nematic to the cholesteric phase.

The effective reorientation rates of the director, $1/\tau_R$, increases with the chirality of the solution, i.e. with the concentration of net *l*-alanine. This is in the direction expected from Eq. (2), since the pitch shortens with increasing concentration of the chiral dopant. In order to determine the exact dependence of P on the net *l*-alanine concentration we require D_T in the same solutions and for the same species for which $1/\tau_R$ was measured. The results of measuring D_T are described in the next section.

B. Translational self-diffusion measurements

The self-diffusion of water and alanine, in several solutions having similar compositions to those used for the determination of τ_R, was measured using the pulsed-gradient spin-echo method. These experiments

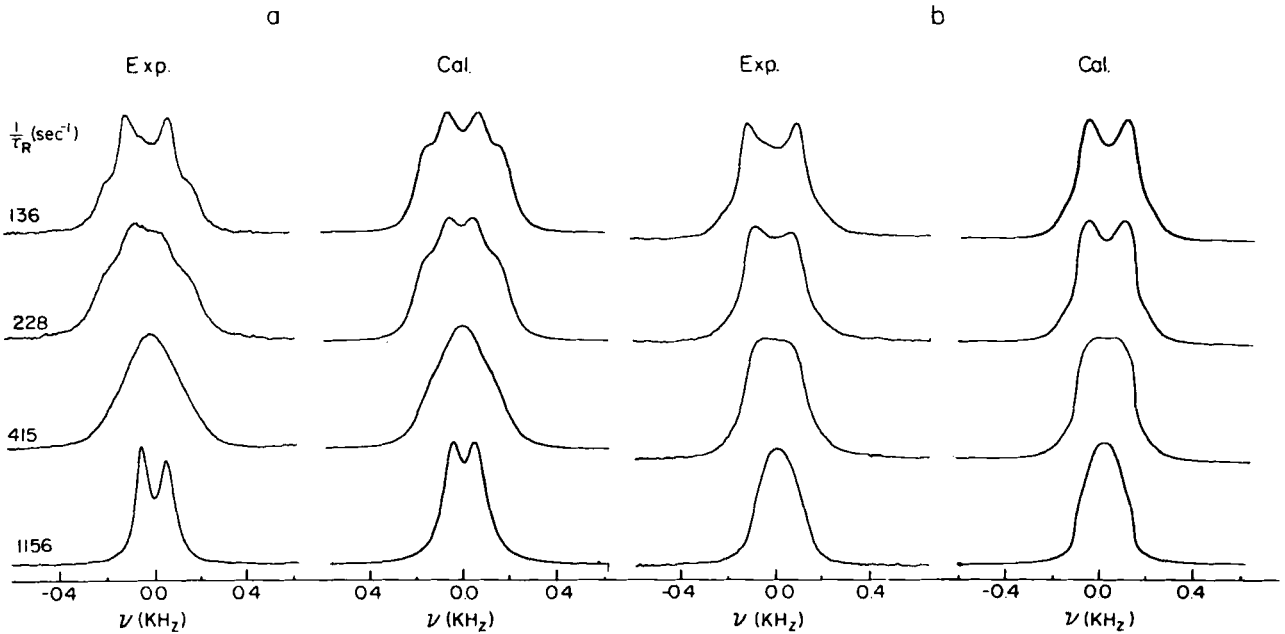

FIGURE 5 Experimental and simulated deuterium NMR spectra of the solvent D_2O in alanine doped DSCG-Water (~14 wt.%) mesophase. The experimental traces on the left, a, were obtained by first aligning the samples in a magnetic field, cooling to 2°C and then rotating by $\pi/2$ before recording the spectra. The traces on the right, b, are also for 2°C and correspond to powder samples with randomly distributed cholesteric domains. The experimental traces from top to bottom correspond to solutions 1, 4, 10 and 11 in Table I. The simulated spectra were calculated as explained in the text using the parameters given in Table II, $\sigma = 5°$ and $1/T_2^c = 13$ Hz.

TABLE II

Results for ν_Q, $1/\tau_R$ and D_T for the solutions listed in Table I and the corresponding calculated pitch (t = 2°C).

Solution No.	net *l*-alanine (molality)	ν_Q (Hz)	$1/\tau_R$ (sec^{-1})	D_T (10^{-5} cm^2/sec)	P (μ)	remarks[a]
1	—	220	—	0.63	∞	
2	0.28	217	136	0.69	19.9	
3	0.45	223	196	b	16.5	
4	0.56	227	228	b	15.3	
5	0.54	245	620	0.23[c]	17.2	ala.
6	0.69	232	262	b	14.3	
7	0.99	223	336	b	12.6	
8	1.11	227	427	b	11.2	
9	1.07	271	170	0.26[d]	11.0	ala.
10	1.13	220	415	0.68	11.4	
11	1.49	230	1156	0.57	6.2	[e]

[a] All results refer to the water constituent except those marked ala., which correspond to alanine.
[b] Not measured.
[c] Interpolated from measurements on alanine in solution Nos. 2 and 10.
[d] Measured on solution No. 10.
[e] This solution contains, in addition to the excess *l*-alanine 4.9 wt.% *d*-lysine.

were done on the proton signals of the constituent molecules as described in section IIB. The measurements on alanine were done in solutions containing normal solute in D_2O, while the self-diffusion of water was determined on the HDO signal of the same solutions due to the small proton content (~3 at.%) in the solvent D_2O. To allow comparison with the τ_R measurements, all self-diffusion experiments were done at 2°C, using 5 mm sample tubes. The spin-echoes were obtained without sample spinning. Examples of such self-diffusion experiments indicating the quality of the results are shown in Figure 6. The calculated values for D_T are summarized in Table II. Several diffusion measurements were done at different orientations of the samples (of type a) with respect to the external magnetic field, but no effect of diffusion anisotropy could be detected within the experimental accuracy. One experiment was also performed in a thin capillary (0.3 mm) and again the same D_T values were obtained as in the 5 mm tubes for the corresponding solution. In fact, for all water diffusion experiments essentially the same result of 0.67×10^{-5} cm^2/sec at 2°C was obtained. The only exception is solution No. 11 for which a somewhat lower D_T value was obtained. This is, no doubt, due to the effect of added lysine and the higher alanine concentration in this solution. Likewise, for the two

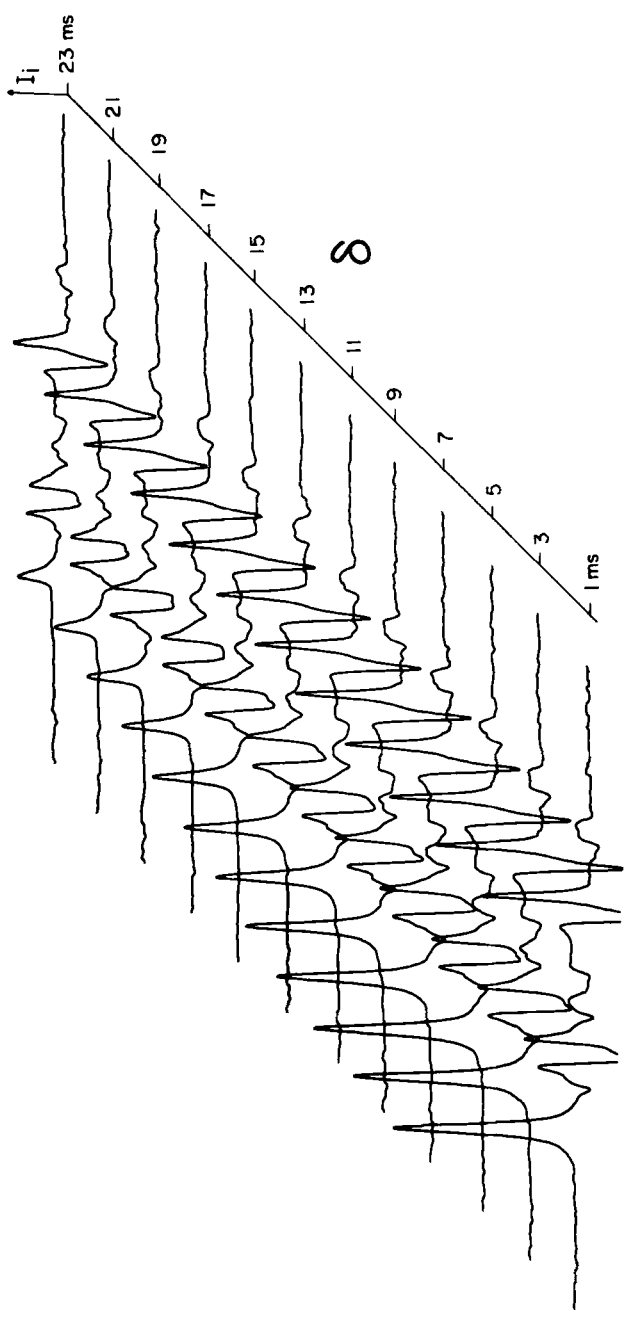

FIGURE 6 A typical pulsed-gradient spin-echo experiment performed on solution 10 of Table I (14.8% DSCG, 10.1% *l*-alanine) at 2.3°C, $\Delta = \tau = 35.9$ ms, $G = 4.6$ G/cm. The FT signals, from left to right, arise from the HDO, alanine—CH and alanine—CH_3 protons. The shape of the alanine signals depends on the spin–spin coupling constant and on Δ. Signal attenuation is due solely to molecular self-diffusion.

solutions for which alanine diffusion was measured (Nos. 2 and 10 in Table II), essentially the same value for D_T (alanine) was obtained.

These results are at variance with those recently obtained by Doane *et al.*[7,12] in certain thermotropic cholesterics. These authors found that the translational self-diffusion constant in cholesterics decreases with the square of the pitch. In the experiments reported here, the pitch changed by a factor of three within the cholesteric mesophase region (and by ∞ if the nematic phase is included). In this region the diffusion rate, according to the predictions of Doane *et al.*, should have changed by more than a factor of ten. As indicated, no such effect was detected.

DISCUSSION

Using the results for $1/\tau_R$ and D_T in Table II, the values for the pitch given in the last column of this table were calculated [Eq. (1)]. It should be noted that D_T was measured on the non-deuterated constituents, while $1/\tau_R$ was determined on the corresponding deuterated species. This effect is not expected to introduce a significant error in the value of P. For example, diffusion measurements on water (97 at.% D_2O), at 25°C gave 1.87×10^{-5} and 1.91×10^{-5} cm^2 sec^{-1} for the D_2O and DHO species respectively.[13,14] The isotope effect on the diffusion of *l*-alanine is expected to be even smaller.

In Figure 7 $1/P$ is plotted versus the net molality of *l*-alanine and compared with the results of Lee and Labes.[3] As expected $1/P$ increases with the concentration of *l*-alanine in both sets of experiments, however there is a discrepancy which increases with decreasing *l*-alanine concentration. For the solutions with long pitches the discrepancy may in part be due to the fact that the NMR lineshape measurements for these solutions are less accurate than for the shorter pitch samples. Also the optical microscopy experiments were done at 20°C while the NMR measurements were for 2°C. However from qualitative observation of the NMR lineshape at higher temperatures and from the temperature dependence of D_T, it is clear that the pitch changes very little in the range 2°C to room temperature, and we therefore feel that the discrepancy might be due to the effect of sample size and shape on the cholesteric structure.

We rule out distortion due to magnetic field effects in the bulk sample experiments because of the good fit between the calculated and experimental NMR spectra. In the optical measurements[3] however, thin rectangular capillaries of 100μ to 300μ inner width were em-

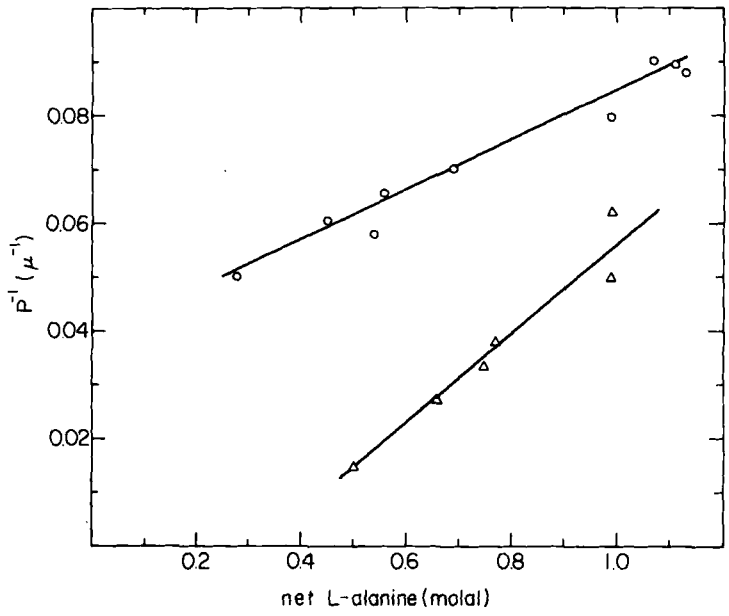

FIGURE 7 Plots of the inverse pitch versus the net *l*-alanine concentration in the cholesteric lyomesophase of DSCG-Water-alanine system. Circles correspond to results from the present work (t = 2°C), triangles to results from Ref. 3 (t = 20°C).

ployed. This range is of the order of the pitch, measured in some of the samples, and thus wall effects can be expected to influence the results. We have therefore performed several NMR measurements, of the same type as described above for the 5 mm tubes, except that thin rectangular capillaries were used in order to check possible wall effects on the alignment and structure of the cholesteric DSCG lyomesophase. As indicated above, we found no effect of sample size and shape on the measurements of D_T. However for samples with low *l*-alanine concentration a significant effect was observed on the NMR lineshape: In Figure 8 are shown examples of spectra obtained with the thin capillaries. The spectra on the left correspond to solution No. 4 of Table I, and contains 5.0 wt.% *l*-alanine. The upper trace (a) was obtained from a rectangular capillary, 0.2 mm thick, by first aligning the sample with the magnetic field parallel to the capillary's flat wall and then recording the spectrum with H perpendicular to it. The middle spectrum (b) was obtained using the reverse order: aligning the sample with H perpendicular to the flat wall and then recording the spectrum in the parallel configuration. For comparison we also show the spectrum obtained using a 5 mm sample tube (trace c), obtained by first aligning

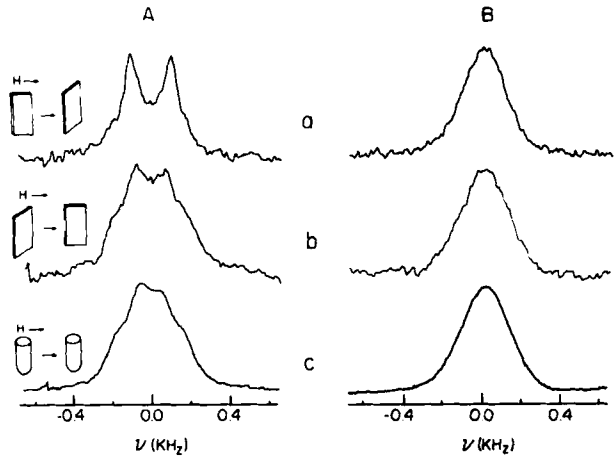

FIGURE 8 Experimental deuterium NMR spectra of the solvent D_2O in alanine-doped DSCG-Water solutions. The spectra on the left correspond to a solution containing 0.56 molal *l*-alanine while those on the right to a solution containing 1.11 molal *l*-alanine (solutions Nos. 4 and 10 in Table I respectively). The bottom traces in each series were recorded in 5 mm tubes by first aligning the samples in a magnetic field and then rotating by $\pi/2$ before recording the spectra. The two upper traces correspond to similar experiments performed on rectangular capillaries. In the upper traces the alignment was done with the magnetic field parallel to the flat wall of the sample and recording the spectra with the magnetic field perpendicular to it, while the middle traces were recorded with the reverse procedure: aligning the sample with *H* perpendicular to the flat wall and recording the spectra with the field perpendicular to it. The dimensions of the rectangular capillaries were 20 × 3 × 0.3 mm for the traces on the right and 20 × 2 × 0.2 mm for those on the left.

the sample and then recording the spectrum at the perpendicular direction. The spectra on the right describe similar experiments for solution No. 10 (containing 10.1 wt.% *l*-alanine) in rectangular capillaries of 0.3 mm thickness.

It may be seen that while traces a and b for the solution containing 10.1 wt.% *l*-alanine are essentially the same as the corresponding trace c, in the solution with lower *l*-alanine content trace b looks very much like trace c, but trace a does not. Clearly in the latter case wall effects distort the cholesteric structure of the mesophase. In this solution a pitch of 15μ (at 2°C) was determined. This corresponds to about a tenth of the capillary width (0.2 mm). For the corresponding experiment on the right hand side of Figure 8, the pitch is 11μ and the width of the capillary 0.3 mm. It appears that the director prefers to align parallel to the capillary glass wall, and of course perpendicular to the magnetic field. When the magnetic field is perpendicular to the flat walls of the capillary, a planar cholesteric structure is formed which ex-

tends from one wall to the other without any deformation. However, when the magnetic field is parallel to the capillary flat side, no simple cholesteric structure can be formed which will satisfy both the tendency of the director to be parallel to the walls and perpendicular to the magnetic field. When the pitch is sufficiently long significant distortions in the sample can be expected as is apparently observed in the upper trace (a) of solution No. 4. It is possible that such distortions are responsible in part for the discrepancy between the results obtained by optical microscopy and the magnetic resonance method.

In summary, we have shown that the magnetic resonance method described above, which combines translational self-diffusion measurements and effective director reorientation, provides a very useful method for determining pitch in bulk cholesteric samples.

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References

1. J. S. G. Cox, G. D. Woodard and W. C. McCrone, *J. Pharm. Sci.*, **60**, 1458 (1971).
2. N. H. Hartshorne and G. D. Woodard, *Mol. Cryst. Liq. Cryst.*, **23**, 343 (1973).
3. H. Lee and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, in press.
4. D. Goldfarb, M. M. Labes, Z. Luz and R. Poupko, *Mol. Cryst. Liq. Cryst.*, in press.
5. P. J. Collings, T. J. McKee and R. McCall, *J. Chem. Phys.*, **65**, 3520 (1976).
6. Z. Luz, R. Poupko and E. T. Samulski, *J. Chem. Phys.*, **74**, 5825 (1981).
7. Z. Yaniv, G. Chidichimo, N. Vaz and J. W. Doane, *Phys. Lett.*, **86A**, 297 (1981).
8. N. Kamezawa, *J. Mag. Res.*, **21**, 211 (1976); **27**, 325 (1977).
9. M. E. Moseley and A. Loewenstein, *Mol. Cryst. Liq. Cryst.*, submitted.
10. E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, **42**, 288 (1965).
11. R. Mills, *J. Phys. Chem.*, **69**, 3116 (1965).
12. G. Karakostas and D. Moroi, *Phys. Lett.*, **87A**, 101 (1981).
13. L. G. Longworth, *J. Phys. Chem.*, **64**, 1914 (1960).
14. R. Mills, *J. Phys. Chem.*, **77**, 685 (1975).