

Ph.D. Thesis

“STRUCTURE, ORIENTATIONAL ORDER AND DYNAMICS OF ROD-LIKE AND BANANA-SHAPED LIQUID CRYSTALS BY MEANS OF ^2H NMR: NEW DEVELOPMENTS”.

By Valentina Domenici

Abstract

The field of liquid crystals (*LCs*) is for me one of the most fascinating aspects of the Science of Materials, on the other hand, Nuclear Magnetic Resonance (*NMR*) represents a very powerful spectroscopy for the large amount of possibilities in performing and projecting new experiments, with the purpose of enlightening both the molecular structure, orientational ordering and dynamics of single molecules.

My Ph.D. research mainly focused on investigating the dynamics of *thermotropic LCs* and the structural properties of a new class of *LCs* called *banana shaped LCs* by means of ^2H *NMR*.

Among the different techniques, *NMR* is probably the most complete to study the dynamics of *LCs*. A detailed overview, including the experimental pulse sequences and theoretical models needed to describe molecular and collective motions, is presented in chapter 1.

The dynamics of rod-like *LCs* in their uniaxial phases, such as the *SmA*, has been investigated by analysing ^2H spin-lattice relaxation times in terms of appropriate diffusional models. These studies, mainly performed in our group in Pisa and in the group of prof. R.Y. Dong in Brandon, Canada, resulted in tens of papers and in a review. Some of the more recent studies have revealed a quite critical problem in determining the diffusion coefficient for the tumbling motions, namely D_{\perp} .

In my thesis this indetermination has been investigated in detail, showing how it depends on the quality and dimensions of the available set of experimental data. Several cases have been investigated and the relaxation data, that have been examined by using an appropriate software developed during my stay in Pisa, guaranteeing a good control on the fitting analysis, are presented and discussed in chapter 2.

Another way to overcome the indeterminacy of D^{\wedge} is to fix some parameters according to the results obtained by means of other spectroscopies. To this aim, 2H NMR relaxation times and Dielectric Relaxation (*DR*) measurements have been quantitatively compared for the first time in this thesis. The advantage is that both spectroscopies allow to access dynamic information on a broad range of frequencies, from low to high frequencies, although the relation between the measured quantities and the molecular properties are not always straightforward in the case of *DR*. For this reason the comparison between *NMR* and *DR* represented an important way to test the theoretical models used to analyse experimental relaxation times, as widely discussed in chapter 3.

Although the sole uniaxial phases have been considered in the discussion so far, one of the most interesting phases in the field of thermotropic LCs is the SmC*, namely the ferroelectric phase, which is biaxial. However, the lack of suitable theoretical models for biaxial phases prevented the analysis of relaxation data in ferroelectric LCs (*FLCs*). In this thesis a new theoretical approach to the analysis of deuterium spin-lattice relaxation times in the SmC* phase and its application to several sets of data for different *FLCs* is reported and discussed in chapter 4.

The interest of these results is connected with the use of ferroelectric systems in LC-Display, Photonics and Laser technology of new generation. In fact, the fast switching properties of *FLCs* in presence of electric and magnetic fields which represent one of the most interesting properties of these materials could be correlated with the very fast reorientation motions, encountered in all the cases examined.

Related to my attention to the rapid development in the field of LC materials through new molecular and macromolecular systems is the choice to study the recently discovered *banana-shaped LCs* by means of 2H NMR, which had not been used so far. The interest on these samples is related to some electrooptical properties, which could be used for new technological applications and, in conjunction with polymeric matrices, to projecting bio-inspired materials. An overview of the literature on the mesophases formed by banana-shaped molecules is presented chapter 5.

Even the isotropic phase of banana compounds turned to be very unusual. This is the central topic of chapter 6, where the 2H NMR line-width trend in the isotropic phase of two banana mesogens has been discussed together with a theoretical interpretation of spin-spin relaxation times (T_2). This

study shows that the dynamics of banana compounds is particularly slow and an explanation of this behaviour in terms of molecular hinderings, which is in agreement with other recent experimental results, is discussed.

Among the still hardly characterizable properties of the mesophases formed by these compounds, the origin of chirality attracted my attention and that represented the input to try to give a contribution by using 2H NMR. I focused my attention on two banana-shaped mesogens, only differing for one substituent on the central ring (a Chlorine atom in the place of an Hydrogen). A quite interesting aspect of these compounds is the sensitivity to single substitutions, in fact the presence of a chlorine atom determines the occurrence of a nematic phase and the disappearance of a typical banana mesophase (B₂). A complete study of molecular structure and orientational ordering properties have been performed for the Chlorinate compound in its nematic phase, by comparing 2H , ^{13}C NMR and Quantum mechanical calculations. Studying the nematic phase of banana-shaped molecules revealed to be very interesting, since this phase seems to have several peculiarities with respect to the *usual* nematic phases, on either orientational order and phase symmetry or dynamic behaviour, as it's shown in chapter 7.

According to this study the question of chirality of banana compounds is related to the rigid core of the molecules. Several works have been published proposing *propeller-like* conformations for the central rigid cores of these molecules, but the differences in energy between planar and twisted conformations are not very significant. We choose to follow a different approach, studying the conformational attributes of typical banana sub-units with much more details. The well known method consisting in analysing 2H NMR spectra of deuterated probes dissolved in LCs was used, where probes had the same molecular structure of banana cores, and LC solvents were nematic and banana-like. This work was presented in chapter 8.