Nuclear magnetic resonance: a powerful tool to study liquid crystals

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ABSTRACT
Nuclear magnetic resonance (NMR) is a spectroscopic technique widely used to investigate materials and soft matter in particular. In this brief review, the main uses of NMR techniques to investigate different aspects of liquid crystals, such as the orientational and dynamic properties, the supramolecular structure and average molecular conformations, are described. In the second part of the paper, the case study of a 'de Vries' liquid crystal is reported and the main results obtained by combining different NMR techniques are discussed.

1. Introduction
Nuclear magnetic resonance (NMR) is a spectroscopic technique widely used to investigate materials. Since the discovery of NMR in 1945, there were an increasing number of techniques and applications to study different aspects of materials with physical, chemical, biological and medical interest. The relationship between NMR and partially ordered systems, mainly liquid crystals, was a great stimulus for the development of specific NMR methods focused on the anisotropic contributions of the interactions at the basis of NMR signal detection. The first study was performed in 1963 by Saupe and Englert [1], by using a nematic phase to orient small molecules, while the first observation of orientational order in nematics oriented in a relatively strong magnetic field was carried out by Lohman and MacLean only in 1978 [2].

To give an idea of the impact of NMR spectroscopy in the field of liquid crystals, a simple search of papers and books can be performed, for instance, by accessing commonly used databases, such as Scopus or Web of Science, as well as scientific archive platforms, such as Google Scholar. An example of simple search is here reported. In Figure 1, the trend of peer-reviewed manuscripts and reviews dealing with liquid crystals published in the last 50 years is shown. Only papers having ‘Liquid Crystal’ in the title have been considered, thus giving a representation in deficit. Only papers reported in the Web of Science database, from January 1967 up to now, have been included in this search. For a better visualisation, data are grouped in 5 decades. The trend of papers dealing with liquid crystals is clearly increasing, starting from 2525 papers published in the first decade (1967–1976) to 23782 published in the last decade (2007–2016).

Among these papers, those ones based on NMR spectroscopy as ‘main experimental technique’ are also reported in Figure 1 (see the red line). In this case, the trend of published papers has a sort of plateau in the central decades (1987–2006), which correspond to the period of the maximum development of novel NMR techniques, followed by a slow decrease in the recent years. The number of papers having ‘NMR’ in the title, in addition to ‘Liquid Crystal’, represents about 2–5% of the total papers dealing with liquid crystals, which is a relatively small percentage. This is because NMR is not a routinely experimental technique, but a more specialist one. In fact, the role of NMR in the field of liquid crystal cannot be just quantified in terms of number of papers, but from their impact to solve specific open questions or unsolved issues, as described in the following sections.

2. NMR basic principles and applications to study liquid crystals
NMR papers and reviews can be classified based on the magnetic nucleus (or nuclei) under investigation. The most studied magnetic nuclei are $^1\text{H}$ and $^{13}\text{C}$, which are typically observed throughout ‘liquid state’ or ‘solution’ NMR techniques in organic compounds, mainly to characterise their chemical composition and purity. In the liquid state, the NMR signal is due to the Zeeman interaction ($H_Z$), corrected by the chemical shielding effect described by the shielding constant, $\sigma$, and to the indirect spin–spin coupling contribution ($H_J$),...
describing the interaction between two neighbouring nuclei.

In liquid crystals, the presence of anisotropy opens up to many different applications of NMR. In this case, in fact, there are other potential contributions to the NMR signal: the direct dipole–dipole interactions \( (H_D) \), due to the dipolar coupling between two spatially neighbouring nuclei, and the quadrupolar interaction \( (H_Q) \) typical of quadrupolar nuclei (with a magnetic spin \( I > 1/2 \)).

In the general case, the total Hamiltonian determining the NMR signal can be written as:

\[
H = H_Z + H_J + H_D + H_Q,
\]

where, in anisotropic systems, the different terms assume a tensorial expression of different complexity depending on the symmetry of the mesophase and on the nuclear spin system. A detailed description of these terms is out of the scope of this brief review, and a comprehensive explanation can be found in many books and reviews on NMR of liquid crystals, such as those reported in references [3–7].

In addition to \(^1\)H and \(^{13}\)C nuclei, another magnetic nucleus widely investigated is deuterium \(^2\)H), which is a quadrupolar nucleus. The limitation related to the very low natural abundance of \(^2\)H was often overcome by synthesising selectively deuterated liquid crystals. When a liquid crystalline molecule is selectively deuterated, the resulting \(^2\)HNMR spectrum is relatively simple, but rich of information, as shown for instance in this review about \(^2\)H NMR studies on liquid crystalline elastomers [8]. More than 30% of the total number of NMR papers dealing with liquid crystals, in fact, contain \(^2\)H NMR experiments (see Figure 2 (a)). Recent advancements in the field of liquid crystals, such as the understanding of the director reorientational behaviour in nematic phases in presence of the electric field [9], the explanation of the supramolecular structure of the twisted nematic phase [10].

Figure 1. Trend of papers with ‘Liquid Crystal’ in the title published in the last 50 years (blue histograms) and trend of papers including in the title ‘NMR’ and ‘Liquid Crystal’ (red line). Data are from the ISI Web of Science database (at 10 June 2016).

Figure 2. Number of papers having the words ‘NMR’ and ‘Liquid Crystal’ in the title published in the last 50 years (a) and in the last 10 years (b). Papers are here divided on the basis of the nuclei investigated: only \(^1\)H NMR (H-1), only \(^{13}\)C NMR (C-13), only \(^2\)H NMR (H-2), both \(^1\)H and \(^2\)H NMR (H-1 & H-2), both \(^1\)H and \(^{13}\)C NMR (H-1 and C-13), both \(^2\)H and \(^{13}\)C NMR (H-2 and C-13), a combination of \(^1\)H, \(^{13}\)C and \(^2\)H NMR (H1, C13 and H2) and other nuclei (data set from ISI Web of Science, at 10 June 2016).
or the development of new techniques used to discriminate between chiral enantiomers [11] were possible thanks to $^2$H NMR studies. Other nuclei that contributed to investigate different properties of liquid crystals are, for instance, $^{129}$Xe [12], $^{19}$F [13], $^{23}$Na [14], $^{15}$N [15] and $^{14}$N [16]. Papers focused on these nuclei represent more than 33% of total papers published in the last 50 years (see Figure 2(a)).

An interesting observation is related to the number of papers in which a multinuclear approach (such as a combination of $^2$H and $^{13}$C NMR techniques) is used. In the last 10 years, in fact, the multinuclear approaches were applied more than in the past (see Figure 2(a) and (b)). Some recent examples of original studies applying multinuclear approaches are reported in references [17–20].

The description of the physical principles of NMR techniques applied to liquid crystals is out of the scope of this brief review. For all these aspects, there are a great number of reviews, chapters and books (see, for instance, references 3–8). However, a simplified description of the main techniques used to investigate different aspects of liquid crystalline materials could be of interest for a larger audience.

Figure 3 is a conceptual map describing the main uses of NMR techniques to explore the conformational, the orientational and the dynamic properties, as well as the details of the structural features of the various mesophases formed by liquid crystals.

The conformational properties of liquid crystalline molecules in their mesophases are commonly investigated by analysing the temperature dependence of $^{13}$C NMR chemical shift isotropy and chemical shift anisotropy (CSA) contributions, as well as $^{129}$Xe NMR chemical shift trend. For relatively simple molecules, more sophisticated approaches imply the combination of predictive atomistic molecular dynamics (MD) simulations and proton liquid crystal nuclear magnetic resonance (LXNMR) residual dipolar coupling measurements, as reported in this recent paper [21].

One of the most interesting properties of liquid crystals, namely, the phase and molecular orientational order can be obtained by analysing the temperature dependence of the $^2$H quadrupolar splittings [22] or the trend of $^1$H–$^{13}$C NMR dipolar splitting obtained by the separated local field (SLF) or the proton-detected local field (PDLF) NMR experiments [23]. In case of fluorinated compounds, $^{19}$F is also a useful nucleus to investigate.

The analysis of the spectral shape of $^2$H NMR spectra of liquid crystals provided an excellent and powerful method to investigate the supramolecular structure of liquid crystals, such as in frustrated phases (TGBA, TGBC* and so on) [24] and ferroelectric (SmC*) phases [25].
Dynamic properties, such as molecular reorientational diffusion, translational self-diffusion and collective motions are mainly investigated by specific NMR approaches, such as NMR diffusometry [26] and NMR relaxometry [27] (which requires specific equipment), or by analysing the spin–spin ($T_2$) and spin–lattice ($T_1$) relaxation times (mainly $^1$H and $^2$H) through specific models [28–30]. In few cases, for instance if molecules are distributed in not homogeneously aligned structures, 2D exchange NMR methods can also be applied [31].

In order to give the feeling of what can be done by combining different NMR methods, the case study of a ‘de Vries’ compound is reported in the following section.

3. A case study: a ‘de Vries’ liquid crystal investigated by means of several NMR techniques

One recent hot topic in liquid crystals is related to ‘de Vries’ liquid crystals and the relationship between their molecular and physical properties [32]. In this respect, NMR gave a contribution with several studies [18,27,33,34] performed on a rod-like ‘de Vries’ compound, namely 9HL (see Figure 4). One of the most fascinating properties of ‘de Vries’ systems is the absence of layer-shrinkage at the SmA–SmC* transition, coupled with a high response to the electric field in the SmA phase, the so called electroclinic effect. Other interesting effects and properties were discovered in several new ‘de Vries’ systems, but few details about the molecular organisation within the ‘de Vries’ SmA phase were known. This was one of the main motivations of applying NMR techniques to investigate ‘de Vries’ liquid crystals.

3.1. $^2$H NMR investigations of the local orientational order in a ‘de Vries’ liquid crystal

The first NMR work on 9HL was performed on a selectively deuterated compound with two equivalent deuterons on a phenyl ring of the aromatic core [33], as reported in Figure 4. $^2$H NMR spectra were recorded by varying the temperature from the isotropic to the SmC* phase and, due to the presence of a single type of deuterons, the spectra are extremely simple (see Figure 4). In the isotropic phase, the $^2$H NMR spectrum is characterised by a single peak, due to the Zeeman interaction. In the SmA and SmC* phases, the anisotropy is at the origin of the typical spectral shape, constituted by a large doublet, $\Delta \nu_q$ ranging from ~13.5KHz to ~17.5KHz (due to the $^2$H quadrupolar interaction) that further splits in a small doublet, $\Delta \nu_d$ ranging from ~1.1KHz to ~1.8KHz (due to the $^1$H–$^2$H dipolar interaction) [33].

The relationships among the measured quadrupolar, $\Delta \nu_q$, and dipolar, $\Delta \nu_d$, splittings and the molecular orientational order parameters, $S_{ij}$, are in general quite complex; however, in this case, several approximations can be introduced. For instance, in the NMR time scale, we can assume that the whole molecule is uniaxial. This

![Figure 4](https://example.com/figure4.png)

**Figure 4.** On the right, structure of the deuterated molecule of 9HL superimposed to the reference axes frames: the principal axes system (PAS) frame $(a,b,c)$, the phenyl axes system (PHE) frame $(x,y,z)$ and the Laboratory system (LAB) frame $(X_{LAB}, Y_{LAB}, Z_{LAB})$. On the left, Series of $^2$H NMR spectra from the isotropic to the SmC* phases obtained on the deuterated 9HL sample at a magnetic field of 7.05 T. The typical dipolar ($\Delta \nu_d$) and quadrupolar ($\Delta \nu_q$) splittings are displayed. Picture is modified from reference [33]. Reprinted by permission of John Wiley & Sons, Inc.
is also justified by the fast reorientational motions affecting the 9HL molecules, as shown in Section 3.4.

A geometrical relation can be easily found between the quadrupolar principal axes system (PAS) frame (a,b,c) and the local phenyl axes system (PHE) frame (x,y,z) (see Figure 4).

All this considered, the measured quantities, \( \Delta \nu_d \) and \( \Delta \nu_q \), can be related to the local orientational order parameters, \( S_{zz} \) and \( \Delta = S_{xx} - S_{yy} \), referred to the deuterated aromatic ring, through the following equations [22]:

\[
\Delta \nu_d = -2K_{DH} \frac{S_{zz}}{r_{DH}^3} \quad \text{(2)}
\]

and

\[
\Delta \nu_q = \frac{3}{2} q_{aa} \left[ S_{zz} \left( \cos^2 \phi - \frac{1}{2} \sin^2 \phi - \frac{\eta}{6} \cos^2 \phi + \frac{\eta}{6} + \frac{\eta}{3} \sin^2 \phi \right) + \Delta \left( \frac{1}{2} \sin^2 \phi + \frac{\eta}{6} \cos^2 \phi + \frac{\eta}{6} \right) \right], \quad \text{(3)}
\]

where \( K_{DH} \) and \( r_{DH} \) are the dipolar coupling constant, equal to 18,434.4 Hz Å\(^3\), and the distance between the deuteron nucleus and the proton in ortho position equals to 2.5 Å. Moreover, \( q_{aa} \) and \( \eta \) are the quadrupolar constants for aromatic deuterons, equal to 185 KHz and 0.04, respectively, while the angle \( \phi \) is fixed to 60°, by assuming that the geometry of the phenyl ring is hexagonal.

The analysis of the temperature dependence of the quadrupolar and dipolar splittings through the above equations allowed us to obtain the temperature dependence of the local order parameter \( S_{zz} \) within each mesophase, that is, the SmA and the SmC*, and the average value of the local biaxiality of the deuterated phenyl moiety.

The analysis of the spectra recorded at 7.05 T (Figure 4 and ref [33]) showed a behaviour very similar to common ferroelectric smectogens [35]. In particular, we noted an increasing tilt angle in the SmC* phase by decreasing the temperature and a SmA–SmC* transition showing a sudden change in the local order parameter and/or the relative tilt of the deuterated phenyl ring with respect to the phase director. These findings were apparently not consistent with other experimental results obtained on the same molecular system.

### 3.2. \(^2\)H NMR investigations at different magnetic fields to get information about the supramolecular structure of the ‘de Vries’ phase

A determinant contribution to understand the supramolecular properties of the 9HL in the SmA and in the SmC\(^*\) phases, came from the \(^2\)H NMR study at several magnetic field strengths [33,34]. In fact, as reported in Figure 5, different behaviours were observed in the two mesophases by increasing the magnetic field.

In the SmA phase, a very unusual magnetic field dependence of the orientational order \( S_{zz} \) was observed, thus indicating a sort of magnetoclinic

![Figure 5. Trends of the main order parameter, Szz, of the sample 9HL, as obtained by analysing \(^2\)H NMR spectra recorded at different magnetic fields (4.25 T, 7.05 T, 11.75 T, 16.45 T and 18.80 T). A sketch of the mesophase structure in different cases is also shown.](image-url)
effect [33], similarly to the electroclinic one. This behaviour was explained by recurring of a new model for the ‘de Vries’ SmA phase, the so-called cluster cone model in analogy with the diffuse cone model [36]. Within this model, the supramolecular structure of the ‘de Vries’ SmA phase can be represented as parallel layers of tilted molecules (with an average tilt θ with respect to the layer normal, similarly to the SmC* phase) grouped in clusters having a short-term correlation (i.e. with the same azimuthal angle, ψ). By increasing the magnetic field strength, the clusters are partially deformed, the layers tilt with respect to the magnetic field while the molecules are aligned along this direction.

In the SmC* phase, the 9HL behaviour at increasing magnetic field strength is similar to common rod-like ferroelectrics [37]. Below a critical value of the magnetic field, \( H_c \), the helical structure is preserved, the helical axis of the SmC* domains is parallel to the magnetic field, and the molecules are tilted. This is at the origin of the apparent decreasing of the local order parameter, \( S_{zz} \), observed at 11.75 T, 7.05 T and 4.25 T. Above the critical field, the SmC* phase supramolecular structure is unwound and the 9HL molecules are aligned along the magnetic field direction. This is the explanation of the increasing trend of \( S_{zz} \) observed in 9HL at 16.45 T and 18.80 T by decreasing the temperature from the SmA to the SmC* phases.

All the above results, however, refer to a particular moiety of the 9HL compound: the deuterated phenyl ring in the aromatic core. The following questions then arise: can we infer these findings to the whole molecule? What is the behaviour of the whole molecule?

### 3.3. \(^{13}\text{C}\) and \(^1\text{H}\)–\(^{13}\text{C}\) NMR experiments to study the conformational properties of a ‘de Vries’ liquid crystal

In typical rod-like liquid crystals, the orientational properties of the aromatic core are usually assumed to be comparable to those of the whole molecule [22]; this approximation can be accepted in particular when the aromatic core is rigid. In the case of 9HL, the aromatic core is constituted by three phenyl rings connected each other by ester groups. The rigidity of the three-ring moiety is not obvious, but further NMR investigations can help solve this point.

Multinuclear NMR experiments of 9HL in the isotropic, in the liquid crystalline phases and in the solid state were performed [18] starting from the assignment of the carbons of the 9HL through a combination of 2D NMR experiments (\(^1\text{H}\)–\(^{13}\text{C}\) HETCOR, \(^1\text{H}\)–\(^{13}\text{C}\) PDLF and \(^{13}\text{C}\)–\(^{13}\text{C}\) INADEQUATE). The combination of these techniques allowed us the determination of the isotropic \( \delta_{iso} \) and anisotropic \( \delta_{aniso} \) components of the \(^{13}\text{C}\) chemical shift \( \langle \delta \rangle \) for each carbon site of the aromatic core.

These quantities are related to the local orientational order parameters, \( S_{zz} \) and \( \Delta = (S_{xx} - S_{yy}) \), defined for each phenyl ring of the core, according to the following equation:

\[
\delta_{aniso} = \langle \delta \rangle - \delta_{iso} = \frac{2}{3} \left[ P_2(\cos(\beta))(\delta_{33} - \delta_{22}) + \frac{1}{2}(\delta_{22} - \delta_{11}) \right] S_{zz} + \frac{1}{3} [\delta_{11} - \delta_{22} \cos^2(\beta) - \delta_{33} \sin^2(\beta)] \Delta,
\]

where the \(^{13}\text{C}\) chemical shift tensor principal elements \( \delta_{11}, \delta_{22}, \delta_{33} \) and their relative orientation (through the angle \( \beta \)) were determined by combining data from the literature and from the 2D PASS NMR experiment [18] performed in the solid state of 9HL.

In this way, the main orientational order parameters, \( S_{zz} \), of the three rings were determined, and their trend within the mesophases was further confirmed by an additional NMR experiment: the \(^1\text{H}\)–\(^{13}\text{C}\) NMR PDLF [18]. From this comparative study, the behaviour of the three-ring core of the 9HL molecule was fully understood showing in the SmA phase that the three rings are almost collinear and they have similar values of \( S_{zz} \) with an average tilt of 5–11° with respect to the normal to the SmA layers. In the SmC*, two close rings continue to be collinear, while the ring close to the lactate lateral chain has a more pronounced tilt with respect to the layer normal. This is an indication of a conformational change at the SmA–SmC* transition and it is also confirmed by the trend of the observed \(^{13}\text{C}\) chemical shift \( \langle \delta \rangle \) of the alpha methylenoxy carbons (see the black and orange arrows in Figure 6) from the SmA to the SmC* phase. The different behaviour of these signals as a function of temperature can be interpreted in terms of the occurrence of a different conformation of the lateral chain, similarly to the case of another ferroelectric liquid crystal [38].

The complete analysis of the temperature-trends of the observed \(^{13}\text{C}\) chemical shift \( \langle \delta \rangle \) of 9HL combined with the \(^2\text{H}\) NMR study of 9HL at different magnetic field strengths was important to come to the following conclusions concerning this peculiar molecular system:

- In the SmA, molecules are tilted with respect to the layer normal and they are organised in clusters each having a coherent orientation. If the magnetic field is above a critical value, these SmA
Figure 6. Series of $^{13}$C NMR spectra of 9HL recorded in the SmA and SmC* phases by decreasing the temperature (top-down). Signals of the aromatic carbons (Ar) and quaternary carbons (Qu) have $^{13}$C chemical shift at higher frequencies (on the left) and those of aliphatic carbons (Al) are at lower frequencies (on the right). Three $^{13}$C signals corresponding to the alpha methyleneoxy carbons are put in evidence throughout different arrows. Picture is modified from ref [18]. Reprinted by permission of John Wiley & Sons, Inc.

Figure 7. On the left. A sketch of the main dynamic processes investigated by NMR on the 9HL compound: overall molecular reorientational motion (ROT), tilt director fluctuations (TDF), self diffusion (SD) and layer undulations (LU). On the right. Frequency dependence of the $^1$H NMR relaxation times, $T_1$, of 9HL at different temperatures, in the SmA and in the SmC* phases. The frequency regions where the various motional processes are dominant are also shown.
clusters are deformed and the molecules align with the magnetic field.

- In the SmC* phase, molecules change their average conformation: the aromatic core has a large tilt with respect to the layer normal, but the lateral chains are in a more extended configuration so that the average molecular length does not change too much passing from the SmA to the SmC* phase.

These findings are in agreement with two of the known models for ‘de Vries’ systems: the cluster cone [33] and the conformational model [39].

3.4. $^1$H NMR relaxometry investigations of the dynamic properties of a ‘de Vries’ liquid crystal

As shown in Section 2, $^1$H NMR relaxometry is a powerful technique to investigate dynamic properties and this was also applied to the 9HL mesogen. This technique allowed us to obtain the frequency dependence of $^1$H NMR spin-lattice relaxation times ($T_1$) at different temperatures from the isotropic to the SmC* phase [27].

Thanks to dedicated equipment, it is possible to cover a wide range of frequencies, from few KHz to hundreds of MHz. This is very important to explore at the same time different dynamic contributions that are active in different frequency regimes. For instance, as shown in Figure 7, the molecular diffusion reorientations (ROT), for instance, the overall rotation of the molecule around its long molecular axis or the reorientations of the phenyl rings around their para axis, are usually very fast motions and the typical frequency is of the order of hundreds of MHz.

On a slightly slower frequency range, there are the translational self-diffusion (SD) motions, responsible of the in plane (faster) and perpendicular to plane (slower) diffusion processes.

On a slower frequency scale (10 to 100 KHz), the collective motions such as layer undulation (LU), order director fluctuation (ODF) and tilt director fluctuation (TDF) motions are dominant. These motions and the relative models describing their frequency and temperature dependences are very specific of the mesophases under study. In the case of the 9HL liquid crystal, for instance, the analysis of the $^1$H NMR dispersion curves (shown in Figure 7) was satisfactory only by assuming the presence of tilted molecules in the SmA phase too, thus giving a further confirmation of the structural model for the ‘de Vries’ phases.

4. Conclusions

This brief review has the aim to share with the liquid crystalline community some considerations about the utility and the actual potentialities of NMR methods to explore many different aspects of this intriguing kind of materials. After a first simplified state of the art of NMR works and applications in this field, a complete case study (i.e. the case of a ‘de Vries’ compound) is presented showing that the combination among different techniques and various detected nuclei (such as $^2$H, $^{13}$C and $^1$H) can give very important contributions in understanding the orientational order and the supramolecular structure, as well as the conformational properties and the MD of liquid crystals.

Disclosure statement

No potential conflict of interest was reported by the author.

Note

1. The last year, 2016, is considered only in part (data are updated at 10 June 2016).

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