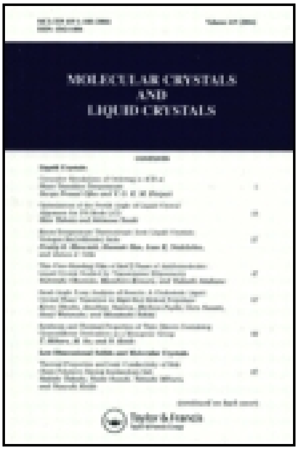

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DIELECTRIC CHARACTERIZATION OF B_N PHASES

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Dielectric Characterization of B_n Phases

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Dielectric data of six different B_n phases formed by banana-shaped molecules are analyzed and discussed with respect to the known results of X-ray measurements. The reorientation about the long molecular axes is discussed with respect to phase transitions. Parallel and antiparallel correlation of the transversal dipole moments in the short range as well as superstructures are detected. Additional AFM and calorimetric investigations are performed. The results of B_3 and B_4 phases prove the existence of dielectric reorientation. Therefore, both modifications cannot be regarded as "ordinary" solids. The existence of the B_8 phase was confirmed.

Keywords: Banana-shaped molecules; mesophases; dielectric investigations; superstructures; AFM

INTRODUCTION

Till now a lot of banana-shaped molecules were synthesized and different mesophases of the B_n type were detected [1-3]. Most of these are characterized and classified by X-ray measurements [4]. Nevertheless

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there are a many open questions related to the order in the short range and the formation of polar superstructures which can be better solved by dielectric spectroscopy and atomic force microscopy [5,6].

EXPERIMENTAL RESULTS

Experiments

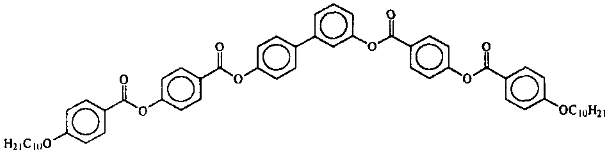
Dielectric investigations were carried out in the frequency range from 1 Hz to 10 MHz using the Solartron-Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. A brass cell coated with gold (d = 0.2 mm) was used as capacitor which was calibrated with cyclohexane. The samples could not be oriented by external magnetic or electric fields. The experimental data of ε' and ε'' were fitted together to the real and imaginary part of equation (1) consisting of two Cole-Cole mechanisms (term 2 and 3), a conductivity contribution (term 4) and term 5 for the description of the capacitance of the double layer at low frequencies

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1+(j\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1+(j\omega\tau_2)^{1-\alpha_2}} + \frac{jA}{f} + \frac{B}{f^N} \qquad (1)$$

with ε_i low and high frequency limits of the dielectric constant, $\omega=2\pi f$ (f - frequency), τ - relaxation times ($\tau=(2\pi f_R)^{-1}$ with f_R relaxation frequency, α - Cole-Cole distribution parameters, the conductivity term A ($\sigma = 2\cdot A\cdot\pi\cdot\varepsilon^0$ (specific conductivity), $\varepsilon^0=8.85\cdot10^{-12}$ As/Vm) as well as B and N as further fit parameters responsible for the capacity of the double layer at the interface sample/gold. For the given summary data of different samples are discussed with respect to known X-ray results.

The B_1 phase

Fig. 1 shows dielectric constants of the banana-shaped sample



1

Cr 392 B_1 439 I (temperatures in K)

in the isotropic (438 K) and the B_1 state (428 K) synthesized at first by Tschierske [7]. There are practically constant ε'-values by changing the frequency in isotropic phase (if the increase of ε' at low frequencies due to the double layer at the interface gold/sample is neglected) and two dispersion ranges at about 1 kHz and 200 kHz in the B_1 phase. The

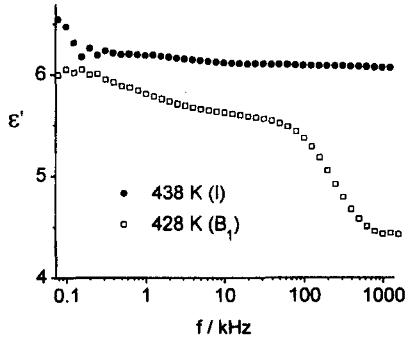
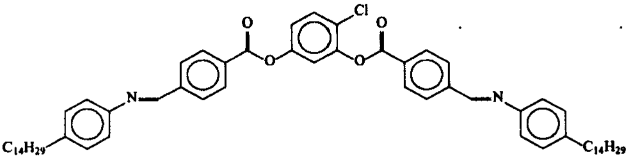


FIGURE 1: Dielectric dispersion of 1 in the isotropic and the B_1 state.

high frequency process is related to the reorientation of the molecules about the long axes, the low frequency process probably to a collective motion [5,6]. It should be pointed out that the dielectric constants in the B_1 phase do not exceed the ε'-values in the isotropic phase at all temperatures. This points to an antiparallel correlation of the longitudinal dipole moments of 1 and it is in agreement with the structure model of a rectangular columnar phase proposed at first by Sekine et al. [4].

The B_2 phase

Dielectric results on the B_2 phase are already reported in the literature [6,8-10]. Similar to the dielectric behavior of the B_1 modification low and high frequency relaxation were detected [8, 9]. Additionally a very fast reorientation of terminal dipoles could be seen at low temperatures [6]. Experimental data on sample 2



2

Cr 341 B_2 398 I

are shown in Figure 2. Contrary to the B_1 phase, an increase of the dielectric constant to about 10 at 10 kHz was measured in the B_2 modification. ε' decreases strongly at the I/B_2 transition. At frequencies of about 200 kHz the dispersion due to the reorientation about the long axes reduces the ε'-values. This process could be also detected in the isotropic phase, but with a stepwise increase of the relaxation time and a much lower intensity [6, 8]. Thus, this absorption at about 2 MHz cannot clearly be seen in Figure 2. We explain the increase of the absorption intensity at the I/B_2 transition as result of the ferroelectric order in the short range. The relaxation frequencies f_R for the reorientation about the long molecular axes (open circles) are also strongly influenced by the phase transition I/B_2 as seen in Figure 3.

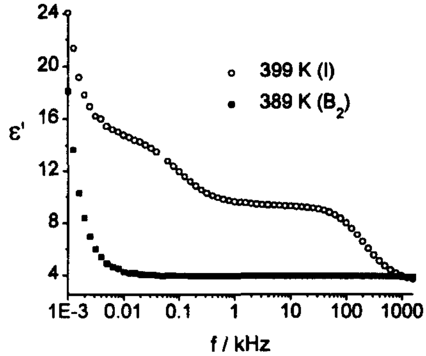


FIGURE 2: Dielectric dispersion of 2 in the isotropic and the B_2 state.

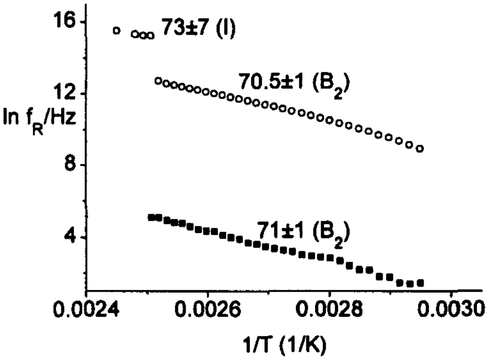


FIGURE 3: Relaxation frequencies of 2 versus the reciprocal temperature. The numbers are activation energies in $kJmol^{-1}$.

Measurements on sample **2a** (similar to **2**, only the terminal $-C_{14}H_{29}$ are substituted by polar octyloxy groups) result in much higher limits for the high frequency dielectric constants ε_2 (see Figure 4). The octyloxy groups show a separate relaxation in the GHz range. This means that the ferroelectric short range order in B_2 is produced only by the stiff middle parts of the molecules.

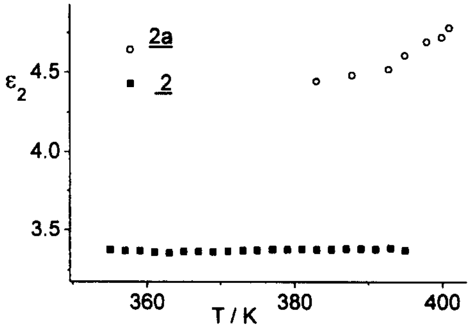


FIGURE 4: High frequency limit of ε' of **2** and **2a**.

The low-frequency absorption, not seen in the isotropic phase, is connected with a collective dynamics within the antiferroelectric layers. In order to prove the existence of a superstructure AFM measurements were carried out. An AFM image obtained on a sample which could be supercooled [11] is presented in Figure 5. At lower magnifications a typical focal-conic texture with additional disclinations between the minima at the surface is observed. In line measurements of Figure 5 steps in the surface profile of one layer are seen. In other samples additionally steps of two and three layers were detected. From these results it can be concluded that there are not very strong interactions between two neighboring layers with antiferroelectric dipole order. Helical super-structures could not be observed.

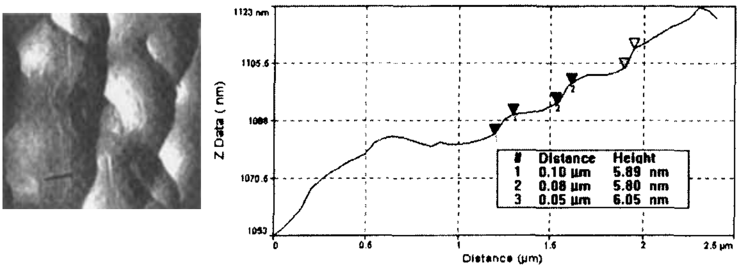
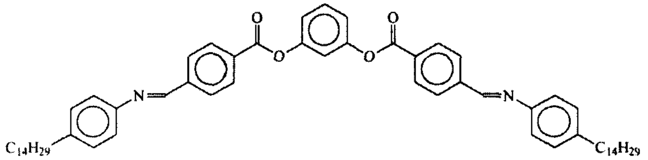


FIGURE 5: AFM-image of a sample in the glassy B_2 state. The line inside of the image represents the part for the line measurements shown right. Steps in the profile are indicated and given in the inset.

The B_3 phase

Sample 3 is a classical "banana-shaped liquid crystal"



3

I 433.4 B_2 396 B_3 330 Cr (by cooling)

synthesized at first by Sekine and coworkers [12]. The B_3 phase exhibit many sharp X-ray pattern. Therefore, it was classified as solid modification [4]. Dielectric constants of all phases are presented in Figure 6. Let us take the dielectric constants in the isotropic phase (solid squares) as reference for the discussion. Again much higher ε'-values in the B_2 phase with the MHz dispersion are detected (open triangles). The low-frequency relaxation at 300 Hz is superimposed by the double layer due to the high conductivity.

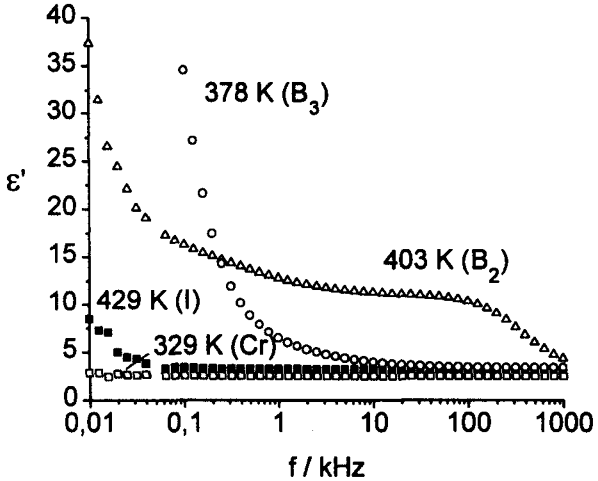
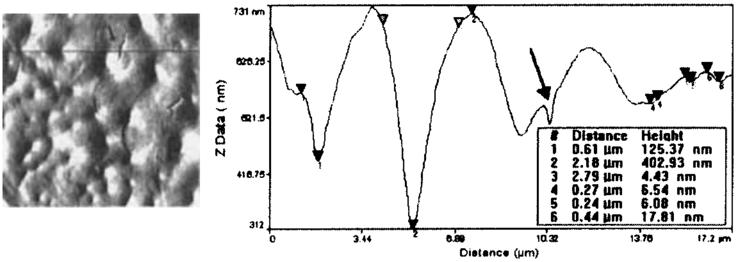


FIGURE 6: Dielectric constants of 3 in different phases.

The solid phase (open squares) shows the lowest dielectric constant. Here all motions are frozen. In the B_3 phase (open circles) higher dielectric constants than in the isotropic state were found. Furthermore a strong increase of ε' at low frequencies is detected which results from a strong increase of conductivity [13] and the corresponding double layer at the interface capacitor/sample. The molecular origin for the increase of conductivity is difficult to understand. The small difference in ε' between the solid, the isotropic and the B_3 phases points to a small net dipole moment of sample <u>3</u>. The higher ε'-value in the B_3 phase may be the result of a local dynamics like in plastic crystals. Thus, one can understand the appearance of many sharp X-ray reflections [4].

An AFM-image of sample <u>3</u> is presented in Figure 7. To obtain this image a thin layer of the sample was heated to 430 K, cooled to 422 K with a rate of 0.5 $Kmin^{-1}$ then cooled with 5 $Kmin^{-1}$ to 400 K and afterwards very fast to room temperature. Surprisingly, the AFM-picture remembers on that of the B_2 phase given in Figure 5. There is a focal conic texture, but the number of disclination lines between the minima is reduced. Furthermore there are cracks in the surface profile. These points to a layered structure deformed due to volume contraction at the phase transition. Probably we are dealing with an epitaxy effect from the B_2 phase, but in any way regular crystals cannot be detected.

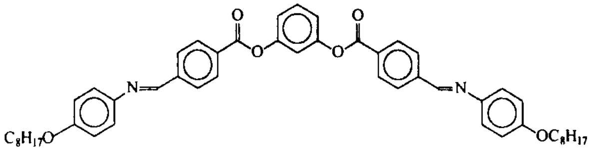


#	Distance	Height
1	0.61 μm	125.37 nm
2	2.18 μm	402.93 nm
3	2.79 μm	4.43 nm
4	0.27 μm	6.54 nm
5	0.24 μm	6.08 nm
6	0.44 μm	17.81 nm

FIGURE 7: AFM-image of a sample in the B_3 state. Along the line inside of the image the line measurement shown right was done. Breaks are indicated by arrows. Steps in the profile are related to the minima of the focal conics (#1-3) and to distances of one layer (#4-6).

The B_4 phase

Dielectric investigations on



4

I 444.3 B_2 425.2 B_3 412 B_4 (by cooling)

are presented in Figure 8. The dielectric constants of the isotropic (solid squares), B_2 and B_3 phases show similar behavior as already presented in Figure 6. The solid state could not be reached, thus there is no chance for a direct comparison as done in Figure 6. Nevertheless

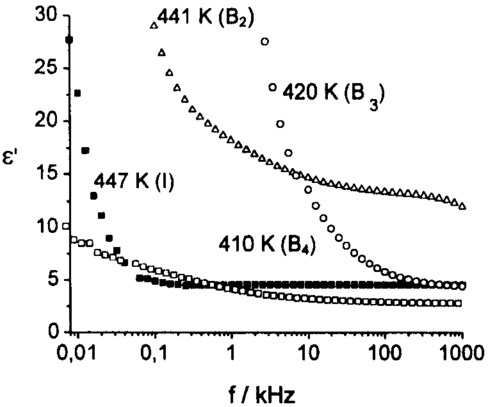
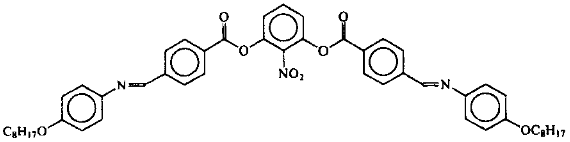


FIGURE 8: Dielectric constants of **4** in different phases.

it is obvious, that the ε'-data in the B_4 phase (open squares) cross those of the isotropic state. The strong increase of the data in the isotropic phase below 50 Hz and in B_4 below 10 Hz is connected with the double layer. This effect could be separated from a low-frequency absorption in B_4 (f_R about 200 Hz). X-ray pattern of the B_4 phase show wide angle reflections with a broad distribution pointing to fluctuations in the lateral distances [4]. Thus, the observed low-frequency absorption may be related to a complete or partial reorientation about the long molecular axes of **4**.

The B_7 and B_8 phases

The B_5 and B_6 phases are not well characterized till now. Interesting results were obtained on the B_7 phase of



5

Cr 393 B_7 457 I

In this case the dipole moments compensate each other in the middle part. Therefore the reorientation about the short axes is difficult to detect. On the other hand the experimental data of **5** can be well fitted under assumption of a low-frequency absorption as it was demonstrated in [5]. The calculated static dielectric constants show a maximum at about 400 K. The directly measured dielectric constants outside of the relaxation range (60 kHz) at cooling and heating are presented in Figure 9. Astonishingly the ε_0-values show a step at about 400 K and seem to be stable up to the beginning of crystallization. This effect could be reproduced by heating. Calorimetric and AFM-measurements support an interpretation as phase transition.

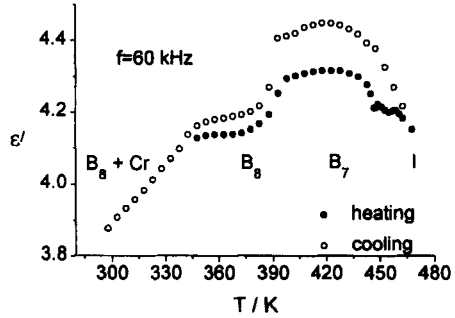


FIGURE 9: Measured dielectric constants of 5.

SUMMARY

At the present stage of investigations one can summarize the results in the following way:

1. In the B_1, B_2, and probably also in the B_4 and B_7 phases the molecules can reorient about their long axes.
2. In the B_1 modification an antiparallel dipolar correlation and in B_2 an ferroelectric short range order was detected.
3. In all phases a restriction of the dynamics with respect to that of the isotropic state is seen.
4. In the B_3 and B_8 phases a clear restriction of the dynamics and a reduction of the dielectric increments was observed. It is possible that only parts of the molecules can rotate in the investigated time

scale. On the other hand the B_3 phase shows an anomalous high conductivity and focal conic domains at the surface.

5. Low-frequency relaxation which are related to super-structures were detected in the B_1, B_2, B_4, and B_7, phases.

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