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$^2$H-NMR Detection of the Pressure Effect on Packing Modulations in a Columnar Liquid Crystal

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Abstract. — The effect of high pressure on the columnar density modulation of the hexaoctyl-ether of rufigallol, resulting from the incommensurability of the aromatic and aliphatic packing, is studied by 1D and 2D $^2$H-NMR spectroscopy. The mobility of the side chains can be used to probe the local packing density along the columns. We show that the numbers of molecules in regions of high and low packing density are strongly dependent both on temperature and on pressure. 2D-exchange NMR spectra show that the rate of exchange between these regions decreases considerably at increasing pressure, which is attributed to an increase of the length scale of the pinched regions. Our findings are consistent with the model proposed by de Gennes to resolve the incommensurability problem. A large decrease in the rate of molecular reorientation about the column axis is observed at the II-III phase transition.

1. Introduction

In 1977 [1] it was first shown that disc-shaped molecules consisting of a rigid planar aromatic core and a number of flexible aliphatic side chains can form stable mesophases in which the discs are stacked on top of each other to form columns. In certain columnar discotic liquid crystals there is evidence from X-ray diffraction for the occurrence of packing modulations along the columnar axis. These observations have first been made by Skoulios et al. [2] on octa(dodecyloxyethyl)phthalocyanine.

In a model proposed by de Gennes [3] the rigid cores and the flexible chains interact with adjacent cores and chains in the column, however, with different equilibrium spacings. In a limited range of the misfit of the equilibrium spacing the frustration can be solved by the establishment of a periodic sequence of regions of high packing of the cores, the “pincements” of Skoulios. Subsequently, a generalized de Gennes model was analyzed by Hood and Caillé [4]. In addition, a numerical analysis by Godrèche and de Seze confirmed the possibility of having a stable structure along the column consisting of these pinched regions [5].

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Recently, in a study [6] of the columnar mesophase II of the hexa-octylether of rufigallol (rufigallol-HOE) by $^2$H-NMR it was shown that the columns consist of rather distinct regions of high and low packing density. The $^2$H-NMR spectra could be explained by a simple model in which the side chains have two states of mobility: large angle and small angle librations, corresponding to low and high local packing densities, respectively. The ratio of the numbers of molecules in regions of high and low density is strongly temperature dependent. X-ray diffraction data presented in the same study did not show evidence for a periodicity in the density along the columns, however. Two-dimensional exchange spectra showed exchange between the regions of different packing densities on a timescale of 1-100 ms, proving that the density modulations are not static.

The purpose of the present study is the investigation of the effect of high pressure on the density modulations in rufigallol-HOE, also using one-dimensional and two-dimensional $^2$H-NMR. The application of pressure makes it possible to distinguish between and compare the effects of temperature and of density. In addition, a number of results concerning the transitions between the mesophases occurring at lower temperature and at high pressure will be presented.

2. Rufigallol-HOE

The discussion in reference [6] of the phase behaviour and of the structure of the hexa-octylether of rufigallol (rufigallol-HOE) may be summarized as follows.

DSC and X-ray diffraction measurements [6, 7] have shown that rufigallol-HOE exhibits a number of mesophases. Below the isotropic phase I, phases II and III have the same hexagonal columnar packing with the molecules reorienting at different rates about the columnar axis. In phase IV the molecular reorientation stops and the columnar packing changes from hexagonal to rectangular, while the molecules form dimers. Eventually, in phase V, the side chains are also frozen, the packing density increases slightly while the columnar packing is preserved. Approximate values of the temperatures of the transitions between the phases I through V as derived from the DSC diagram in reference [6] are 370, 304, 292 and 275 K, respectively.

In the present study we use rufigallol-HOE, selectively deuterated at the α-position of the side chains (see Fig. 1a), the preparation of which is described in reference [6]. Oxygen is removed by flushing the probe containing the sample several times with high-purity nitrogen gas. Aligned samples, in which the domains have a planar distribution of the columnar directors perpendicular to the magnetic field, are prepared by slowly cooling (< 2 K/h) the sample in the magnetic field from 380 K in the isotropic phase I through the transition (at 370 K) to the mesophase II and further down to 340 K in a nitrogen atmosphere. The degree of the alignment achieved can be estimated from the $^2$H-NMR spectra (see Sect. 7). Depressurizing the sample from 1 kbar to ambient pressure generally results in a slight misalignment, after which the aligning procedure described above is repeated. All $^2$H-NMR experiments discussed in the following have been performed on a carefully aligned sample.

3. Experimental

All $^2$H-NMR experiments have been performed at 41.43 MHz using a home-built spectrometer and a high-pressure NMR probe designed for a pressure up to 10 kbar [8]. The central part of the probe is a cylindrical beryllium-copper pressure vessel (outside diameter 55 mm, inside diameter 11 mm), which contains the rf coil and a sample container made out of Kel-F. We use a cylindrical sample of length 6.5 mm and diameter 6 mm.

The pressure is generated outside the NMR probe. High-purity nitrogen gas is used as a pressurizing medium, which is transferred via a capillary transfer tube to the sample inside
Fig. 1. — (a) The hexa-octyl-ether of rufigallol (rufigallol-HOE), selectively deuterated at the α-position. (b) A characteristic quadrupole echo spectrum of rufigallol-HOE, taken at 340 K and 4 kbar. The peaks are labelled by the letters (a-d), and the corresponding quadrupole splittings are indicated in the figure. Note that the outer side chains (2, 4, 7 and 9) give rise to the inner doublets (a) and (b) while the inner side chains (3 and 8) are responsible for the outer doublets (c) and (d).

the probe. A 0.8 mm diameter hole at the top of the container allows the transfer of the gas. The probe is placed in a thermostat, constructed inside the 89 mm bore of a 6.4 T magnet (Oxford Instruments). The temperature is measured using a calibrated four-lead platinum thermometer (Heraeus). The temperature can be controlled from about 90 to 400 K with an accuracy of ±0.01 K. The design of the high-pressure instrumentation generally follows the one described earlier [9]. The pressure is measured with an accuracy of 5 bar.

One-dimensional $^2$H-NMR spectra are obtained using the quadrupole echo technique [10–12] with a time interval $t_1$ between the pulses of 30 – 100 μs. The length of the 90° pulses is 4 μs. The time domain signals are obtained using quadrature detection with a sampling rate of 500 kHz. To minimize spectral distortions a phase cycling scheme is used [13]. Prior to Fourier transformation the time domain signal is shifted to start from the echo maximum, using spline functions [13].

Two-dimensional exchange spectra are obtained using a five-pulse sequence [14, 15] with $t_1$ increments of 6 μs. The size of the time domain matrices is increased from $43 \times 256$ to $256 \times 256$ by zero filling before Fourier transformation. The time delay between scans is 0.35 s.

The $^2$H-spin-lattice relaxation process is investigated using a saturation sequence consisting of ten π/2 pulses (at 1 ms intervals) which, after a variable delay time, is followed by a quadrupole echo sequence (with $t_1 = 25 \mu s$). $T_1$ is determined from the amplitude of the echo as a function of the delay time. The “apparent” transverse relaxation time $T_2^*$ is obtained from the decay of the quadrupole echo amplitude as a function of the time interval $t_1$ between the pulses.

4. Lineshape Analysis

Figure 1b shows the characteristic shape of the one-dimensional $^2$H-NMR spectrum of oriented α-deuterated rufigallol-HOE (Fig. 1a) in phase II. As has been discussed in reference [6] one can schematically account for this shape in the following way.
The NMR frequency of the deuteron is determined by its quadrupole interaction with the electric field gradient (EFG) present in the carbon-deuteron chemical bond. The EFG tensor is approximately axial about the C–D bond; the quadrupole coupling constant \( \delta_Q = \frac{3}{5} e^2 q Q / h = 55 \text{ kHz} \) [16]. The EFG’s at the deuteron sites become axial about the director when molecular reorientation faster than the quadrupole constant about the director occurs. With all molecules perpendicular to the director the quadrupole frequency shift \( \omega_Q / 2\pi = \pm \frac{1}{2} \delta_Q (3 \cos^2 \theta - 1) \) \((3 \cos^2 \beta - 1)\) is only orientation dependent through \( \theta \), the angle between the magnetic field \( B \) and the symmetry axis of the averaged EFG, and \( \beta \), the angle between the carbon-deuteron chemical bond and the director. With the director perpendicular to the magnetic field \( B \), \( \omega_Q \) is only determined by the conformation at the \( \alpha \)-carbon of the side chain with respect to the molecular plane. C–D-bonds in an in-plane-trans conformation (see Fig. 2 of [17]) have \( \beta = 35.3^\circ \) which will result in frequencies \( \omega_Q / 2\pi = \pm 28 \text{ kHz} \). Additional libration about both C–O axes further reduces \( \omega_Q \). In an out-of-plane-trans conformation \( \beta \) is close to the magic angle 54.7° which gives \( \omega_Q \sim 0 \).

NMR spectra of molecules with selectively deuterated side chains revealed [6] that the side chains 3 and 8 give rise to doublets (c) and (d) (see Fig. 1b). At the \( \alpha \)-carbon of these chains, located between two adjacent chains, the conformation is in-plane-trans. One can explain doublets (c) and (d) by assuming that they arise from side chains with and without substantial libration in the in-plane-trans conformation, respectively. Doublets (a) and (b), arising from chains 2, 4, 7 and 9, can be accounted for by assuming conformational exchanges between \( \sim 25\% \) in-plane-trans and \( \sim 75\% \) out-of-plane-trans. The additional reduction in doublet (a) as compared to (b) is accounted for by assuming additional libration in both conformations.

The important point to note (as has been pointed out in Ref. [6]) is that the 1D-spectrum clearly shows that each type of side chain assumes mainly two states of mobility, obviously corresponding to regions of higher and lower packing densities along the columns. Therefore, the amplitudes of the linepairs (c) and (d) and of the pairs (a) and (b) may be assumed to be roughly proportional to the numbers of molecules in regions of low and high packing densities, respectively.

The 1D-spectra can be simulated with the help of a computer program, discussed in detail in reference [18], in which a number of refinements is introduced in the schematic model for the motion discussed above. The program calculates the \(^2H\)-NMR frequency in both chain conformations while the effect of librations about the C–O bonds, reorientation about the molecular axis, misorientation of the molecules in the column and misalignment of the columns can be taken into account. The algorithm represents a transformation of the EFG tensor at the site of the deuteron from its principal axis system to the laboratory axis system. The transformation consists of a sequence of six rigid rotational transformations, in which the \( z \)-axis consecutively lies along C–D, along O–C, along C–O, perpendicular to the molecular disc, along the column axis, perpendicular to the column axis and, finally, along the external magnetic field. In addition, dipolar broadening is introduced. As will be shown in the next section, the spectra simulated with this simple model describe the measured spectra satisfactorily.

5. 1D \(^2H\)-NMR Quadrupole Echo Spectra

Experimental 1D \(^2H\)-NMR spectra as a function of temperature and close to atmospheric pressure, namely about 3 bar, are shown in Figure 2. These spectra are in perfect agreement with the spectra at 1 bar, presented in reference [6]. 1D spectra as a function of pressure up to 4500 bar have been obtained at 320, 330 and 340 K. The data at 340 K are also shown in Figure 2. Clearly visible is the dependence both on temperature and on pressure of the amplitudes of the (c) and (d) lines and somewhat less visible those of the (a) and (b) lines. These amplitudes
reflect the temperature and pressure dependence of the numbers of molecules in regions of low and high density along the columns. There is also an increase of the splittings of most doublets at higher pressure and at lower temperature. In comparison with the data obtained as a function of temperature in which the density decreases at increasing temperature, the spectra obtained as a function of pressure contain the effect of density changes only.

The experimental spectra have been analyzed by comparison with the results obtained by simulation of the spectra with the help of a slightly modified version of the computer program mentioned above. A quadrupole coupling constant $\delta_Q = 55.5$ kHz results in the best fits. The molecular reorientation about the director is considered to be fast. In order to limit the number of variables we have made the following choices, which result in acceptable fits for all values of $p$ and $T$ in phase II. All side chains have librations with equal amplitudes.
Fig. 3. — The mole fractions and librational amplitudes of the contributions (a-d) as a function of temperature (at 3 bar) and pressure (at 340 K), resulting from the best fit of the simulations to the experimental spectra. All lines are linear least squares fits, except for $x_b$ as a function of temperature, which is fitted by a second order polynomial.

The mole fractions and librational amplitudes, resulting in the best fit to the experimental spectra taken as a function of temperature and pressure, are shown in Figure 3. The mole fractions $x_b (= 1 - x_a)$ and $x_d (= 1 - x_c)$ are the fractions of molecules giving lines b and d, respectively. The values of $x_d$ can be obtained quite accurately. The dependence of $x_d$ on temperature and pressure is shown in Figures 3a and 3b.

The determination of $x_b$ is rather inaccurate. This is partly due to the considerable overlap of lines a and b, particularly at high temperature and low pressure. Moreover, the simulation of the a and b lines requires the choice of the additional parameter $R$. As may be seen directly from the spectra in Figure 2, $x_b$ is smaller than $x_d$ at low temperature and at high pressure. In the framework of our model this means that the number of outer chains undergoing large angle librations in both conformations is less sensitive to the local density in the column. Therefore, the $x_b$ may be expected to show a weaker dependence on temperature and pressure. It should be noted, however, that the dependence of $x_b$ on temperature and pressure as obtained from our spectra simulations and shown in Figures 3a and 3b is strongly influenced by our choice.
Table I. — Quadrupolar splittings $\Delta$ of the (a-d) doublets as a function of temperature at 3 bar.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta_a$ (kHz)</th>
<th>$\Delta_b$ (kHz)</th>
<th>$\Delta_c$ (kHz)</th>
<th>$\Delta_d$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310.0</td>
<td>6.3 ± 0.2</td>
<td>18.6 ± 0.4</td>
<td>37.4 ± 0.3</td>
<td>57.9 ± 0.4</td>
</tr>
<tr>
<td>320.0</td>
<td>6.1 ± 0.2</td>
<td>19.8 ± 0.4</td>
<td>36.9 ± 0.3</td>
<td>55.7 ± 0.4</td>
</tr>
<tr>
<td>330.0</td>
<td>5.9 ± 0.2</td>
<td>19.5 ± 0.4</td>
<td>36.9 ± 0.3</td>
<td>53.2 ± 0.4</td>
</tr>
<tr>
<td>340.0</td>
<td>6.6 ± 0.2</td>
<td>18.1 ± 0.4</td>
<td>37.1 ± 0.3</td>
<td>49.8 ± 0.4</td>
</tr>
<tr>
<td>350.0</td>
<td>6.8 ± 0.2</td>
<td></td>
<td>37.4 ± 0.3</td>
<td>46.4 ± 0.4</td>
</tr>
<tr>
<td>360.0</td>
<td>7.1 ± 0.2</td>
<td></td>
<td>38.3 ± 0.3</td>
<td></td>
</tr>
</tbody>
</table>

Table II. — Quadrupolar splittings $\Delta$ of the (a-d) doublets as a function of pressure at 340 K.

<table>
<thead>
<tr>
<th>$p$ (bar)</th>
<th>$\Delta_a$ (kHz)</th>
<th>$\Delta_b$ (kHz)</th>
<th>$\Delta_c$ (kHz)</th>
<th>$\Delta_d$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>6.6 ± 0.2</td>
<td>17.6 ± 0.4</td>
<td>37.1 ± 0.3</td>
<td>50.0 ± 0.4</td>
</tr>
<tr>
<td>502</td>
<td>6.8 ± 0.2</td>
<td>18.3 ± 0.4</td>
<td>36.9 ± 0.3</td>
<td>51.3 ± 0.4</td>
</tr>
<tr>
<td>1019</td>
<td>7.0 ± 0.2</td>
<td>19.3 ± 0.4</td>
<td>36.6 ± 0.3</td>
<td>52.5 ± 0.4</td>
</tr>
<tr>
<td>1499</td>
<td>7.1 ± 0.2</td>
<td>19.0 ± 0.4</td>
<td>36.6 ± 0.3</td>
<td>53.7 ± 0.4</td>
</tr>
<tr>
<td>2019</td>
<td>7.3 ± 0.2</td>
<td>19.3 ± 0.4</td>
<td>35.9 ± 0.3</td>
<td>53.5 ± 0.4</td>
</tr>
<tr>
<td>2503</td>
<td>7.6 ± 0.2</td>
<td>19.8 ± 0.4</td>
<td>35.9 ± 0.3</td>
<td>54.2 ± 0.4</td>
</tr>
<tr>
<td>2998</td>
<td>8.1 ± 0.2</td>
<td>20.0 ± 0.4</td>
<td>36.4 ± 0.3</td>
<td>54.2 ± 0.4</td>
</tr>
<tr>
<td>3512</td>
<td>8.5 ± 0.2</td>
<td>20.3 ± 0.4</td>
<td>36.1 ± 0.3</td>
<td>53.7 ± 0.4</td>
</tr>
<tr>
<td>3996</td>
<td>8.8 ± 0.2</td>
<td>20.3 ± 0.4</td>
<td>35.9 ± 0.3</td>
<td>54.2 ± 0.4</td>
</tr>
<tr>
<td>4500</td>
<td>9.3 ± 0.2</td>
<td>20.5 ± 0.4</td>
<td>36.4 ± 0.3</td>
<td>54.9 ± 0.4</td>
</tr>
</tbody>
</table>

of the ratio $R$, independent of temperature and pressure; this result, therefore, is not very reliable.

As can be seen in Figure 3, the observed increase of the quadrupole splittings of most doublets at increasing pressure or decreasing temperature (see Tabs. I and II) can be taken into account by a reduction of the librational amplitudes.

Because molecular reorientation about the director is considered to be fast, the model does not allow us to describe the extra intensity outside the (d) lines due to the slowing down of the molecular reorientation. The extra intensity between the (c) and (d) lines in the experimental spectra with respect to the simulated spectra is an indication of a small contribution of molecules in between the two possible states considered for the side chains.

6. 2D $^2$H-NMR Exchange Spectra

Two-dimensional exchange spectra essentially show the joint probability $P(\omega_1, \omega_2; t_m)$ that a deuteron has frequency $\omega_1$ before and frequency $\omega_2$ after a mixing time $t_m$ [19,20]. 2D-exchange experiments have been performed to study the effect of pressure on the exchange between the regions of different packing densities. We have conducted experiments at 320 K and 330 K and pressure values up to 3 kbar with mixing times of 5 and 20 ms (see Fig. 4). The spectra show
Fig. 4. — Experimental 2D spectra as a function of pressure at 330 K. The mixing time is 5 ms at 3 bar and 20 ms in all other cases. The repetition time is 350 ms and the acquisition time for each spectrum is 142 h.
Table III. — The exchange time constant $\tau$ between the (c) and (d) lines, as a function of temperature and pressure. The errors are derived from the 10% error estimated in the diagonal and cross-peak amplitudes.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (bar)</th>
<th>$\tau$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320.0</td>
<td>10</td>
<td>27.0 (+6.5,-5.4)</td>
</tr>
<tr>
<td>319.8</td>
<td>983</td>
<td>33.0 (+7.7,-6.4)</td>
</tr>
<tr>
<td>330.0</td>
<td>10</td>
<td>4.00 (+1.10)</td>
</tr>
<tr>
<td>330.0</td>
<td>1000</td>
<td>10.0 (+3.6)</td>
</tr>
<tr>
<td>330.0</td>
<td>1977</td>
<td>22.1 (+5.5)</td>
</tr>
<tr>
<td>330.0</td>
<td>2992</td>
<td>29.3 (+6.9,-5.8)</td>
</tr>
</tbody>
</table>

an exchange process within the inner doublets (a) and (b) and within the outer doublets (c) and (d). In view of the model proposed above we see an exchange between side chains with small and large librational amplitudes, i.e. side chains in regions of high and low local packing densities, respectively, indicating changes in the density modulations along the columnar axis. The application of pressure has a profound effect on the amplitudes of the cross-peaks.

The exchange time constant $\tau$ has been determined as a function of temperature and pressure, following the procedure described in reference [21]. The cross-peak amplitudes $a_{cd}$ and $a_{dc}$ and the diagonal-peak amplitudes $a_{cc}$ and $a_{dd}$ are determined by fitting the peaks with two-dimensional Gaussians with equal widths. The uncertainties in the amplitudes are estimated to be $\sim 10\%$. The spin-lattice relaxation times of the (c) and (d) lines are assumed to be equal, and dipolar cross-relaxation is neglected.

The results are displayed in Table III and Figure 5. The values found for $\tau$ at 320 and 330 K at ambient pressure agree within the estimated errors with the previous results from reference [6] (shown in Fig. 5a). The data obtained as a function of pressure are shown in Figure 5b. We see a substantial increase in $\tau$ at increasing pressure, i.e. at an increased overall density along the columns, the exchange rate between regions of low and high local density is reduced.

Comparison of the 1D spectra (see Fig. 2) with the diagonals ($\omega_1 = \omega_2$ axes) of the 2D spectra show that the spectral lines in the former are much broader than in the latter. The excess intensity appears in the 2D spectra outside the diagonal, even at short mixing times (e.g. Fig. 4a). This indicates frequency exchange “within” the diagonal lines on a timescale $\tau < 5$ ms. The exchange could be in librational amplitudes or in the molecular orientation with respect to the magnetic field.

7. Phase Transitions

In relation with the investigation of the effect of pressure on the density modulations in phase II, it is of interest to know the location of the II-III phase transition line in the $p$-$T$ phase diagram. In order to investigate the II-III transition as a function of temperature and pressure we have measured $^2$H-quadrupole echo spectra. On cooling down (in steps of 2 K) from 310 K (phase II) at 3 bar we observe a broadening in the quadrupole echo spectra, discontinuous between 300 and 298 K (see Fig. 6a), which we associate with the II-III phase transition. The discontinuous broadening is caused by a discontinuous decrease in the rate of reorientation of the molecules about the molecular axis, as a result of which the line shape broadens into a superposition of
spectra corresponding to conical distributions of the EFG axes. The discontinuous decrease in the reorientation rate is also very clearly reflected in the behaviour of $T_2^*$ (defined as the time constant of the approximately exponential decay of the quadrupole echo maximum) which increases by more than an order of magnitude at the II→III transition (see Fig. 7). Above the phase transition the decay of the echo maximum is mainly caused by the attenuation factor [12,22]; the contribution of transverse relaxation by dipole-dipole coupling is only minor. From the strong attenuation just above the transition one may see that the reorientation rate has decreased to a value of the order of $\delta_Q$. Therefore, the sudden increase of $T_2^*$ at the transition reflects a further large decrease in the reorientation rate. The II-III transition shows a rather large hysteresis. The transition temperature derived from the $T_2^*$-discontinuity observed on cooling is 299 K. At increasing temperature the III→II transition is found at 304 K. The latter value is in good agreement with the temperature of the peak in the DSC data [6], also obtained at increasing temperature.

Near the II-III transition temperature we do not observe a discontinuous change in the spin-lattice relaxation time $T_1$ (see Fig. 7), indicating no sudden change in (chain) motions with frequencies near $\sim 41$ MHz.

On applying pressure, the II→III phase transition is found at 320 K and 5 kbar (see Fig. 6b), which gives a rough indication of the II→III transition line in the $p$-$T$ diagram (see Fig. 8). However, the III→II transition is observed at 330 K and 1.5 kbar, again indicating a very large hysteresis. Upon arrival in phase II the macroscopic alignment is maintained.

Fig. 5. — (a) Previous measurements [6] of the exchange time constant $\tau$ as a function of temperature (○) as compared to: (b) $\tau$ as a function of pressure at 320 K (○) and 330 K (△). The lines are linear least squares fits.
Fig. 6. — The II—III phase transition is indicated by the broadening of the quadrupole echo spectra, caused by a discontinuous decrease in the molecular reorientation rate. (a) The transition at 299 K and 3 bar. (b) The transition at 320 K and 5000 bar.

Upon further cooling to 280 K we do not see changes in the lineshape, nor discontinuities in $T_2^*$ or $T_1$. In particular, we find no indication of the III→IV phase transition occurring at $\sim 292$ K [6].

At 260 K, in phase V, we observe a wider spectrum with a different shape (see Fig. 9a). This spectrum can be simulated with good agreement by taking a superposition of conical distributions of the C–D bonds corresponding to an immobile core and immobile side chains, with a Gaussian distribution of the molecular axes with $\sigma = 8^\circ$ and assuming all $\alpha$-carbons of the inner side chains in an in-plane-trans conformation and a fixed ratio 25% in-plane-trans and 75% out-of-plane-trans for the outer side chains. The simulated spectrum is rather sensitive to the relative population of the conformations for the outer side chains; the estimated error is $\pm 5\%$.

The spectra taken in the range from 280 to 298 K (phases III and IV) can be simulated to a good approximation as well (see Fig. 9b), mainly by allowing a rapid ($> \delta_Q$) exchange of the outer side chains (sites 2, 4, 7 and 9) between the in-plane-trans and out-of-plane-trans conformations. Acceptable fits are obtained with $15 \pm 10\%$ of the inner side chains having a librational amplitude of $\sim 12^\circ$ and $50 \pm 10\%$ of the outer side chains having a librational amplitude of $\sim 20^\circ$. Furthermore, a Gaussian distribution of the molecular axes with $\sigma = 15^\circ$ is assumed.
Fig. 7. — The time constant $T_2^*$ (see text) and spin-lattice relaxation time $T_1$ as a function of temperature at 3 bar. The II$\rightarrow$III phase transition at 299 K is clearly indicated by the increase of $T_2^*$ from $\sim 40 \mu$s to $\sim 600 \mu$s. The lines through the $T_2^*$ data above and below 299 K are linear least squares fits. The curve through the $T_1$ data is merely a guide to the eye.

![Graph showing $T_2^*$ and $T_1$ vs. temperature](image)

Fig. 8. — The $p$-$T$ diagram with approximate II$\rightarrow$III transition lines. As can be seen, the transition has a rather large hysteresis. The arrows indicate the paths taken during transitions.

![Graph showing $p$-$T$ diagram](image)

From this discussion we can conclude that the molecular reorientation rate about the molecular axis decreases discontinuously at the II$\rightarrow$III phase transition, with the side chains retaining their mobility. At the IV$\rightarrow$V transition the rate of exchange of the side chains (of the now immobile core) between an in-plane-trans and out-of-plane-trans conformation changes from
the fast limit (where one has motional averaging of the corresponding EFG’s) to the slow limit. Furthermore, in phase V the side chains show no substantial libration at the α-carbon.

We introduced a Gaussian distribution of the angles between the molecular axes and the magnetic field. We observe that, on passing from phase II to phase V, the standard deviation σ of the distribution decreases. This reflects the increase in ordering on lowering the temperature. It has to be noted that from the spectra we cannot distinguish between a deviation of the molecular axis from the column axis and a deviation of the column axis from a direction perpendicular to the magnetic field. Therefore, the value σ = 8° obtained in phase V represents an upper limit to the uncertainty in the perpendicular alignment of the columns.

8. Discussion

With the NMR experiments discussed in this paper the packing densities along the columns are observed in an indirect way by means of the mobility at the α-carbons of the side chains. The spectra do not provide a measure for the changes of the molecular distances. The effect of pressure on the fractions of molecules present in regions of high and low densities in phase II is quite large, as is the effect of temperature (as was shown in Ref. [6]). As has been discussed in Section 5 the pressure effect is most accurately observed in the change in the mole fraction x₄₅.

For an analysis knowledge of the effect of pressure on the stacking density in the columns is needed. Such data, requiring an X-ray experiment at high pressure on an oriented sample, are not available. An order of magnitude estimate can be made from the behaviour of the II-III
phase transition. One may assume that the variable mainly determining this transition, which is characterized by a sudden decrease of the rate of molecular reorientation, is the average distance $d$ between molecules in the column. From the value $2.0 \times 10^{-3}$ Å K$^{-1}$ of the linear expansion coefficient it follows that at ambient pressure the decrease in $d$ from 320 K to the transition point at 299 K is 0.044 Å, while $d = 3.49$ Å at 310 K (see Ref. [6]). From the phase diagram in Figure 8 one may assume that approximately the same reduction is caused by a pressure increase of 5000 bar. Therefore, the effect of pressure on the stacking density is only small.

The large effect on the density modulation can very well be explained on the basis of the numerical simulations at zero temperature made by Godrèche and de Seze [5]. Starting from a Lennard-Jones type interaction between discs and harmonic chain-chain and disc-chain interactions of the same size, they arrive at a structure of the density modulation and show the stability of pinched regions of more than two molecules in a narrow range ($\sim 1.4$ to 1.6) of the ratio $r$ of the optimum chain-chain distance and the optimum disc-disc distance. They also nicely demonstrate that the length of the pinched regions depends very strongly on $r$. Although in rufigallol-HOE we estimate $r$ to be slightly smaller, namely about 1.3, we believe that these results provide an essentially correct model for the density modulations in rufigallol-HOE.

The application of external pressure amounts to a variation of the optimum chain-chain distance. Although this variation is only of the order of one percent in the pressure range considered, the large variation with pressure of the number of molecules in the pinched regions in rufigallol-HOE is probably caused by the strong sensitivity of the length of the pinched regions to the ratio $r$. A further numerical study could possibly show in which way the properties change at finite temperature and what the effect is of using more realistic shapes and amplitudes of the interactions.

The exchange observed in the 2D spectra could be caused by a time dependence of the sizes of the regions of different density and/or of the location of their boundaries. In both cases it is reasonable to assume that the life-time of a molecule in a region increases with the region’s size. It appears that the rate of exchange decreases with increasing pressure. This is consistent with a picture in which the pressure variation of the fraction of molecules in pinched regions is mainly due to the variation in size of these regions.

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References

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