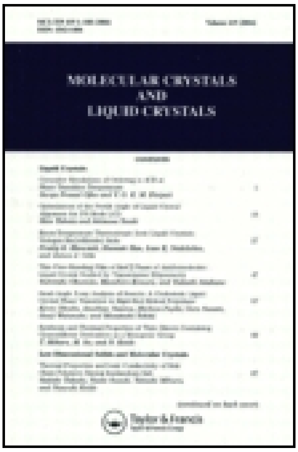

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# In Spectroscopic Study of the Electric Field Induced Phase Transition of a Ferroelectrically Switchable Columnar Dibenzopyrene

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# IR SPECTROSCOPIC STUDY OF THE ELECTRIC FIELD INDUCED PHASE TRANSITION OF A FERROELECTRICALLY SWITCHABLE COLUMNAR DIBENZOPYRENE

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**Abstract** Fourier transform infrared spectroscopy of a ferroelectrically switchable columnar liquid crystalline dibenzopyrene has been performed in the wavenumber range of 450-4000 $cm^{-1}$ as a function of temperature and applied electric field. The sample was edge-on aligned by the electric field. At 10 V/μm, a sudden change of the C=O band intensity is observed, whereas no strong field dependence of the aromatic bands was detected. Earlier electrooptical observations evidenced a phase transition at this field strength. The temperature dependence of the intensities reveals a preferential orientation of the aromatic cores parallel to the direction of the electric field in the columnar phase. This orientation vanishes when heating into the isotropic liquid. The temperature dependence of the C=O band frequency is similar to the behaviour reported for smectic phases of calamitic molecules.

## Introduction

The first switchable ferroelectric columnar liquid crystal was discovered in 1992 by Bock and Helfrich[1,2]. After the first columnar phases had been reported by Chandrasekhar et al. in 1977[3], it was soon realized that such phases of tilted chiral disc-like molecules can be ferroelectric[4]. However, electric switching of such ferroelectric columnar phases was thought to be impossible[5]. The switchable compound studied in detail by Bock and Helfrich shows not only the wished bistable switching at moderate voltages, but also a field induced phase transition to a metastable ferroelectrically switchable high field phase[2]. These authors infer the structures of the low field

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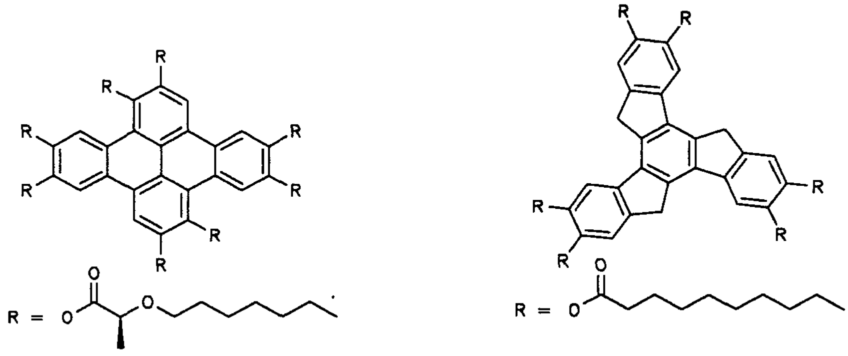
and high field phases from their different spontaneous polarizations, optical tilt angles, and refractive index anisotropies. We study the infrared spectra of this material with a view to finding further information on the phase structures as well as measuring the change in quadrupolar order of different parts of the molecule at the field induced phase transition. The main advantage of IR spectroscopy compared to other techniques is its ability to deliver separate data on the orientation of the flexible chains, the rigid core, and the dipolar groups. The dependence of both the absorption intensities and the frequencies of maximum absorption on electric field and temperature can be followed, yielding information on intramolecular conformational changes and on changes of the relative orientation of the columns.



D8m*10    X6n10

D - 388K - I    Cryst - 341K - N - 358K - D(tilted) - 411K - D(hexagonal) - 553K - I

Fig. 1: Structural formulae and phase transitions of the compounds investigated

## Experimental

The structural formula of the discotic liquid crystalline material 1,2,5,6,8,9,12,13-octakis-((S)-2-(heptyloxy)-propanoyloxy)-dibenzo-[e,l]-pyrene designated as D8m*10 is shown in Fig. 1. The clearing temperature of this material is approximately 388 K. No phase transition above a temperature of 248 K could be detected. using DSC. The chiral material D8m*10 was sandwiched between two ITO coated ZnSe windows (resistivity 2 kΩcm). The cell thickness was fixed to 8 μm using mylar spacers and checked using interference fringes superimposed on the infrared vibrational spectra. The texture of the mesophase between crossed polarizers when the sample was cooled from its isotropic phase consisted of a characteristic flower-like domains with some grey to black areas (see Fig. 2a). In the flowers, the columns are parallel to the glass and form circles around the flower centre. Each flower centre is the centre of a black extinction cross, because the liquid crystal does not change the polarisation of the transmitted light where the principal axis of its dielectric constant in the cell plane coincides with the polarizer or the analyser directions. The sample was found to achieve a uniform edge-on alignment (column axes parallel to the glass) (Fig. 2b) after subjecting the cell to an alternating electric field of 20 V/μm at 10 Hz in the columnar phase at 373 K for about 3 hours. This edge-on alignment remained stable after the field was switched off.

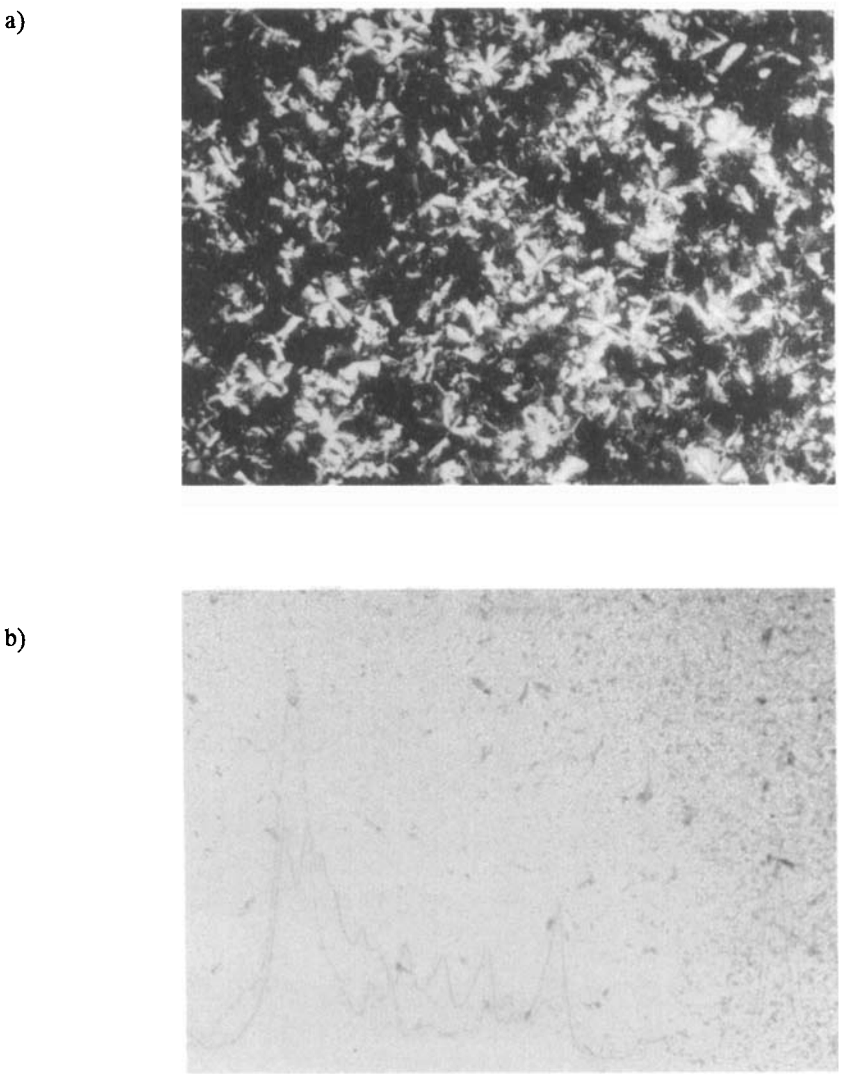


Fig. 2: The texture of D8m*10 between crossed polarizers at T=293K: a) fresh sample; b) after alignment at a. c. bias of 20 V/μm at 10 Hz in the columnar phase at 373K for about 3 hours. See Color Plate X.

A BioRad FTS-60A FTIR spectrometer with a nitrogen cooled MCT detector has been used for IR measurements. A total of 64 scans were added to compute an absorbance spectrum with a resolution of 0.25 $cm^{-1}$ in the wavenumber range 500-4500 $cm^{-1}$. IR spectra were recorded as a function the DC bias in the range 0 to 170 V at temperature from 300 to 450 K. The temperature increment was kept at about 5 K, except close to the transition temperature from the columnar to the isotropic phase. Here the temperature was incremented by 2 to 3 K. A temperature controller (Oxford Instruments ITC4) was used to stabilize the temperature to within 0.1 K. The spectra of the ZnSe windows at different temperatures have been subtracted from the measured sample spectra. The spectra were smoothed, and base corrections where applied to them.

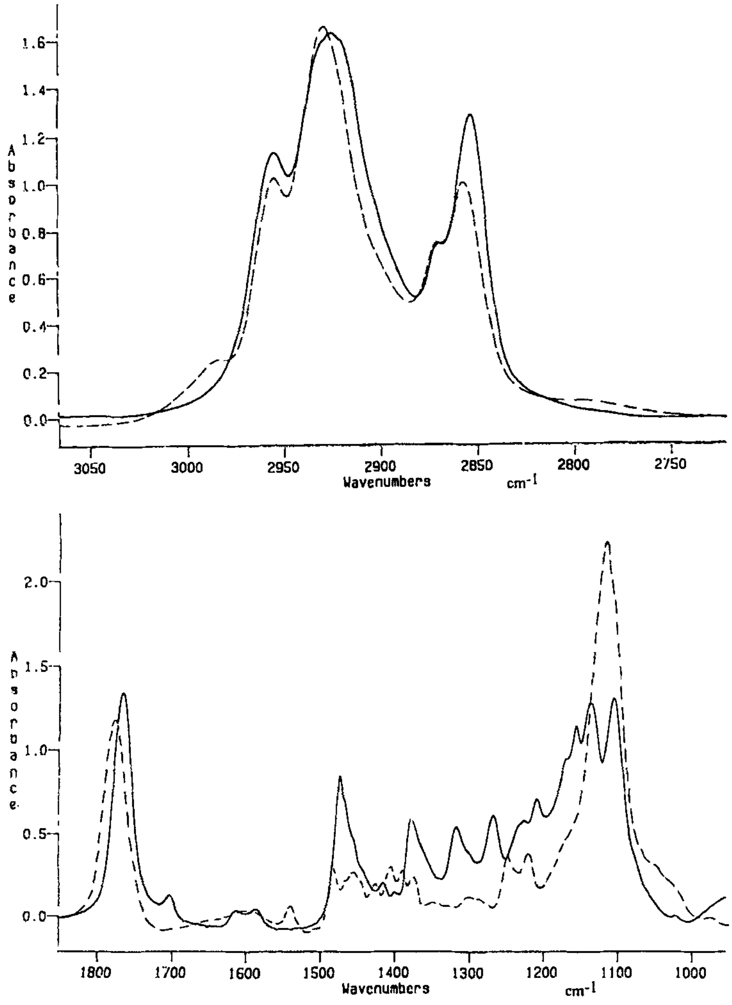


Fig. 3: IR spectra of D8m*10 (dotted line) and 6Xn10 (solid line) at T=343K.

We also investigated the IR spectra of side-on aligned (column axes perpendicular to the glass) 2,3,7,8,12,13-hexakis-decanoyloxy-truxene[6] (structural formula shown in Fig. 1) designated as X6n10 for comparison. This compound has a structural arrangement similar to D8m*10 but does not exhibit ferroelectricity and can ideally be used for the band assignments.

## Results

The spectra of D8m*10 and X6n10 at 340 K without applied field are shown in Fig. 3. The most intense bands are found to lie in the wavenumber range 2700-3000 cm$^{-1}$ (alkyl chain vibrations), 1700-1800 cm$^{-1}$ (C=O stretch vibration) and 950-1200 cm$^{-1}$ (C-O-C stretch vibrations).

In the spectrum of D8m*10, all bands corresponding to benzene ring vibrations and core-oxygen vibrations are of very low absorbance. This behaviour is different from the one previously found for other discotic liquid crystals investigated by Vij and co-workers[7,8]. One of the small peaks in the frequency range of benzene ring vibrations was nicely isolated from the others and therefore could be precisely integrated.

The intensity of the bands assigned to the benzene ring vibrations (in the range 1500-1650 cm$^{-1}$) and to the core-oxygen vibration (approximately 1250 cm$^{-1}$) are temperature dependent, increasing when heating to the isotropic phase to a value far higher than in the the columnar phase. A similar increase has been found for the C-O-C vibrations. All our measurements of the absorbance intensity dependence on temperature were repeatable. The temperature dependence of the peak intensity and of the frequency of the maximum absorbance for the isolated benzene ring vibration ($\nu$ = 1540 cm$^{-1}$) and the carbonyl stretch vibration ($\nu$ = 1777 cm-1) are shown in Figs. 4-7. We see from Figs 4 and 5 that the dependence of the peak intensity on temperature for these bands is similar: Near the phase transition to the isotropic liquid, the absorbance decreases abruptly, and then, on further heating, increases to values that were beyond the detection range of our apparatus. We find that the frequency of the benzene ring vibration band shifts slowly to lower frequencies with increasing temperature (Fig. 6), whereas the frequency maximum of the C=O stretching vibration does not change between 300 and 365 K. When heating into the isotropic liquid, the latter increases rather sharply by 5 cm$^{-1}$, and then again remains constant at higher temperatures (Fig. 7).

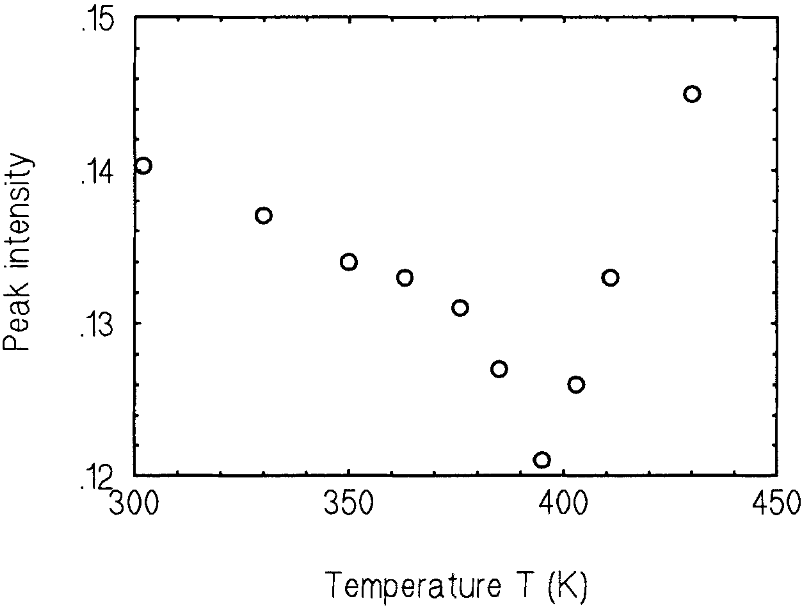


Fig. 4: Peak intensity changes for the benzene ring vibration near 1540 $cm^{-1}$.

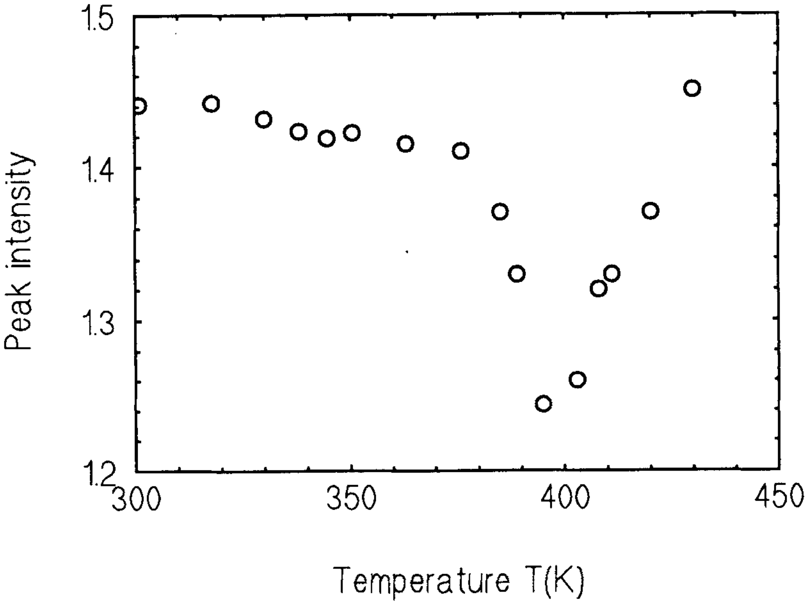


Fig. 5: Peak intensity changes for the C=O stretch vibration near 1777 $cm^{-1}$.

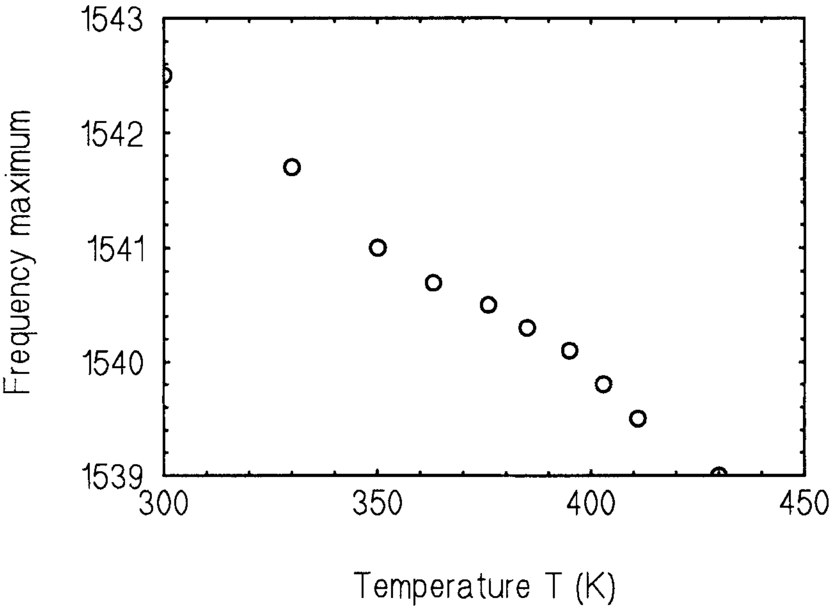


Fig. 6: Frequency changes for the benzene ring vibration near 1540 $cm^{-1}$

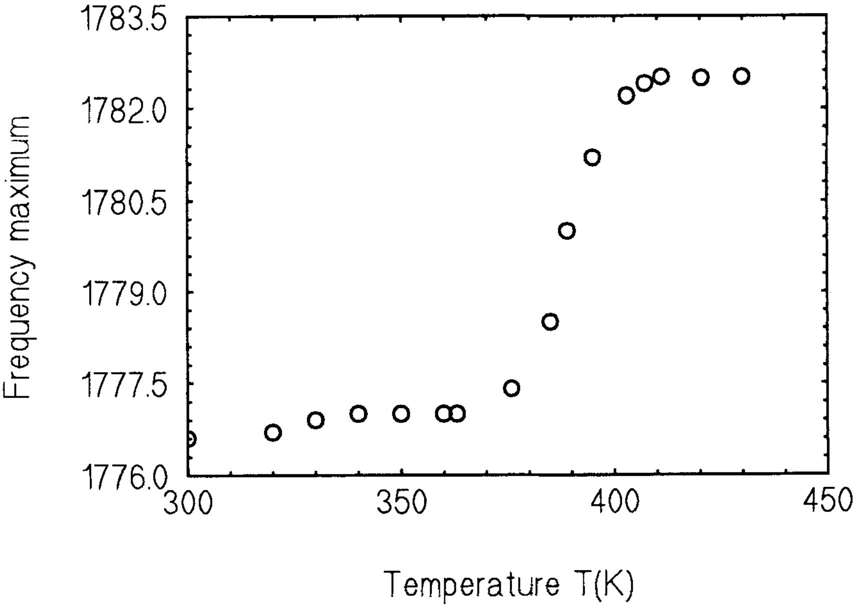


Fig. 7: Frequency changes for the C=O stretch vibration near 1777 $cm^{-1}$.

Now we discuss the intensity and frequency of the IR bands as a function of the electric field. We find that the DC bias only influences the C=O bond. The intensity of the isolated benzene ring vibration remains constant when the field is increased, and also all further less isolated bands seem not to be influenced by the applied field, as far as can be detected. The peak intensity of the C=O (carbonyl group) as a function of the increasing electric field is shown in Fig. 8. The most prominent feature of this figure is the sharp decrease of the peak intensity when the field is increased above about 10 V/μm. The same field strength was also found by Bock and Helfrich[2] for the phase transition inferred from a discontinuous change of the tilt angle, the spontaneous polarization and the birefringence colour. The IR absorption decreases at this field strength to about 80% of the low field value. Above and below 10 V/μm, the C=O absorption intensity is only weakly field dependent, decreasing continuously with increasing field strength.

When the electric field is subsequently increased and decreased, we observe around 10 V/μm a hysteresis of the peak intensity versus the field strength. The field dependence of the C=O band intensity is similar at different temperatures, except that the width of the hysteresis decreases with increasing temperature.

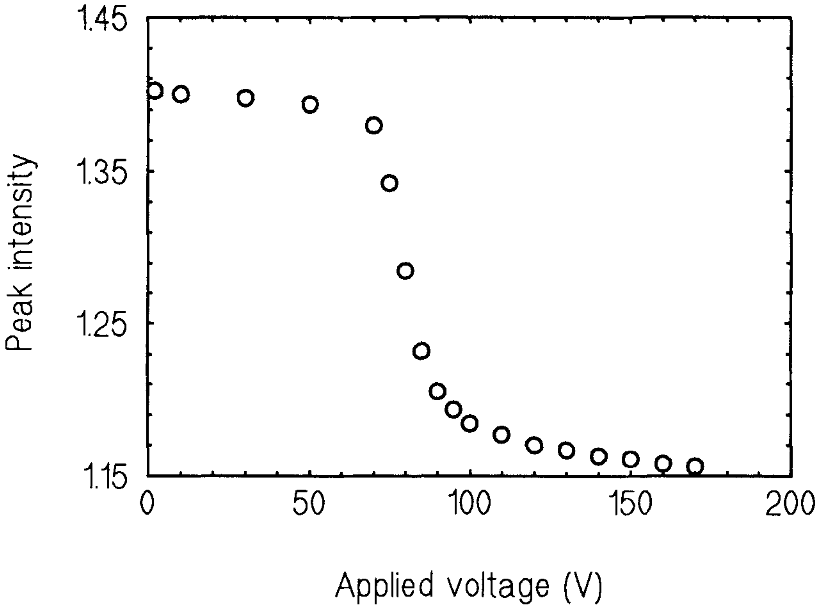


Fig. 8: Dependence of the peak intensity of the C=O band on d.c. bias for D8m*10 at T=371K.

## Discussion

The infrared absorption spectrum of D8m*10 shows two isolated peaks that correspond to the two regions of the molecule whose orientations are of the greatest interest, namely the aromatic core and the dipolar chiral chain head. This enables us to gain some insight into the conformational changes of the two most important parts of the compound in its columnar phase.

The ***temperature dependence of the intensity*** of the core signals as well as the C=O vibration indicates that in the field-aligned columnar phase, both the aromatic cores and the carbonyl groups are oriented preferentially perpendicular to the glass plates. When heating into the isotropic phase, this preferential orientation vanishes after an intermittent decrease of the absorbance near the clearing temperature. Unfortunately, we could not determine the maximum intensity of the completely randomly oriented liquid at very high temperatures. So we are not able to infer quantitatively the mean orientation of the cores in the columnar phase and in the isotropic liquid just above the clearing point. The orientation preferentially parallel to the windows of the core normals in the field-aligned sample is in accordance with the model for the columnar states of D8m*10 suggested by Bock and Helfrich[2] (Fig. 9). We do not undestand at all the sharp intermittent decrease of the intensities near the clearing temperature.

The ***temperature dependence of the frequency*** of the C=O vibration, namely the jump to a higher frequency at the clearing point is easily explained by a lower interaction between the carbonyl and aromatic electrons in the isotropic liquid. Such frequency shifts of aromatic ester C=O vibrations at the clearing temperature are known from smectic liquid crystals[9].

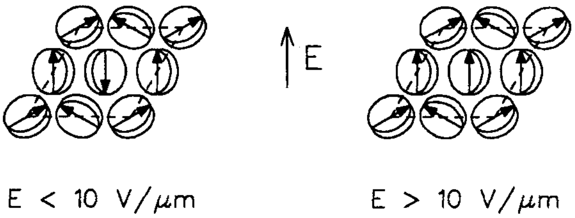


Fig. 9: The two structures proposed by Bock and Helfrich for the low field and high field phases. View along column axes.

A ***field dependence of the intensity*** was not observed for the core band, supporting the model of Bock and Helfrich depicted in Fig. 9. This model implies that the phase transition is brought about only by a 180° rotation of the tilt direction in some of the columns, and such a 180° rotation should not change the IR absorption intensity. On the other hand, the considerable decrease of the C=O band intensity at the field induced phase transition is not explained by this model, as conformational changes within the molecules were not taken into account. The reason for this decrease may be a conformational change or a rotation of the tilt direction of some columns about an angle different from 180°, but such a rotation about an angle other than 180° may be ruled out because the aromatic band intensity does not change. So the conformation of the molecules seems to change at the phase transition, and this conformational change is necessarily linked to a second change, e. g. a 180° rotation of some columns, because it is discontinuous.

Bock and Helfrich[2] measured a tripling of the polarization at the phase transition to the high field phase, and therefore suggested the phase structures of Fig. 9. At the transition between these two phases, the spontaneous polarization should triple because of the change of the tilt direction pattern alone (as can be verified by adding the arrows in Fig. 9), and therefore they did not suppose any conformational changes within the column. Our IR data reveal such a conformational change including the dipolar carbonyl groups, and this should cause an additional increase of the spontaneous polarization, because the angles between the carbonyl dipoles and the axis of the electric field become smaller. We did not yet invent a convenient model to estimate the magnitude of this increase.

The weak but detectable continuous decrease of the C=O band intensity with increasing field strength within each of the two columnar phases supports suggestions of Rey-Lapon et al.[10] and of Samulski et al.[11] regarding the flexibility of the alkyl chains for discotic liquid crystals. The ester group can change its relative orientation with respect to the ring without bringing about a change in the overall molecular orientation.

## Conclusion

Whereas we can explain only in part and tentatively the intriguing temperature dependence of the infrared spectrum of D8m*10, we extract valuable informations from its field dependence: The field-induced phase transition between the two ferroelectric phases of this compound does not affect the quadrupolar order of the aromatic cores, whereas the one of the chiral dipolar chain heads increases considerably when passing from the low field to the high field phase. This suggests that the transition does only imply 180° rotations of columnar tilt directions, and that the conformation of the dipolar chiral groups is affected considerably by these rotations.

Further investigations, especially the determination of the peak intensities in the isotropic liquid phase at temperatures far above the clearing point, are needed to gain quantitative informations about the quadrupolar order of the aromatic cores and the chiral dipolar groups. It will also be helpful to investigate the field dependence of the infrared spectra of the simpler smectic phases showing a field-induced phase transition, namely the antiferroelectric SmC* phase and the SmC*γ phase.

## Acknowledgement

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