

Visco-Elastic Parameters of a Liquid Crystal with a Nematic-Nematic Transition

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This work comprises Electro-Optical (EO) and proton NMR studies of a dimer liquid crystalline system that exhibits a phase transition in between two different nematic phases: the conventional nematic phase (N_u) and the called twist-bend nematic (N_{TB}). The liquid crystal studied is the compound CBC9CB.

The EO studies consist of capacitance and optical transmission measurements in thin samples of the liquid crystalline compound, while subjected to electric fields which are able to induce Fréedericksz transitions. From the simulation of these results based on the description of the nematic as a continuous medium, it was possible to determine the elastic constants involved in the induced Fréedericksz transition as well as the dielectric constants and refraction indices in the N_u phase. Due to the high field threshold and high viscosity shown by the compound in the N_{TB} phase, it was not possible to obtain useful measurements with the EO technique. Our results suggest that the bend constant can take negative values in the N_{TB} phase since in the N_u phase this constant is small and tends to decrease with decreasing temperature.

From the proton NMR spectra analysed, we obtained the order parameter in the N_u phase and the data from the N_{TB} phase showed that there is a change of conformation relative to the N_u phase. It was also observed from the proton NMR spectra in the twist-bend nematic that at 7T the director is aligned by the magnetic field while at 0.78T the alignment is only partial.

Keywords: Nematic, twist-bend nematic, dimer, twist-bend distortions, Fréedericksz's transitions, proton NMR spectroscopy

INTRODUCTION

The uniaxial nematic phase (N_u) is the most symmetric of all the liquid crystalline mesophases, having only orientational molecular order along a single axis. Since 1970, nematic phases with more complex structures have been proposed and, giving the example of the biaxial nematic phase (N_B), experimentally observed [1].

Recently, it has been observed in several organic compounds of molecules formed by two mesogenic bodies connected by a flexible chain (dimers) an unknown nematic phase named N_{TB} which presents, at equilibrium, a non uniform director field. This is considered to be due to the existence of a spontaneous twist-bend deformation [2]. For this kind of structure, it has been proposed that at least one of the elastic constants characteristic of the uniaxial nematic phase had assumed a negative value, due to the likelihood of the constituent molecules in forming an arc-shaped conformation [3].

The compound used in this work is the dimer α,ω -bis(4,4'-cyanobiphenyl)nonane (CBC9CB). Few studies have been reported about it in particular. Namely, Tripathi *et al.* [4] did a high-resolution adiabatic scanning calorimetry study on mixtures with 4-pentyl-4'-cyanobiphenyl (5CB) and, more recently, Dong *et al.* [5] report that a nematic potential modelled by two independent Maier-Saupe terms is successful in fitting observed dipolar couplings from solute NMR.

Other odd spaced bimesogenic dimers have been under heavy investigation in recent years, namely the dimers

CBC7CB and CBC11CB, which differ from ours only in the size of the flexible alkyl chain [6–9]. Meyer *et al.* [10] also extended the twist-bend nematic model to describe the electro-optics properties of this phase.

We intend to contribute to the ongoing investigations on liquid crystal dimers presenting the N_{TB} phase. As stated earlier, the molecular structure of this phase is not yet fully understood and several hypothesis are being proposed and open for discussion.

We focused our investigation on a single odd spaced bimesogenic dimer, CBC9CB, by measuring its elastic constants, dielectric constants and indices of refraction, using a well-established technique [11] based on induced Fréedericksz transitions [1, 12] and monitoring the sample's capacitance and birefringence.

Our study differs from a similar one recently published on a similar dimer called CBC11CB [7]. Besides the experimental technique that is different, we also went further and investigated the behaviour at the uniaxial nematic phase at four different frequencies. With regard on how the elastic constants were obtained, we did not resort to a retardation method as Balachandran *et al.* [7] did. Instead, we measured directly the capacitance of the cell and the light transmitted through it.

At the time this work has begun, the results obtained by Balachandran *et al.* [7] were not yet known. The initial approach on the study of the dimer CBC9CB was independently done.

Complementary to this, we obtained proton Nuclear Magnetic Resonance (NMR) spectra at several tempera-

tures within both nematic phase ranges and for different magnetic fields. These spectra in the N_{TB} phase are interpreted in terms of the presence of a tilt angle of the molecular rigid segments in the molecular frame, and a different alignment of the director depending upon the external magnetic field.

MATERIAL STUDIED: CBC9CB

The liquid crystal dimer CBC9CB is composed of two polar cyanobiphenyl (CB) mesogenic units linked by a flexible alkyl chain of nine carbon atoms [2, 4]. The compound was synthesized in the Department of Chemistry at the University of Hull (United Kingdom) [4] and its chemical structure and phase sequence are shown in Figure 1.

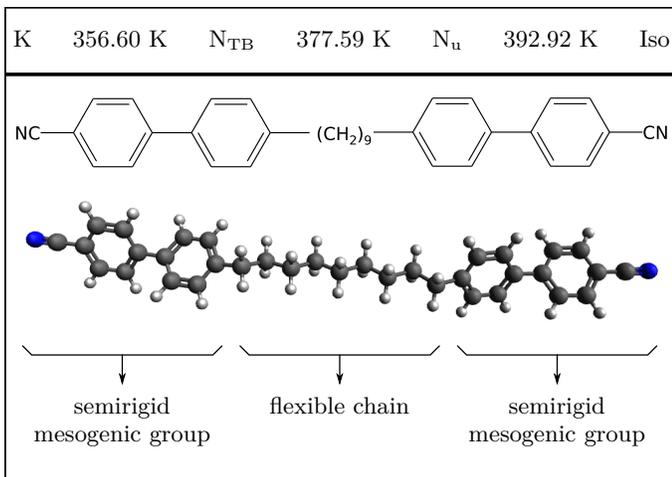


Figure 1. Chemical structure and phase sequence of the dimer α,ω -bis(4,4'-cyanobiphenyl)nonane (CBC9CB). Transition temperatures presented here are those reported by Tripathi *et al.* [4].

It is known that, upon cooling from the isotropic phase, the compound CBC9CB exhibits an uniaxial nematic phase (N_u) and an unknown nematic phase prior to crystallization. Those phases were detected by observing textures obtained with Polarised Optical Microscopy (POM) and by Differential Scanning Calorimetry (DSC) results. Afterwards, they were confirmed by X-Ray Diffraction (XRD) on a magnetically aligned sample. High-resolution Adiabatic Scanning Calorimetry (ASC) was used for the investigation of the two nematic phases of the pure compound CBC9CB and its mixture with 5CB up to 40 wt %. In the case of the pure compound, the transition from the isotropic to the uniaxial nematic and the lower temperature nematic was confirmed to be a weakly first order transition. On the other hand, in the case of the mixtures with 5CB, it was found that they exhibit the same two nematic liquid-crystalline

mesophases on cooling from the isotropic phase and no additional phases. The transition between the two nematic phases was found to be first order until a concentration of 5CB up to 40 wt %. Above this concentration the phase transition was not observed. [4]

EXPERIMENTAL METHODS

The experimental techniques that were used to characterize the dimer CBC9CB will now be addressed. These include POM, an Electro-Optical (EO) setup that allows us to measure some dimer's properties such as the elastic constants, and proton NMR spectroscopy. Here only the EO setup will be discussed.

First of all, let us make a note on how the liquid crystal dimer was contained and handled. As usual in this kind of experimental proceedings, the liquid crystalline material was contained in Indium Tin Oxide (ITO) coated glass with appropriate treatment to induce either planar or homeotropic surface alignment. The glass cells were labelled as they were filled as $h001$, $h002$ and $h003$. The first two were purchased from INSTEC (USA) and the last one from E.H.C. (Japan). According to the manufacturer, the Liquid Crystal (LC) chamber thickness are those summarized in Table I.

Table I. Summary of the LC cells used. Their thickness values presented here are those the manufacturer reports. For more information, please refer to manufacturer's brochure.

| Cell Label | Cell Gap (μm) | Alignment |
|------------|----------------------------|-------------|
| $h001$ | 8.7 | Planar |
| $h002$ | 9.0 | Homeotropic |
| $h003$ | 50 ± 10 | Planar |

Electro-Optics

An home built electro-optical setup was used to study the electric and optical properties of the compound CBC9CB. This setup, depicted in Figure 2, is composed of a HeNe laser ($\lambda = 632.8\text{nm}$) equipped optical bench associated with a function generator and a voltage amplifier. Sample temperature is maintained with a computer controlled oven with 0.2°C stability.

This electro-optic setup allow us to record both the tension applied and the current going through the sample, as well as the intensities of the outgoing laser beams split according to their polarization. This enables us to determine LC's capacitance and to investigate its birefringent behaviour, at different temperatures. Capacitance is determined measuring both the AC voltage applied to the LC cell and the current going through it. To

EXPERIMENTAL RESULTS AND DISCUSSION

POM Studies

Although we did not get into details about this experimental method here, it is still important to address what have been observed with it.

POM is here used to get a first touch with the compound being studied. As already mentioned, knowing the transition temperatures of our CBC9CB samples is important and we can not trust entirely in the values reported previously (recall Figure 1) because these samples could have become degraded or contaminated at some extend. We also needed to test if the glue used to seal the cells was resistant enough in the temperature range we were willing to reach.

In the first place, the glue seemed to hold in the temperature ranged covered. A fast scan running throughout the mesophases presented by CBC9CB showed that the transition temperatures were very close to the expected ones, although a bit lower than the values referenced by Tripathi *et al.* [4].

We obtained for the N_{TB} - N_u -Iso phase sequence the following transition temperatures:

$$N_{TB} \quad 378.3 \text{ K} \quad N_u \quad 393.8 \text{ K} \quad \text{Iso}$$

The temperatures obtained above may be affected by a calibration error of up to 2 K, but they serve our purpose of checking the integrity of the sample.

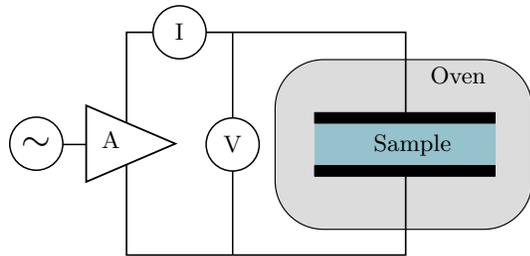
In Figure 3 we illustrate the N_u - N_{TB} phase transition. Notice that sample's texture changes stand out clearly. In the lower temperature nematic phase, the texture starts acquiring some stripes which develop into a more entangled pattern as the temperature goes down.

As a final note, it is important to say that during the last months we checked sample's integrity several times, again by measuring these phase transition temperatures. This temperature did not change significantly so we concluded that sample degradation was not a problem during the extent of this work.

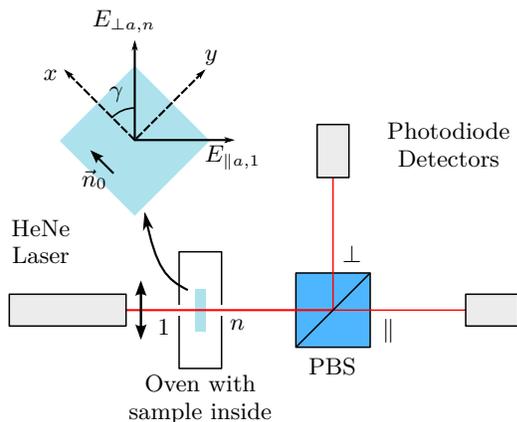
Capacitance and Optical Studies of Elastic and Dielectric Properties

The experimental data recorded with the help of the digital oscilloscope HS4 from TiePie engineering was processed in order to obtain the measurements of cell's capacitance, resistivity and light transmission. Fitting these quantities it is possible to determine the physical parameters that characterize our nematic system, such as the splay and bend elastic constants, the dielectric anisotropy constants and refractive indices.

The splay and bend constants were determined in the N_u phase from the capacitance fits. The following plots



(a) Electrical setup. An AC voltage is applied to the LC cell to induce the Fréedericksz transition.



(b) Optical setup. The linearly polarized HeNe laser beam hits the sample orthogonally. The outgoing beam is split by the PBS cube into orthogonal and parallel components and their intensities are read by photodiode detectors.

Figure 2. Experimental setup. In this schematic we separate the electrical and optical setups for a better understanding. The close up on cell in (b) is seen from the laser perspective.

induce the Fréedericksz transition the Alternate Current (AC) voltage amplitude is varied in steps and simultaneous measurements of voltage and current are performed at each step using a computer controlled Handyscope HS4 from TiePie engineering (see Figure 2a). On the other hand, birefringence is determined recording the perpendicular and parallel polarized beam intensities (relative to the incident linearly polarized beam) coming out of the beam splitter polarizing cube receiving the laser light that has passed orthogonally through the LC cell as shown in Figure 2b. These beam intensities are registered by two other channels of the same digitizing scope. The LC cell is placed perpendicular to the incident laser beam with the cells rubbing direction making an angle of 45° with the incident linearly polarized beam direction of polarization. [13]

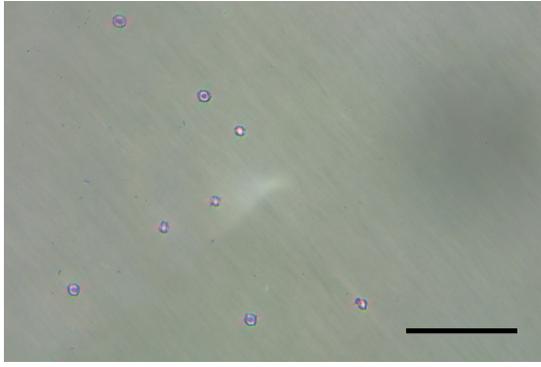
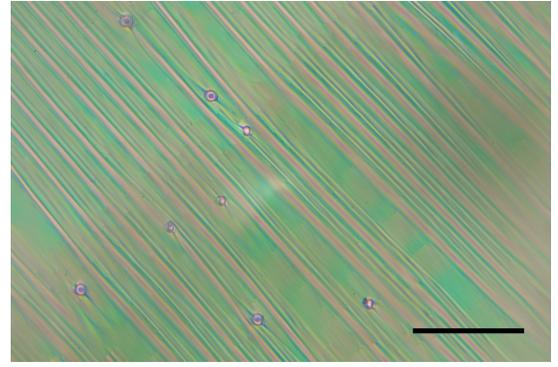
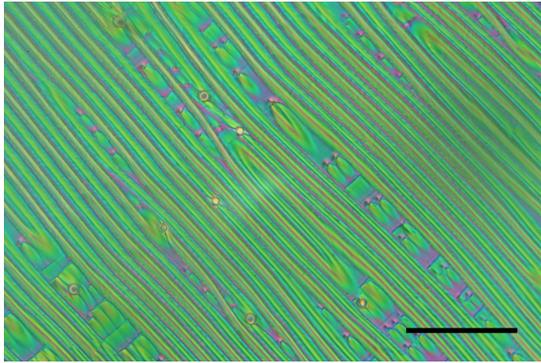
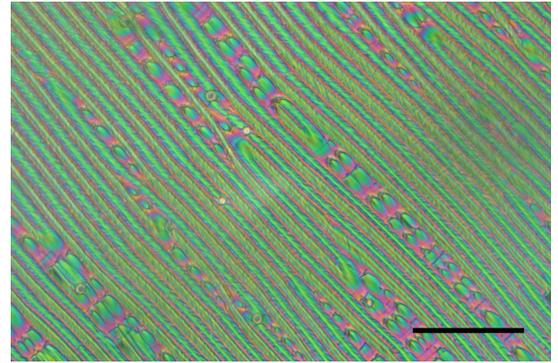
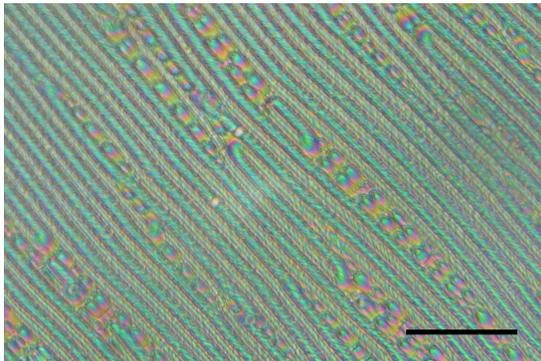
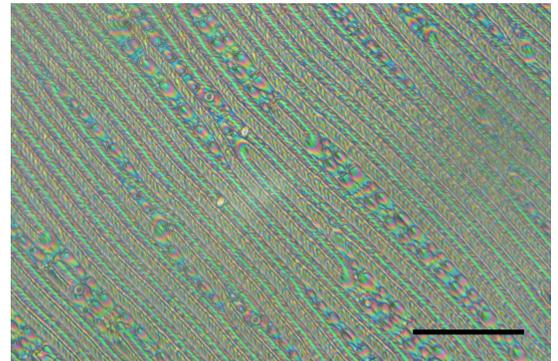
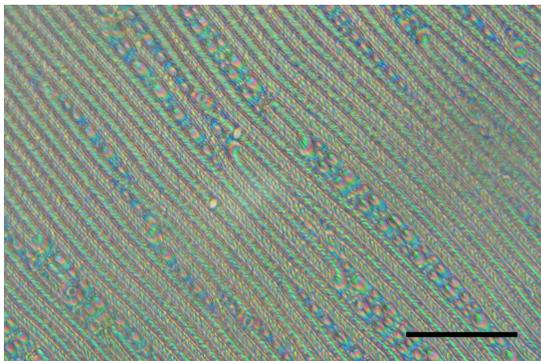
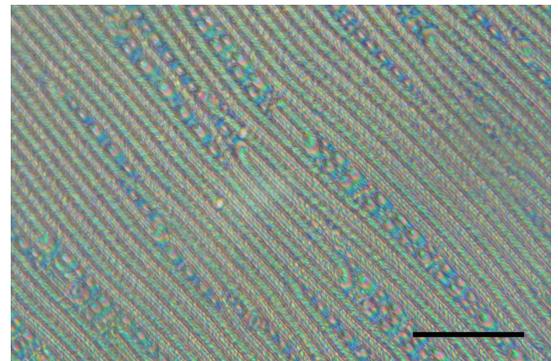
(a) $T = 380.3$ K(b) $T = 379.5$ K(c) $T = 378.7$ K(d) $T = 377.3$ K(e) $T = 373.2$ K(f) $T = 366.0$ K(g) $T = 361.5$ K(h) $T = 358.7$ K

Figure 3. Transition N_u - N_{TB} cooling at 2 K/min from the isotropic phase. The length of the black bar is 100 μm .

show the dependence with temperature of both splay and bend elastic constants (Figure 4), dielectric constants (Figure 5), conductivity (Figure 6) and nematic refraction indices (Figure 7).

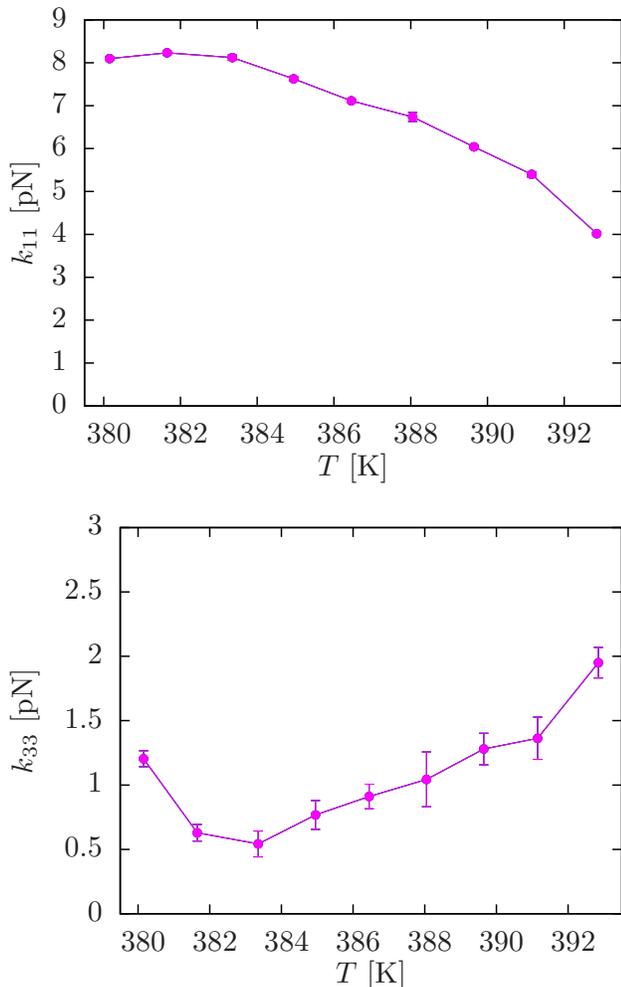


Figure 4. Splay and bend elastic constants obtained from a simultaneous fit of the capacitance at 30, 40, 60 and 100kHz.

The elastic constants shown in figure Figure 4 are in agreement with those observed with similar dimers [6–9]. Increasing K_{11} as the temperature is lowered is expected, but having $K_{33} < K_{11}$ with a decreasing tendency for K_{33} is far from expected for a nematic. But this has been observed for similar dimers also. This too leaves open the possibility for a negative bend elastic constant at the N_{TB} phase. This behaviour is not the expected one because when comparing with a well known system in the N_u phase, such as 5CB which has a rigid molecular core identical to each of those two in the dimer branches, we have both K_{11} and K_{33} rising with decreasing temperature and also $K_{33} > K_{11}$ [14]. So, although both CBC9CB and 5CB exhibit a N_u phase, K_{33} behaviour is quite different between these two materials in that phase.

Also of note is the tendency for the K_{33} constant to rise again near the N_{TB} - N_u phase transition. Adlem *et al.* [9] have also reported this behaviour, but its origin remains open for discussion.

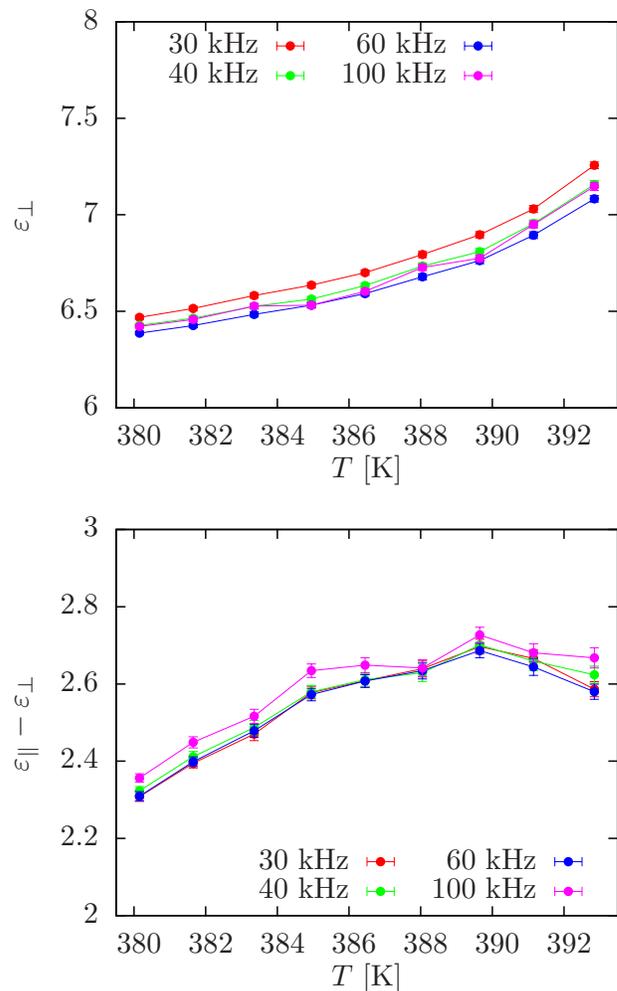


Figure 5. Normal permittivity and dielectric anisotropy obtained at 30, 40, 60 and 100kHz.

Dielectric constants measurements have also been done by Balachandran *et al.* [7] for the dimer CBC11CB. Although harder to spot in their results, there seems to be a decreasing tendency in dielectric anisotropy for both dimers. This behaviour goes against the one expected. Taking 5CB into account once again, dielectric anisotropy increases when lowering the temperature. On the other hand, ϵ_{\perp} behaves as expected. [14]

Regarding the refractive indices we obtained in the N_u and, once again, comparing with 5CB data, the behaviour measured is the expected: increasing $n_e - n_o$ with decreasing temperature. The values measured are also in agreement with those obtained for 5CB. [14]

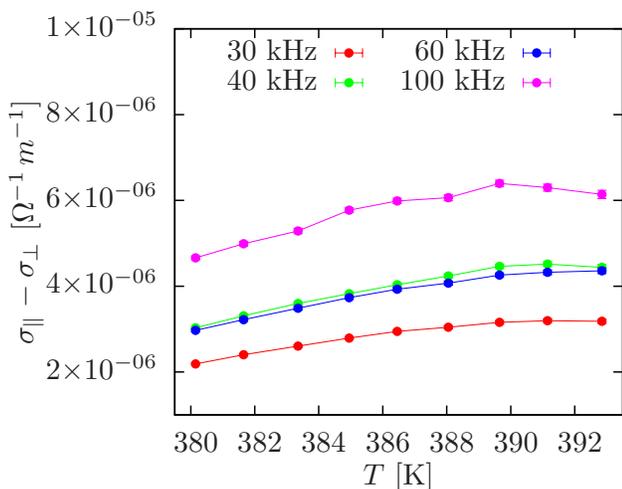
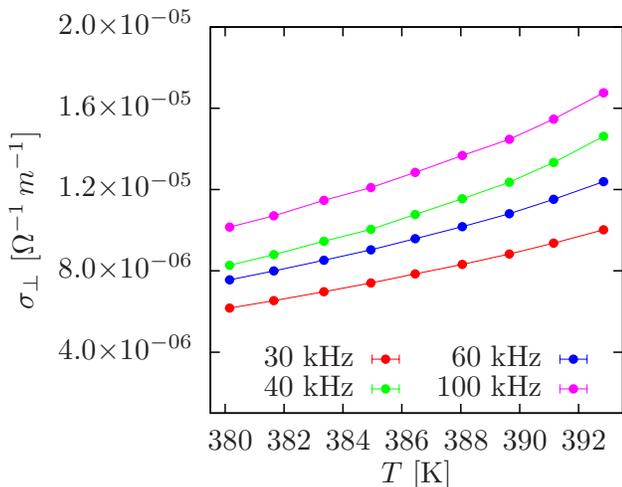


Figure 6. Conductivity obtained at 30, 40, 60 and 100kHz.

NMR Study of the Molecular Alignment in CBC9CB Mesophases

^1H NMR spectra were recorded at regular temperature intervals in both mesophases and at two distinct field strengths: 0.78 T and 7 T, henceforth denominated by low field and high field for simplicity. These treated spectra are presented in Figure 8.

Looking at the spectra recorded at different temperatures at high fields we can see that the overall shape does not change significantly, indicating that the changes may simply derive from the order parameter evolution with the temperature. Following this hypothesis we consider one spectrum in the high temperature phase as the reference spectrum and fit it to the other temperature spectra considering that the order parameter has changed accordingly. Because of the odd shape change revealed for lower field, we will focus only in the higher field data for the moment.

We start by choosing for the reference spectrum the

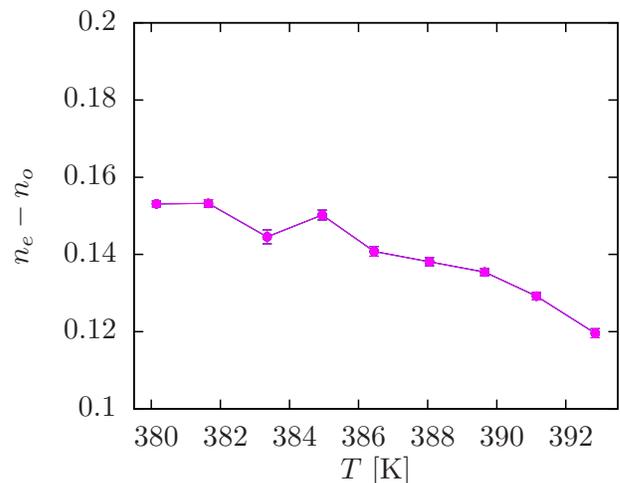
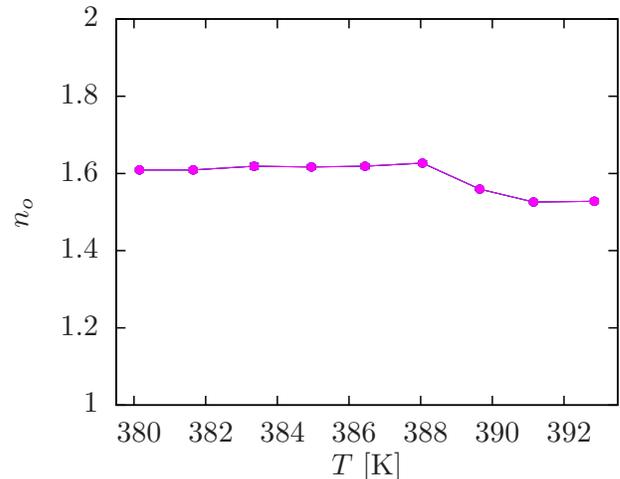


Figure 7. Normal refraction index and optical anisotropy obtained from a simultaneous fit of the optical transmission at 30, 60 and 100kHz.

spectrum recorded at the temperature of 381 K in the known N_u phase. To fit the different spectra at high field we consider a fitting function $G'(\omega')$, based on the reference spectra $G_r(\omega)$ linearly interpolated with its argument scaled by a factor A , $\omega' = \omega/A$, and its amplitude scaled by a factor B , $G' = B G_r$. This approach is justified by the fact that the dipolar Hamiltonian responsible for the dipolar spectral splitting is in good approximation proportional to the nematic order parameter S .

Our interest lies into parameter A for it is related to the nematic order parameter S . In the high temperature nematic phase this parameter should be proportional to the nematic order parameter S . We have obtained a rough estimate of this proportionality constant through a direct evaluation of the order parameter from the average spectra splitting due to the dipolar interaction between the proton pairs in the core benzene rings and by using published data on the proton spectra and the nematic order

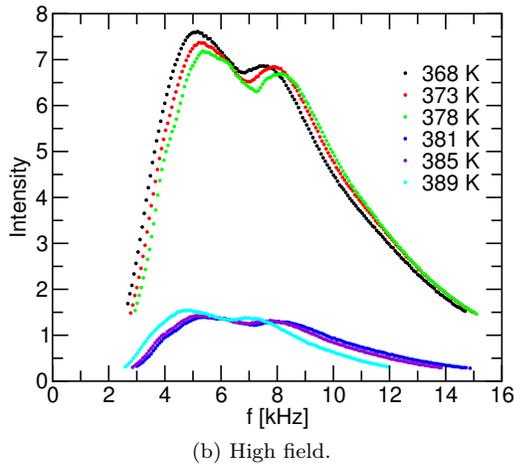
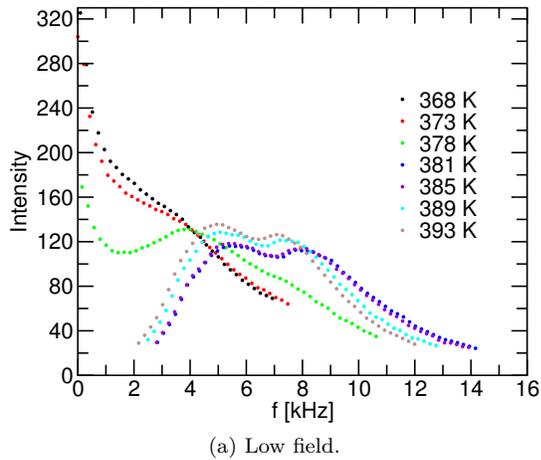


Figure 8. ^1H NMR spectra obtained.

parameter of 5CB, which has a molecular core identical to each dimer of CBC9CB.

To describe the temperature dependence of the order parameter in the high temperature nematic we have considered a Haller law [15], this law will later be extended to the N_{TB} phase also. These results for high field are shown in Figure 9. The analysis will not be addressed here. For full details, please refer to the full text.

The angle $\Delta\beta$ translates the occurrence of a significative conformation change of the molecule in the N_{TB} phase relative to the N_{u} phase, which is also responsible for the appearance in the N_{TB} phase of a non-equivalence between the two deuteriums linked to the first chain carbons in selectively deuterated CBC9CB [16].

Fitting $\Delta\beta$ in the N_{TB} phase to a Haller type law produces the results shown in Figure 9b. Using this $\Delta\beta(T)$ dependence leads to the fitting result shown in Figure 9c for the full range of temperatures studied. We verify that the model used translates our experimental data very well. This lead us to conclude mainly that, in N_{TB} phase, there is a significant conformation change relative to the N_{u} phase and it probably corresponds to a tilt-

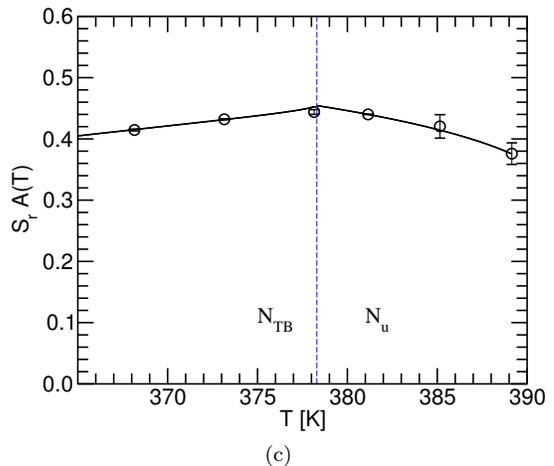
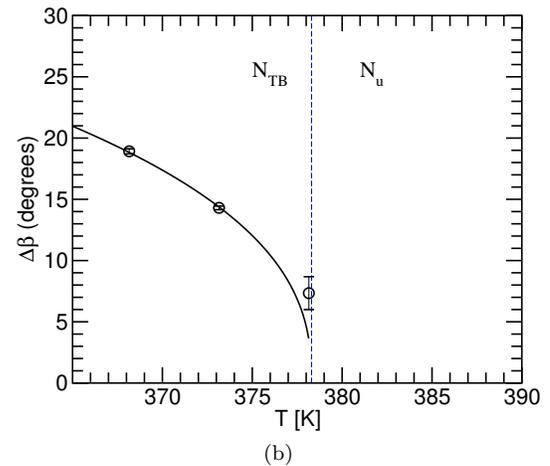
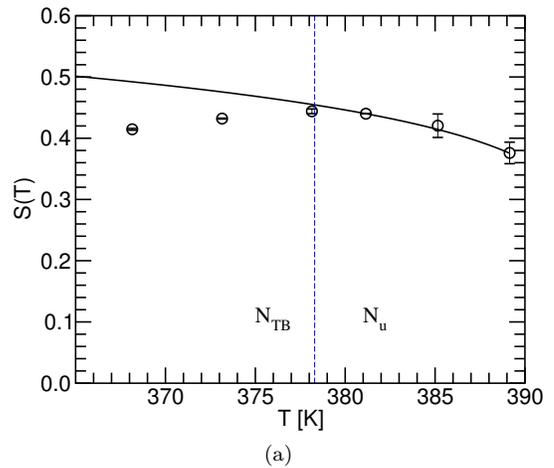


Figure 9. Temperature dependence of the nematic order parameter in a range that covers both CBC9CB dimer mesophases. In (a) experimental data in N_{u} is fitted to an Haller law; (b) presents an Haller law fit to the angle $\Delta\beta$, which can be seen as an order parameter of the $N_{\text{TB}}-N_{\text{u}}$ transition; (c) shows the full fit taking into account the temperature dependence for $\Delta\beta$ obtained in (b).

ing increase of the benzene rings para-axis relative to the

most ordered molecular axis. This tilting increase may be linked with the twist-bend configuration proposed for the LC molecules in the N_{TB} phase [3].

Regarding the analysis of the low field spectra, the fits in the N_u phase to $G(\omega, S, \Delta\beta)$ are shown in Figure 10. These were executed exactly as in the high field case by taking the spectrum at $T = 381$ K as reference.

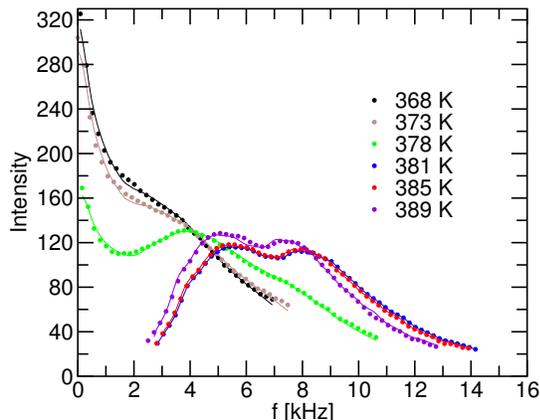


Figure 10. Fits of the spectra obtained in low field to the reference spectrum at $T = 381$ K.

The values of the fitting parameter A obtained in the N_u phase are within error similar to those obtained in the high magnetic field experiment.

In the N_{TB} phase the spectra are very different from those in the N_u phase, indicating that the director is not aligned with the external magnetic field but instead it is distributed over different orientations relative to this field. To fit these spectra we must consider the superposition of the spectra arising from different domains with their director making different angles with the external field. If the director is not aligned with the external field the dipolar splitting becomes reduced by a factor which depends on the angle θ between the director and the field. Therefore, the fits in the N_{TB} phase depend upon an orientation distribution probability $P(\theta)$. This distribution was approximated to a series expansion in Legendre polynomials up to the 10th order, but considering only even terms due to the $\vec{n} = -\vec{n}$ symmetry. The fits in the N_{TB} phase are also shown in Figure 10 and the corresponding $P(\theta)$ in Figure 11. These results show that, for fields of 0.78 T, the director in the N_{TB} phase is not uniform as observed also in POM images of this phase while, for fields of 7 T, the director becomes aligned by the field.

From the angular distributions present in Figure 11 one can also see that there is a huge difference when going from 373 K to 378 K. We think it is safe to say that the θ distribution for $T = 378$ K somehow reveals an intermediate distribution between the perfect alignment with the field situation (N_u phase) and the alignment charac-

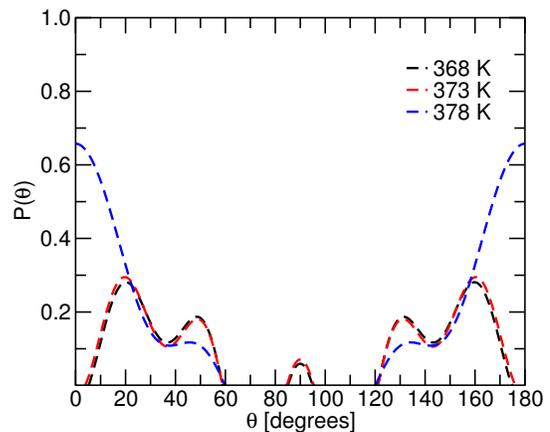


Figure 11. Orientation distribution in θ for the N_{TB} phase at low magnetic field.

teristic of the low temperature nematic. In the latter, for instance at 373 K, likely θ orientations move away from $\theta = 0$ thus indicating a configuration for the director that is not aligned with the B_0 field of the spectrometer. Between 373 K and 368 K distributions it is hard to tell the difference. This leads us to consider that the structure reached may be the most stable for lower temperatures into the N_{TB} phase.

As a final note, recall that such an evolution of the director field when lowering the temperature right after the N_u - N_{TB} phase transition and into the N_{TB} was in fact observed during our POM studies. Back in Figure 3 watch as the pattern observed evolves from simple stripes to a more entangled texture along those initially formed stripes.

CONCLUSIONS

Bimesogenic dimers like CBC9CB have become very interesting in the past few years due to the presence of an unusual nematic phase, whose physical characteristics are not yet fully understood.

The studies made on this dimer in particular when performing this thesis evidenced the fact that there still exist important doubts concerning what could be the cause of the spontaneous bend-like conformation the material seemed to acquire in the N_{TB} phase. Namely, our measurements of the splay and bend elastic constants are coherent with those obtained by independent investigations on similar dimers and support the idea of a decreasing bend elastic constant as the system is cooled into the N_{TB} phase, although not excluding the possibility of negative values.

Our observations under POM showed a huge texture change when the transition N_{TB} - N_u occurs. The textures observed in every phase is consistent with those reported for similar dimers. In particular, the texture in

N_{TB} phase resembles a somehow twisted conformation of the director.

We also confirm a high viscosity in this lower temperature nematic phase for this compound. Besides the need of a much stronger field to be able to change the orientation of the director, it was observed that, after switching off the electric field applied, there was no visual evidence of the nematic returning to its original configuration state during several minutes. Observations on the dimer α,ω -bis(4,4'-cyanobiphenyl)undecane (CBC11CB) mention that it takes a few hours to return to its original state [7].

The NMR study showed that a significant conformation change sets in the N_{TB} phase relative to the N_u phase. Also, while a 7 T field can align the director in the N_{TB} phase, a 0.78 T field is not sufficient to do it. In the N_{TB} phase at low field, the distribution of director orientations is not uniform but shows a well defined structure at each temperature suggesting that the director field adopts a non-uniform preferred configuration.

Looking back at what we initially intended to do and what we could indeed achieve over past months, it is clear that a lot of research is still needed to fully understand this unique nematic phase.

Although our motivation was to try to fully explore the N_{TB} phase, our experimental approach revealed to be insufficient to switch the director in this phase because a higher electric field was needed and the cell in which the LC was contained could not withstand it. This restricted our electro-optic study to the uniaxial nematic phase. Because of this, further investigation in the N_{TB} is still required and may certainly be the next step for a future work. In particular, we plan to explore magnetically induced Fréedericksz transitions in the N_{TB} phase to directly access the elastic constants in this phase and verify the hypothesis that one or more Frank elastic constants take negative values.

Regarding the results from the analysis of the NMR spectra, we intend to develop a model of orientational order in this system capable of explaining our proton NMR results along with deuterium data obtained with selectively deuterated CBC9CB and reported at ECLC2013 [16]. In particular, we want to precisely identify the

molecular conformation changes that seem to onset at the N_u - N_{TB} phase transition.

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