

## Contribution of proton NMR relaxation to the investigation of molecular dynamics in columnar mesophases of discotic and polycatenar molecules

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**Abstract.** We present in this work a review concerning wide frequency range  $T_1$  proton NMR relaxation studies performed in compounds exhibiting columnar mesophases, namely the  $\text{Col}_{\text{ho}}$  mesophase in the case of a liquid crystal of discotic molecules and the  $\phi_{\text{h}}$  mesophase in the case of a liquid crystal of biforked molecules. These NMR relaxation studies were performed combining conventional and fast field cycling NMR techniques in a frequency range between 100 Hz and 300 MHz. The possibility of probing such a large frequency range has provided a way to effectively distinguish the influence, on the  $T_1$  relaxation profiles, of the different molecular movements observed in this type of mesophases. In addition, we present a comparison between the molecular dynamics in columnar ( $\phi_{\text{h}}$ ) and lamellar (SmC) mesophases exhibited by the same biforked compound.

**Keywords.** Liquid crystals; NMR relaxation; molecular dynamics.

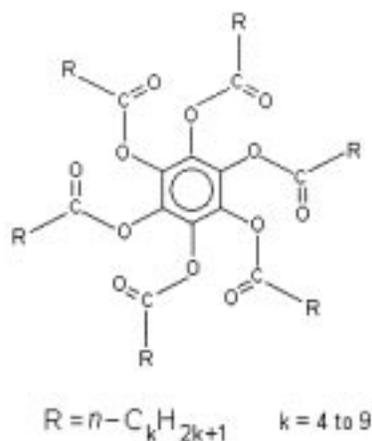
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### 1. Introduction

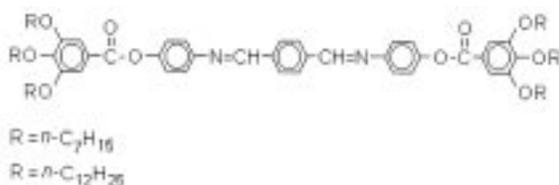
The discovery of a columnar mesophase exhibited by some compounds of the series of discotic molecules, presented in figure 1, was reported for the first time in the literature in 1977 by the Bangalore Group [1]. In the detected mesophase called  $\text{Col}_{\text{hd}}$  the discotic molecules are organized in columns forming a two-dimensional hexagonal lattice in the plane perpendicular to the columnar axis. The index 'd' in  $\text{Col}_{\text{hd}}$  means that the molecules are positionally disordered inside a column.

After this important discovery, the synthesis and characterization of new different types of compounds of disc-like molecules were reported. In fact, with this type of molecules with a flat rigid core surrounded by aliphatic chains it was also possible to observe columnar hexagonal ordered mesophases ( $\text{Col}_{\text{ho}}$ ) [2,3], different types of columnar rectangular mesophases [3–5], oblique columnar mesophases [5,6], nematic, cholesteric mesophases [7] and in very peculiar cases a smectic phase of disc-like molecules [8].

In 1985, a new class of thermotropic liquid crystalline compounds called phasmids was described in the literature [9]. The molecules of these compounds (see figure 2) present



**Figure 1.** Molecular structure of the first discovered series of compounds of disc-like molecules exhibiting columnar ( $Col_{hd}$ ) mesophases.



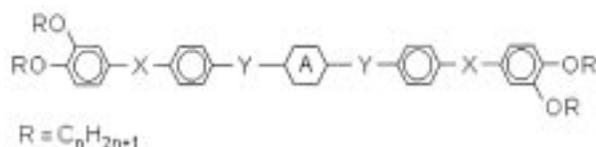
**Figure 2.** Molecular structure of the first discovered series of mesogenic compounds of phasmidic molecules.

a rod-like rigid core ending on two half-disc-shaped moieties formed by three aliphatic chains attached to both terminal sides (actually, the origin of the name *phasmidic* comes from the resemblance of this molecular structure with the so-called insect).

With this first system it was possible to observe, in one case, the existence of a columnar oblique mesophase and, in another case, a phase transition between a columnar oblique mesophase and a columnar hexagonal mesophase. However, it is important to remark that in the columnar mesophases of these systems, a columnar plateau is not formed by a single molecule, as in the case of disc-like molecules, but by an aggregation of some molecules [10]. In the case of the columnar hexagonal mesophase of the phasmidic molecules ( $\phi_h$  phase) it was proved, taking into account X-rays and dilatometric measurements, that the average number of molecules by plateau, arranged side by side, is close to three (18 chains by plateau) [10].

Following the discovery of phasmidic molecules, a new class of thermotropic liquid crystalline compounds, of the so-called biforked molecules, was described in the literature for the first time in 1986 [11]. The molecules of these compounds present a rod-like rigid core, as in the case of phasmidics, ending on both sides by two aliphatic chains. In this first report concerning biforked molecules five series of compounds were synthesized and characterized (see figure 3).

With some of the compounds having short chains it was possible to detect the existence of lamellar smectic C phases, while for others it was possible to observe in the same



**Figure 3.** Molecular structure of the first discovered series of mesogenic compounds of biforked molecules.

compound nematic and smectic C mesophases in different temperature ranges. For the compounds with long chains, the nematic or smectic C mesophases are not detected and a columnar mesophase similar to the  $\phi_h$  phase of phasmidic molecules can be observed. For compounds with intermediate chain length different types of polymorphism are detected. For one particular compound, it was possible to observe the existence of a peculiar columnar phase, a cubic phase and finally a smectic C phase on decreasing the temperature from the isotropic phase. However, we must remark that for other biforked compounds, direct phase transitions between the smectic C phase and the columnar hexagonal ( $\phi_h$ ) phase were reported afterwards [12] and carefully studied by X-ray dilatometry and NMR [13,14]. It was verified that in the  $\phi_h$  phase of the biforked compounds the average number of molecules side by side in each columnar plate is about 4.5 (average of 18 chains by plateau as in the phasmidic compounds) [13]. The phasmidic molecules and the biforked molecules are, in general, called as polycatenar molecules. These polycatenar molecules fill the gap between calamitic and discotic molecular shapes. In fact, in general, it is possible to observe lamellar mesomorphic structures with calamitic molecules and columnar structures with discotic molecules. With the polycatenar mesogens it is possible to observe lamellar and/or columnar mesophases. In the case of the biforked molecules both structures can be observed with the same compound as described previously [12,15].

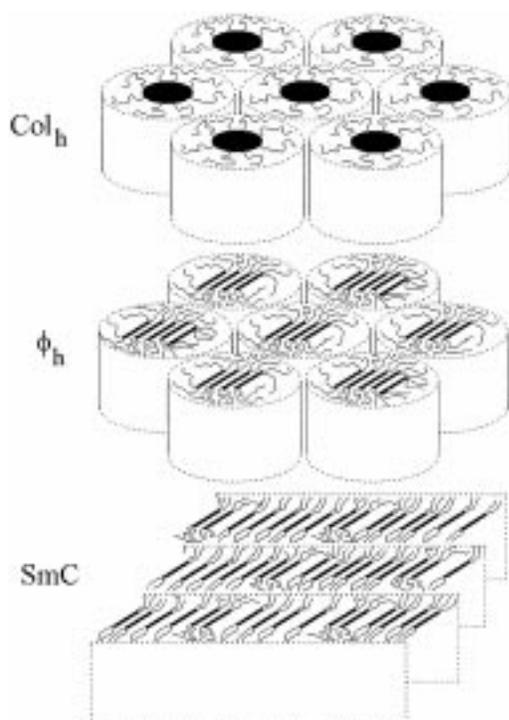
In this paper, we present a review concerning wide frequency range proton  $T_1$  NMR relaxation on columnar mesophases. The reference systems are two different kinds of compounds exhibiting columnar mesophases, namely a compound of disc-like molecules showing a  $Col_{ho}$  mesophase [2] and a compound of biforked molecules showing a  $SmC-\phi_h$  phase transition [12]. Additionally, the study of the biforked compound allows for the comparison of the molecular dynamics behaviour in columnar ( $\phi_h$ ) and lamellar ( $SmC$ ) phases exhibited by the same compound. In figure 4, a schematic representation of the structure of the three described mesophases is seen.

We will show how NMR spin-lattice relaxation studies performed in large frequency domains are important to the study of molecular dynamics in liquid crystals and how, in some cases, they can be useful in understanding the structure of the mesophases.

## 2. Nuclear magnetic relaxation in liquid crystals

### 2.1 A general view

Proton spin-lattice relaxation studies are particularly useful in obtaining a general view of the relative importance of different molecular motions, observed in different mesophases [16,17], especially when a wide frequency range is explored [18,19]. In this work, the  $T_1$  NMR relaxation studies presented were performed at frequencies ( $\nu$ ) from 100 Hz to



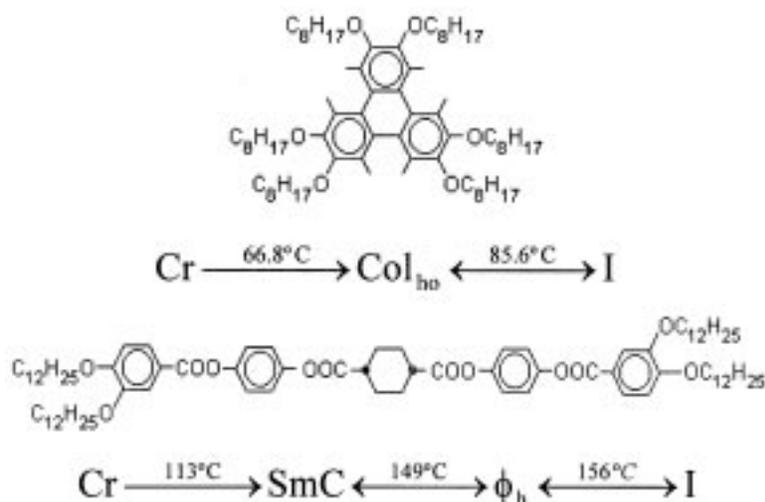
**Figure 4.** Schematic representation of the  $\text{Col}_h$ ,  $\phi_h$  and  $\text{SmC}$  phases.

300 MHz, combining conventional and fast field cycling NMR techniques. We must remark that only with field cycling techniques it is possible to perform systematic relaxation measurements for frequencies below the MHz range [18]. The possibility of probing such a large frequency range has provided a way to effectively distinguish the influence on the relaxation profiles of the different molecular movements and to estimate their characteristic time-scales [18].

Usually, the relaxation dispersion profile may be analysed considering the sum of different contributions  $(1/T_1)_i$  to the overall relaxation rate  $(1/T_1)$  [20].

$$\frac{1}{T_1} = \sum_i \left( \frac{1}{T_1} \right)_i \quad (1)$$

In the case of liquid crystalline phases, the  $(1/T_1)_i$  contributions for the global relaxation  $1/T_1$  profile are, in general, associated with molecular local rotations/reorientations, translational self-diffusion and collective movements. From many significant proton relaxation studies performed in the past, in different types of mesophases exhibited by different kinds of liquid crystals it is possible to conclude that, in general, collective motions are dominant in the low frequency range, translational self-diffusion is dominant in an intermediate frequency range and rotations/reorientations are dominant in the high frequency range [17–19]. It is also very important to remark that other kind of motions associated with very peculiar mesophases can also show their signature in the relaxation profiles [21].



**Figure 5.** Molecular structures and phase sequences of liquid crystals of the disc-like molecules ( $\text{C}_8\text{HET}$ ) and of the biforked molecules discussed in this work.

Several theoretical studies describe how the relaxation profiles associated with the different types of movements depend on the molecular shape and structural details of the mesophase [17] as we will see in §2.3.

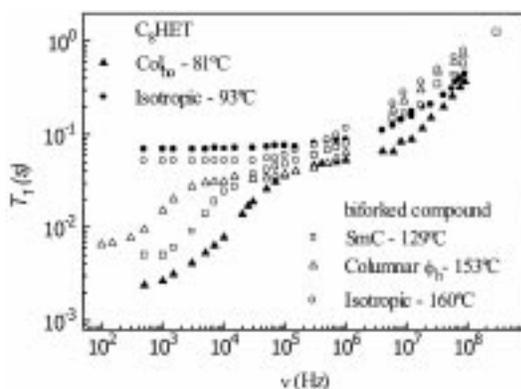
## 2.2 NMR relaxation results obtained in different types of mesophases

In this section, we will present a detailed qualitative analysis of the nuclear magnetic relaxation results of the spin lattice-relaxation time  $T_1$ , as a function of the frequency  $\nu$ , obtained in the isotropic and  $\text{Col}_{\text{ho}}$  columnar mesophase of the discotic compound  $\text{C}_8\text{HET}$ , and in the isotropic, smectic C and columnar  $\phi_{\text{h}}$  phases of the biforked compound referred to in this work. The molecular structures and phase sequences of these two compounds are presented in figure 5 [2,12].

In order to illustrate the influence of phase structure on the proton spin-lattice relaxation, we present in figure 6 the  $T_1$  dispersion characteristic profiles obtained for the phases described above. It is clear that the observed  $T_1(\nu)$  depends on the type of phase.

The comparison between the  $T_1(\nu)$  profiles obtained in the isotropic phases of both compounds shows that they are quite identical and clearly different from those observed for the three studied mesophases. In fact, in the isotropic phases of both compounds, a large plateau is observed for frequencies lower than  $\sim 100$  kHz. The clearly different behaviour of  $T_1(\nu)$  detected in all mesophases for that frequency range must be associated with the structure of the phase and with the existence of a specific relaxation mechanism not present in the isotropic phase. This is the case of collective motions, which is generally the relaxation mechanism dominant in the lower frequency regimes as described in §2.1.

From the observation of the  $T_1(\nu)$  profile presented in figure 6 it is also possible to conclude that above  $\sim 10$  MHz a similar behaviour (regular monotonic increase) of  $T_1(\nu)$



**Figure 6.**  $T_1$  vs. proton frequency,  $\nu$ , in the isotropic,  $Col_{ho}$ ,  $\phi_h$  and SmC phases of the compounds presented in this work.

is detected in all phases. This means that a ‘similar’ relaxation mechanism is observable in all phases for this frequency range. As described in §2.1 and taking into account the facts described in the literature [17] it is possible to say that this is the case of rotations/reorientations, which are the most effective motions that relax the protons in liquid crystals at the high frequency regime.

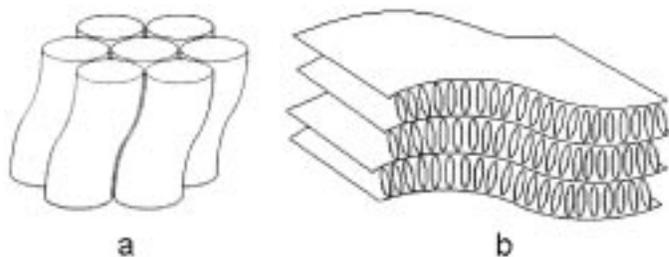
The comparison of  $T_1(\nu)$  results presented in figure 6 for the SmC and  $\phi_h$  mesophases in the frequency range  $\sim 3 \times 10^4$ – $10^6$  Hz clearly show that the results are very similar for both mesophases ( $T_1$  decreases slightly with decreasing  $\nu$ ). The data points are approximately parallel. The small shift observed is essentially due to the temperature difference between the two phases. This means that the most important relaxation mechanism in this frequency range is similar for both mesophases; in general as described in §2.1 in liquid crystals, in the intermediate frequency range, translational self-diffusion is the predominant relaxation mechanism.

However, for frequencies lower than  $10^4$  Hz, the behaviour of  $T_1(\nu)$  for the SmC and  $\phi_h$  mesophases is clearly different. This means that collective motions present a different physical behaviour in the two mesophases.

Moreover, the behaviour of  $T_1(\nu)$  in the mesophases of the biforked compound and in the  $Col_{ho}$  mesophase clearly diverge for frequencies smaller than  $7 \times 10^4$  Hz. In fact, in the  $Col_{ho}$  mesophase it is also observed that a small decrease of  $T_1$  between  $10^6$ – $7 \times 10^4$  Hz similar to that observed in the other mesophases, corresponding to the dominant contribution of self-diffusion in this frequency range. However, for the  $Col_{ho}$  mesophase, for values of  $\nu$  smaller than  $7 \times 10^4$ , a clear decrease of  $T_1$  with  $\nu$  is observed. This behaviour must be associated with a strong importance of the collective motions for higher values of  $\nu$  than those observed for the mesophases of the biforked compound. These results will be discussed in the next section.

### 2.3 Relaxation models for the $Col_{ho}$ phase

The contribution of the reorientational/rotational relaxation mechanism in the columnar phases of the discotic compound is described by a generalization of the Woessner model



**Figure 7.** Schematic representation of the collective movements observed in columnar and lamellar mesophases, respectively columnar deformations and layer undulations.

[22]. This approach [14,23] considers a combination of the discotic core and chains reorientational movement each of which is characterized by two correlation times for transversal and longitudinal rotations,  $\tau_{\perp}$ ,  $\tau_{\parallel}$ ,  $\tau_{\perp}^C$ ,  $\tau_{\parallel}^C$ , respectively, as described in [23].

The contribution of the molecular translational self-diffusion mechanism to the overall proton relaxation rate in the  $\text{Col}_{\text{ho}}$  mesophase of the discotic compound is explained by a model presented by Zumer and Vilfan [24]. In this model, diffusion is described by sequences of random jumps of the molecules from one column to an adjacent one. These movements are characterized by the average time between jumps,  $\tau_D$ , which determine the diffusion coefficients,  $D_{\parallel}$  and  $D_{\perp}$ , taking into account the structure of the phase that determines the mean lengths for single diffusive jumps.

The contribution of collective movements to the relaxation rate in the case of the  $\text{Col}_{\text{ho}}$  phase of the discotic compound is explained by a model presented by Zumer and Vilfan [24] that takes into account bending and compression of the columns characterized by the corresponding elastic parameters,  $K_3$  and  $B$ , respectively, and the effective viscosity  $\eta$  (see figure 7a). As is generally considered in director fluctuation models, the collective modes are limited by minimum and maximum lengths which correspond, at the limit, to the dimensions of a molecule and a single domain, respectively. This gives rise to high and low cut-off frequencies, respectively, in the  $T_1$  frequency dispersion. In this case [24] due to the asymptotic behaviour of  $1/T_1(\nu)$  in the low frequency regime, only the high cut-off frequency  $\omega_c$  is necessary to be taken into account.  $\omega_c$  is given by

$$\omega_c = 2\pi\nu_c = \frac{K_3 q_{\parallel}}{\eta} \quad \text{with} \quad q_{\parallel} = \frac{2\pi}{d}, \quad (2)$$

where  $d$  is the average distance between neighbouring molecules inside a column.

#### 2.4 Relaxation models for the $\text{SmC}$ and $\phi_h$ mesophases of biforked compounds

In the case of the biforked compound, the rotational/reorientational relaxation mechanism is explained by the model previously referred [14] taking into account both the different geometry of the core (rod-like vs. disc-like) and the particular orientation of its main symmetry axis relative to the phase director [14,23]. As in the case of the  $\text{Col}_{\text{ho}}$  phase, two pairs of correlation times, for longitudinal and transversal motions of the core and chains,  $\tau_S$ ,  $\tau_L$ ,  $\tau_X^C$ ,  $\tau_L^C$ , respectively, must be considered [14].

In the case of the SmC phase of the biforked compound, the molecular translational self-diffusion relaxation mechanism is explained by a random jump model, in which diffusion is described as a combination of intra- and inter-layer jumps. The corresponding diffusion coefficients,  $D_{\perp}$  and  $D_{\parallel}$ , are determined by the characteristic times between jumps,  $\tau_{\perp}$  (in layer) and  $\tau_{\parallel}$  (between layers), and by the type and characteristic lengths (mean lateral molecular distance and layer spacing) of the smectic phase considered [25].

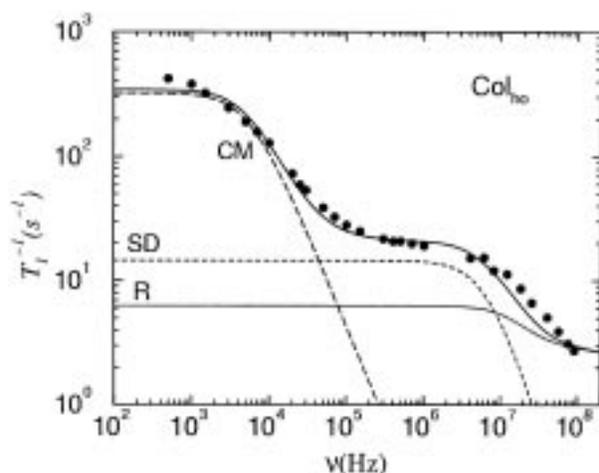
Due to the similarity between the SmC and the  $\phi_h$  phase of the biforked compound at local level [13] (see figure 4), it was considered as a hypothesis that the molecular translational self-diffusion model used to describe the SmC phase can be applied to the  $\phi_h$  phase. In fact, as described in §2.1, the  $T_1$  frequency dependence is quite similar for these two phases in the intermediate frequency range. We must stress that the model used to explain the proton relaxation due to self-diffusion is basically a local model in the sense that the results of the diffusion process are determined by the random jumps of the molecules to adjacent positions [25,26]. This justifies the assumption made, which, as will be seen in the discussion, was coherently verified by the analysis of the experimental results. Obviously, the diffusion model used for the Col<sub>ho</sub> phase is not appropriate in this case, because the columnar aggregates (corresponding to the discs in the Col<sub>ho</sub> phase) are, in this case, composed of several molecules, which do not have any plausible physical reason to diffuse together.

In the case of the  $\phi_h$  phase of the biforked compound, the columnar hexagonal symmetry of the phase justifies the use of the model previously adopted to explain the contribution of collective motions to the relaxation in the Col<sub>ho</sub> phase of the discotic compound [14,23,27]. Contrary to what happens with the diffusion mechanism, the movements are collective and the entities involved are not the individual molecules but rather, in this case, the ensemble of columns that are considered as a continuous anisotropic medium. This justifies, in principle, the assumption that the same model (columnar deformations [24]) applies to both columnar phases [14,23]. Again this is verified by the analysis of the experimental results.

The contribution of collective movements to the relaxation rate in the case of the SmC phase of the biforked compound is described by a mechanism where the layer undulation movements (see figure 7b) are the dominant collective modes [28]. This mechanism gives a contribution to the relaxation rate proportional to the inverse of the Larmor frequency as was verified by the experimental results. As in other collective movement models, low and high cut-off frequencies appear, due to limits in the wavelength of the collective modes considered. The high cut-off frequency ( $\nu_{CH}$ ) is imposed at the limit by the molecular dimensions and the limit to the low cut-off frequency ( $\nu_{CL}$ ) is determined by the dimensions of a single smectic domain.

### 3. Analysis of experimental results

The analysis of the experimental results is made by fitting expression (1) corresponding to the sum of the three different contributions to the relaxation rate to the measured  $1/T_1(\nu, T)$  values. For each mesophase, the fits were performed by the minimization of  $\chi^2$  taking into account the compatibility between physical parameters for all the temperatures involved. This means that, for one mesophase, all the data obtained at different temperatures are fitted together by a single expression  $1/T_1(\nu, T)$  which includes the variation of the physical parameters with the temperature. For instance, in the case of thermally activated



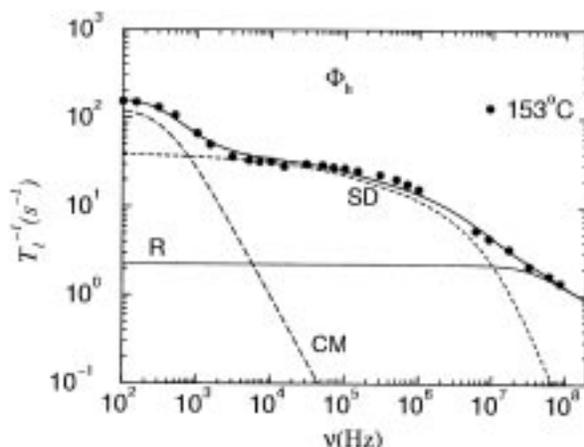
**Figure 8.** Fit of the relaxation rate ( $1/T_1$ ) data as a function of the frequency ( $\nu$ ) in the  $Col_{ho}$  phase ( $T = 81^\circ C$ ) of the compound of disc-like molecules, using the models described in §2.3 for the contributions of local molecular rotational reorientations (R), translational self-diffusion (SD) and collective movements (CM).

mechanisms, the characteristic times associated with the movements must obey the Arrhenius law with the same activation energy. Additionally, some of the parameters involved in the models were obtained from the literature considering measurements performed by other experimental methods as, for instance, X-rays [2,3,12].

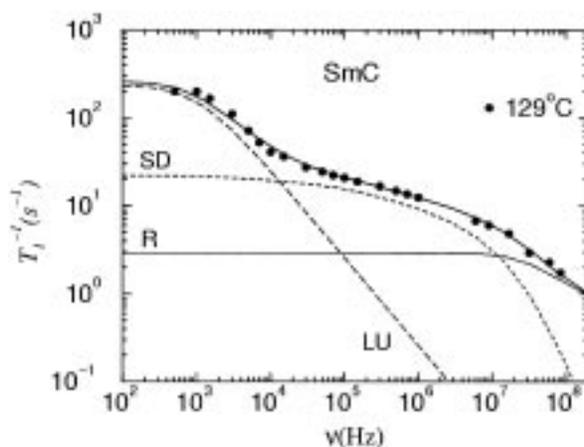
### 3.1 $Col_{ho}$ phase of $C_8HET$

As an example, in figure 8 we present the fit of the  $1/T_1$  theoretical models to the experimental data obtained for the  $Col_{ho}$  phase ( $T = 81^\circ C$ ) of the compound  $C_8HET$ . The results corresponding to this fit confirm clearly the assumptions presented before, concerning the importance of the different molecular motions to the relaxation rate in different frequency ranges [23]. From these fits it was possible to conclude that:

- The high cut-off frequency,  $\nu_c$ , for the collective modes corresponding to the deformation of the columns is close to 28 MHz.
- The characteristic times between diffusive jumps,  $\tau_D$ , are of the order of  $10^{-8}$  s and the diffusion coefficients,  $D_\perp$  and  $D_\parallel$ , associated with molecular movements in directions both perpendicular and parallel to the columns are of the order of  $10^{-10}$   $m^2 s^{-1}$  and  $10^{-12}$   $m^2 s^{-1}$ , respectively.
- The correlation time associated with the global rotations of the molecules around the columnar axis  $\tau_\parallel$  is of the order of  $10^{-9}$  s, while the correlation time for reorientations out of the average disc plane,  $\tau_\perp$  is of the order of  $10^{-8}$  s. The correlation times associated with the rotations of the chains around transversal ( $\tau_\perp^C$ ) and longitudinal ( $\tau_\parallel^C$ ) axis attached to the core are of the order of  $10^{-11}$  s and  $10^{-12}$  s respectively.



**Figure 9.** Fit of the relaxation rate ( $1/T_1$ ) data as a function of the frequency ( $\nu$ ) in the  $\phi_h$  phase ( $T = 153^\circ\text{C}$ ) of the compound of biforked molecules, using the models described in §2.4 for the contributions of local molecular rotational reorientations (R), translational self-diffusion (SD) and collective movements (CM).



**Figure 10.** Fit of the relaxation rate ( $1/T_1$ ) data as a function of the frequency ( $\nu$ ) in the SmC phase ( $T = 129^\circ\text{C}$ ) of the compound of biforked molecules, using the models described in §2.4 for the contributions of local molecular rotational reorientations (R), translational self-diffusion (SD) and collective movements (layer undulations (LU)).

### 3.2 $\phi_h$ and SmC phases of the biforked compound

Similar to §3.1, we present in figures 9 and 10, fits of  $1/T_1(\nu, T)$  in the  $\phi_h$  ( $T = 153^\circ\text{C}$ ) and SmC ( $129^\circ\text{C}$ ) phases of the biforked compound [14]. As in §3.1, the contributions of the different molecular motions to the relaxation rate for different frequency ranges are in agreement with the general comments presented earlier. From the analysis of the fits for the  $\phi_h$  phase it is possible to conclude that:

- The high cut-off frequency for the collective modes (columnar deformations) detected in the  $\phi_h$  phase is  $\nu_{CH} = 2$  MHz – one order of magnitude smaller than in the  $Col_{ho}$  phase of the discotic compound  $C_8HET$ .
- The best fits (like the one presented in figure 9), using the model of molecular translational self-diffusion in smectics with liquid-like layers [25] are obtained with  $D_{\perp}/D_{\parallel} \sim 1$ . These results are compatible with the existence of intra- and inter-columnar diffusive movements. For  $D_{\perp}/D_{\parallel} \sim 0$ , the fits are clearly of inferior quality [14]. The characteristic time between diffusive jumps,  $\tau_{\perp}$ , is of the order of  $10^{-8}$  s and the diffusion coefficients,  $D_{\perp}$  and  $D_{\parallel}$ , associated with lateral and longitudinal molecular movements are of the order of  $10^{-12}$  m<sup>2</sup> s<sup>-1</sup>.
- The correlation times associated with the rotations of the molecular core around transversal ( $\tau_S$ ) and longitudinal ( $\tau_L$ ) molecular axis are of the order of  $10^{-9}$  s and  $10^{-10}$  s respectively. The corresponding times for the chains,  $\tau_S^C$  and  $\tau_L^C$ , are of the order of  $10^{-11}$  s and  $10^{-12}$  s, respectively.

From the analysis of the fits for the SmC phase it is possible to conclude that:

- The low and high cut-off frequencies associated with the collective modes (layer undulations) detected in the SmC phase are respectively  $\nu_{CL} = 2$  kHz and  $\nu_{CH} = 380$  MHz.
- The characteristic time between intra-layer diffusive jumps,  $\tau_{\perp}$ , is of the order of  $10^{-9}$  s and the diffusion coefficients,  $D_{\perp}$  and  $D_{\parallel}$ , associated to intra- and inter-layer diffusion movements are of the order of  $10^{-11}$  m<sup>2</sup> s<sup>-1</sup>.
- The results concerning the rotations/reorientation mechanism are similar to those obtained for the  $\phi_h$  phase, the values of the correlation times obtained for this phase are compatible with a global interpretation for both phases considering an Arrhenius law with an activation energy of 16 kJ mol<sup>-1</sup>.

#### 4. Discussion and conclusions

We may draw the first conclusion by comparing the results obtained for the proton  $T_1$  relaxation obtained in the mesophases considered in this work. The most general features associated with the molecular dynamics behaviour in liquid crystal phases are still verified in the case of these systems showing columnar mesophases. We have three relaxation mechanisms: collective motions, molecular translational self-diffusion and rotations/reorientations – with prevailing contributions to the relaxation rate at low ( $\nu \lesssim 1$ –50 kHz), intermediate ( $1$ –50 kHz  $\lesssim \nu < 10$  MHz) and high ( $\nu > 10$  MHz) frequency regions, respectively.

If we compare the characteristics of the rotations/reorientations mechanism in the two types of columnar mesophases analysed – mono-molecular section ( $Col_{ho}$ ) and poly-molecular section ( $\phi_h$ ) – and in the SmC phase of the biforked compound, we verify that, more than the structure of the mesophase (lamellar/columnar), the shape of the molecule is determinant for the behaviour concerning rotational reorientation movements. In fact, in the case of the biforked compound, both the lamellar and columnar mesophases show the same behaviour at high frequencies, the only difference between the two phases is simply

explained by the effect of the temperature in a thermal activated mechanism. The introduction of a model, which considers a separation of the reorientational movements of the molecule as a whole, from the rapid reorientations of the chains was in part justified by a large number of protons of the chains, which largely exceeds that of the core in the systems considered in this work [14]. If the assumption that the movements of the chains in the range of two orders of magnitude is faster than those represented by the frame attached to the core is correct, then the results reported earlier of the correlation times associated with rotations would have been verified. Another interesting comparison can be made between the reorientations/rotations movements of the biforked and discotic molecules: while, in the case of biforked molecules, the ratio between transverse and longitudinal reorientational movements is compatible to what may be expected due to the molecular anisometry [29,14], in the case of the  $\text{Col}_{\text{ho}}$  phase of the discotic compound, the rotations around the columnar axis are more than one order of magnitude faster than the out-of-disc plane reorientations, which may not be simply justified by the molecular dimensions. This result can be explained if we consider the rotations around the columnar axis to be free (the columnar cores are separated by a medium of liquid-like aliphatic chains), while the reorientations out of the molecular disc plane are constrained by the piling up of the discotic cores in the columns.

If we compare the results concerning molecular translational self-diffusion in the systems presented here, we verify that self-diffusion in the  $\text{Col}_{\text{ho}}$  mesophase of discotic molecules is explained by a mechanism specific for columnar phases of discotic molecules [24], while in both the columnar  $\phi_{\text{h}}$  phase and in the SmC phase of the biforked mesogen molecular self-diffusion may be explained by a mechanism typical of lamellar phases of calamitic molecules [25]. In fact, we verify by fitting the relaxation rate (mesophases SmC and  $\phi_{\text{h}}$  of the biforked compound) obtained by using this model described in [25], that this assumption is in good agreement with the experimental data, as shown in figures 9 and 10. For the  $\phi_{\text{h}}$  phase, different assumptions were tested relative to the ratio between transverse and longitudinal diffusion. The best fits were obtained with ( $D_{\parallel}/D_{\perp} \sim 1$ ) for the lamellar phase. It is worthwhile to stress that this may be explained by the short range similarities between the two phases as cross-verified by other experimental techniques [13]. Finally we may compare the transverse/longitudinal diffusion ratio in the phases of biforked molecules with that of the columnar phase of the discotic molecules: while in the first case we have similar diffusion coefficients in both directions, in the last we verify that inter-columnar diffusion (characterized by  $D_{\perp}$ ) is about two orders of magnitude more efficient than diffusion in the direction of the columnar axis (characterized by  $D_{\parallel}$ ). Actually this is explained by the random jumps inter-columnar permeation model used in the data analysis. When a molecule jumps from one position to another in a different column it travels a distance of 23 Å (corresponding to the hexagonal lattice parameter) in the direction perpendicular to the column and only a distance between 0 and 3.6 Å (corresponding to the nearest position of a molecule in the same column) in the direction of the columnar axis.

If we now consider collective movements, we may verify that the relaxation results in both columnar mesophases –  $\text{Col}_{\text{ho}}$  mesophase of discotic molecules and  $\phi_{\text{h}}$  mesophase of biforked molecules – are explained by the same model (deformations of the columns) with the results in the SmC phase of biforked molecules clearly compatible with the layer undulation mechanism. It was verified that fits with models different from those theoretically predicted for the corresponding mesophases give unreasonable values for the

physical parameters involved. For instance, if we apply to the  $\phi_h$  columnar phase, a model corresponding to layer undulations, we obtain similar values for low and high cut-off frequencies, which is obviously physically unreasonable.

The other conclusion that can be drawn from a comparison of columnar phases of both discotic and biforked mesogens, is obtained through the analysis of the high cut-off frequencies  $\nu_c$  as presented in expression (2). The results obtained for this frequency in the  $\text{Col}_{ho}$  phase of discotic molecules and  $\phi_h$  phase of biforked molecules are respectively of 28 MHz and 2 MHz. Taking into account (2) and considering an average value between molecules,  $d$  (distance between neighbouring molecules in a column and lateral distance between molecules in a smectic layer  $\sim 3.6\text{--}5 \text{ \AA}$ ) corresponding to the shortest possible wavelength mode for these phases, we conclude that the ratio  $K_3/\eta$  is one order of magnitude greater in the  $\text{Col}_{ho}$  phase of the discotic compound than in the  $\phi_h$  phase of the biforked compound. Using these results, the elastic constants  $K_3$  of the columnar mesophases may be determined by measuring the effective viscosity.

Finally, we may say that the results obtained for the systems presented in this work may be summarized as follows: The rotations/reorientations relaxation mechanism is primarily determined by the molecular shape; molecular translational self-diffusion is mostly influenced by the short-range structure of the mesophase, which is still strongly dependent on the molecular shape (diffusion of disc-like molecules is quite different from that of the elongated molecules even if both the phases are alike); collective motions are ruled by the long-range structure of the mesophase (mesophases with the same symmetry and molecules of different shape behave similarly, mesophases of different symmetry, formed by the same molecules behave differently).

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