NMR Study of the Twist-Bend Nematic Phase

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Liquid crystalline dimer systems have been extensively studied in recent years as candidates for having the Twist-Bend nematic phase (Ntb), in which the director is distributed in an oblique helicoid, maintaining a constant oblique angle with the helix axis. The CBC9CB compound exhibits the uniaxial Nematic (Nu) phase at temperatures below the isotropic phase range and, at lower temperatures, a periodically modulated nematic phase which, according to recent studies, seems concordant with the Ntb phase. In this work, we will characterize this molecular system in both nematic phases using proton and deuterium NMR spectroscopy. Simulation of proton spectra from the terminal mesogenic groups along with quadrupolar splittings from the carbon-deuterium (CD) bonds in the chain positions adjacent to the mesogenic groups allowed for the determination of the Saupe order tensor for the mesogenic groups. We concluded that, in the Ntb phase, the mesogenic group’s nematic order parameter remains approximately constant. The change in the orientation of the most ordered molecular axis, leaving the symmetry plane defined by the aforementioned CD bonds in the Nu-Ntb phase transition, along the verification that the molecular biaxiality assumes a non null value in the Ntb phase are the main factors that account for the change in the molecular orientational order.

Keywords: Nematic, Twist-Bend Nematic, Proton and Deuterium NMR spectroscopy, Saupe Order Tensor

I. INTRODUCTION

So far, in the entire history of liquid Crystals, only four distinct nematic ground states have been found, for achiral molecular systems the uniaxial nematic (Nu) and the biaxial nematic; for chiral molecules the helical nematic and the blue phases. In 1973, however, Meyer suggested the theoretical possibility that molecular interactions that favour bend deformations might lead to a twist-bend nematic phase, in which the director will have an helical distribution with a constant tilt angle between $0$ and $\frac{\pi}{2}$. This theoretical prediction sparked interest in banana-shaped molecules that may actually exhibit this new twist-bend phase (Ntb). Molecular dimers at relatively low temperatures can behave like these bent shaped mesogens and they could be candidates for this phase. For instance, the liquid crystal dimer CBC7CB as of 1993 had already been reported to have a high temperature uniaxial nematic phase followed by a lower temperature smectic phase, which was odd since similar compounds only exhibited an uniaxial nematic phase. In this way, the authors in [1] made a comprehensive study of this compound in order to verify if this intermediate phase was actually the twist-bend nematic phase, and arrived at results that agree with this interpretation. More recently, Robles-Hernández et al. [2] focused on the study of the liquid crystal dimer system CBC9CB, which was also reported to have a nematic-bend nematic phase transition and is the compound that is going to be studied in this work, and obtained very similar results that also agree with the existence of periodically modulated structures. Both papers demonstrate, through deuterium NMR, that the two carbon-deuterium (CD) bonds at the terminal methylene groups of the linking chain lose their equivalence when entering the Ntb phase. The authors in [3] went even further and demonstrated that all the methylene groups in the linking chain of the CBC7CB compound in the Ntb phase have non equivalent bonds, except for the central group because of its two-fold symmetry.

The existence of the helical distribution in these dimer system is, however, still under debate. Some authors, [4], argue that even though the helical distribution of the director is consistent with the experiments, there is no direct evidence of its existence. The authors allege that if such a structure existed, then the spectrum, after a rotation of $90^\circ$ toward an axis perpendicular to the magnetic field, should be a superposition of peaks corresponding to the continuous helix. Instead what they obtained was a typical spectrum of the perpendicular orientation relative to the magnetic field of a uniformly oriented director. If we assume that the diffusion of the molecules is fast enough, then these global heli-conical structures could still be possible. However, they propose an alternative interpretation of the phase where the molecular packing creates domains that assume predominately twisted and chiral conformations. This interpretation is also expanded in [5].

Regarding the potential applications of this phase, the authors in [6], after studying a possible extension of the twist-bend nematic model to incorporate electro-optic effects in the CBC7CB compound, found that the director tilt had ultra fast response times ($\sim 1\mu s$) to an applied electric field. In the same year, there was also a study in [7] of the optical response of the Ntb phase, where it was reported that a linear optical response to an applied electric field was detected, with a switching time of $4\mu s$, for periodic electric excitation. In this way, it is evident that this phase shows promise it will have technological applications, namely in the display industry.
The primary objective of this thesis is to understand the molecular orientational order of the CBC9CB in the Nu and Ntb phase. We will achieve this by being able to explain, in detail, the $^1$H NMR spectra and the quadrupolar splitting results reported in [8] by A. Hoffmann et al.. In order to achieve this objective, we start by investigating the phase sequence of this compound through polarising optical microscopy (POM). Then we will proceed with an preliminary analysis of the $^1$H NMR spectra that expands upon the work presented in [12]. In the final section, we will present a numerical model that is able to simulate both the $^1$H NMR spectra in conjunction with the deuterium splittings, published in [8], along with a discussion of its results and their implications on the molecular orientational order of this system.

II. THEORETICAL BACKGROUND

Matter presents itself in different states of aggregation, the more common ones being the crystalline solid (Cr), the isotropic liquid (Iso) and the gas state. The liquid crystal (LC) state shares mechanical properties with the liquid state since it is a fluid phase, however this phase possesses optical, electric and magnetic properties characteristic of crystalline solids. The molecules in all liquid crystal phases diffuse much like molecules in liquids, however, they maintain some degree of orientational order (nematic LC phases) and sometimes even positional order (smeectic and columnar phases) [13].

The amount of orientational order in a LC is smaller than that of a crystal and it stems from the fact that the molecules have a slight tendency to orient themselves in a direction, defined by a pseudo vector $\mathbf{n}$. This orientational order is only possible because molecules that possess these phases are anisometric. This orientational order causes some physical properties of a LC system along the direction of the director to be different from directions perpendicular to it.

A. Order in Nematic LCs

As previously mentioned the orientational order in liquid crystal is not nearly so perfect as in a solid therefore we can define a nematic order parameter $S$ that quantifies this degree of molecular alignment:

- Isotropic Liquid (no alignment): $S = 0$
- Nematic: $-\frac{1}{2} \leq S \leq 1$
- Crystalline Solid (perfect alignment) $S = 1$.

Each molecule in a mesogenic compound can have the orientation of its most ordered axis defined by a set of angular variables $(\theta, \phi, \psi)$ as represented in figure 1. To obtain the nematic order parameter $S$ we have to compute the ensemble average (represented by the $\langle \rangle$ symbol) of:

$$S \equiv \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle.$$  \hspace{1cm} (1)

The temperature dependence of this order parameter in uniaxial LCs not close to the critical temperature, $T_C$, where the transition from liquid crystal to isotropic liquid occurs, can be approximated by the Haller Law: [13]

$$S = S_0 \left(1 - \frac{T}{T_C}\right)^\alpha,$$  \hspace{1cm} (2)

where the parameter $S_0$ is a scaling factor and $\alpha$ is a material constant. The parameter $T_C$ is temperature at which the order parameter would reach zero if its continuous decrease were not aborted by the discontinuity due to the first-order transition to the isotropic phase [13]. It is noteworthy to point out that the temperature $T_f$ is very close to the temperature $T_C$.

The distribution of orientations in the system can be quantified by a distribution function $f(\theta, \phi, \psi)$, knowing this function it is possible to calculate $S$ directly:

$$S = \int_\Omega \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right) f(\theta, \phi, \psi) d\Omega.$$  \hspace{1cm} (3)

Orientational order plays a fundamental role in LCs in relation between the tensorial molecular $(mol)$ properties and the corresponding macroscopic $(mac)$ tensorial properties. Generalizing the concept of order parameter, we arrive at the Saupe order matrix,

$$S_{\alpha\beta}^{ij} = \left(\frac{3}{2} \cos \theta \alpha \cos \beta \beta - \frac{1}{2} \delta_{ij} \delta_{\alpha\beta}\right),$$  \hspace{1cm} (4)

which allows that relation to be expressed as:

$$A_{\alpha\beta}^{mol} = \left(\frac{2}{3} S_{\alpha\beta}^{ij} + \frac{1}{3} \delta_{\alpha\beta} \delta_{ij}\right) A_{\alpha\beta}^{mol},$$  \hspace{1cm} (5)

where $A_{\alpha\beta}^{mol}$ and $A_{\alpha\beta}^{mol}$ are the tensorial components of some physical properties in the laboratory and molecular frames, respectively and $i, j$ represent the axis in the laboratory frame and $\alpha, \beta$ the axis of the molecular frame. In the Super order matrix $\cos \theta \alpha \beta$ are the direction cosines relating the molecular and laboratory frames. In the particular case of NMR in a high magnetic field the quantities that will determine the spectra only depend on the $zz$
components in the laboratory frame (where the magnetic field lies) of specific tensorial variables. In this context the Saupe order matrix, $S^{zz}_{\alpha\beta}$, becomes the relevant order variable. This tensor describes, in a molecule fixed frame, the order of the laboratory fixed frame’s frame $z$ axis to which the director is parallel in oriented samples. Note that $S^{zz}_{zz}$ describes how the axis of greatest order is related to the director, which coincides with our definition of nematic order parameter. In its principal frame this matrix is diagonal and only dependent on $S$ and an additional parameter $D = S_{zz}^{zz} - S_{yy}^y$ that defines the molecular biaxiality:

$$S^{zz}_{\alpha\beta} = \begin{pmatrix} \frac{D-S}{2} & 0 & 0 \\ 0 & \frac{D+S}{2} & 0 \\ 0 & 0 & S \end{pmatrix}$$ (6)

Since the orientation of this frame is usually unknown we must consider a rotation from a molecular frame we define in the molecule to this principal frame. This change of frame is carried out through a congruent transformation using the Euler angles $(\phi, \theta, \psi)$ defined according to [15]$.^1$ In this way the Euler angles also represent molecular parameters of the system.

### B. Nuclear Magnetic Resonance

NMR is an experimental technique that allows us to measure the interaction of a system of nuclear spins, with intrinsic magnetic moment and angular momenta, with an external magnetic field, mediated by the absorption and re-emission of electromagnetic radiation. This process depends on the magnetic environment of the spins and since this environment is dependent on the characteristics of the electronic cloud, measuring these interactions and analysing the energy spectrum of the NMR Hamiltonian allows us to probe the molecular structure of a given sample which is the focus of this work. Additionally, though it will not be the focus of this work, the energy transfer between spins and between spins and the lattice is associated with relaxation times, that can also provide valuable insight regarding molecular dynamics.

In high field NMR, the Zeeman term, $\hat{H}_z$, of the Hamiltonian ends up being dominant while the remaining terms: the dipolar, $\hat{H}_d$, the indirect dipolar interaction, $\hat{H}_I$, the quadrupolar, $\hat{H}_q$, and the chemical shift $\hat{H}_s$ interactions can be treated as a perturbation. In the context of liquid crystals the molecules undergo rapid translational and rotational diffusion motions which causes the perturbing Hamiltonian to be the result of an averaging process over these motions that causes interactions between spin of different molecules to be averaged out. Additionally since some interactions are inversely proportional to the distance between the spins to the power of three which means nuclei that are far from each other have an almost neglectable interaction, allowing us to consider small groups of spins and neglect interactions between groups within each molecule. Considering these approximations and neglecting the indirect dipolar interaction term due to its small value for interacting protons, the Hamiltonian terms for a group of identical spins take the form$^2$:

$$\hat{H}_z = -\hbar \sum_{k=1}^{N} \gamma_k B_{0,z} \hat{I}_{k,z}$$ (7)

$$\hat{H}_s = \sum_k \gamma_k h B_{0,z} \hat{I}_{k,z} \left[ \sigma_k^{10} + \langle \sigma_{k,zz}^s \rangle \right],$$ (8)

$$\hat{H}_q = \sum_k \frac{3 \epsilon Q_k (V_{k,zz})}{4 k (2I_k -1)} \left( \hat{I}_{k,z} \right)^2 - \frac{1}{3} I_k (I_k + 1) ,$$ (9)

$$\hat{H}_d = \sum_{k<l} \frac{-\mu_0}{4\pi} \gamma_k \gamma_l h^2 (N_{kl,zz}) \cdot \left[ \hat{I}_{k,z} \hat{I}_{l,z} - \frac{1}{4} (\hat{I}_{k,+} \hat{I}_{l,-} + \hat{I}_{k,-} \hat{I}_{l,+}) \right],$$ (10)

where $I_k$ is spin of the nucleus, $\hat{I}_k$ the spin angular momentum operator, $\hat{I}_z = \hat{I}_x + i \hat{I}_y$, $\hat{I}_+ = \hat{I}_x - i \hat{I}_y$ are the raising and lowering operators of angular momentum and $\epsilon Q_k$ is the quadrupole moment of the nucleus $k$. In addition, $\langle N_{kl,zz} \rangle \equiv \frac{1}{3(n_{kl,z})^2 - 1}$, with $n_{kl,z}$ being the $z$ component of the unitary vector established between the nuclei $k$ and $l$, and $\langle V_{k,zz} \rangle$ is the $zz$ component of the electric field gradient tensor at the nucleus site.

Considering that the director $n$ is aligned along the $z$ axis of the laboratory frame, which is the case for LC samples with positive magnetic susceptibility anisotropy, we can use the Saupe order matrix when spins $k$ and $l$ belong to the same molecular segment, i.e.:

$$\langle N_{kl,zz} \rangle = \sum_{\alpha,\beta} \left( \frac{2}{3} S_{\alpha\beta}^{zz} + \frac{1}{3} \delta_{\alpha\beta} \right) N_{kl,\alpha\beta}$$ (11)

$$\langle V_{k,zz} \rangle = \sum_{\alpha,\beta} \left( \frac{2}{3} S_{\alpha\beta}^{zz} + \frac{1}{3} \delta_{\alpha\beta} \right) V_{k,\alpha\beta}.$$ (12)

If the spins $k$ and $l$ change their relative distance due to a conformation change, then expressions (11) and (12) can be used in an approximate way by considering an average molecular conformation to which a molecular frame is attached and the quantities $N_{kl,\alpha\beta}$ and $V_{k,\alpha\beta}$ in equations (11) and (12) are replaced by their corresponding averages over the spanned conformations. The quantities $N_{kl,\alpha\beta}$ and $V_{k,\alpha\beta}$ can be related to their values in their principal molecular frame through congruent transformations. The quantity $V_{k,\alpha\beta}$ has its principal axis defined along the bond that connects an atom, in our case a carbon atom $C$, to the deuterium, D. In this frame, $V_{k,A,B}$

$^1$ A more common definition of these angles would be $\phi, \theta, \psi$. We chose to change notation to ensure that the parameters were not to be confused with the angular parameters that define the orientation of the molecule relative to the director.

$^2$ For the simulation of the $^1H$ NMR spectra we neglect the indirect dipolar interaction since its contribution is only of the order of several hertz.
much smaller than \( S \) and since the molecular biaxiality is a molecular quantity. In the last of the equality we considered \( \eta \) to be not very large \[16\] and for the CD bonds in the methylene group of our system we considered \( \eta = 0 \).

Finally, it is worth adding that if we are able to define a molecular frame as the principal frame of the Saupe order tensor and since the molecular biaxiality \( D \) is, in general, much smaller than \( S \) it can, sometimes, be neglected we end up with the following equations for the line splittings:

\[
\Delta \tilde{v}_{kl,d} = \frac{3\pi \mu_0}{8\pi^2} \gamma^2 \hbar \left( \frac{1}{r_{kl}} \right) S \left[ 3 \left( \frac{1}{2} \cos^2 \beta_{kl} - \frac{1}{2} \right) \right],
\]

\[
\Delta \tilde{v}_{k,q} = \frac{3}{4\pi} \frac{e^2 q_k Q_k}{\hbar L_k(2I_k - 1)} S \left[ 3 \left( \frac{1}{2} \cos^2 \beta_{kl} - \frac{1}{2} \right) \right],
\]

with the angles \( \beta_{kl} \) being the polar angles that defines the orientation of the inter-nuclear vector when the molecular frame is written using spherical coordinates \[17\], see figure 2.

Now that we have defined the high field Hamiltonian and how we relate the splittings with the orientational order of the system, it is possible to use first order time independent perturbation theory to calculate the NMR absorption spectra\[^3\]. The positions of the spectral lines in the spectra will correspond to transitions that obey the selection rule \( \Delta m = 1 \), with \( m \) being the spin magnetic quantum number. The area of each peak will be given by:

\[
W_{m_j \rightarrow m_j+1} = \frac{2\pi}{\hbar} \left| \langle I, ... m_j + 1 ... | I_j^+ | I, ... m_j ... \rangle \right|^2 \delta(\Delta E - \hbar \omega_1)
\]

provided that during the time scale \( \tau \) of the perturbation the spin populations change only a small amount and the possible states between which absorption can occur must be spread over a range \( \Delta E \) such that \( \Delta E >> \frac{1}{\tau} \) \[18\].

### III. EXPERIMENTAL INTERLUDE

The liquid crystal dimer \( \alpha, \omega - \text{bis}(4,4’ - \text{cyanobiphenyl}) \) nonane, CBC9CB, studied in this work belongs to the CBCnCB series and is known to present a periodically modulated nematic phase referred to as Ntb phase. It consists of two mesogenic groups linked by a flexible chain. The mesogenic units are cyanobiphenyl (CB) groups and the flexible is odd alkyl chain composed of nine carbon atoms \[12\]. The compound was synthesized in the Department of Chemistry at the University of Hull in the United Kingdom \[6\].

NMR spectroscopy studies were carried out in a Bruker Avance II 300 setup that generates a static magnetic field through a superconducting magnet. The setup is comprised of an operator console, a console, a switcher/pre-amplifier and the magnet system that includes the superconducting magnet, a probe head that houses the radio-frequency coil, the tuning and matching rf circuits and the sample’s heating/cooling oven, and a shim system located around probe head.

Lastly it is worth mentioning that all the experimental work was performed Laboratório de Cristais Líquidos e Ressonância Magnética Nuclear of the Complex Fluids, NMR and Surfaces Group, Center of Physics and Engineering of Advanced Materials, CFNMRS-CeFEMA, at IST.

### IV. EXPERIMENTAL RESULTS

#### A. Preliminary NMR Study

As a first approach to study the orientational order in both nematic phases with \(^1\)H NMR we carried out an analysis which improves on the one performed in \[12\]. The acquired spectra, in a magnetic field of \( T = 7.04T \), are represented in figure 3. The isotropic to uniaxial nematic phase transition occurred at 399.1 ± 0.8K\[^4\] which is higher than the temperatures recorded in the Polarising Optical Microscopy (POM) studies (395 ~ 396K) and those reported in \[4\]. This seems to indicates that

\[^3\] The Fourier transform of the transverse complex magnetisation \( M_s(t) + iM_\phi(t) \) following the application of a time oscillating radio frequency field that causes the net magnetisation in the laboratory frame to rotate \( \frac{2}{\pi} \) radians, gives the absorption spectra of the nuclear spin Hamiltonian \[15\] p. 179.

\[^4\] This error was estimated through a linear calibration with a thermocouple that was previously calibrated with the boiling and freezing point of distilled water.
the magnetic field may induce some order in the system which increases the phase transition temperature\(^5\).

Looking at the spectra in the figure 3 we can see that the overall shape does not change significantly and, therefore, to study the evolution of the order parameter we followed a procedure identical to the one in 12 with some improvements. The procedure consists of choosing a reference spectrum at a specific temperature and proceed to fit the other temperatures with a function \(G'(\omega)\) defined as the piecwise linear interpolation of the reference spectrum \((G(\omega))\) but with its argument shifted by a factor \(\omega_0\), scaled by a factor \(A\) and its amplitude scaled by a factor \(B\), that is \(G'(\omega) = B \cdot G(\frac{\omega - \omega_0}{\alpha})\). The fits were carried out using the Levenberg-Marquardt minimization method [20] (implemented in [21]), disregarding a percentage of the lowest data, in order to suppress the contribution of the tails and the central region of the spectra. Our interest lies in the parameter \(A\), since this hypothesis assumes the spectra evolution with temperature is due to the evolution of the product of the order parameter \(S\) by a molecular dependent parameter with temperature. A plot that depicts the evolution of this parameter with temperature is represented in 4a. We find indications that the transition Nu-Ntb occurs in between temperatures. Ntb-Nu phase transition

\[ \Delta \beta(T) = \beta(T) - \beta_r \]

is a proportionality factor, \(P_2\) is the second degree Legendre polynomial and \(\beta(T)\) is the the angle represented in 2 and \(\beta_r\) is the value of \(\beta(T)\) in the Nu phase. We assume that \(\beta_r\) is temperature independent and, therefore, the \(P_2(\cos(\beta(T)))\) parcel can be dropped in the Nu phase. In the Ntb phase, defining \(\Delta \beta(T) = \beta(T) - \beta_r\) to account for a temperature dependent additional tilting beyond \(\beta_r\) and using a zeroth order approximation we end up with:

\[ A(T) \approx K \cdot S(T) \cdot \left[ \frac{3}{2} \cos(\Delta \beta) - \frac{1}{2} \right]. \]

The parameter \(\Delta \beta\) translates the occurrence of a significant change in the orientation of the most ordered molecular axis molecules which is associated with the onset of the Ntb phase 12. Using an Haller type law to fit the high temperature region of the Nu phase we are able to obtain \(\Delta \beta\) as a function of temperature. The results are represented in 11. By further examination of figure 11 we can conclude that this orientational change starts occurring before the Nu-Ntb phase transition, which explains a decrease in \(A(T)\) before the transitions as one approaches the Ntb-Nu from above. When the phase transition occurs the rate of change of this angle it varies discontinuously. This variation could be associated with a change in the molecular packing that possibly occurs at the phase transition.

V. MODEL AND NUMERICAL IMPLEMENTATION

We next built a model and its numerical implementation from more fundamental principles able to describe the \(^1\)H NMR spectra and, along with deuterium NMR data available in the literature on the same compound, characterise the orientational order in the system. The main provision of this model was to simulate the \(^1\)H NMR spectrum along with the quadrupolar splittings from a oriented monodomain liquid crystal sample, considering the molecular structure conformation and orientational order. In order to simulate the spectrum we must first construct the Hamiltonian. Since we are in high field NMR the Zeeman term is dominant and the remaining terms can be treated as a perturbation. It is also noteworthy to point out that the quadrupolar interaction has a null contribution for the proton absorption spectra. The summations in the NMR Hamiltonian include all the spins in all the molecules, however, due to fast self-diffusion the interaction between spins of different molecules are averaged out and only contribute to the broadening of the resonance lines. Additionally the

\[ T_1 = T_C \]

with \(A(T)\) given by:

\[ A(T) = K \cdot S(T) \cdot \frac{P_2(\cos(\beta(T)))}{\sqrt{P_2(\cos(\beta_r))}}, \]

where \(K\) is a proportionality factor, \(P_2\) is the second degree Legendre polynomial and \(\beta(T)\) is the the angle represented in 2 and \(\beta_r\) is the value of \(\beta(T)\) in the Nu phase. We assume that \(\beta_r\) is temperature independent and, therefore, the \(P_2(\cos(\beta(T)))\) parcel can be dropped in the Nu phase. In the Ntb phase, defining \(\Delta \beta(T) = \beta(T) - \beta_r\) to account for a temperature dependent additional tilting beyond \(\beta_r\) and using a zeroth order approximation we end up with:

\[ A(T) \approx K \cdot S(T) \cdot \left[ \frac{3}{2} \cos(\Delta \beta) - \frac{1}{2} \right]. \]

\(^5\) High magnetic fields are known to have effects in the phase transition of compounds that exhibit the Ntb phase 19.

\(^6\) We initially considered \(T_1\) as a free parameter but it yielded a temperature smaller than \(T_C\), which is physically impossible. In this way we chose this approximation since \(T_C\) is the lower bound of \(T_1\).
state space for a spin group with \( N \) spins has dimension of \( D = (2I + 1)^N \), with \( I = \frac{1}{2} \). In this way, a scalability problem in the simulation also becomes obvious, the Hamiltonian matrices have size \( 2^N \times 2^N \). To handle this problem we considered that our system is composed of three separate molecular groups (see figure 5), the first one, represented in blue (B), corresponding to the mesogenic group defined by the aromatic rings and the first methylene group, the second one, represented in red (R), is the majority of the linking chain composed of the remaining methylene groups expect for the central methylene which by itself define a third molecular group, represented in green (G). This assumption is not unmerited because we do not expect that the linking chain should have as much orientational order as the mesogenic body. Finally the central group also had to be differentiated from the rest of the chain, since the CH bonds in this group are NMR equivalent in both Nu and Ntb phases \( 7 \). No interaction between protons of different groups will be considered. It is also noteworthy to point out that we are only effectively simulating half of the molecule, because we assume the linking chain has enough internal mobility to ensure that the two halves of the molecule are equivalent to NMR, as considered also by other authors studying dimer systems with NMR \( 1, 8, 22 \) and is suggested by the proton and deuterium data on these systems. The molecular frame we considered is also represented in figure 5 in which the z axis is aligned with the longest molecular axis and the y axis is defined so that the yOz plane defines a symmetry of the carbon hydrogen (CH) bonds of the flexible chain. The x axis was simply defined as to be perpendicular to the yOz plane.

In order to calculate the Hamiltonians we need to supply the quantities \( \langle V^i_{zz} \rangle \) for the quadrupolar, \( \sigma_{k,zz}^{iso} \) and \( \sigma_{k,zz}^s \) for the chemical shift and \( \frac{3\langle H_{zz} \rangle^2 - 1}{r_{zz}} \) for the dipolar Hamiltonians, for each spin and spin-spin interaction.

Regarding the chemical shift term, it is noteworthy to point out that this simulation was computed considering the rotating frame which means, quantum mechanically, that the contribution of the Zeeman Hamiltonian in the Eigenvalue calculation is suppressed and thus the spectra will be centered around zero Hz instead of the Larmor frequency. However we have to consider a contribution of offset to the resonance. In this model, we considered two different chemical shift coefficients as fitting parameters, one for the protons in aromatic groups, that usually have a characteristic chemical shift contribution, and one for the protons in the methyl chain, which all have the same hybridisation and hence we predict that their contribution to the chemical shift will be similar. This consideration was due to the fact that the chemical shift is associated with the movement of the electronic cloud around the nuclei which induces local magnetic fields that oppose the external magnetic field and are usually characteristic of certain functional groups in a molecule. By doing this approximation, we effectively include off resonance effect in these coefficients and consider both terms \( \sigma_{k,zz}^{iso} \) and \( \sigma_{k,zz}^s \) to be indistinguishable.

FIG. 4: The blue dotted lines indicate the temperature at which Nu-Ntb occurred according to our POM studies. The violet dot dashed line indicates the last temperature in which Nu-Ntb occurred according to our POM studies. The violet dot dashed line corresponds to the temperature reported in \( 5 \), respectively.

The deuterium splittings published in \( 22 \) were equal and the violet dot dashed line indicates the last temperature in which the deuterium nuclei 1 and 2. Henceforth we will use this notation as a subscript to distinguish the different assignments. The represented yOz plane defines the plane of symmetry of the CH bonds of the flexible chain.

FIG. 5: Ball and stick representation of the simulated system. The pink (P), blue (B), and green (G), correspond to the molecular groups defined in the simulation. The blue \( (xyz) \) and red \( (x'y'z') \) corresponds do selected and principal molecular frames. In a orange shade we highlighted the deuterium nuclei 1 and 2. Henceforth we will use this notation as a subscript to distinguish the different assignments. The represented yOz plane defines the plane of symmetry of the CH bonds of the flexible chain.

Finally the central group also had to be differentiated from the rest of the chain, since the CH bonds in this group are NMR equivalent in both Nu and Ntb phases \( 7 \). No interaction between protons of different groups will be considered. It is also noteworthy to point out that we are only effectively simulating half of the molecule, because we assume the linking chain has enough internal mobility to ensure that the two halves of the molecule are equivalent to NMR, as considered also by other authors studying dimer systems with NMR \( 1, 8, 22 \) and is suggested by the proton and deuterium data on these systems. The molecular frame we considered is also represented in figure 5 in which the z axis is aligned with the longest molecular axis and the y axis is defined so that the yOz plane defines a symmetry of the carbon hydrogen (CH) bonds of the flexible chain. The x axis was simply defined as to be perpendicular to the yOz plane.

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Regarding the quadrupolar interaction, we will use the quadrupolar splittings reported in \( 22 \) of a deuterated molecule (the protons in the first methylene group of the linking chain were substituted by deuterons, see figure 5). In order to calculate the splittings, we need to use a congruent transformation to change the principal frame of the electric field gradient tensor to molecular frame.
Subsequently we can calculate the splitting using the following equation:

$$\Delta \nu_k = \frac{3}{2} \sum_{k, \alpha \beta} \left( \frac{2}{3} S_{\alpha \beta}^{zz} + \frac{1}{3} \delta_{\alpha \beta} \right) \left( \frac{eQ}{2\hbar} V_{k, \alpha \beta}^m \right).$$

(20)

Since the Saupe order tensor is dependent on $S$, $D$ and the angular parameters $\alpha, \beta, \delta$ and we have two deuterated nuclei, we can establish a system of two equations for five unknowns:

$$\Delta \nu_1 = a_{11}(\alpha, \beta, \delta, \nu_q) S + a_{12}(\alpha, \beta, \delta, \nu_q) D,$$

(21)

$$\Delta \nu_2 = a_{21}(\alpha, \beta, \delta, \nu_q) S + a_{22}(\alpha, \beta, \delta, \nu_q) D.$$

(22)

We have chosen to solve for $S$ and $D$ since they are linear in these parameters. In this way, $S$ and $D$ can be determined from the quadrupolar splitting and the angles $\alpha, \beta, \delta$. However we also expect that the biaxiality parameter $D$ will be much smaller than the $S$ [24]. As a starting point we considered the angle $\delta$ that minimizes the molecular biaxiality parameter $D$ using the Brent routine explained in detail in [20]. The remaining parameters $\alpha$ and $\beta$ will be considered as fitting parameters. In this way we are able to obtain all the the molecular parameters of the mesogenic molecular group. We will consider that $D = 0$ and, for simplicity, $\delta = 0$ (since they are coupled) for the remaining groups. Additionally, we assume $\beta$ is the same for all molecular groups and that $\alpha$ is the same for the flexible chain and mesogenic body while its fixed at $\pi/2$ for the central CH$_2$ group. This ensures that the CH bonds of this group never lose their NMR equivalence. The flexible chain and central CH$_2$ will both have independent order parameters left as a fitting parameter.

Now that we have established how we take into account, in our simulation, the quadrupolar splitting we are going to discuss the generation of the coefficient $\langle N_{kl,zz} \rangle$ in order to calculate the dipolar Hamiltonian. The quantity $\langle \frac{1}{r_{kl}^2} (3n_{kl} \otimes n_{kl} - \delta_{alpha} \beta) \rangle$ can be easily calculated for each pair of interacting spins in each molecular group simply using each protons position, determining the inter proton normalised vector, $n_{kl}$ and computing the tensor product. In our model we only consider one average coformation, however, we considered fast $\pi$ flips of both benzene rings and also considered the orientation of each one of them in the molecular planes is defined by two angles that are fitting parameters. The coupled $\pi$ rotations were obtained simply rotating both benzene rings along the axis defined by its bonds to the rest of the molecule by an angle $\theta$. Taking into account spin flips means that we have to consider two possible conformations of the aromatic rings, calculate the $\langle \frac{1}{r_{kl}^2} (3n_{kl} \otimes n_{kl} - \delta_{alpha} \beta) \rangle$ tensor for all pairs of interacting spin and then calculate the average tensor. Finally, similarly to the quadrupolar interaction we have to change from the molecular frame to the laboratory frame by contracting this tensor with the Saupe order tensor,

$$\langle 3(n_{kl,zz})^2 - 1 \rangle = \sum_{\alpha \beta} \left( \frac{2}{3} S_{\alpha \beta}^{zz} + \frac{1}{3} \delta_{\alpha \beta} \right) \frac{1}{r_{kl}^2} (3n_{kl} \otimes n_{kl} - \delta_{alpha} \beta).$$

(23)

the over bar indicates an average over the $\pi$ flips of the rings. Since in this analysis, we are considering that this mesogenic group adopts one preferred conformation, the Saupe order matrix relates to that conformation.

Now that all the necessary quantities for the different parcels of the Hamiltonian were discussed, we are able to build it. Subsequently, we have to compute its eigenvalues and eigenvectors. In order to do so, we used the Jacobi algorithm, described in [20].

After calculating the eigenvalues $E_i$ and eigenvectors $|\psi_i\rangle$ of the Hamiltonian, proceed to the calculation of the absorption spectra taking into account equation (17) indicating that the area of the peak corresponding to each transition is proportional to

$$W_{ij} \propto \kappa \langle |\psi_j| \hat{I}_t \hat{I}_i |\psi_i\rangle^2 \delta(\Delta \omega - \hbar \omega),$$

(24)

with $\kappa$ being a proportionality constant and $\Delta \omega = E_i - E_j$ with $E_j$ and $E_i$ being eigenvalues of the final and initial state, respectively. Due to spin-spin relaxations each allowed transition in the spin system will contribute to the absorption spectra with a shape function centered at the transition frequency $\omega = \frac{\hbar}{\epsilon_i}$, with an area given by [24]. The width of the shape function is parametrized by a line broadening parameter $LB_{ij}$ and the shape function is assumed to be Lorentzian. In this way, our simulated free induction decay is given by:

$$\phi(t) = \kappa \sum_{i=1}^N \sum_{j<k} W_{ij} e^{-\left[ \frac{1}{2} (t - t_j)^2/\epsilon_i + LB_{ij} \right]^t},$$

(25)

with $\kappa$ being, once again, a proportionality constant and $LB_{ij}$ the broadening coefficients.

Most of the $LB_{ij}$ coefficients should be correlated and, therefore, we divided the spins in four different groups and considered that each group has its broadening coefficient $K_i$ [7]. The groups considered were: one for the spins in the aromatic rings, one for the spins in the first methylene group, which in spite of having a chemical environment different from the aromatic ring should have its orientation strongly coupled with them, one for the remaining flexible chain and, finally, one for the central methylene group, whose CD bonds, as we previously mentioned, do not lose their NMR equivalence which causes the orientational order of this group to be different than the rest of the chain. Each eigenstate is a linear combination of produced states of up and down spins, in this way to estimate the contribution of each spin flip to a given transition we may calculate the following quantity:

$$X_{kij} = |\langle \psi_j | \hat{I}_k^+ \hat{I}_i | \psi_i \rangle|^2,$$

(26)

where $\hat{I}_k^+ = \mathbb{1}_1 \otimes \ldots \otimes \mathbb{1}_n \otimes \ldots \otimes \mathbb{1}_N$. Finally $LB_{ij}$ simply becomes

$$LB_{ij} = \sum_{k=1}^N X_{kij} K_k / \sum_{k=1}^N X_{kij},$$

(27)

[7] The dipolar interaction is dominant in the transverse relaxation of the signal and consequently the broadening of the transitions.
with $K_i$ being the previously defined spin dependent broadening coefficients.

After computing the signal, in order to produce the spectra we calculated the Fourier transform of the signal. We chose to use the Fast Fourier Transform algorithm, explained in detail in [20].

Lastly, regarding the fitting algorithm, the Least square minimisation we used to run these simulations was the Levenberg-Marquardt, adapted to use the Eigen library [24], discussed in [20]. It is also worth noting that to match the intensities of both simulated and experimental spectra we multiplied our simulation by a linear function and left both slope and constant offset as fitting parameters. In this way, our model considered fourteen different fitting parameters.

To define the error of each data point in the spectra, we considered the standard deviation of the data corresponding to high absolute values of frequency in which the spectra has already decayed to zero. The error of the fitting parameters is estimated through the covariance matrix computed in the Levenberg-Marquardt method [25]. However, since some parameters are obtained through the splitting equations (21) and (22) ($S$ and $D$) and through a minimisation routine ($\delta$). The error of these parameters is obtained by calculating the standard deviation of distribution of solutions computed by generating Gaussian distributions of the necessary parameters required to compute them. Finally, regarding the splittings transcribed from [8], the error these parameters was approximated by the maximal reasonable deviation when digitising the data of the aforementioned reference.

VI. FITTING RESULTS

After introducing the numerical model that is able to explain both the proton and deuterium NMR data, we will focus on presenting and discussing the results we obtained. The model we developed has several fitting parameters increasing the chances that the topology of $\chi^2$ as a function of the free parameters will include several local minima. Since both the proton and deuterium NMR results vary monotonously with temperature, for results that had similar $\chi^2$ we favoured results that were locally monotonous. Additionally, we do not have information regarding which CD bond corresponds to which orientation parameter together with $\beta$. However, we do not have information regarding which CD bond corresponds to which angular parameters, while $\alpha$ and $\delta$ exhibit a symmetric evolution between assignments. It is also worth mentioning that these parameters stabilize at about $T = 365K$ remaining approximately constant at lower temperatures while $\beta$ continues to increase as temperature decreases. These angular parameters together with $D$ are the main mechanism that causes the change of profile in the spectra.

In the previous chapter we mentioned the parameter $\delta$ was obtained minimising $D$. In order to ensure that this condition was not being too restrictive we relaxed it and fitted the experimental data in some representative temperatures. The results we obtained matched the minimums we had obtained before and did not result in a significant decrease in the $\chi^2/n.d.f.$ (n.d.f.=number of experimental points - number of fitting parameters), which means our results with $D$ minimized are compatible with the best $\chi^2/n.d.f.$.

VII. CONCLUSIONS

In this work we presented a proton and deuterium NMR study of the CBC9CB liquid crystal dimer system. We focused on the describing the molecular orientational order of this system in the Nu and Ntb phase.

In our preliminary analysis of the proton NMR spectra we concluded that in the high temperature region of the Nu phase, the horizontal scaling of the spectra fits well an Haller-type law. However before the onset of the Ntb...
phase the spectra is no longer modelled solely by this law and we have to take into account the variation of angle $\beta$, see figure 2. In a zeroth order order approximation we concluded that the difference between $\beta$ in the Nu phase and at a given temperature in the Ntb phase increases with decreasing temperature. After the onset of the Ntb phase, this difference increases almost linearly with decreasing temperature.

Using our numerical model we were able draw some conclusions regarding the molecular orientational order in the Ntb phase and the Nu-Ntb phase transition. In this temperature range we concluded that the order parameter of the mesogenic group remained almost constant. This result is not contradictory with our previous interpretation since far away from the Nu to isotropic liquid phase transition the order parameter, according to an Haller type law, should exhibit little variation. The order parameter $S$ of the flexible chain, without the central CH$_2$, which defines the second most important contribution to the spectra, has a very similar behaviour to the order parameter of the mesogenic group, in spite of being slightly lower. This indicates that these two molecular groups are still significantly correlated. We also concluded that the main mechanism that induces the change of $^1$H NMR spectrum and the quadrupolar splittings is the change in the orientation of the principal molecular frame, along with molecular biaxility parameter ceasing to be null in the Ntb to Nu phase transition. The angular parameter $\beta$, which describes the angle between the principal molecular frame’s $z$ axis, to which the director is, on average, parallel to, and the $z$ axis of the molecular frame we defined, which is parallel to the para-axis of the benzene rings, increases almost linearly with decreasing temperature. This behaviour matches the results we obtained in our preliminary study, with an approximate description of $\beta$. It is also noteworthy to point out that in the Ntb phase the $z$ axis of the principal
molecular frame leaves the plane of symmetry defined by the two CD bonds of the deuterated CH$_2$ (see figure 3). We believe that these results are in agreement with a collective molecular arrangement in twisted and bent chiral domains, in the Ntb phase, because this packing suggests that the mesogenic groups are be packed in a tilted-twisted configuration. This configuration is coherent with our results since the most ordered molecular axis, associated with the mesogenic group, establishes an angle $\beta$ with the para-axis of the benzene rings and leaves the plane of symmetry defined by the CD bonds. Additionally, this packing is compatible with the molecules acquiring some biaxiality ($D \ll 0$) which is also in agreement with our results.

When comparing the results of both assignments we conclude that they were mutually compatible in almost all relevant parameters except in the angular parameters $\alpha$ and $\delta$ that define the orientation of the principal molecular frame and in the molecular biaxiality parameter $D$. These results, however, seem to exhibit a symmetry between assignments, arising probably from the simple quadrupolar splitting exchange between both assignments.

As future work, it would be interesting to carry out additional NMR studies that could provide uncorrelated information to restrict the free parameters of our model to further validate our results. Studies that could provide this type of information would be double quantum $^1$H experiments and the carbon 13 absorption spectra. In addition, it would also be interesting to use our model and study the evolution of the orientational order in the lower temperatures of the Nu phase, since our preliminary study indicates that the orientation changes of the principal molecular frame start occurring in those temperatures, this provided we also could obtain the evolution of the quadrupolar splitting with temperature in that region or other independent NMR data. Other issues still persist in this phase, since in the literature the elastic constants have yet to be measured in the Ntb phase, a study of the magnetically induced Fréedericksz transitions, in this phase, would be very important. Additionally, it would also be relevant to measure the dielectric permittivity in these conditions where we can ensure that the director is aligned with the magnetic field, as the measurements reported in literature seem to overlook the director alignment in the Ntb phase leading to incorrect values being reported for the dielectric permittivities in this phase.