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Visualization of enantiomers through deuterium NMR in cholesterics Optimization of the chiral liquid crystal solvent

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Thermotropic cholesteric liquid crystals made of mixtures of cholesteric esters and of a $\Delta\chi<0$ nematic (ZLI 2806) may be used as NMR solvents to visualize enantiomers. Proton decoupled deuterium NMR spectra of a racemic mixture show that the quality of the spectra strongly depends on the temperature and on the nature and the concentration of the ester. A relationship between the spectral resolution and the presence of textural defects in the mesophase is also discussed. The best results, both for spectral resolution and enantiomeric separation, were obtained with a 45/55 by weight mixture of cholesteryl butyrate and ZLI 2806 at 368 K.

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1. Introduction

We have recently reported [1] that it is possible to visualize enantiomers through deuterium NMR in a thermotropic cholesteric liquid crystal solvent. This differentiation originates in the fact that, in such an anisotropic chiral medium, the molecular order parameters for each of two enantiomers, can be different. This is the reason why we named this phenomenon the differential ordering effect of enantiomers.

The quadrupolar splitting, $\Delta\nu_Q$, is the largest anisotropic interaction in deuterium NMR. Because it depends on the molecular order parameters, a difference of order induces different quadrupolar splittings for each enantiomer. The expression for $\Delta\nu_Q$ is

$$\Delta\nu_Q = \frac{1}{2I(I+1)} Q_C[3S_{aa} + \eta(S_{bb} - S_{cc})],$$

where Q_C is the quadrupolar coupling constant, η is the asymmetry parameter of the quadrupolar coupling tensor and $S_{ii} = \frac{1}{2}\langle 3\cos^2\theta_1^i - 1\rangle$ are the order parameters of the principal axes a, b and c of the electric field gradient at the deuterium site.

However, to distinguish between enantiomers with small differences in their $\Delta\nu_Q$ values, the cholesteric solvent must be homogeneously oriented in the magnetic field H_0, so that the deuterium spectra show distinct pairs of peaks instead of overlapping powder patterns. Pure cholesterics are known to exhibit thermodynamically stable textural defects [2], disturbing the molecular orientation. Generally, magnetic fields used in NMR are not high enough to overcome these kinds of defects, thus hindering the achievement of high resolution NMR spectra. Visualization of enantiomers in such solvents requires the preparation of a cholesteric phase that is as homogeneous as possible and free of textural defects.

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To obtain a useful cholesteric NMR solvent, we have selected the following characteristics:

(i) The cholesteric phase must have a negative anisotropy of the diamagnetic susceptibility to align the helix axis to lie parallel to the magnetic field [3].
(ii) The phase must be as fluid as possible to allow fast molecular tumbling.
(iii) The pitch of the solvent must be as large as possible, because the helicity is the main hindrance to a good orientation.
(iv) The solvent must be cholesteric over a large temperature range in order that the molecules dissolved in the phase do not alter the liquid crystal properties too much.

The four above remarks grouped together have guided us to select cholesterol derivatives in the form of halides and esters (see figure 1) as the chiral solvent. In order to increase the fluidity of the solvents and the liquid crystal temperature range (figure 2), these derivatives have been mixed with a nematic material (ZLI 2806 purchased from E. Merck) consisting of a eutectic mixture of cyanobicyclohexyl derivatives (see figure 1). The purpose of the following study is to look for the mixture that allows one to obtain the best NMR enantiomeric separation when used as a solvent.

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2. Experiments and results

The first experiments were realized with a mixture made of a 60/40 ratio by weight of cholesteryl iodide and ZLI 2806; this derivative of cholesterol is known to induce a very weak helicity when mixed with a nematic (intrinsic pitch $\approx 33\,000$ Å [4]). With this solvent, the deuterium spectra were well resolved with a linewidth of 8 Hz in the deuterium NMR, but the time required for a good orientation in the magnetic field was very long (4 to 5 hours) and the observed differences in the quadrupolar splitting between enantiomers were very small. Cholesteryl chloride and bromide gave similar results [5]. Thus it appears that the helicity of the mixture does not really influence the

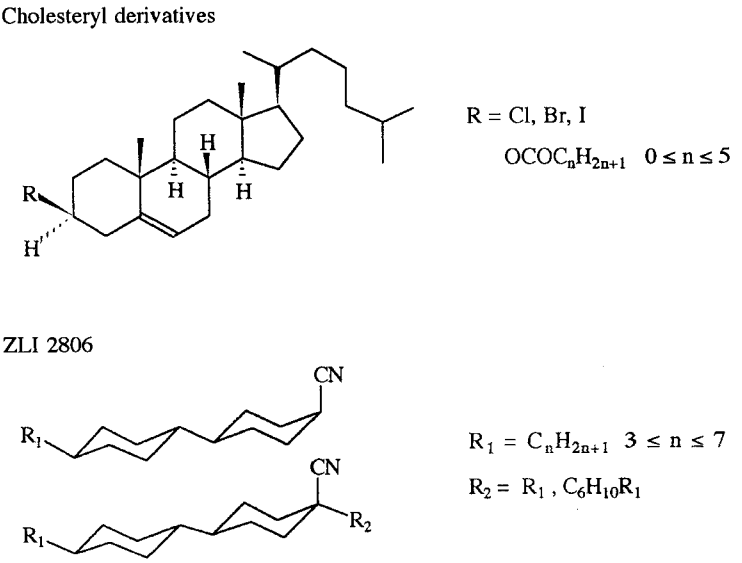

Figure 1. Cholesteryl derivatives and ZLI 2806.

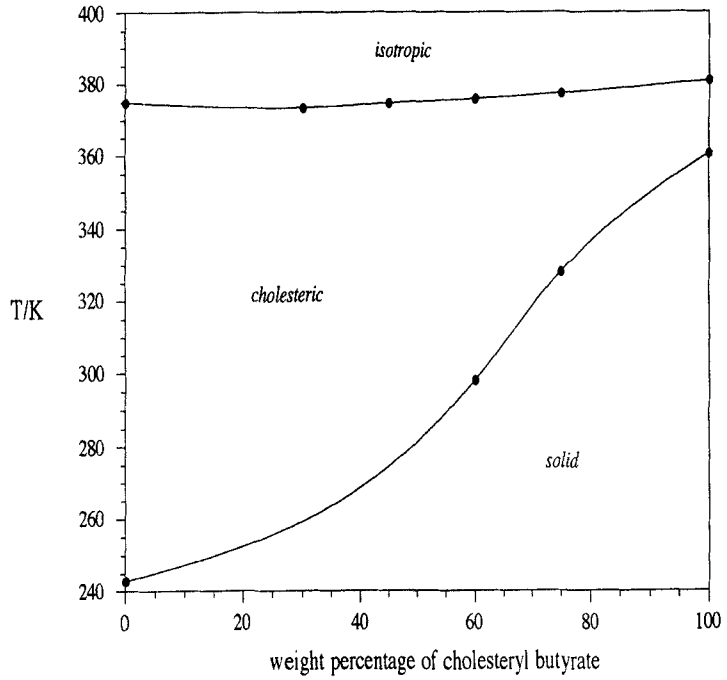

Figure 2. Phase diagram for the mixtures made of cholesteryl butyrate and ZLI 2806. The transition temperatures have been obtained from DSC measurements.

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orientational quality, because cholesteryl chloride (pitch $\approx$ 3400 Å) and bromide (pitch $\approx$ 4200 Å) [6] have much stronger twisting powers than the iodide. In these three cases, the necessary times for obtaining a good orientation of the sample, and consequently a high resolution spectrum, are about the same, and much too long to be useful.

On the other hand, the first experiments using a mixture involving a 44/56 molar ratio of cholesteryl propionate and ZLI 2806 also gave good NMR high resolution spectra, and this mixture only required very short orientation times (around 1 min) [5]. Therefore, to optimize the NMR solvent, we prepared mixtures of cholesteryl esters, from the formate to the hexanoate, with ZLI 2806 in different relative concentrations. The test molecule used was the 1-deuterio-1-(2-methylphenyl)ethanol, a material that exhibits a large enantiomeric separation. Its concentration was 3 per cent by weight in each sample.

In order to compare all the spectra, we define a quality factor F. According to the principle that a better NMR solvent gives a larger difference in the quadrupolar splittings between enantiomers ($\Delta\nu_Q^S - \Delta\nu_Q^R$), and a smaller half sum of the transitions linewidth $\Delta\nu_{1/2}^S$ and $\Delta\nu_{1/2}^R$, we define F as

$$F = \frac{|\Delta\nu_Q^S - \Delta\nu_Q^R|}{\frac{1}{2}(\Delta\nu_{1/2}^S + \Delta\nu_{1/2}^R)}.$$

Thus the larger F is, the better is the solvent.

For each mixture, the variation of the quality factor, F, with temperature has been studied. In figure 3, the results obtained for the best mixture of each ester are shown.

The analysis of this graph leads to the following conclusions:

(i) The largest quality factor is obtained for a mixture of cholesteryl butyrate and ZLI 2806 in a 45/55 ratio by weight at 368 K. The temperature is critical.

(ii) The quality factors are always higher for esters possessing an extended chain with an even number of carbon atoms rather than an odd number. This recalls the well-known even–odd effect in liquid crystals.

(iii) The mixture made of 60 per cent of cholesteryl propionate and 40 per cent of ZLI 2806 also exhibits a good quality factor. Although its F value is not as high as the maximum value for the butyrate mixture, it has a broader cholesteric temperature range which can make this mixture easier to use.

To correlate these results obtained with the different experimental parameters (nature of the ester, concentration, temperature), the dependence of the difference in the quadrupolar splittings, $|\Delta\nu_Q^S - \Delta\nu_Q^R|$, and the dependence of the averaged linewidth, $\frac{1}{2}(\Delta\nu_{1/2}^S + \Delta\nu_{1/2}^R)$ on the temperature are represented in figures 4(*a*) and (*b*).

The difference in the quadrupolar splittings, $|\Delta\nu_Q^S - \Delta\nu_Q^R|$, increases almost linearly with the concentration of cholesteryl ester but, obviously, does not depend on the nature of the ester. Meanwhile, for the same ester concentration (i.e. 45 per cent), the averaged linewidth is strongly modified by the ester used. Thus it appears that the quality factor variation is mainly due to the evolution of the averaged linewidth.

In order to show that the NMR resolution is linked to the presence of textural defects in the phase, we have examined different mixtures of cholesteryl butyrate–

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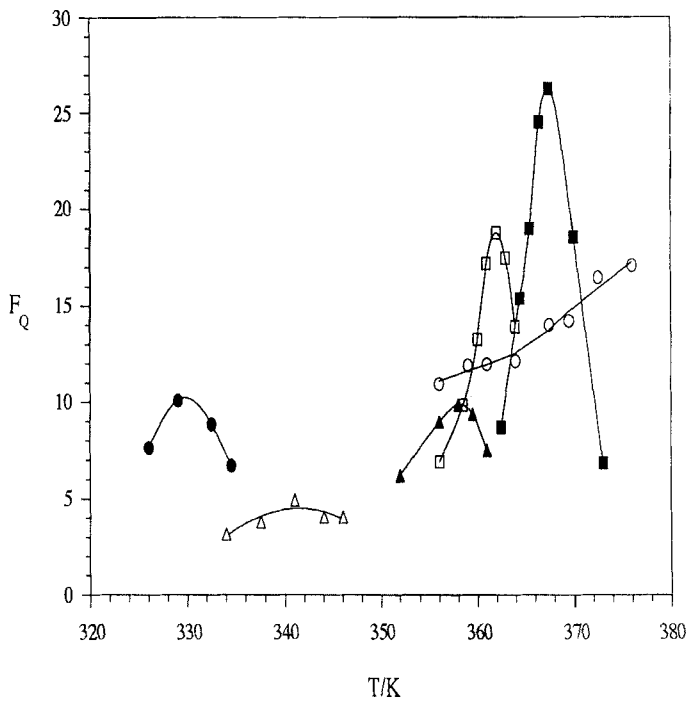

Figure 3. Temperature evolution of the quality factor F of the best mixture of each ester. (●), Ch–formate 80 per cent; (□), Ch–acetate 70 per cent; (○), Ch–propionate 60 per cent; (■), Ch–butyrate 45 per cent; (▲), Ch–valerate 45 per cent; (△), Ch–hexanoate 45 per cent.

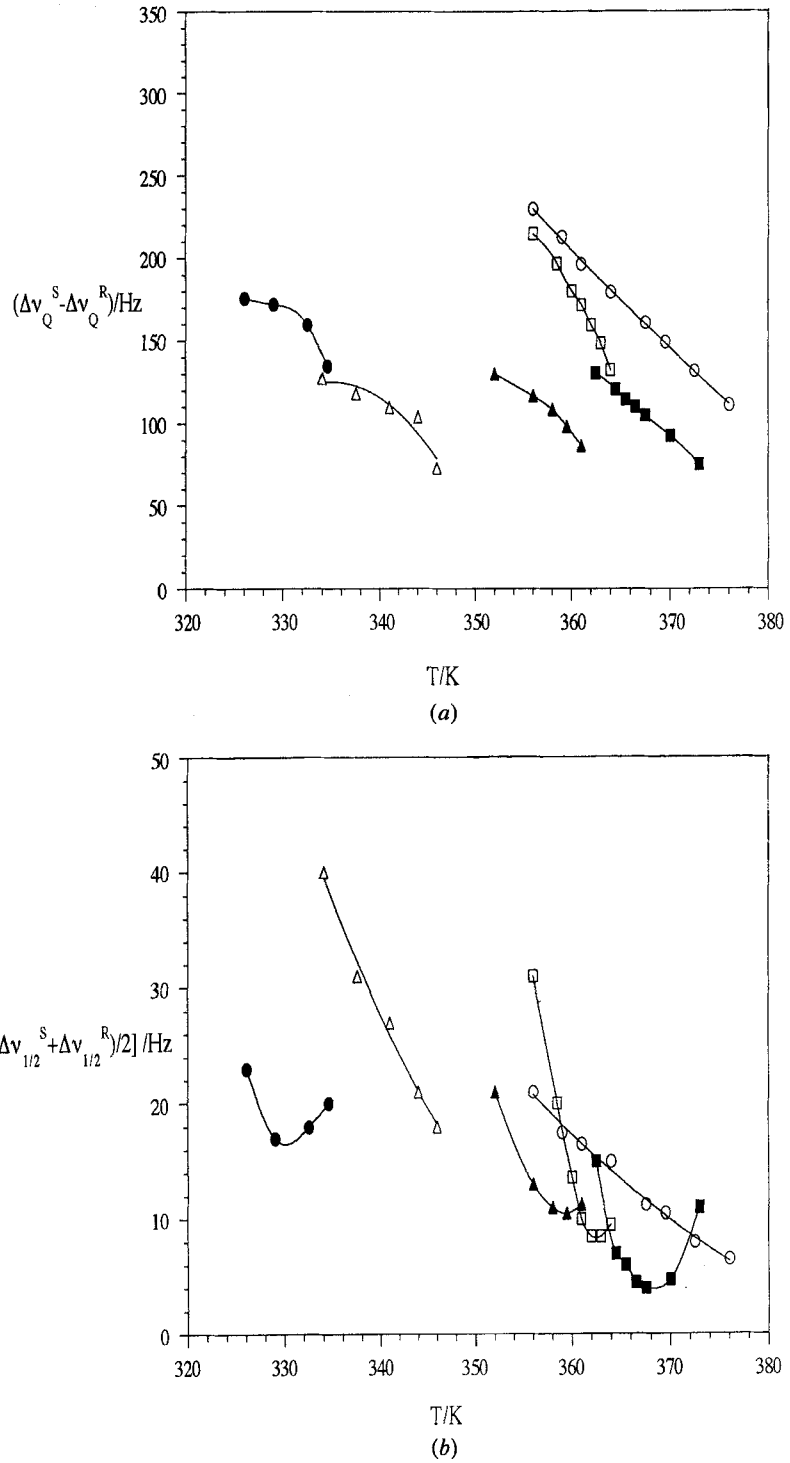

Figure 4. (*a*) Temperature evolution of the difference in the quadrupolar splittings between the enantiomers dissolved in the different mixtures. (*b*) Temperature evolution of the averaged linewidth. Ester abbreviations and symbols as in the legend to figure 3.

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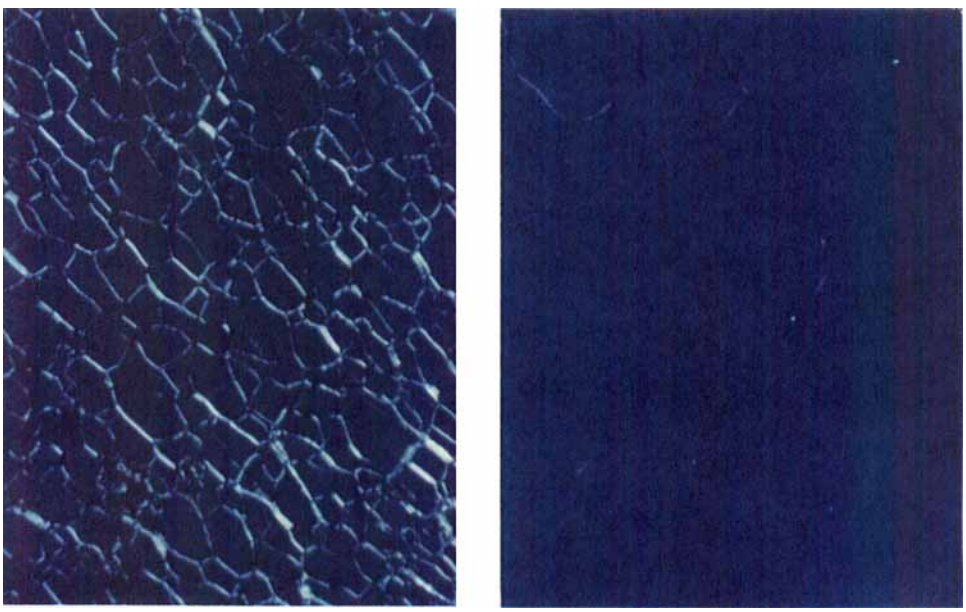

(*a*) (*b*)

Figure 5. Photomicrographs of the textures obtained by polarizing microscopy for the cholesteric phases of (*a*) pure cholesteryl butyrate, and (*b*) a mixture of cholesteryl butyrate (45 per cent) and ZLI 2806 (55 per cent).

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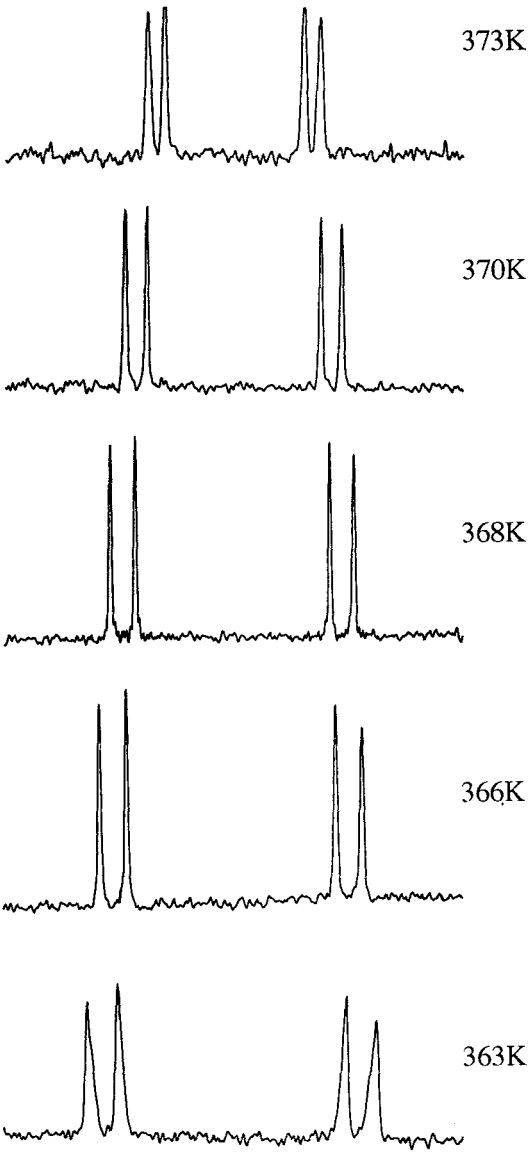

Figure 6. Temperature evolution of the proton decoupled deuterium NMR spectrum of 1-deuterio-1-(2-methylphenyl)ethanol in the mixture of 45/55 per cent by weight of cholesteryl butyrate and ZLI 2806.

ZLI 2806 using polarizing optical microscopy. As shown in figure 5, the number of textural defects decreases dramatically from pure butyrate to the 45/55 per cent by weight mixture of cholesteryl butyrate and ZLI 2806, where only very few strings of focal-conics remain. This absence of textural defects is shown by the noteworthy quality of the NMR spectrum (see figure 6). Regarding the origin of this absence of textural defects, one possible answer could be that the signs of some viscoelastic coefficients of the components of the mixture are different, leading therefore to near-zero values for these coefficients at a particular temperature and concentration.

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3. Conclusions

The work described here has permitted us to optimize a cholesteric solvent that gives a good enantiomeric separation through high resolution proton decoupled deuterium NMR. It is made of a 45/55 per cent by weight ratio of cholesteryl butyrate and ZLI 2806. This mixture exhibits very few textural defects at 368 K. The quality of the spectra seems to be closely related to these defects. This solvent allowed us to visualize the resolution of a large number of chiral deuteriated compounds by NMR. A study of other cholesteric phases is presently underway in this laboratory in order to improve the spectral quality further.

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