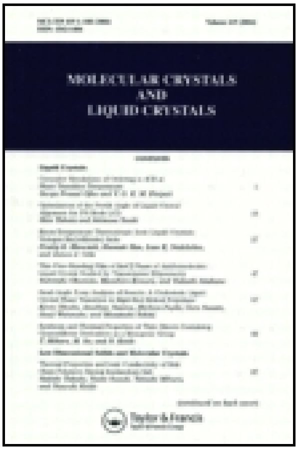

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Thermotropic Lamellar-to-Columnar Phase Transition Exhibited by a Biforked Compound

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Thermotropic Lamellar-to-Columnar Phase Transition Exhibited by a Biforked Compound

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In this work we present a structural study of the smectic $C(S_C)$ and columnar (Col_h) liquid-crystalline phases exhibited by a biforked molecule. This study was performed by means of dilatometry and X-ray diffraction measurements performed at different temperatures. Following these measurements, molecular packing within lamellar and columnar mesophases of this compound is discussed; finally, a mechanism for the lamellar-columnar transition is proposed.

Keywords: Phase transition; X-ray diffraction; Biforked compound

1. INTRODUCTION

It is well known that classical columnar mesophases are easily obtained with disk-like molecules [1]. The columns are formed by the piling of the flat cores of the molecules, the molten aliphatic chains filling the space between the columnar cores. Columnar mesophases are also found with phasmidic molecules which can be considered as formed by long rigid aromatic cores (containing in general five rings) with three chains at both ends [2]. In the columnar mesophases of these phasmidic compounds, the columns are

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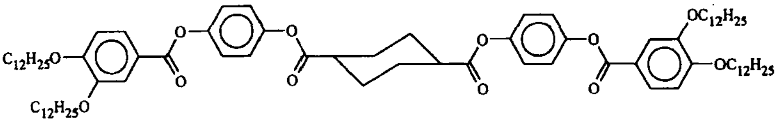
*Corresponding author.

formed by the piling of clusters of three molecules [3]. Biforked molecules are one of the several examples of liquid-crystalline compounds with molecular shapes deviating also from the usual rod of disc-like ones [4–6]. Molecules of this particular kind are composed by an elongated rigid core with two aliphatic chains attached to each end. Previous studies have shown that this type of molecular architecture gives rise to very interesting polymorphisms which may include nematic, lamellar, cubic and columnar liquid-crystalline phases [5–9].

Several studies have already been published in order to understand the polymorphic behaviour as a function of molecular parameters of polycatenar compounds. For example, the introduction into the centre of the rigid core of flexible segments such as oxymethylene (CH_2O —) groups destroys the mesomorphic behaviour [9, 10], whereas the introduction of two methylene (CH_2 —CH_2 —) groups at the last junction between the rings is very much in favour of the occurrence of columnar mesophases [10]. On the other hand, the presence of a lateral substituent on one of the rings in the rigid core suppresses the occurrence of columnar mesophases to the benefit of smectic and/or nematic phases [11], strongly suggesting that the internal packing of polycatenar molecules in the columnar cores is mainly due to efficient van der Waals interactions between the rigid cores. Moreover, the ratio between the number n_c, of carbon atoms of the paraffinic moiety of a molecule and the number of phenyl rings, n_ϕ, forming the core has been invoked also to predict the nature of the mesophase that this type of compound could exhibit [12]; for example, this ratio n_c/n_ϕ should be larger than 9 so that columnar mesophases could be observed.



The compound studied in this work, with the following phase transitions: $K \xrightarrow[113°C]{} S_C \xleftrightarrow[149°C]{} \mathrm{Col}_h \xleftrightarrow[156°C]{} I$ belongs to the family of the biforked molecules. Moreover, it has the particular feature of exhibiting both smectic $C(S_C)$ and columnar (Col_h) mesophases as a function of temperature [8]. A better understanding of the relationships between the polymorphic behaviour and the molecular structure for such systems is the main objective of this structural study, in order to be precise about the molecular arrangement in both mesophases and to pin down the mechanism of the lamellar-columnar phase transition, which has been described as a breaking of the smectic lamellae into finite ribbons [12, 13].

2. STRUCTURAL STUDY

2.1. Experimental

X-ray diffraction and dilatometry were used to obtain the structural details of the mesophases described. The X-ray diffraction results were obtained from powder samples using a Guinier camera or a Debye-Scherrer camera equipped with a bent quartz monochromator (Cu-$K_{\alpha 1}$ radiation) and an electric oven. The patterns were registered photographically or with a gas curved counter "Inel CPS 120" associated with a data acquisition computer system. The temperature of the sample was controlled within ±0.05°C.

The dilatometry technique used was developed by Kovacs for the study of polymers [14] and afterwards applied to liquid crystals [15]. The measurements were performed with a high precision home-built apparatus, automatically computer controlled, including data-acquisition and temperature control within ±0.03°C [16].

The molecular lengths and intramolecular distances were evaluated using the "Sybyl" software of Tripos.

2.2. Results and Discussion

The X-ray diffraction results obtained with the liquid crystal powder samples at different temperatures are characteristic of S_C and columnar mesophases (see Figs. 1 and 2). In the S_C phase, the patterns contain a sharp Bragg reflection in the small angle region, associated with the smectic layer spacing, and a diffuse reflection in the wide-angle region corresponding to a distance of about 4.6 Å. In the Col_h columnar phase, the patterns contain three sharp Bragg reflections in the ratio $1 : \sqrt{3} : \sqrt{4}$ in the small angle region, corresponding to a two-dimensional hexagonal columnar lattice, and a diffuse reflection at about 4.7 Å in the wide-angle region.

The variation of the molecular volume V_m as a function of temperature T obtained by dilatometry is presented in Figure 3. The variation with temperature of the layer spacing d in the S_C phase and of the intercolumnar distance, a, in the Col_h phase are represented in Figure 4. The variation with temperature of the spacing corresponding to the lateral intermolecular interaction (D) (determined by integration of the diffuse reflection in the wide-angle region with the trapezium-method, after subtraction of the baseline) is shown in Figure 5.

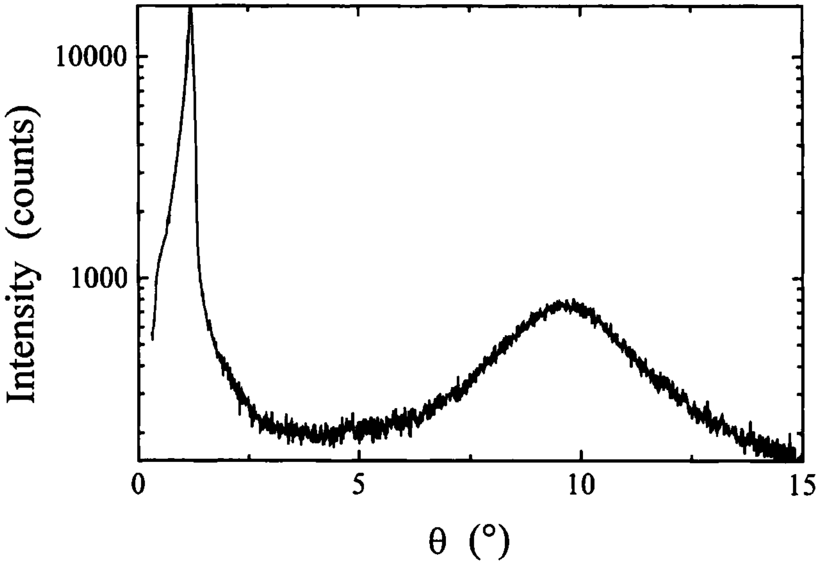


FIGURE 1 X-ray diffraction pattern at 135°C in the S_C phase.

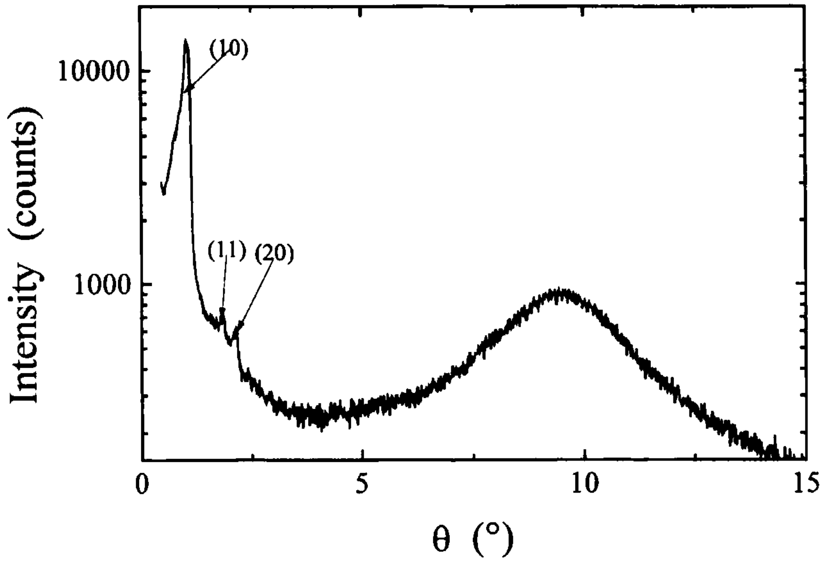


FIGURE 2 X-ray diffraction pattern at 152°C in the Col_h phase.

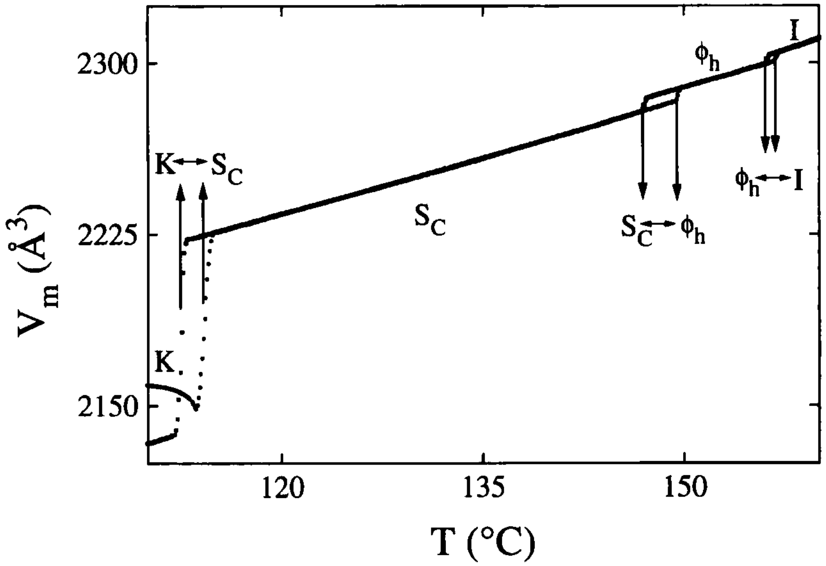


FIGURE 3 Molecular volume as a function of temperature.

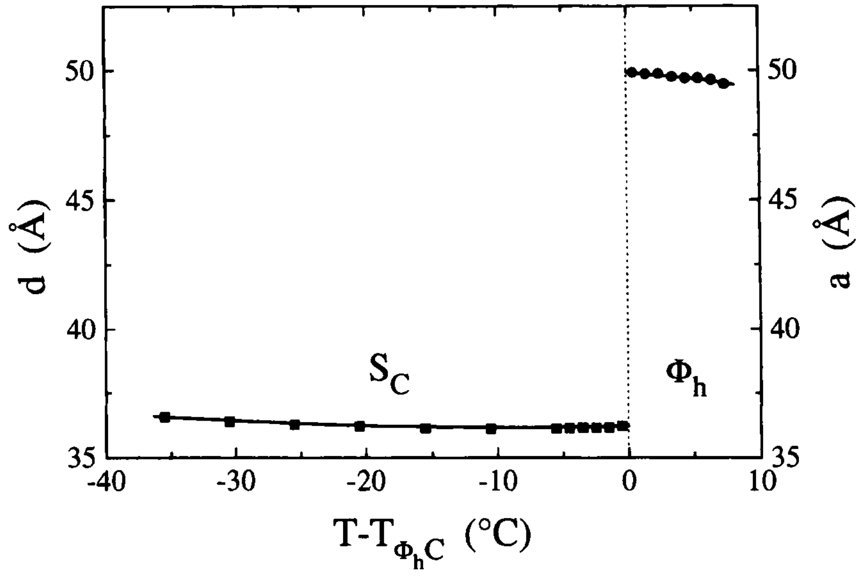


FIGURE 4 Layer spacing, *d*, in the S_C phase (filled squares) and intercolumnar distance, *a* in the Col_h phase (filled circles) as a function of temperature.

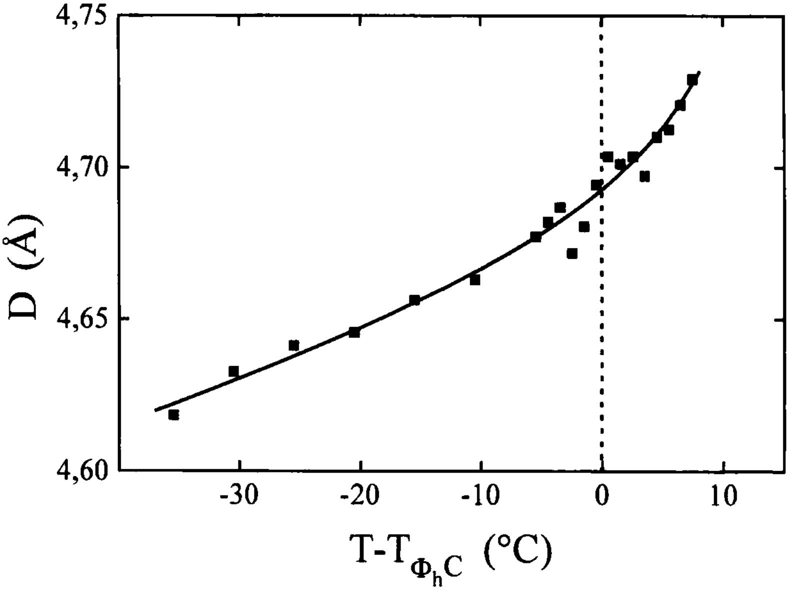


FIGURE 5 Spacing corresponding to the lateral intermolecular interaction as a function of temperature.

2.2.1. Smectic C Phase

Usually, the tilt angle in the smectic *C* phase may be determined from the ratio between the layer spacing and the molecular length. In the present case, this results in a mean tilt angle Ψ close to 53°, showing no significant temperature dependence. However, it has to be pointed out that Ψ is an average tilt angle for the whole molecule, while different tilt angles should correspond to different molecular moieties. For the work under consideration, these tilt angles can be deduced from the values of the molecular area *S*. In general, for a lamellar system such as a smectic *C* mesophase, particularly when the molecules are symmetrical with identical aliphatic chains at their extremities, the molecular area *S* has a very simple geometrical sense. It represents the average surface per molecule in the plane of the smectic layers [17]. Clearly, the molecular area is directly related to the molecular volume V_m and to the layer spacing *d* by $S = V_m/Nd$, where *N* is Avogadro's number. It should be emphasized that *S* must not be confused with σ which is the average area per molecule in a plane perpendicular to the long axis of the molecule [18]. The latter offers a specific measure of the compactness in the lateral packing of the molecular arrangement. Of course, when the molecules are tilted at an angle Ψ with respect to the layer normal, σ is given by $\sigma = S\cos(\Psi)$. The variation of S as a function of temperature for the biforked compound under study is represented in Figure 6. The observed slightly convex variation of S with temperature is due to the non strictly linear variation of d with T.

To determine the tilt angle Ψ_C of the aromatic cores, the lateral bulkiness, σ_C, of the rigid cores has been estimated from the average lateral distance D. σ_C is found to vary between 24.5 and 25.5 Å^2 depending upon temperature, and Ψ_C has a value of 66° with no significant temperature dependence. As for the aliphatic end chains, their lateral bulkiness, σ_{CH}, has been estimated from the volume of one methylene unit in liquid linear alkanes and from the classical methylene "zig-zag" length. σ_{CH} is found to vary between 22.8 and 23.3 Å^2 for one aliphatic chain, and therefore the mean tilt angle of the terminal chains, Ψ_{CH}, is about 42° with a very small temperature dependence (1.5° over the 40°C temperature range of the S_C phase).

It has to be noted that the tilt angle of the aromatic cores is fairly large, 66°. However, it is about the same as for other polycatenar molecules in their crystalline phase [18], suggesting that the lateral van der Waals interactions between the rigid cores remain similar in the crystalline and smectic phases. On the other hand, the mean tilt angle of the aliphatic chains is also relatively large, 42°, when compared with that observed (a few

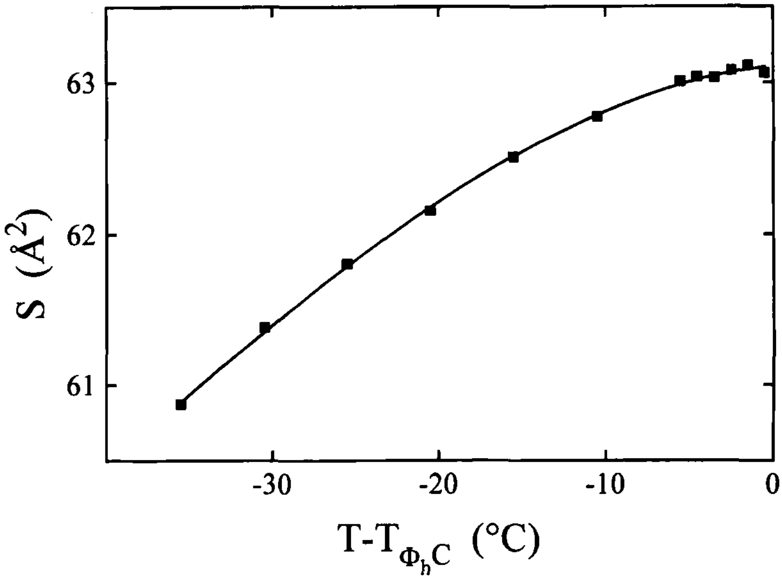


FIGURE 6 Molecular area in the S_C phase as a function of temperature.

degrees) in the crystalline phase of similar polycatenar molecules. As a matter of fact, when smectic layers are formed by sublayers of different nature exhibiting a pronounced amphipathic character and flat interfaces, the stability of the structural organisation increases as the area of the interface decreases. For biforked compounds, this would correspond to aliphatic chains oriented normal to the smectic planes and to tilt angles of about 50–60° for the aromatic cores, corresponding to the difference in the lateral bulkinesses of both molecular moieties. This seems to be the case for the crystalline phases, showing that the basic concept of amphipathy between rigid aromatic parts and disorganised aliphatic chains has to be considered also in the solid phases of these compounds. Nevertheless, in the smectic *C* phase of the compound under study, the tilt angles of both molecular moieties are much larger. This behaviour can result from layer undulations as in water surfactant systems, when the area of the hydrophobic part exceeds that of the hydrophilic one [19].

2.2.2. Columnar Mesophase

The general description of the molecular packing in the columnar phase of polycatenar molecules is based on a model previously proposed for a hexacatenar compound [3] which considers the transverse section of the columns to be constituted by several calamitic rigid cores disposed side by side and surrounded by the corresponding disorganised aliphatic end chains. The number of molecules in a slice of a column depends upon the number and the length of the terminal aliphatic chains; three molecules are found for six-chain phasmids, four to five molecules for biforked mesogens.

As pointed out above, the X-ray diffraction patterns obtained at different temperatures in the Col_h phase are characteristic of a hexagonal columnar structure. With the assumption that the spacing corresponding to the lateral intermolecular interaction (D, see Fig. 5) is identical to the mean intracolumnar periodicity h, the average number of calamitic rigid cores associated in a columnar core can be calculated from the ratio between the volume of the hexagonal cell and of the molecular volume, by using the following relation developed in Ref. [3]:

$$n = \frac{\frac{\sqrt{3}}{2} a^2 h}{V_m} \qquad (1)$$

where a is the distance between the axes of two neighbouring columns and V_m the molecular volume.

The values of n obtained (decreasing from 4.43 to 4.36 with increasing temperature) are not significantly different from 4.5 and are weakly temperature dependent. This number ($\cong$ 4.5 molecules in each elementary cluster of the column) would correspond to an average paraffinic crown formed by 18 alkyl chains. Now, considering a disc of diameter 30 Å equal to the length of the rigid core, its circumference corresponds precisely to 18 times the ideal distance between molten aliphatic chains ($\cong$ 5.2 Å). This result is also in perfect agreement with data already reported for hexacatenar and pentacatenar compounds containing central rigid cores of same length; the values of n found for these compounds were respectively 3 and 3.6, thus corresponding in both cases to 18 chains around the central core [5]. From the general agreement between all the data relative to the columnar mesophase of different polycatenar materials, it seems then natural to consider that columnar cores have a diameter corresponding to the length of the rigid core of the molecules, the clusters of rigid cores piling one over another and the aliphatic end chains forming a liquid matrix around. The local order and the possible orientational correlation between neighbouring molecules of adjacent columns will be considered in next section.

2.2.3. Smectic-to-Columnar Phase Transition

The low enthalpy and volume changes observed at the smectic-to-columnar phase transition, the almost identical shape and position of the diffuse reflection in the wide-angle region, and the similarity between the self-diffusion and reorientational rotations movements in the S_C and Col_h phases, verified by NMR molecular dynamics study [20] indicate that the transition cannot imply a significant change in the local structure.

This similarity found in the local structure combined with the structural models proposed for the S_C and the Col_h phases suggest the model presented in Figure 7 for the smectic-to-columnar phase transition. This model was proposed for the first time [21] by the authors of this paper and is also referred to in a recent review paper [11] about polycatenar mesogens. In the S_C phase (see Fig. 7a), the sublayer formed by the rigid cores undergoes undulations, in order to keep the rejection of the aliphatic parts from of the rigid cores' sublayer efficient enough, when the sublayer thickness is maximum. The difference in the transverse areas of both molecular moieties is compensated when the sublayer thickness is minimum, by the correlated shift in the positions of the rigid cores. With increasing temperature, the volume of the alkyl chains and therefore the amplitude of the layer

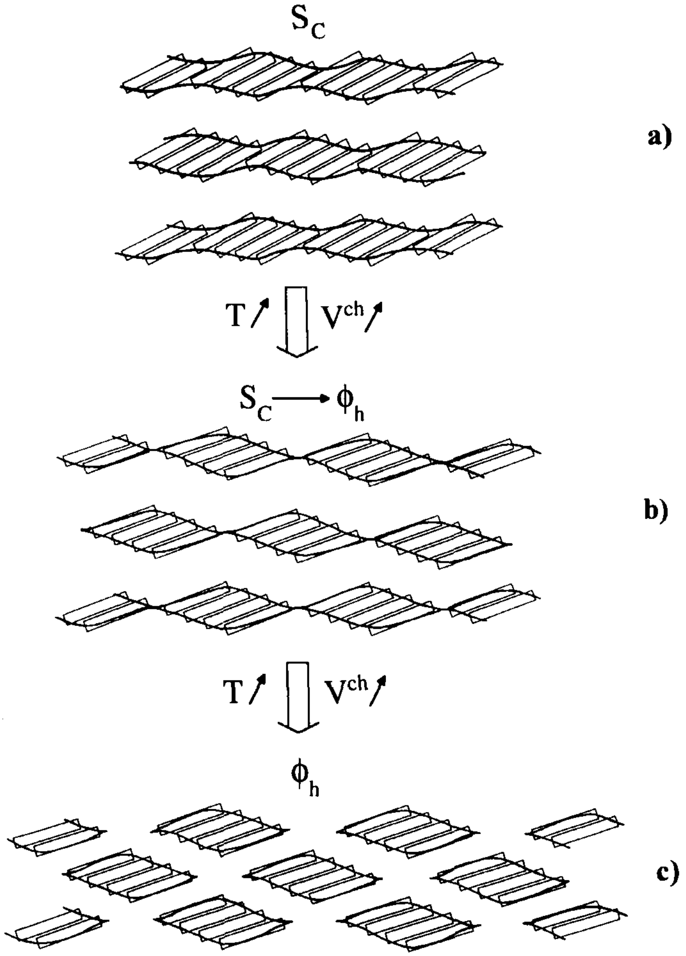


FIGURE 7 Structural models of a) the S_C phase, with undulations of the hard cores' sublayer; b) the S_C-Col_h phase transition; c) the Col_h phase (see text).

undulations increase. At the smectic-to-columnar phase transition, the amplitude of these undulations reaches the whole thickness of the rigid cores' sublayer (see Fig. 7b). Above the transition, these sublayers have broken into columns, separated by the aliphatic chains forming a continuous medium (see Fig. 7c).

The first order character of the smectic *C*-to-columnar phase transition implies that there is still a discrepancy between the surface covered by the surrounding alkyl chains and the one enveloping the columnar cores at the transition. However, the small latent enthalpy and the small volume jump observed at the transition seem to indicate that this remaining discrepancy is small. Moreover, a small expansion of the discrepancy with decreasing temperature follows from the low temperature dependencies of Ψ_C and Ψ_{CH}– see part **2.2.1.** – (in consistency with the about 1.2 percent of variation of the alkyl chains section over the same temperature range deduced from volume measurements on liquid paraffins [22]).

Despite the small transitional effects, the temperature dependence of V_m (see Fig. 3) reveals that the transition is associated to an important thermal hysteresis, which is even higher than that associated generally with the melting-crystallisation process (in general, the transitions between liquid-crystalline phases are perfectly or almost perfectly reversible in temperature). This can be expected from the amphipathy of both molecular moieties, as the aliphatic medium between the columnar cores forms an energetic barrier against their fusion in smectic sublayers. It can therefore be considered that this fusion is reached for a higher contraction of the aliphatic medium than that corresponding to the separation of the smectic sublayer into columns, as in that case such an energetic barrier would not have to be overcome.

There are a few studies on homologous series of biforked compounds [5–9]. They show that the transition from the smectic *C* to the hexagonal columnar phase is induced by increasing the chain length, an experimental observation consistent with our model. Thus, on the one hand, the occurrence of layer undulations may be interpreted as resulting from a compromise between the natural lateral positions of neighbouring rigid cores and the "propensity" of the aliphatic tails to stretch along the rigid cores' direction. On the other hand, studies on homologous series of classical bicatenar smectogenic compounds [23] confirm the basic idea that the amphipathy and the confinement in adjacent sublayers of both molecular moieties is enhanced by increasing the chain length. Consequently, the weight of the amphipathic forces inducing the stretching along the rigid core director increases with increasing chain length, resulting in the enhancement of the undulation amplitude.

It is interesting to note that according to the mechanism of the lamellar-to-columnar transition proposed above, the orientation of molecules should be very similar in neighbouring columns close to the transition. This feature is in fact supported by a previous NMR molecular dynamics study [20]. In that study, the S_C and Col_h phases were compared considering the contributions of the different possible molecular movements to the overall proton nuclear magnetic relaxation rate, namely collective movements, molecular self-diffusion and reorientational rotation.

On the one hand, the contributions of collective movements (which dominate the low frequency region) are clearly distinct in each of these phases revealing the long-range structural difference between them (the characteristic collective movements in the S_C and Col$_h$ phases are respectively layer undulations and column deformations). On the other hand, relaxation data associated with self-diffusion and rotational reorientations are compatible with a similar description of both phases indicating a local resemblance between them. This observation is specially relevant when we consider the results of the self-diffusion contribution (which dominates the medium frequency range) because of its intermolecular characteristics. In fact, the description of the self-diffusion relaxation mechanism depends on the geometric arrangement of the molecules. The good agreement between the data in the Col$_h$ phase with the self-diffusion model for the S_C phase (leading to similar values of the diffusion constant) favours the picture where the lamellar-columnar phase transition mechanism preserves the local parallelism between the molecules belonging to neighbouring columns (leaving something like a short range reminiscence of the layers which form the S_C phase).

Thus, it is possible to consider that in the columnar mesophase, close to the lamellar-columnar transition, neighbouring molecules belonging to adjacent columns could be approximately parallel to each other. However, the hexagonal symmetry of the columnar mesophase implies that all orientations of the rigid cores are possible within a columnar domain. This can be achieved through a small and regular change of molecular orientations from one cluster to the adjacent one along the columnar axis, the change in orientation being small enough in order not to perturb too much the natural van der Waals interactions between the rigid cores of the molecules. It is also reasonable to think that increasing temperature favours the isotropic orientation of the clusters and thus, the circular shape of the columnar cores formed by the rigid parts of the molecules especially when approaching the transition to the isotropic phase. Moreover, the hysteresis observed by dilatometry (see Fig. 3) is also an indication that the molecular orientations within the cluster should be different on increasing and decreasing temperature. Indeed, the condensation of the columnar mesophase into the lamellar smectic *C* phase implies, most probably, that the molecular orientations inside the clusters between adjacent columns should be approximately the same close to the transition. So, the need for molecular orientational correlation between columns can also explain the hysteresis in the phase transition on decreasing the temperature.

3. CONCLUSION

For a biforked compound exhibiting smectic *C* and columnar hexagonal mesophases, the variation of the structural parameters and of the specific volume were measured as a function of temperature. From the interpretation of the results in the smectic *C* phase, the existence of undulations of the rigid cores' sublayer was postulated, resulting in a packing model very close to the one of the smectic *C* antiphase previously proposed for monocatenar compounds. In the columnar hexagonal phase, the repetition units along the columnar axis were shown to contain $\cong 4.5$ molecules. The undulations in the smectic *C* phase should be the precursors of the columns, the breaking of the smectic layers occurring when their amplitude reaches the whole sublayer thickness. The existence of molecular orientational correlations between neighbouring columns close to the transition results from the breaking of smectic lamellae into ribbons [24], and can explain the strong hysteresis observed for the columnar to lamellar transition. Moreover these orientational correlations are in agreement with a previous NMR molecular dynamics study on the same compound.

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