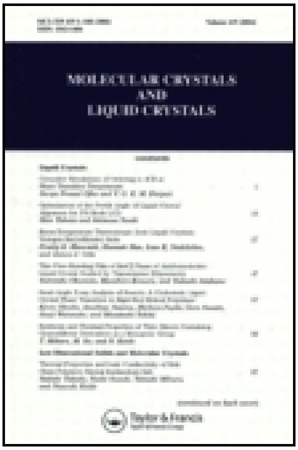

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Contribution of Proton NMR Relaxation to the Investigation of Molecular Dynamics and Molecular Organisation in Liquid Crystalline Phases

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Contribution of Proton NMR Relaxation to the Investigation of Molecular Dynamics and Molecular Organisation in Liquid Crystalline Phases

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We present in this paper some general remarks concerning proton Nuclear Magnetic Resonance studies carried out in particular phases of calamitic, polycatenar and discotic molecules and we show how these studies can be used to understand the molecular dynamics in different types of mesophases. We also illustrate how these studies can contribute, in some cases, to test the validity of molecular organisation models proposed in the literature to describe particular structures detected by X-ray diffraction.

Keywords: liquid crystals; NMR relaxation; molecular dynamics; structural models

INTRODUCTION

The discovery of the first thermotropic calamitic liquid crystal was reported by Reinitzer in 1888[1]. Following this discovery, nematic, cholesteric and different types of monolayered smectic phases were identified and described in the literature[2]. In addition, new types of smectic A phases with layer thickness varying from one to two molecular lengths were detected for the first time in cyanobiphenyl mesogens[3,4]. In this kind of systems the reentrance phenomena[5] were also discovered for both nematic and smectic mesophases[6]. The presence of a strong polar terminal group in these molecules is clearly associated with their thermotropic behaviour. Besides, particular calamitic molecules with lateral dipoles, associated with chiral features, may exhibit particular lamellar phases such as

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ferro[7,8] anti-ferro[9,10] and ferri-electric[10] phases and also the TGB_A mesophase[11,12] – the liquid crystal phase analogous to the Abrikosov flux lattice phase of superconductors[13].

In 1977, the discovery of a columnar mesophase formed by disc-like molecules[14] considerably increased the knowledge of the variety of possible forms of liquid crystalline molecular organisation. With this kind of molecules it is possible to observe different types of columnar organisation[14,15] and also nematic[16], cholesteric[17] and, in very particular cases, smectic mesophases[18].

In general, it is possible to say that lamellar and columnar structures are characteristic of mesophases detected with calamitic and discotic molecules, respectively. The intermediate situation between these two types of systems is filled by polycatenar mesogens described for the first time in the literature in 1985[19]. These compounds present very interesting polymorphisms[19,20,21,22,23] including columnar mesophases (ϕ phases) where the transverse section of a column is formed by a group of molecules arranged side by side[24,25,26]. The average number of molecules, k, in the transverse section of one column depends on the number of chains in each molecule, being $k=3$ in the case of the phasmidic (hexacatenar) mesogens and $k=4.5$ in the case of the biforked (tetracatenar) compounds. In addition, some terms of biforked mesogens homologous series present a rather peculiar polymorphism in which transitions between lamellar and columnar mesophases may be observed as a function of the temperature[26,27,28].

The identification of the structure of all the referred mesophases generally results from a combination of experimental techniques in which X-ray diffraction plays a determinant role[29]. In complex cases, dilatometric measurements are very useful to a better understanding of the local molecular organisation[30]. On the other hand, studies of molecular order and dynamics, which are also of major interest for the characterisation of the liquid crystal phases, may be subsequently performed using different techniques including nuclear magnetic relaxation[31,32], among others[33]. Generally, the molecular dynamics studies follow the identification of the structure of the mesophase, since the molecular dynamics properties of a phase are strongly conditioned by the molecular organisation. However, in particular cases, the set of techniques usually applied to the structural study of the mesophases reveals some limitations in determining univocally the form of molecular organisation under investigation. In these cases, different models, compatible with the available structural data, are discussed and complementary experimental techniques are required in order to test their validity. In particular, NMR techniques can be successfully used[26,34,35,36,37] as we will see hereafter.

In this paper, we present general comments concerning some proton NMR relaxation results obtained with different compounds of calamitic, discotic and polycatenar molecules and we show how NMR spin-lattice relaxation studies performed in large frequency domains are useful to study the molecular dynamics in liquid crystals. We will illustrate here that some specific details of particular but well characterised mesophases, like the TGB_A phase, can show a clear signature in the relaxation profiles[38]. We will also show how the proton NMR relaxation results can contribute, in some cases, to the test of the validity of molecular organisation models proposed in literature to describe some particular structures determined by X-ray diffraction. These complementary approaches have proved to be very useful for the study of structural details of some of the mesophases considered herein, in particular the partial bilayer smectic A phase, S_{Ad}[35], and also the columnar mesophases formed by polycatenar molecules[36].

2 - NUCLEAR MAGNETIC RELAXATION IN LIQUID CRYSTALS

2.1 – A general view

Nuclear magnetic resonance can be considered as an important tool for the study of the molecular order and dynamics in liquid crystal phases. In particular, proton and deuteron NMR relaxation studies have been used in the past to identify different molecular motions in different types of mesophases[32].

Proton spin-lattice relaxation studies are important because general informations concerning different types of molecular motions can be obtained especially when classical and fast field-cycling NMR techniques are combined[31,39]. It should be remarked that, in general, different molecular motions with different time scales can show their characteristic signatures in the proton relaxation profiles, when a broad enough domain of Larmor frequencies is explored. In fact, in the past twenty years many significant proton relaxation studies have been performed using both techniques in different types of mesophases exhibited by calamitic[35,38,40,41], disc-like[42] and polycatenar molecules[36].

Deuteron NMR studies are, in general, site specific and consequently very useful to clarify, in a precise way, the molecular movements associated with intra-molecular relaxation mechanisms[32,43]. This is the case of the fast local molecular rotational reorientation movements. Nevertheless, although very useful, these ^2H relaxation studies are insensitive to the intermolecular relaxation mechanisms like translational self-diffusion. In this case, using the techniques described above, non-selective proton nuclear relaxation can be important in order to have an insight concerning these motions. In addition, we must remark that ^{2}H relaxation measurements are usually performed in the MHz domain and some molecular motions, such as director fluctuations in most cases, don't give a significant contribution for the relaxation rate ($1/T_1$) in this frequency range[44]. Therefore, proton NMR relaxation can be very important for the characterisation of collective motions, especially when the relaxation measurements are performed in large frequency domains, combining standard and fast field-cycling techniques. ^{2}H and ^{1}H relaxation measurements are complementary and it is very important to combine, if possible, the information obtained from both kind of measurements; but it is also clear that both techniques are limited in scope.

We must remark that several theoretical studies describe how the relaxation profiles associated with the different types of movements depend on the structural details of the mesophase[32]. For instance, the contribution of the director fluctuations mechanism for the relaxation rate is quite different in nematic, smectic A or columnar mesophases[45,46]. Also, some specific molecular movements, typical of the structural characteristics of particular mesophases, result in a signature detectable in the nuclear magnetic relaxation profiles[35–38].

Usually, the relaxation dispersion profile may be analysed considering the sum of different contributions $(1/T_1)_i$ to the overall relaxation rate $(1/T_1)$[47].

$$1/T_1 = \Sigma\ (1/T_1)_i \tag{1}$$

In the case of liquid crystals, molecular rotational reorientations, translational self-diffusion and collective movements, if present, are the most important movements which contribute to the relaxation rate. However, as pointed out before, other relaxation mechanisms, associated with the nature of particular mesophases can also be detected by NMR relaxation[35,38].

2.2 – NMR relaxation results obtained in different types of mesophases

Along with a description of some specific structures and models of particular mesophases, we will present in this section a detailed analysis of nuclear magnetic relaxation results obtained with systems constituted of:

- Calamitic molecules with a strong terminal dipole exhibiting nematic and partial bilayered smectic A mesophases and showing the double reentrance phenomenon.
- Calamitic molecules with a chiral centre showing the TGB_A mesophase;
- Biforked molecules showing smectic C and columnar Φ_h mesophases. These results are compared with those obtained in a columnar D_{ho} mesophase.

As an example and in order to illustrate the influence of the phase structures on the proton spin-lattice relaxation we present in figure 1 some T_1 dispersion profiles obtained in the nematic, smectic A_d, smectic C and columnar hexagonal Φ_h phases of two liquid crystalline compounds considered hereafter (see molecular structures and phase sequences in sections 2.2.1 and 2.2.3).

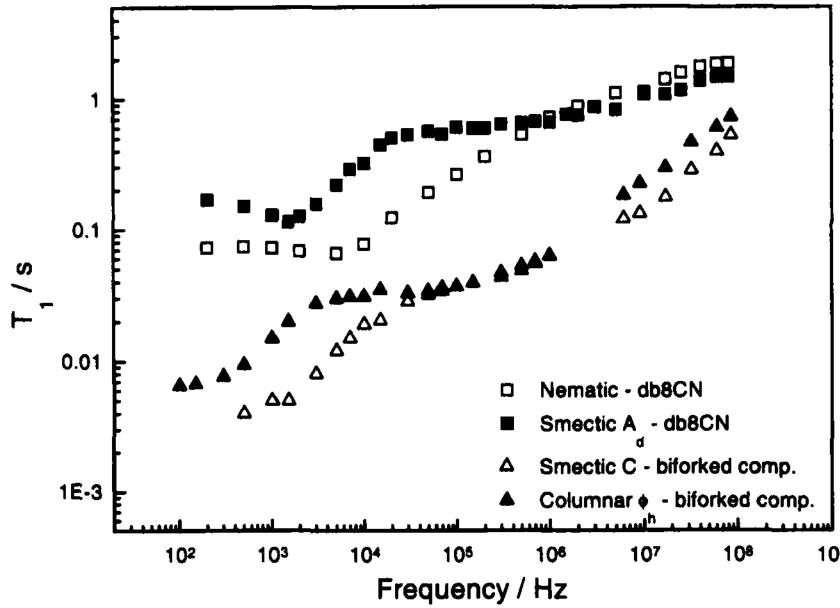


FIGURE 1 T_1 dispersion in the nematic (T = 195°C) and S_{Ac} (T = 165°C) phases of DB8CN Sym and in the smectic C (T = 119°C) and ϕ_h (T = 153°C) phases of the biforked compound presented in the text

It is clear that the observed T_1 dispersion depends on the type of mesophase. The range of T_1 values can vary from 40–400 ms to 100–1500 ms depending on the material. This variation is associated with a large number of physical parameters, including molecular mass and dimensions, viscosity coefficients, elastic constants, etc.[32]. On the other hand, there are also very clear differences in the overall T_1 frequency dependence that reflect the particular structure of each mesophase. These differences, as we will see hereafter, result from the influence of the structural characteristics of the mesophase on the different molecular motions detected by NMR relaxation.

From the observation of figure 1 it is possible to conclude that above 10 MHz a similar behaviour (regular monotonic increase) of $T_1(\nu)$ is detected in all phases.

This means that in this domain a "similar" relaxation mechanism is observable in all the mesophases considered. On the other hand, in all the other frequency ranges the T_1 dispersion profiles are different from phase to phase. The differences between the T_1 dispersion curves presented in figure 1 reveal the influence of the molecular organisation of the mesophases on the observed molecular motions. In particular, translational self-diffusion and collective motions depend on the constraints imposed by the phase structure.

In cases where different molecular organisation models are compatible with the available structural data, NMR relaxation results may be of great help in the confirmation of each of the models considered. Actually, different structural models will lead to different theoretical predictions for the T_1 dispersion associated with the allowed molecular motions, permitting to identify those compatible with the experimental NMR relaxation data. From the presented results, we will comment on similarities and differences associated with the various relaxation frequency T_1 dispersions. Some specific relaxation mechanisms will also be discussed.

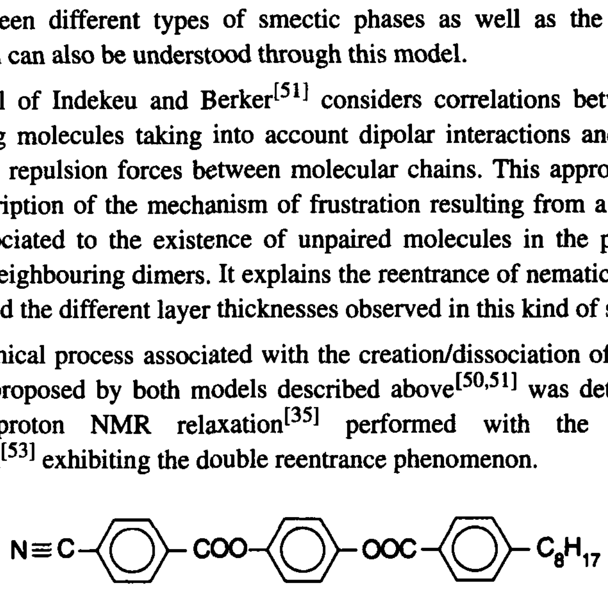
2.2.1 - Molecules with strong terminal dipoles. The Nematic and Smectic mesophases

The detection of the partial-bilayer smectic A (S_{Ad}) phase in a compound with a strong polar terminal group[3] can be considered as the first important mark for the chemical and physical research concerning these systems, where the tendency of the molecules to form pairs, due to the interaction between the terminal dipoles, plays an important role[3-6,48]. The detection of the reentrance phenomena[6] for both nematic and smectic phases and the existence of different types of smectic phases[3–6] in this kind of systems constituted a very important problem, which remained an open question during a considerable period and was the subject of different theoretical approaches[48,49,50,51]. One of them considers the competition between the classical smectic A order parameter and an antiferroelectric order parameter associated to the formation of pairs due to the dipolar interaction[48]. However, this phenomenological approach is unable to describe the details of some of the mesophases at the molecular scale, as pointed out in [52]. Nevertheless, at the molecular scale, these systems can be described by taking into account the interactions between neighbouring molecules and the consequent possible types of local molecular organisation.

Two interesting models of this kind, introduced by Guillon and Skoulios[50] and Indekeu and Berker[51], respectively, successfully describe[34] the polymorphisms observed in this kind of systems. For instance, according to the Guillon and Skoulios model[50] in the partial bilayer smectic A phase the layers are composed by a mixture of monomers and head-to-head molecular pairs (dimers) resulting from the coupling between the terminal dipoles. This model assumes a dynamic process where the dimers are constantly being formed and dissociated. The intermediate layer thickness between one and two molecular lengths is a function of the relative number of monomers and dimers. This process explains the variation of the layer thickness with temperature as an evolution of the proportion between single molecules and pairs. A qualitative description of the transitions between different types of smectic phases as well as the reentrance phenomenon can also be understood through this model.

The model of Indekeu and Berker[51] considers correlations between three neighbouring molecules taking into account dipolar interactions and excluded volume type repulsion forces between molecular chains. This approach allows for the description of the mechanism of frustration resulting from a dynamical process associated to the existence of unpaired molecules in the presence of occasional neighbouring dimers. It explains the reentrance of nematic and smectic phases and the different layer thicknesses observed in this kind of systems.

The dynamical process associated with the creation/dissociation of molecular aggregates proposed by both models described above[50,51] was detected by a study of proton NMR relaxation[35] performed with the compound DB8CNSym[53] exhibiting the double reentrance phenomenon.



$$\mathrm{Cr} \xrightarrow{125^\circ\mathrm{C}} S_{A1} \xleftrightarrow{142^\circ\mathrm{C}} N_{re} \xleftrightarrow{157^\circ\mathrm{C}} S_{Ad} \xleftrightarrow{186^\circ\mathrm{C}} N \xleftrightarrow{238^\circ\mathrm{C}} I$$

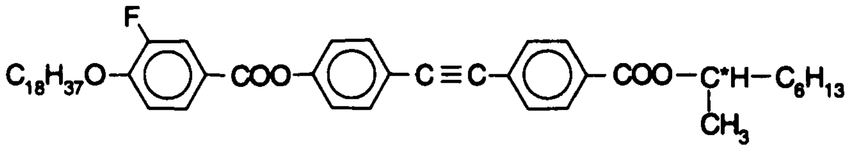
The T_1 dispersion profiles presented in figure 1, concerning the nematic and S_{Ad} mesophases, correspond to the higher temperature mesophases exhibited by this compound. As pointed out before, the only frequency region where $T_1(\nu)$ is identical, in both types of mesophases, is the high frequency range ($\nu \geq 10$ MHz), where reorientational motions give the most important contribution for the relaxation. In the nematic mesophase there is a plateau in the T_1 dispersion in the low frequency range, which is less evident in smectic Ad phase. For intermediate frequencies (10 kHz $\geq \nu \geq$ 10 MHz) T_1 strongly increases in the nematic phase till the MHz range, while in the S_{Ad} mesophase a clear increasing of T_1 is only detected in the kHz domain, followed by a kind of plateau detected till the MHz range. These behaviours observed in the T_1 dispersion at low and intermediate frequencies are essentially due to the differences on the type and relative importance of collective and translational self-diffusion movements detected in nematic and smectic A mesophases. The collective motions in the S_A mesophases are essentially due to layer undulations and the frequency range where this kind of motions are predominant is clearly shorter in the S_A mesophases than in the nematic phases. This is essentially due to the smaller number of degrees of freedom for director fluctuations in the S_A phases and to the fact that only splay and layer compression have non-divergent elastic constants. The low frequency plateau is caused, in both cases, either by a low cut-off on the long wavelengths of the collective fluctuation modes or by a local field limit imposed on the relaxation. The plateau detected at intermediate frequencies in the S_{Ad} mesophase is associated to the dominance of the translational self-diffusion relaxation[35]. It is important to point out that the contributions of self-diffusion movements for the relaxation in smectic and nematic mesophases are quite similar[54]. They are less evident in the intermediate frequency range of the nematic phase because they are masked by the stronger contribution of the collective motions in this phase[35].

No major differences between the reentrant and non-reentrant nematic and smectic phases is observed in the spin-lattice relaxation dispersion[35]. However, a joint interpretation of the T_1 results for all the mesophases of DB8CN Sym studied, revealed that it is necessary to consider an additional relaxation mechanism clearly present in S_{Ad} mesophase but also detected in the nematic higher temperature mesophase, where at a local scale some reminiscence of S_{Ad} is detected[55]. This additional relaxation mechanism was associated to the dissociation/recombination of the molecular aggregates whose existence is proposed in the models described in literature to explain the S_{Ad} phase structure[50,51]. The NMR relaxation study predicts a characteristic time for the dissociation/recombination process of the order of 10^{-8} s[35]. This quantitative result is in agreement with a previous prediction resulting from an NMR study of molecular order[34] based on the analysis of proton and deuterium NMR spectra performed in a chain deuterated cyano compound, exhibiting S_{Ad} and reentrant nematic mesophases. In fact, in this study, it was estimated that the mean lifetime of the molecular aggregates predicted by the two described models[50,51] must be shorter than the NMR observation time (of the order of the microseconds).

We must remark that without the introduction of the additional relaxation mechanism associated to the dynamical process predicted by Guillon-Skoulios[50] and Indekeu-Berker[51] it would not be possible to obtain a complete and correct interpretation of all the relaxation results concerning all the studied mesophases[35]. The signature of this mechanism is clearly evident in the S_{Ad} mesophase where the existence of dynamical aggregates could explain the observed layer thickness.

2.2.2 - The Twist grain boundary smectic A (TGB_A)

The particular structure of the TGB_A mesophase, where there are smectic A blocks of dimension l_b arranged in a helical way[11], is clearly reflected in the T_1 relaxation results obtained with a compound ($18FBTCO_1M_7$) exhibiting S_C^* and TGB_A mesophases[38]:



$$Cr \xrightarrow{67°C} S_{C^*} \xleftrightarrow{93°C} TGB_A \xleftrightarrow{97°C} I$$

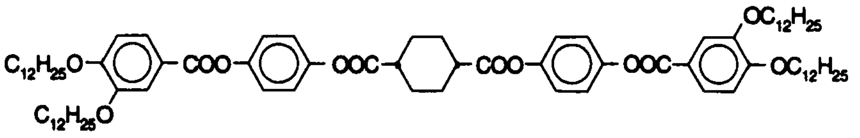
In fact, in the TGB_A mesophases, between two adjacent smectic blocks, rotated of an angle $\Delta\alpha$, there is a grain boundary region[11] which clearly affects the nuclear magnetic relaxation as described in [38]. The $T_1(\nu)$ profiles obtained in the S_C^* and TGB_A mesophases are similar to those represented in figure 1 for the S_{Ad} and S_C mesophases. This means that apparently similar relaxation mechanisms are present in the mentioned mesophases.

Usually, at the S_A-S_C^* transition, the $T_1(T)$ profiles obtained at different Larmor frequencies show the same type of behaviour namely a continuous decreasing of T_1 with decreasing temperature[41]. However, in the case of the TGB_A-S_C^* transition, different $T_1(T)$ behaviours were detected for different Larmor frequencies[38]. For frequencies larger than 9 MHz, the usual behaviour detected at the S_A-S_C^*[41] transition was observed. For frequencies equal or smaller than 1 MHz a completely different behaviour was observed. In fact, in the TGB_A mesophase T_1 increases with decreasing temperature for the low frequencies, while in the S_C^* phase the usual behaviour of decreasing of T_1 with decreasing temperature was observed. This result means that an additional relaxation mechanism must be considered in order to explain the detected behaviour. Actually, considering only the usual mechanisms contributing to the T_1 relaxation profiles in the S_A mesophases, it was not possible to explain the relaxation results in the TGB_A mesophase, a kind of frustrated S_A mesophase. As explained in [38], the additional relaxation mechanism detected in the TGB_A mesophase in the low frequency domain is associated with the molecular self-diffusion through the grain boundaries. Translational molecular motions between adjacent blocks are clearly affected by the existence of such a kind of barriers. In fact, it is possible for a molecule to cross the grain boundary region from one smectic block to an adjacent one by a kind of self-diffusion movement. When the molecules cross this region along a direction parallel to the helical axis, they need to rotate of an angle $\Delta\alpha$ (the angle between adjacent blocks). The movement from one smectic block to the next one is a kind of reorientational motion mediated by translational displacements. These molecular rotations inside the grain boundaries are in principle executed by steps.

We should remark that without the introduction of this particular mechanism, clearly associated with the structure of the TGB_A mesophase, it would not be possible to obtain a correct interpretation of the relaxation data in the low frequency domain. This significant result reflects the structure of the TGB_A mesophase and could be considered as an additional proof concerning the real importance of the Nuclear Magnetic Relaxation studies. Dielectric relaxation studies performed in a TGB_A mesophase were used to detect a new relaxation mechanism associated to the molecular movements in the grain boundary regions[56], in agreement with the NMR results described in [38].

2.2.3 - Biforked Mesogens showing S_C and ϕ_h mesophases

The polymorphisms exhibited by polycatenar mesogens depend on several characteristics of the molecular architecture, namely the length and flexibility or rigidity of the core and naturally on the number, position and length of the end chains[23]. As stated before, some biforked compounds of appropriate chains' length, such as the one with the following molecular structure and phase sequence[28]:



$$Cr \xrightarrow{113°C} S_C \xleftrightarrow{149°C} \phi_h \xleftrightarrow{156°C} I$$

present lamellar-to-columnar phase transitions[27]. In these cases, the detailed study of the structure and molecular dynamics in both the lamellar and columnar phases, near the phase transition, can be very important to elucidate the structure of the special columnar phase (ϕ) characteristic of this type of mesogens.

In this case, DSC experiments show that the lamellar-to-columnar transition enthalpy is fairly low[28], which is compatible with a structural change between the S_C and ϕ_h phase, where some similarity, at least at a local scale, is maintained[26]. This experimental result favours the model presented in [24] suggesting the possibility that the S_C-ϕ_h transition corresponds to the segmentation of the smectic layers in parallel stripes, which give rise to the columns in the ϕ_h phase[26].

As previously mentioned, T_1 dispersion curves, corresponding to the S_C and ϕ_h phases of this compound[36] are presented in figure 1. From a global analysis of the obtained NMR relaxation results[36], it was possible to identify the characteristic frequency ranges associated to the different types of molecular movements present in both the lamellar and columnar phases: as in other liquid crystal phases, collective movements, molecular translational self-diffusion and rotational reorientations are dominant at low, medium and high frequencies, respectively. The contribution of this study to the identification of the structural characteristics of the ϕ_h phase results from the comparison between the T_1 dispersion results in the S_C and ϕ_h phases. The molecular dynamics behaviour in the S_C phase of biforked molecules is quite similar to that of equivalent phases of calamitic molecules, apart a slightly more complex description of the rotational reorientation movements due to the extra terminal aliphatic chains. We can also find a similar behaviour in the S_{Ad} phase described herein, except for the existence of the dimer formation/dissociation mechanism[35] that is obviously absent in the case of the biforked molecules. Actually, if we compare the T_1 dispersion curves corresponding to the S_{Ad} phase of the DB8CN Sym and the S_C phase of the biforked compound presented in figure 1, we will notice a roughly similar frequency dependence behaviour (even if the order of magnitude of T_1 is different due to, among other factors, the difference in molecular mass and size): an increasing of T_1 in the low frequency region (which may be attributed, through a detailed analysis, to a law of $T_1(\nu)$ associated with smectic layer undulations); a plateau in the medium frequency region, from ~2×10^4 Hz to ~1 MHz, in both curves, and finally a region of monotonic increase above the MHz range. For the ϕ_h phase, we find at high frequency a dynamical behaviour completely similar to that of the S_C phase[36], which is expected as the rotational reorientations movements are not strongly influenced by the structure of the phase. This can be observed in figure 1 noticing that the T_1 evolution above 10 MHz is almost perfectly parallel for the S_C and ϕ_h phase. The shift between the two curves is due to the temperature's difference between the two phases and it can be easily explained by the expected Arrenhius dependence. On the other hand, in the low frequency range we see that there is a clear difference between the results obtained in the two phases. As the collective movements are dominant in this frequency range, we conclude that this difference is due to the different collective movements observed, resulting from distinct long range molecular order in the columnar and lamellar phases[36].

The most relevant contribution of the referred NMR study[36] to the elucidation of the structure of the ϕ_h phase results from the analysis of the molecular translational self-diffusion movements. This kind of motion in liquid crystal phases is generally described as a random jump process of the molecules between neighbouring positions, which modulates the relaxation. Necessarily, this depends on the phase structure at a local scale, which determines the possible positions for the diffusive jumps to occur. Therefore, different phase structures will lead to different relaxation dispersion curves in the intermediate Larmor frequency range where, in most cases, the translational self-diffusion mechanism dominates the relaxation process. The important result in this case is that the same model, which describes the relaxation due to the translational self-diffusion process in smectics with liquid-like layers, successfully fits the T_1 dispersion in both the *smectic* C and the ϕ_h phase of biforked molecules. The similarity between the relaxation results in these two phases becomes evident from the observation of the curves in figure 1, where we may verify the coincidence of T_1 results in the intermediate frequency range. This is in agreement with the structural model proposed by Guillon, Skoulios and Malthête[24] and with the description of the lamellar-to-columnar phase transition proposed in [26] where a similar structure at a local scale is assumed for both phases, as it can be observed in figure 2. This conclusion is reinforced by the comparison of the T_1 dispersion results in the ϕ_h phase with those obtained for the columnar hexagonal phase, D_{ho}, of discotic molecules of the compound C_8HET[37,42].

In spite of presenting the same global structural characteristics – columnar hexagonal – (which justifies the similar behaviour in the low frequency range, where collective movements dominate the relaxation process) the frequency dispersion in the intermediate frequency range is very different in the two columnar-hexagonal phases. In fact, Zumer and Vilfan[46] previously described the translational self-diffusion process in the D_{ho} phase as an inter-columnar jump permeation process. The analysis of NMR results rules out this description in the case of the ϕ_h phase. This is, indeed, expected because there is no plausible physical mechanism for the groups of biforked molecules, which correspond to the discs of the D_{ho} phase, to diffuse together from column to column (see figure 2b). Actually, according to the description of the ϕ_h phase and the lamellar-to-columnar phase transition presented before, the local "environment" of a biforked molecule in the ϕ_h phase, includes the neighbouring molecules in the same column and the nearby molecules in adjacent columns, being all these molecules on average parallel to each other as in the precursor lamellar phase. Comparing figures 2a and 2b we may assume that the inter-layer self-diffusion movements characterised by the coefficient $D_\parallel$ in the smectic phase, as described in [36], correspond necessarily in the ϕ_h phase to inter-columnar diffuse movements. The smectic intra-layer self-dif-

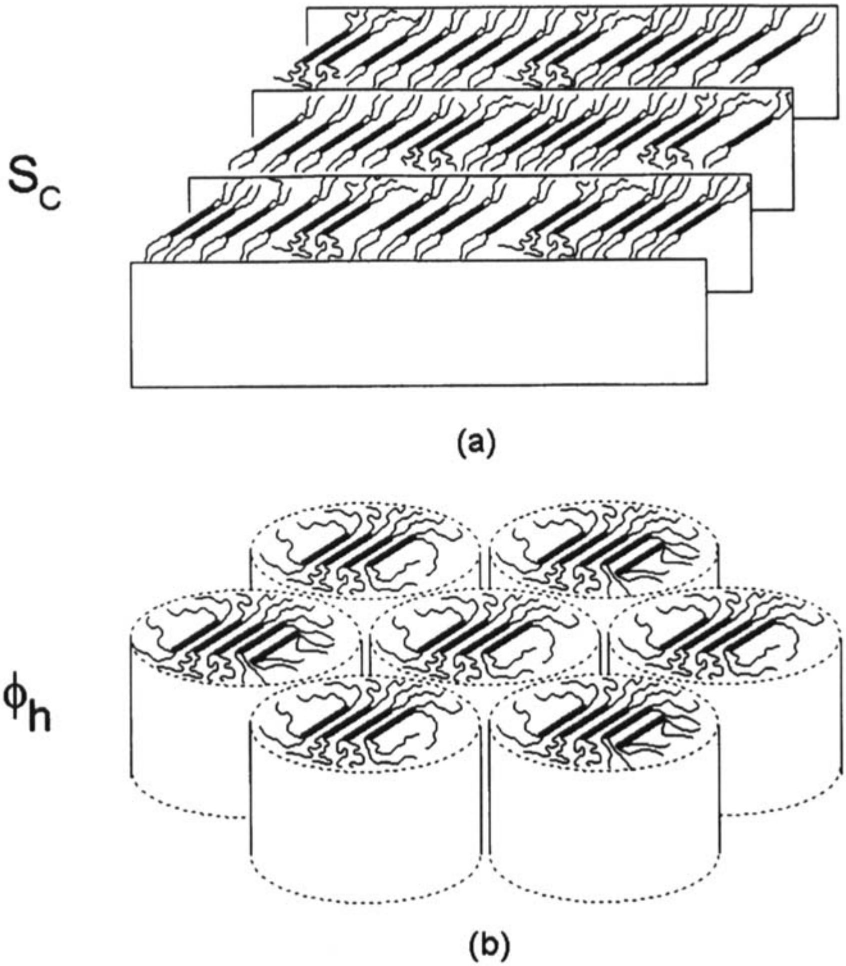


FIGURE 2 Schematic view of the molecular organisation in the mesophases of the biforked compound referred in the text. a) smectic C phase, b) ϕ_h phase

fusion movements, characterised by the coefficient $D_\perp$[36] correspond most probably to intra-columnar diffusive movements.

CONCLUSION

As a conclusion, it is possible to say that, in general, the molecular motions present in different types of mesophases, with different characteristic time scales, can show their particular signature in the $T_1(\nu)$ proton relaxation profiles when classical and fast field-cycling NMR techniques are combined. From these studies it is possible to understand how molecular motions are influenced by the local structure of the different mesophases. This is particularly clear in the case of the TGB_A phase.

It was also described how these relaxation studies can contribute, in some cases, to test the validity of molecular organisation models proposed in literature to describe some specific structures determined by X-ray diffraction, namely the partial bilayer smectic S_{Ad} and the columnar phases formed by polycatenar molecules.

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References

[1] F. Reinitzer, *Wiener Monatsch. Chem.*, **9**, 421(1888), *Liq. Cryst.*, **5**, 7 (1989).

[2] G.W. Gray, J.W. Goodby, *Smectic Liquid Crystals* (Leonard Hill, Glasgow, London and Philadelphia, 1984).

[3] G. W. Gray, J. E. Lydon, *Nature* **252**, 221 (1974).

[4] J. E. Lydon, C. J. Coakley, *J. Physique Colloq.* **36**, C1–45 (1975).

[5] P. E. Cladis, *Phys. Rev. Lett.* **35**, 48 (1975).

[6] F. Hardoin, G. Sigaud, M. F. Achard, H. Gasparoux, *Sol. State Commun.* **30**, 265 (1979); F. Hardoin, A. M. Levelut, *J. Physique* **41**, 41 (1980); F. Hardoin, N. H. Tinh, M. F. Achard, A. M. Levelut, *J. Physique Lett* **43**, 327 (1982).

[7] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Physique Lett.* **36**, 69 (1975).

[8] N. Clark, S. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).

[9] A. M. Levelut, C. Germain, P. Keller, L. Liebert, *J. Physique* **44**, 623 (1983).

[10] A. D. L. Chandani, Y. Ouchi, H. Takezoe, A. Fukuda, K. Terashima, K. Furukawa, and A. Kishi, *Jap. Journal of Appl. Phys.* **28/7**, L-1261 (1989); ibdi, *Jap. Journal of Appl. Phys.* **28/7**, L-1265 (1989).

[11] S. Renn, T. Lubensky, *Phy. Rev. A* **38**, 2132 (1998).

[12] J. W. Goodby, M. A. Waugh, S. Stein, E. Chin, R. Pindak, J. Patel, *Nature* **337**, 449 (1989).

[13] P. G. de Gennes, *Solid State Commun.* **10**, 753 (1972).

[14] S. Chandrasekhar, B. Shasdashiva, K. Suresh, *Pramana* **9**, 471 (1977).

[15] C. Destrade, M. C. Mondon, J. Malthete, *J. Phys. Colloq.* **C3**, 40, (1979);C. Destrade, M. C. Mondon, Nguyen H. Tinh, *Mol. Cryst. Liq. Cryst* **49**, 169 (1979); Nguyen H. Tinh, H. Gasparoux, C. Destrade, *Mol. Cryst. Liq. Cryst* **68**, 101 (1981).

[16] J. Billard, *Liquid Crystals of One and Two Dimensional Order*, ed. W. Heldrich and G. Heppke, Springer Series in Chem Phys. **11**, 383 (1980).

[17] C. Destrade, Nguyen H. Tinh, J. Malthete, J. Jacques, *Phys. Lett.* **79A**, 189 (1980).

[18] A.C. Ribeiro, A.F. Martins, A.M. Giroud-Godquin, *Mol. Cryst. Liq. Cryst. Lett.*, **5**, 133 (1988); K. Ohta, H. Muroki, A. Takagi, K.I. Hatada, H. Ema, I. Yamamoto, and K Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **140**, 131(1986).

[19] J.Malthête, A. M. Levelut, H.T. Nguyen, *J.Phys. Lett.(Paris)* **46**, L875 (1985).

[20] J. Malthête, H.T. Nguyen, C. Destrade, *Liq. Cryst.* **13**, 171 (1993).

[21] H.T. Nguyen, C. Destrade, A. M. Levelut, J.Malthête, *J.Phys. (Paris)* **47**, 553 (1986).

[22] H.T. Nguyen, C. Destrade, J. Malthête, *Adv. Mat.*, **9**, 375 (1997).

[23] A.M. Levelut, J. Malthete, C. Destrade, H.T. Nguyen, *Liq. Cryst*, **2**, 877 (1987).

[24] D. Guillon, A. Skoulios, J. Malthête, *Europhys. Lett.* **3**, 67 (1987).

[25] S. Diele, K. Ziebarth, G. Pelzl, D. Demus, W. Weissflog, *Liq. Cryst.*, **8**, 211 (1990); D. Guillon, in *Structure and Bonding, Liquid Crystals II*, Springer-Verlag Berlin, Heidelberg, New York, **41** (1999).

[26] D. Guillon, B. Heinrich, A.C. Ribeiro, C. Cruz, H.T. Nguyen, *Mol. Cryst. Liq. Cryst.* **317**, 51 (1998).

[27] W. Weissfolg, M. Rogunova, I. Letko, S. Diele, G. Pelzl, *Liq. Cryst.*, **19**, 541 (1995); C. Destrade, H.T. Nguyen, C. Alstermark, G. Lindsten, M. Nilsson, B. Otterholm, *Mol. Cryst. Liq. Cryst.*, **180B**, 265 (1990).

[28] H.T. Nguyen, C. Destrade, J. Malthête, *Liq. Cryst.* **8**, 797 (1990).

[29] P.S. Pershan, *Structure of Liquid Crystal Phases*, World Scientific (1988).

[30] A.J. Kovacs, *Ric. Sci. Suppl.*, **25**, 668 (1955); D. Guillon and A. Skoulios, *C.R. Acad. Sci. Paris*, **C278**, 389 (1974).

[31] C. G. Wade, *Ann. Rev. Phys. Chem* **28**, 47 (1977).

[32] R.Y. Dong, *Nuclear Magnetic Resonance of Liquid Crystals* (Springer Verlag, 2nd ed. 1997) and references therein.

[33] G. Vertogen, W.H. de Jeu, *Thermotropic Liquid Crystals Fundamentals* (Springer-Verlag, 1988).

[34] J. L. Figueirinhas, C. Cruz, A. C. Ribeiro, Nguyen Huu Tinh, *Mol. Cryst. Liq. Cryst.* **212**, 263 (1992).

[35] P.J. Sebastião, A.C. Ribeiro, H.T. Nguyen, F. Noack, *J. Physique II* **5**, 1707 (1995).

[36] C. Cruz, J.L. Figueirinhas, P.J. Sebastião, A.C. Ribeiro, F. Noack, H.T. Nguyen, B. Heinrich, D. Guillon *Z. Naturforsch.*, **51a**, 155(1996).

[37] C. Cruz, A.C. Ribeiro, *Mol. Cryst. Liq. Cryst.*, **331**, 75 (1999).

[38] J. L. Figueirinhas, A. Ferraz, A. C. Ribeiro, H. T. Nguyen, and F. Noack, *J Phys. II France* **7**, 79 (1997).

[39] F. Noack, *NMR Basic Principles, Aplications*, Springer-Verlag Berlin (1978); F. Noack *Prog. in NMR Spectroscopy*, **18**, 171 (1986).

[40] K. H. Schweikert and F. Noack, *Z. Naturforsch.*, **44a**, 597 (1989); F. Noack, K. H. Schweikert, in *The Molecular Dynamics of Liquid Crystals* (Kluwer Academic Publishers, Netherlands, 1994).

[41] J.L. Figueirinhas, A. Ferraz, A.C. Ribeiro, H.T. Nguyen, F. Noack, *Ferroelectrics*, **146**, 123 (1993); A. Ferraz, J. L. Figueirinhas, P. J. Sebastião, A. C. Ribeiro, H. T. Nguyen, F. Noack, *Liq. Cryst.*, **14**, 415 (1993).

[42] C. Cruz, P.J. Sebastião, J. Figueirinhas, A.C. Ribeiro, H.T. Nguyen, C. Destrade, and F. Noack, *Z. Naturforsch.* **53a**, 823 (1998).

[43] P. A. Beckmann, J. W. Emsley, G. R. Luckhurst, D. L. Turner, *Molec. Phys.*, **59**, 97 (1986); T.M. Barbara, R.R. Void, R.L. Void, M.E. Neukert, *J. Chem. Phys.*, **82**, 1612 (1985); J. M. Goetz, G. L. Hoatson, R. L. Vold *J. Chem. Phys.*, **97**, 1306 (1992); Ronald Y. Dong, L. Friesen, G. M. Richards, *Mol. Phys.*, **81**, 1017 (1994); R.Y. Dong, J.W. Emsley, K. Hamilton, *Liq. Cryst.*, **5**, 1019 (1989).

[44] F. Noack, M. Notter, W. Weiβ, *Liq. Cryst.*, **3**, 907 (1988); P. J. Sebastião, A. C. Ribeiro, H. T. Nguyen, F. Noack, *Z. Naturforsch.*, **48a**, 851 (1993).

[45] P. Pincus, *Sol. State Commun.*, **7**, 415 (1969); R. Blinc, M. Burgar, M. Luzar, J. Pirs, I. Zupancic, S. Zumer *Phys. Rev. Lett.*, **30**, 1192 (1974); R. Blinc, M. Luzar, M. Vilfan, M. Burgar, *J. Chem. Phys.*, **63**, 3445 (1975); I. Zupancic, V. Zagar, R. Rozmarin, I. Lesvtik, F. Kogovsik, R. Blinc,, *Sol. State Commun.*, **18**, 1591 (1976); P. Ukleja, J. Pirs, J.W. Doane, *Phys. Rev. A*, **14**, 414 (1976); J.W. Doane, C.E. Tarr, M.A. Nickerson, *Phys. Rev. Lett.*, **33**, 620 (1974).

[46] S. Zumer, M. Vilfan, *Mol. Cryst. Liq. Cryst.*, **70**, 39 (1981).

[47] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press Oxford, 1961).

[48] J. Prost, *J. Phys. Paris* **40**, 581 (1979); J. Prost, P. Barois, *J. de Chim. Phys.* **80**, 65 (1983).

[49] P. E. Cladis, R. K. Bogardus, A. Aadsen, *Phys. Rev. A*, **18**, 2292(1978); A. J. Leadbetter, J. C. Frost, J.P. Gaughan, *J. Phys. Paris*, **40**, 375 (1979); L. Longa, W.J. de Jeu, *Phys. Rev. A*, **26**, 1632 (1982); N.V. Madhusudana, J. Rajan, *Liq. Cryst.*, **7**, 31 (1990).

[50] D. Guillon, A. Skoulios, *Mol. Cryst. Liq. Cryst.*, **91**, 341 (1983); D. Guillon, A. Skoulios, *J. Physique*, **45**, 607 (1984).

[51] J. O. Indekeu, A. N. Berker, *Phys. Rev. A*, **33**, 1158(1986); J. O. Indekeu, A. Nihat Berker, *J. Phys. France*, **49**, 353 (1988).

[52] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, 1993), pp 575.

[53] H.T. Nguyen, C. Destrade, *Nouv. J. Chim* **5**, 337 (1981).

[54] S. Zumer and M. Vilfan, *Phys. Rev. A*, **17**, 424 (1978); M. Vilfan and S. Zumer, *Phys. Rev. A*, **21**, 672 (1980).

[55] F. Hardouin, A.M. Levelut, G. Sigaud, M.F. Archard, N.H. Tinh, H. Gasparoux, *Symmetries and Broken Symmetries*, N. Boccara (Idset), 231 (1981).

[56] H. Xu, P. Yu Panarin, J. K. Vij, A. J. Seed, M Hird, and J. W. Goodby, *J. Phys.: Condens. Matter* **7**, 7443 (1995).