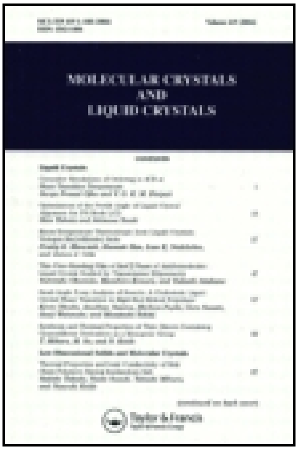

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Molecular Dynamics in Columnar Phases Exhibited by Compounds of Discotic and Biforked Molecules, A Comparative Study from NMR Results

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Molecular Dynamics in Columnar Phases Exhibited by Compounds of Discotic and Biforked Molecules. A Comparative Study from NMR Results

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In this work we compare the outstanding features of the molecular dynamics behaviour as observed by NMR in different columnar mesophases. Columnar mesophases of monomolecular transverse section (e.g. the D_{ho} phase of discotic molecules) and of polymolecular transverse section (e.g. the ϕ_h phase exhibited by polycatenar mesogens) are compared. In addition, recent studies on mesophases formed by biforked molecules allow us for the comparison of the molecular movements in lamellar and columnar mesophases formed by the same molecules.

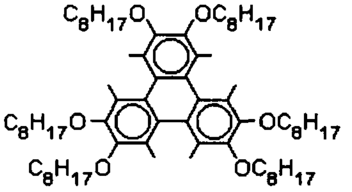
Keywords: NMR; Relaxation; Columnar; Polycatenar; Discotic; Biforked

INTRODUCTION

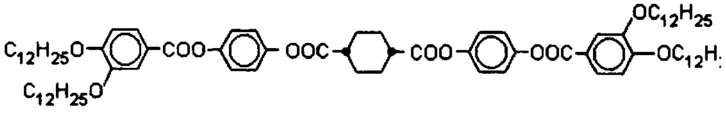
A large number of NMR relaxation studies of molecular dynamics in thermotropic liquid crystals has been reported for more than 20 years [1]. However, only a few among those concern columnar phases. One possible reason for this fact may be associated to the additional complexity of these systems when compared with the nematic and smectic phases of calamitic liquid crystals. Nevertheless, efforts have been made to provide tools for the interpretation of NMR relaxation data in columnar systems of discotic molecules [2] and some experimental results have been presented that confirm the usefulness and adequacy of the proposed models [3].

As in other systems, the application of the fast field-cycling NMR technique [4] combined with high frequency conventional NMR allows for the realisation of proton relaxation studies in a very wide range of Larmor frequencies (from nearly zero Hz to hundreds of MHz). The possibility of scanning such a large domain of frequencies has provided a way to effectively distinguish the influence of the different molecular movements generally observed in liquid crystal systems, on the proton spin-lattice relaxation.

In this work we present for the first time, the comparison of previous NMR molecular dynamics studies in the compounds shown in Fig 1.



$$K \xrightarrow[66.8^{\circ}C]{} D_{ho} \xleftrightarrow[85.6^{\circ}C]{} I$$



$$K \xrightarrow[113^{\circ}C]{} S_C \xleftrightarrow[149^{\circ}C]{} \phi_h \xleftrightarrow[156^{\circ}C]{} I$$

FIGURE 1 Molecular structures and phase sequences of the studied compounds, respectively discotic (C_8HET) and biforked

As we may see in the phase sequences presented in Fig. 1, both these compounds exhibit columnar hexagonal mesophases, namely the D_{ho} phase in the case of compound of discotic molecules (C_8HET)[5] and the ϕ_h phase in the case of the liquid crystal of biforked molecules[6]. As shown in Fig. 2, the difference between these two columnar phases is the local structure of the columns – monomolecular transversal section in the D_{ho} phase and polymolecular transversal section in the ϕ_h phase. In addition we also present the comparison between the relaxation results in the ϕ_h and S_C mesophases exhibited by the biforked compound.

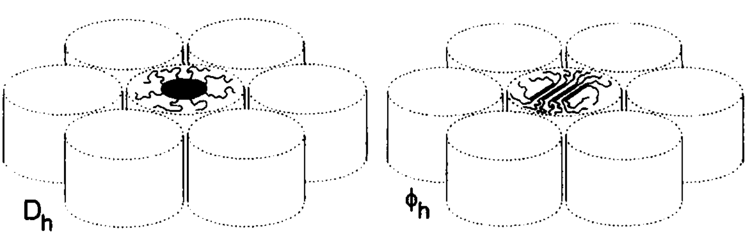


FIGURE 2 Schematic representation of the D_h and ϕ_h phases

In the comparison between the D_{ho} and ϕ_h phases we are dealing with phases of similar symmetry (columnar hexagonal) formed by different molecules and with different arrangements at local level. On the other hand, when comparing the ϕ_h and S_C mesophases we are confronting two phases of quite different arrangements (respectively columnar and lamellar) formed by the same molecules and with relatively similar structure at local level[7]. The intent of this work was to determine how these structural differences reflect on the molecular dynamics behaviour of the respective liquid crystalline systems.

COMPARATIVE ANALYSIS AND DISCUSSION OF NUCLEAR MAGNETIC RELAXATION RESULTS

The comparison of the molecular dynamics in the referred systems - discotic and biforked molecules[8, 9] - is summarised in Table 1. For both systems and in all the mesophases, the molecular dynamics was interpreted by the addition of three different contributions to the spin lattice relaxation rate, namely collective modes - CM, self-diffusion - SD and rotational reorientations - ROT. Furthermore we must remark that the theoretical models used to describe the relaxation mechanisms in different mesophases are clearly associated with the structure of those phases.

		Biforked Molecules S_C phase 	Biforked Molecules Φ_h phase 	Discotic Molecules D_{ho} phase 
Low Freq.	**CM** Collective Movements	Layer Undulations	Columnar Elastic Deformations	Columnar Elastic Deformations
Medium Freq.	**SD** Translational Self-diffusion	Self-diffusion in Smectics with Liquid-like Layers	Self-diffusion in Smectics with Liquid-like Layers	Self-diffusion in Columnar Mesophases
High Freq.	**ROT** Local Molecul. Rot.-Reorient.	Global rot.-reor.+ Chains reorient.	Global rot.-reor.+ Chains reorient	Global rot-reor+ Chains reorient

TABLE 1 Contributions of different relaxation mechanisms to the overall relaxation rate - comparison between the studied systems of biforked and discotic molecules

For both systems and in all the mesophases, the referred mechanisms - collective movements, self-diffusion and local molecular rotational reorientations – dominate the relaxation rate at low, medium and high frequency ranges, respectively.

In both the columnar phases and also in the S_C phase of the biforked molecules the relaxation results[8, 9] are compatible with an interpretation of the local molecular rotational reorientation movements based on a generalisation of the Woessner model[10] adapted to liquid crystalline systems and considering relative reorientations of the chains with respect to the molecular core [8, 9]. However, relatively to this type of movements, we find a significant difference between the behaviour of the columnar phase of discotic molecules and the studied phases of biforked molecules:

While in the studied ϕ_h and S_C phases, the relation between the characteristic times for transversal and longitudinal reorientations are satisfactorily explained by the geometrical anisotropy of the core [11], in the D_{ho} phase, the rotational reorientation movements of the disk-like molecules around the axis of the columns are considerably faster [8] then those around a transversal axis (in the plane of the disk).

This may be understood considering the structural characteristics of the columnar mesophase of discotic molecules. Considering that the columnar cores are separated by the disordered aliphatic medium, the rotation of a molecule around the column longitudinal axis corresponds to a movement between equally probable positions. Contrary, relatively to rotations of a molecular core around an axis in the plane of the disc, there is obviously an average preferred position of the molecule imposed by *the pilling up* of the cores along the column axis which strongly constrains this movement [8].

This argument is not valid in the case of the ϕ_h phase because, in that case, the transverse section of each column is formed by several molecules, which may move individually.

The description of self-diffusion was different in the two studied columnar phases. Actually, the model of inter-columnar permeation diffusive movements used to describe this mechanism in the columnar phase of discotic molecules [2] is not suitable to the ϕ_h phase. That model describes self-diffusion in the columnar phase as a process of random jumps of the discotic molecules between neighbouring positions in adjacent columns. In the ϕ_h phase, there is no physical reason for the groups of molecules, comparatively corresponding to the discs of the D_{ho} phase, to diffuse together from column to column. Even if these phases globally show a similar liquid crystalline arrangement (columnar hexagonal) they are obviously different at local level. Our relaxation data on the ϕ_h and S_C phases of the referred liquid crystal of biforked molecules, together with a study of the corresponding columnar-lamellar phase transition by X-ray diffraction and dilatometry, indicate that the ϕ_h phase have some resemblance at local level with the contiguous lamellar mesophase [7]. This fact justifies the success of the approach of describing self-diffusion in the ϕ_h phase with the model normally used for lamellar phases [12]. The contribution of the self-diffusion to the relaxation rate in the S_C phase of the biforked compound was perfectly explained using this model [9].

Finally, in what concerns collective movements, the same model, (which takes into account bending and compression of the columns) [2] was applied successfully to both mesophases. Actually this is expectable, as this type of movements are specially influenced by the long-range structural characteristics of the mesophases, which are similar (columnar hexagonal) in the considered cases. These collective movements are significantly different from those observed in the S_C mesophase of the biforked compound, in which the contribution to the relaxation rate was taken into account considering the model of layer undulations [13].

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