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Mobility changes of side chains ascribed to density modulations along columnar structures detected by 2D NMR

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Abstract. — The molecular dynamics and phase transitions of a columnar liquid crystal based on hexaether-substituted rufigallol mesogens were studied by a combination of X-ray scattering as well as 1D and 2D solid-state NMR spectroscopy. A correlation of the anisotropic molecular motion, with the molecular symmetry and the phase symmetry was established. 2D-exchange NMR spectra revealed a slow dynamic process involving the side chains, which is attributed to changes in the packing density of the molecules along the column. In this way the packing problem of columnar liquid crystals resulting from the incommensurability of the aromatic core moieties and the aliphatic side chains is solved as proposed by de Gennes.

1. Introduction.

The columnar packing of flat organic molecules able to form discotic liquid-crystalline phases is of interest in order to understand their often unusual electronic and magnetic properties. In particular, it has been pointed out [1, 2] that the columnar mesophase, as realized by rigid aromatic molecules having six to eight flexible aliphatic side chains, poses packing problems because of the incommensurability of the aliphatic and aromatic moieties' packing (Fig. 1).

Fig. 1. — Density waves along the columns as proposed by de Gennes [1].
One of the possible ways to overcome this problem is the establishment of density modulations along the columns. Another possibility which is frequently observed is an inclination of the molecules in the columns. Such tilted columnar phases are indeed observed in discotics with ester side chains which are known to prefer out-of-plane conformations of the first carbon with respect to the ring. In contrast discotics with ether side chains which tend to in-plane conformations typically organize in non-tilted columns [3]. As pointed out by de Gennes, in a mobile mesophase such density modulations should also lead to dynamic packing fluctuations along the columns. Other modes of motion in highly ordered hexagonal columnar mesophases are the axial rotation of the molecules around the molecular axis and internal motions, due to the mobility of the side chains [4, 5]. Diffusion of the molecules between different columns only plays a minor role in columnar phases [6]. In this investigation we have chosen the rufigallol mesogen rather than the standard triphenylene. Its lower two-fold symmetry imposes another packing problem since the molecular and phase symmetries do not coincide [7] (Fig. 2). The ether-substituted rufigallol mesogens exhibit highly ordered hexagonal \((D_{ho})\) mesophases and when going down in temperature they show a strong tendency towards polymorphism [8]. In figure 3 the DSC curve of the octyl substituted rufigallol mesogen studied is displayed together with an arbitrarily chosen nomenclature for the phases encountered. In this paper we focus on NMR-investigations of phase II, the \(D_{ho}\) phase; in addition the phases at lower temperatures were characterized by X-ray diffraction.

The main points of interest of our study are the density modulations mentioned above. If these have a well developed periodicity, they can lead to sharp X-ray reflections as discussed.

![Diagram of columnar packing of the \(D_{ho}\) mesophase and the discotic liquid crystal Hexaoctanoyl-rufigallol. The different positions of deuteration are marked (\(\alpha\): \(\alpha\)-position of side chains, \(C\): core deuterated mesogen).](image-url)
2. in liquid the X-ray in liquid 223 K/mn. The 200 and Fig. N° I dynamic methylene evaporation state was synthesized. In addition, the deuterated deuterated undeuterated synthesized spectra process geometry different motional fluctuations. The C-position should render information on the molecule's motion as a whole, whereas the α-deuterated samples should give insight into the motional behaviour of the side chains. Furthermore, angular-dependent spectra of macroscopically aligned samples reveal the orientation distribution function as well as specific conformations [10].

In addition, the correlation times of the motional process can be determined. If the dynamic process to be studied is sufficiently slow, 2D-exchange spectra [11] give information about the geometry of ultraslow motions [12]. Here, 2D-exchange NMR is used to detect packing fluctuations that interchange the motional behaviour of side chains within the columns in the liquid crystalline phase. However, before we describe these experiments, we analyze the motional behaviour of both the core and the side chains as reflected in conventional 1D spectra.

2. Experimental.

The synthesis of the columnar liquid crystals followed the routes as described in [8]. Rufigallol was prepared by condensation of gallic acid monohydrate in sulfuric acid monohydrate [13] and subsequently esterified in acetic anhydride after which it was recrystallized from acetic acid (yield 48%). The hexa-ethers were prepared by adding 14 mmol hexaacetate-rufigallol, 223 mmol of the appropriate 1-bromo-alkane and 30 g anhydrous, finely powdered K₂CO₃ to 200 ml methylisobutylketone and refluxing for 70 h. Filtering of the inorganic salts and evaporation of the solvents yielded the crude product which was purified by column chromatography (toluene, silica) and recrystallization from ethanol (yield 85%). The core-deuterated rufigallol mesogen was conventionally obtained by repeated recrystallization of the undeuterated mesogen from deutero-trifluoro-acetic acid. The deuterated alkyl chains were synthesized according to standard procedures [14]. All the ²H-NMR-spectra (except for the 1D spectra in Fig. 5, labelled C) shown below were taken from samples with all their alkyl chains deuterated at the α-position. For assignment purposes samples selectively deuterated in
specific side chains (2,7 or 3, 4, 8, 9, respectively) were synthesized by a regioselective dealkylation of the alkyl chains in 2- and 7-position adjacent to the quinone with BCl₃ [15] and subsequent reetherification with the appropriate alkyl bromide.

All compounds were characterized by ¹H and ¹³C NMR. The phase behaviours were studied using a Zeiss Axiohot polarization microscope equipped with a Linkam TMS 90 hot stage. Calorimetric studies were performed with a Mettler DSC 30. Typical heating and cooling rates were 10 K/min.

The θ-θ X-ray diffractograms were measured on a Siemens Kristalloflex diffractometer with collimator widths of 0.3 mm. The diffraction patterns of the aligned samples were recorded on a system consisting of a Rigaku 18 kW rotating anode source with pinhole collimation set-up combined with a rapid two-dimensional Xe-ionization detector (Siemens) [16]. Cu-Kα radiation was selected by a graphite crystal monochromator.

All NMR measurements were performed on a Bruker CXP-300 spectrometer operating at a magnetic field of 7 T. The one-dimensional spectra were taken with the solid-echo pulse sequence [17] using a time delay of 30 μs between the two pulses.

The length of the 90° pulse was slightly shorter than 3 μs. The data processing and acquisition of the 2D spectra have been described in detail elsewhere [18]. 2D-exchange spectra were recorded in phase II (see Fig. 3) at temperatures between 310 and 340 K. The 2D spectra and some of the 1D spectra were recorded on oriented samples. Due to the negative anisotropy of the diamagnetic susceptibility the mesogens tend to align with the molecular director perpendicular to the magnetic field. The orientation of the mesogen in a planar distribution of domains [10, 4] for which the NMR-spectra of the oriented sample were taken, could be obtained easily by slowly cooling (2 K/h) the sample inside the magnetic field from the isotropic (phase I) to the desired temperature. Uniaxially aligned samples, used for the X-ray measurements, were obtained by additional slow rotation (2 rot mn⁻¹) around an axis perpendicular to the magnetic field. Since in the planar orientational distribution all directors are aligned perpendicular to the magnetic field, it was not necessary to go through the effort of aligning the sample uniaxially for the NMR-measurements.

3. X-ray measurements.

Two-dimensional diffractograms obtained with the incident X-ray beam perpendicular to the director are shown in figure 4. The diffraction patterns of phase II and phase III are essentially the same except when mentioned otherwise. Therefore, only the diagram of phase III is shown and discussed according to general assignment [19]. Reflections on the equatorial line arise from the packing of the columns whereas reflections on the vertical arise mainly from intracolumnar packing. The arc-shaped reflections at the widest angles are attributed to the disc repeating distance inside a column which is temperature dependent with a value of 3.49 Å at 310 K and a linear expansion coefficient of α = 2.0 × 10⁻³ Å/K. The halo with intensity around the full circle, but with a maximum intensity on the vertical is caused by the amorphous alkyl side chains which are mainly located in the plane of the molecule. Also, four weak reflections distributed on the edges of a cross can be observed at lower temperatures in phase III, which may be explained by some helical twisting of the side chains with a pitch length of approximately 7 Å. When going down in temperature into phase IV the main difference is the change in the packing of the columns. The hexagonal columnar packing changes into a rectangular arrangement. Additionally new reflections appear on the vertical with a spacing of 5.9 Å indicating the formation of dimers, which might be due either to a specific geometrical arrangement of the molecules with regard to the side chains and/or to a stacking distance modulation as was found before [2]. When going down in temperature again to phase V, the parameters of the rectangular packing change considerably and the previously
Fig. 4. — X-ray diffractograms obtained by exposing the sample with the incident beam perpendicular to the column director $n$. 
amorphous halo is replaced by sharp reflections which center around the vertical as well as the horizontal axis. Furthermore cross reflections appear indicating a correlation between the stacking of different columns. We now have a true crystal which was not analyzed in more detail, since no single crystals are obtained by this method. Nevertheless we may conclude that the main contribution of the heat of crystallization at the transition from phase IV into phase V is caused by the crystallization of the side chains, and the basic columnar structure is preserved.

The parameters of the columnar packing together with a least-squares fit for the two rectangular packings and the packing parameters are given in Table I. The calculated area in the plane of the columnar grid per molecule, $A_{\text{col}}$, is also given.

Table I.

<table>
<thead>
<tr>
<th>III hexagonal</th>
<th>IV rectangular</th>
<th>V rectangular</th>
</tr>
</thead>
<tbody>
<tr>
<td>h k exp.</td>
<td>h k</td>
<td>h k</td>
</tr>
<tr>
<td>10 20.530</td>
<td>11 20.663</td>
<td>10 20.766</td>
</tr>
<tr>
<td>11 11.784</td>
<td>20 17.516</td>
<td>15 15.243</td>
</tr>
<tr>
<td>20 20.194</td>
<td>22 10.337</td>
<td>10 10.38</td>
</tr>
<tr>
<td>20 20.194</td>
<td>22 10.337</td>
<td>10 10.38</td>
</tr>
<tr>
<td>31 10.661</td>
<td>31 10.661</td>
<td>9.47 9.57</td>
</tr>
<tr>
<td>13 8.533</td>
<td>13 8.533</td>
<td>9.29 9.03</td>
</tr>
</tbody>
</table>

All units are given in Å.

As stated in the introduction our main interest is the change in packing density along the columns. Our X-ray experiments give no direct evidence of this phenomenon, in contrast to the original finding [2], where the occurrence of an additional reflection was attributed to a periodic density modulation. However, if one deals with aperiodic density modulations, this gives rise to line broadening and diffuse scattering effects only. In fact, the observed reflections assigned to the intracolumnar stacking have strongly temperature-dependent widths of 2-3° which are compatible with density modulations. As will be shown below they show up clearly in the NMR.

4. 1D NMR solid-echo spectra.

Figure 5 depicts an overview of temperature dependent spectra of the deuterated C-position and α-position. Firstly, the close overall similarity between the spectral narrowing for the C- and α-position is worth mentioning. This indicates that the motions of the core and the side chains in the region close to the aromatic core are coupled considerably. In phases IV and V the full Pake spectrum for the C-position demonstrates the absence of rapid rotational motions with amplitudes larger than 5° of the whole molecule. Furthermore, 2D NMR measurements not shown here also rule out large angular motions at very low rates [29].

In phases II and III the fast rotation of the molecules around the columnar axis leads to a reduction of the spectral width by a factor of 2 [4] for the C-position. The lower intensities of the spectra and the distortions of the spectral shape in phase III indicate that the rates of the rotations are of the order of the quadrupolar coupling constant of 250 kHz [5, 9, 17]. Non-
perfect ordering of the molecules leads to additional spectral narrowing. The order parameter $S$, determined as described in reference [20], is 0.96 at 325 K and 0.88 at 365 K-values typical for $D_{ho}$ phases [20].

The spectrum of the $\alpha$-position in phase IV indicates mobility of the side chains. However, as the core is still quite rigid, the full spectral width is retained because only specific conformations can be explored. The spectrum can be quantitatively reproduced by the assumption of the libration-model discussed in section 5 with the same parameters as that for the low-temperature spectra in phase III, but without the columnar rotation being active.

In figure 6 a series of spectra of the oriented, $\alpha$-deuterated mesogen in the high temperature mesophases (II and III) is displayed. We notice two doublets at high temperatures in phase II and four doublets in phases II and III where one doublet appears only as a shoulder of the inner doublet at lower temperatures. For convenience in figure 7 these doublets with quadrupolar splittings of (a) 6 kHz, (b) 19 kHz, (c) 36 kHz and (d) 56 kHz are marked by the letters a-d. NMR spectra of samples selectively deuterated at the $\alpha$-position of the side chains (not shown) revealed clearly that each individual site gives rise to two quadrupolar splittings (a, b) or (c, d) [30]. The splittings (a) and (b) arise from the side chains having only one vicinal side chain (positions 2, 4, 7, 9, in Fig. 7).

Those side chains located in between two adjacent side chains (positions 3, 8) exhibit larger quadrupolar splittings (c, d) because steric hindrance is stronger and allows less conformational freedom than for the positions having only one adjacent side chain.

It is important to note that the steadily increasing intensity of the narrower doublets with increasing temperatures at the expense of the broader doublets cannot be accounted for by a spectral averaging effect like an exchange with increasing rate between two conformations [21]. This would lead to averaged lines intermediate between splittings at low temperatures. Likewise, it does not correlate with any phase transition. Thus, the additional doublets must arise from an additional conformational species intrinsic to the mesophase, the amount of which increases at the lower temperatures at the expense of the species at higher temperatures.
5. Conformations and mobility of the side chains.

In order to quantify these observations, the NMR lineshapes have to be related to molecular parameters. There are two conceptually different types of motions by which the quadrupolar splittings can be reproduced: conformational changes within the rotational isomeric state model [22], and the librational model [23]. In addition to these two types of motions which are both likely to occur in phases II and III one has to take into account the rotations of the mesogens around their columnar axis. Hence in order to simulate the spectra of oriented samples one needs a fair amount of parameters (for the molecular orientation and each individual type of motion).

Fig. 6. — Experimental and simulated solid-state $^2$H-NMR spectra of the mesogen deuterated in the $\alpha$-position of the side chain at different temperatures in phases II and III. The mesogen is oriented in a planar distribution of domains. The simulations for the experimental spectra assume discrete states of libration. Details about the simulations are given in [29].
Fig. 7. — Peak assignment for the spectra of figure 6. The peaks are numbered by the letters (a)-(d). Note that the outer side chains (2, 4, 7, 9) give rise to the more motionally narrowed inner doublets (a, b), while the doublets (c, d) are accounted to the inner side chains (3, 8).

Here we restrict our simulations to the spectra in phase II, where both, the axial rotation is fast and the mobility of the side chains is high. Therefore only the quadrupolar splittings are of interest. Moreover in the following section it will become clear that details of the line shape simulations do not influence our analysis of the 2D exchange NMR spectra in terms of dynamic packing fluctuations. In order to limit the number of parameters, we use a simple librational model [23-25], which takes into account librations of the deuterated side chains which are fast on the time scale of a 1D experiment. This model has been shown to successfully describe the quadrupole splittings for side chains in discotics [24]. In order to simulate the quadrupolar splittings of doublet (d) (see Fig. 7) we assume an in-plane-trans conformation (see Fig. 2 of Ref. [23]) for the side chains without substantial conformational mobility. To reproduce the quadrupolar splitting of the doublet (c) librational amplitudes of about ± 24° within the in-plane-trans conformation are sufficient. The peaks (a) and (b) could not be assigned to a single conformation (with or without additional librations) so conformational exchanges between an in-plane and an out-of-plane trans conformation (Fig. 2 of Ref. [24]) were assumed. Therefore, one concludes that the in-plane-trans conformation is populated to about 20%. In order to account for the additional reduction in (a) as compared to (b) a libration of about ± 29° is assumed.

In figure 6 experimental and simulated spectra of oriented samples based on this model are displayed. Considering the simplicity of our approach the agreement is highly satisfactory although the fits are not exact. Hence the 2H-NMR spectra clearly reveal that each type of side chain assumes two different states of mobility with temperature-dependent populations. In view of the packing problem of columnar phases [1] described in the introduction, it is only
natural to assign these different states of mobility to regions of higher and lower packing density along the columns (see Fig. 1).

6. 2D-NMR exchange spectra as indicators of packing fluctuations.

If density modulations as shown in figure 1 exist, they are expected to change their position along the column such that a given rufigallol unit finds itself exchanging between regions of higher and lower density. In fact, such a dynamics was addressed in reference [1] as a

![Diagram](image)

Fig. 8. — Experimental 2D spectra of the compound deuterated in α-position. The spectra were taken with the oriented compound at 321 K for the mixing times of (a) 5 ms, (b) 25 ms, and (c) 50 ms. The waiting time after each scan was 0.5 s and the overall acquisition time for one spectrum was between 8 and 12 h.
particularly interesting aspect for future investigations. The time scale of this exchange is expected to be longer than that of the side chain mobilities as revealed in the 1D lineshapes discussed above. Such additional ultraslow modes of motion in phase II can be detected by 2D-exchange NMR spectroscopy [11, 26]. 2D-exchange spectra can be seen as two-time distribution functions [12], i.e. along one dimension a frequency before a mixing time \( t_m \) is displayed, while along the other dimension the frequency corresponding to the same species after the mixing time is displayed. If no exchange processes take place during \( t_m \), all spectral intensity is centered on the diagonal, while in case of exchange spectral intensity can be found off-diagonally.

The 2D-exchange spectra of the oriented sample (Fig. 8) show clearly that there is a slow exchange process between the inner and the outer doublets: exchange between doublets (a)

![Experiment and Simulation](image)

**Fig. 9.** — Experimental and simulated spectra of the oriented mesogen for a short (5 ms) and an intermediate (50 ms) mixing time. The simulations are based on discrete states of libration. The discrepancies between the experiment and the simulation for the short mixing time give evidence of the existence of a distribution for each librational state. Note also that exchange within this distribution is visible for the experimental spectrum with the short \( t_m \) (cf. text).
and (b) and between (c) and (d). In fact, due to the increased spectral resolution of 2D-NMR [26], the doublet (b) is nicely resolved from (a). The spectra can be fitted by choosing suitable sets of parameters for the quadrupolar splittings as described above for the 1D spectra, and subsequent fitting of the calculated to the experimental cross-peak intensities. An example is presented in figure 9 showing that a fair agreement is obtained, in particular for long mixing times, where the exchange is most pronounced (Fig. 9b). Another way is simply determining the relative cross-peak and diagonal-peak intensities by integration and determining the jump exchange rates or correlation times, $\tau_c$, according to reference [11]. This has the advantage that no assumption on the mechanism of molecular motion is necessary. In fact, both approaches yield similar results in our case.

From a series of temperature and mixing-time dependent spectra, correlation times for the exchange were determined and an activation plot is displayed in figure 10. Note that the correlation times are in the range between 1.5 and 75 ms and indeed are longer by several orders of magnitude than the correlation times of the side chain motions and rotational motions of the aromatic core around the columnar axis leading to motional narrowing, i.e. 0.1 $\mu$s.

Within 20 K, $\tau_c$ for the slow exchange process changes by almost two orders of magnitude. If one would assume a simple Arrhenius behaviour one would obtain an apparent activation energy of 165 kJ/mol and a preexponential factor of about $2 \times 10^{-29}$ s. These physically meaningless values show that the motional process detected here cannot be ascribed to simple molecular dynamics showing Arrhenius behaviour, but indeed to a process involving a large number of molecules and leading to a significant entropic change. Such a process is realized by dynamic packing fluctuations along the columns. The conformational freedom monitored by 1D $^2$H-NMR thus serves as a sensitive indicator of the packing density along the column, and 2D-exchange NMR proves that the density modulations are not static, but their positions fluctuate on a time scale of 1-100 ms. Likewise, the temperature-dependent fractions of chains with different side chain mobilities are easily ascribed to temperature-dependent lengths of the respective regions of different packing density.

![Activation plot: correlation times determined by spectrum simulations and integration vs. the inverse temperature.](image)

Fig. 10. — Activation plot: correlation times determined by spectrum simulations and integration vs. the inverse temperature.
It is remarkable that such two distinguishable states of motional behaviour have not yet been found in similar discotic mesogens like side chain deuterated triphenylenes which have been extensively investigated already [4, 5, 10]. We attribute this to the fact that in the rufigallol mesogen the side chains are much more densely packed as compared to the triphenylenes where only two side chains are fixed to each benzene ring. The high density of side chains in the rufigallol leads to an increase of the incommensurability of the side chains and the aromatic core, so that the effect becomes visible.

Considering just two states of mobility of the side chains represents an oversimplification in view of the packing model proposed by de Gennes (Fig. 1). In addition to the mobilities associated with higher and lower packing densities, these should be interfacial regions with intermediate mobilities leading to quadrupole splittings between the prominent peaks.

Indeed the experimental spectra exhibit intensity between the splittings (a) and (b) as well as (c) and (d); compare, in particular, the « almost diagonal » 2D spectra in figures 8a and 9a. Moreover, the slight off-diagonal exchange intensity in the spectra for short $t_m$ cannot be accounted for by considering just two states and the exchange rate which fits the exchange peaks observed for longer $t_m$ cf. figure 10. However, such off-diagonal intensity is to be expected if the regions of higher and lower packing density diffuse along the column. Then for short mixing times, exchange mainly involves the interfacial regions with intermediate chain mobility as observed. In fact, a similar behaviour has been found when monitoring chain diffusion between the crystalline and amorphous regions in polyethylene by 2D-exchange NMR [27]. There the conformations in the interfacial regions, intermediate between those in the crystalline and amorphous regions, are clearly detected too.

7. Summary.

By combining the results from the solid-state NMR and X-ray measurements, the picture sketched in figure 11 about the columnar packing in rufigallol emerges. In the liquid-crystalline phases II and III, the effective molecular symmetry is cylindrical due to fast rotation about the columnar axis and the columns pack in a hexagonal manner. Packing problems caused by the incommensurability of the aromatic core and aliphatic side chains are solved by a density modulation along the columns. It is important to note that the reorientational motion of the core is faster by several orders of magnitude than the dynamic exchange between the packing regions (dynamic packing fluctuations). Our preliminary X-ray results, in contrast to the original findings [2], show no clear indication of periodic density waves. However, they also do not exclude density modulation without a pronounced periodicity. One might be tempted to ascribe our finding to the « trivial » case also discussed in reference [1]: the mean density fits the chain packing (less dense medium) and the 1D stacking undergoes density fluctuations as in other columnar phases but of larger amplitude. Then one would expect a continuous variation of mobility with the most probable being intermediate, rather than two pronounced states of mobility, the probability of the intermediate being low. A similar statement holds to the possibility that the density modulations is due to local helical twisting [31], which would not be put in evidence by X-ray diffraction. At this point it is important to notice that the dynamic packing changes observed in our NMR experiments indirectly by a change of side chain dynamics might actually be very small in terms of molecular distances. Thus, X-ray contrast should be low. X-ray measurements with high resolution could help to further support our model.

In phase IV the columnar rotation is frozen such that the molecular symmetry now has a pronounced effect on the packing symmetry. We observe a phase where the side chains are fully mobile and the columns are packed quite rigidly. The rectangular columnar packing thus obtained resembles a situation sometimes called condis-crystalline [28]. Moreover, the
incommensurability problem apparently is solved by the formation of dimers along the column. Phase V eventually is a conventional crystalline phase where the columnar packing is preserved. In such a way it is possible to keep the macroscopic alignment of the mesophase even in the crystalline phase. Upon heating again the mesophase is regained with the same degree of macroscopic alignment.

Acknowledgments.

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