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Multiple dielectric relaxations in liquid crystals, their analysis and interpretation

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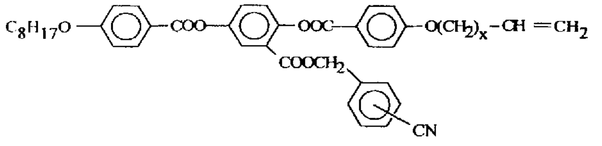
Dielectric measurements on laterally substituted molecules were carried out in the frequency range 10 Hz to 10 MHz. In these systems, the main part of the molecules exhibits only a very small dipole moment in the direction of the *para*-axis, whereas the lateral substituent is strongly polar. Depending on the position of the dipole (*o*, *m*, *p*), a more or less strong dipolar correlation in the parallel direction was detected. The absorption data at higher frequencies were fitted to two Cole–Cole mechanisms. The low frequency relaxation was interpreted as angular vibration of the dipole moment of the lateral group, and the high frequency one as the reorientation about the *para*-axis of the main part of the molecule and of the lateral group. The appearance of two high frequency mechanisms is unexpected and demonstrates that in complicated molecules the dynamics also become differentiated.

1. Introduction

It is generally accepted that in liquid crystals composed of non-optically active rod-like molecules, two main relaxation mechanisms are observed: the reorientation of the molecules around their short and their long axes [1]. Thereby the reorientation around the shorter molecular axis can be well described by a simple Debye-mechanism [2]. The dipolar reorientation around the molecular long axis is a complicated mechanism often fitted to the empirical Havrilag–Negami equation [3, 4]. Dielectric experiments on samples with a high glass temperature have now shown that the high frequency relaxation can be separated into a more cooperative process showing WLF behaviour and a local one which follows the simple Arrhenius equation [5]. This experiment suggests that the perpendicular dipoles of complicated molecules do not reorient all together. In order to confirm this idea, laterally substituted molecules with strong dipoles in the branch were synthesized and investigated by dielectric relaxation spectroscopy. Dielectric measurements were performed on oriented samples in the two main directions, parallel (||) and perpendicular (⊥) to the director **n**.

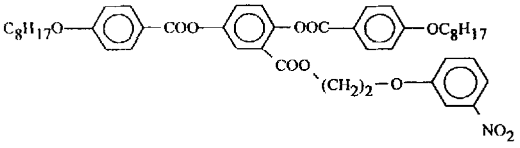
2. Samples

For our experiments the following samples were used (see table 1)



A

and one compound in which the 'spacer' is elongated by one $-CH_2O$-unit.



B

Cr 390 (S_A 379 N 387) I (K)

The whole substituent in the 2-position of the central core is designated in the text that follows as the lateral substituent. The synthesis of the samples is described elsewhere [6].

3. Experiments

Dielectric measurements were performed in the frequency range $10–10^7$ Hz using a HP 4192A impedance analyser. The metal capacitor had a separation distance of 0·2 mm and an area of about 2 cm^2 and was calibrated with cyclohexane. The samples were oriented in a magnetic field of 0·6 T. Figure 1 shows the static dielectric constants of the first three samples.

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Table 1. Phase transition temperatures in K of the samples **A1–A3**.

Sample	Position of CN	x	Cr		S_C		S_A		N		I
A1	*o*	9	●	364	–	–	–	–	(●	363)	●
A2	*m*	9	●	354	(●	330)	●	361	●	373	●
A3	*p*	4	●	387	–	–	●	408	●	412	●

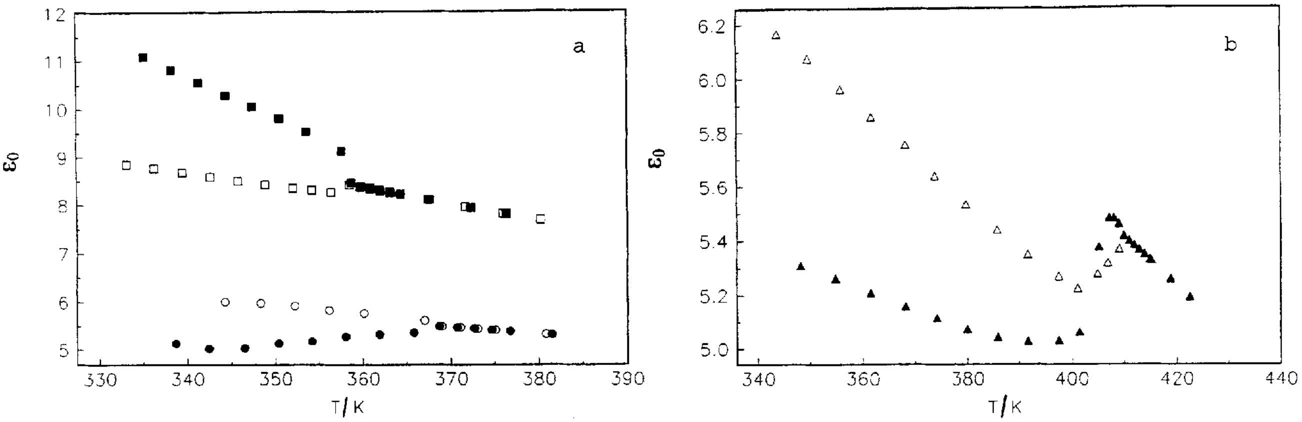

Figure 1. (*a*) Static dielectric constants of the samples **A1** (boxes) and **A2** (circles); the solid points (■, ●) are related to $\varepsilon \parallel n$ ($\varepsilon_{\parallel 0}$ in the LC phases) and the open points (□, ○) to $\varepsilon \perp n$ ($\varepsilon_{\perp 0}$ in the LC-state); in the isotropic phase ($\varepsilon_{0,\mathrm{is}}$) both directions are equivalent: (*b*) static dielectric constants of **A3**.

The *ortho*-(**A1**) and *meta*-(**A2**) derivatives exhibit 'normal' dielectric behaviour with respect to the Maier–Meier theory [7]. From a first inspection of formula **A**, it is surprising that for the *ortho* derivative **A1**, $\Delta\varepsilon_0 > 0$ was detected. This confirms a conformation in which the strong CN dipole is nearly parallel to the *para*-axis of the central core. The static dielectric constant $\varepsilon_{\parallel}$ as function of the frequency in the supercooled nematic phase at $T = 335{\cdot}3$ K is shown in figure 2. There is an absorption in the MHz range, an increase of $\varepsilon_{\parallel}$ at $f < 1$ kHz due to the formation of double layers (conductivity effect) and a very small dispersion range at about 10 kHz with a dielectric increment of $\Delta_{\parallel} \approx 0{\cdot}03$. The expected intensive dielectric absorption at low frequencies connected with the reorientation of the CN dipoles by rotation of the entire molecules could not be observed, even at higher temperatures. Therefore, one has to conclude that this motion can be seen at higher frequencies.

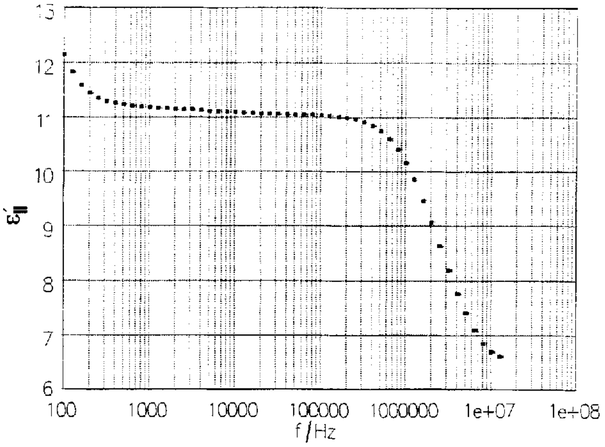

Figure 2. Dielectric constant parallel to the director ($\varepsilon'_{\parallel}$) of sample **A1** versus the frequency.

The decrease in the static dielectric constant $\varepsilon_{\parallel 0}$ of the *para*-compound **A3** on cooling cannot be explained by a change of the orientation, because $\varepsilon_{\parallel 0}$ becomes smaller than $\varepsilon_{\perp}$ with decreasing temperature. Therefore, one has to assume an antiparallel dipolar correlation in the short range order produced by repulsive forces between the non-rod-like molecules [8]. In order to confirm this, dielectric absorption measurements at low frequencies were carried out. Two absorption curves for sample **A2** are presented in figure 3.

The increasing intensity of $\varepsilon''_{\parallel}$ at low frequencies is the result of the electrical conductivity. In order to separate the low frequency absorption from the conductivity, the experimental data at the low frequency side ($f_R \geqslant 10^6$ Hz) were fitted to a simple power Af^n ($n < 0$) and a Cole–Cole process, that taken together are:

$$\varepsilon'' = Im\left\{\varepsilon_\infty + \frac{\Delta}{1 + (\mathrm{i}f/f_R)^{1-h}}\right\} + Af^n \qquad (1)$$

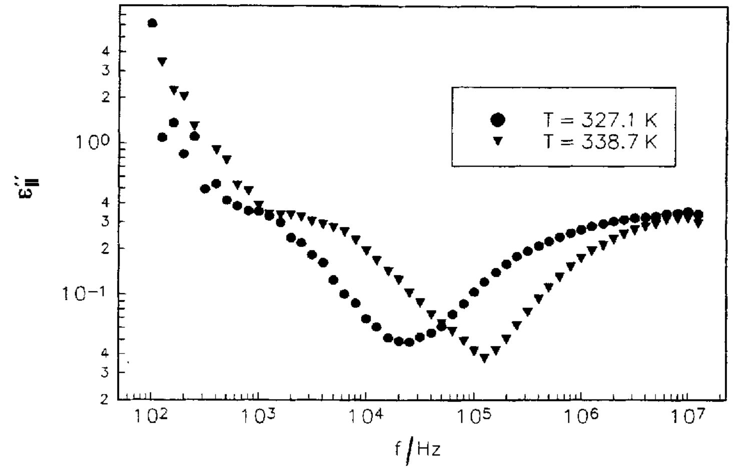

Figure 3. Two experimental absorption curves for sample **A2** in the parallel direction at two temperatures.

with Δ = dielectric increment, ε_∞ = high frequency limit of the dielectric constant, f = frequency, f_R = relaxation frequency, h = Cole–Cole distribution parameter. Only such data were taken into account for which $\varepsilon'' < 1$ and $f < 4f_R$.

Figure 4 shows the dielectric increments $\Delta_\parallel$ of this relaxation process which can be described well for samples **A2**, **A3** and **B** by a simple Debye relaxation ($h = 0$). From this it is obvious that compounds **A1** and **A2** exhibit different dipole moments, μ_1, in the direction of the *para*-axis of the central core, because $\Delta_\parallel \approx \mu_1^2$. For **A2**, **A3** and **B** only small $\Delta_\parallel$-values in the nematic phase were observed. In the transition range N/S$_A$, $\Delta_\parallel$ decreases rapidly and with further decreasing temperature, it cannot clearly be separated from the conductivity part given in equation (1). This indicates a strong tendency to an antiparallel orientation of μ_1 with decreasing temperature for the three samples mentioned above.

The Arrhenius plot of the low frequency mechanism for **A** and **B** in different phases is presented in figure 5. The expected steps in f_R occur at the phase transition I/N and also changes in the slope at the N/S$_A$ transitions. It should be mentioned here that this relaxation process could not be found in the perpendicular direction. This experimental result confirms the existence of a well oriented sample.

Due to the high viscosity of the samples, the reorientation process around the *para*-axes is shifted to lower frequencies. Therefore, we have been able to obtain accurate data on oriented samples. For this high frequency relaxation in the parallel direction, equation (1) was also applied as a first fit. In this case the term Af^n was used to describe the beginning of the low frequency absorption. From the low frequency side, only data with $\varepsilon''_\parallel < \varepsilon''_{\parallel\max}/3$ were taken into account. $\varepsilon''_{\parallel\max}$ means the maximum in the dielectric loss of the low frequency absorption discussed above. Experimental data and fitted data for the sample **A2** are given in figure 6. It can be seen that the fitted curve in figure 6 is not in good agreement with the experimental data, especially for the slope at 6×10^4 Hz and 2×10^6 Hz, as well as for the maximum. Of course a better fit would be obtained by

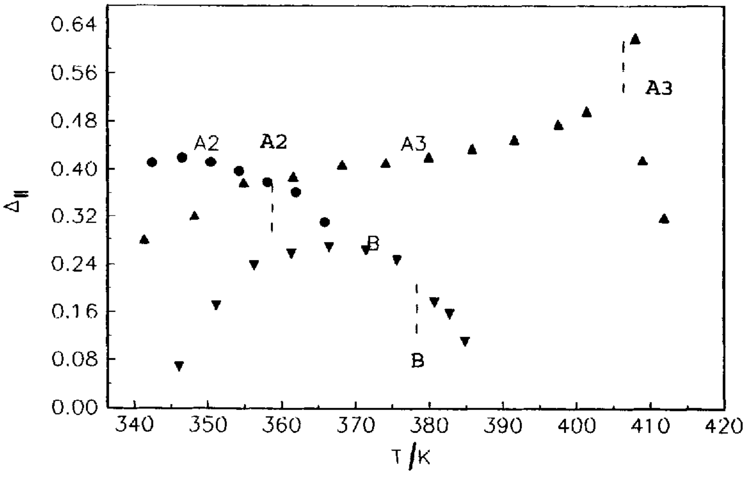

Figure 4. Dielectric increments at different temperatures for the low frequency relaxation detected only in the parallel direction for the samples **A2**, **A3** and **B**. The phase transition temperatures N/S$_A$ are indicated by broken lines.

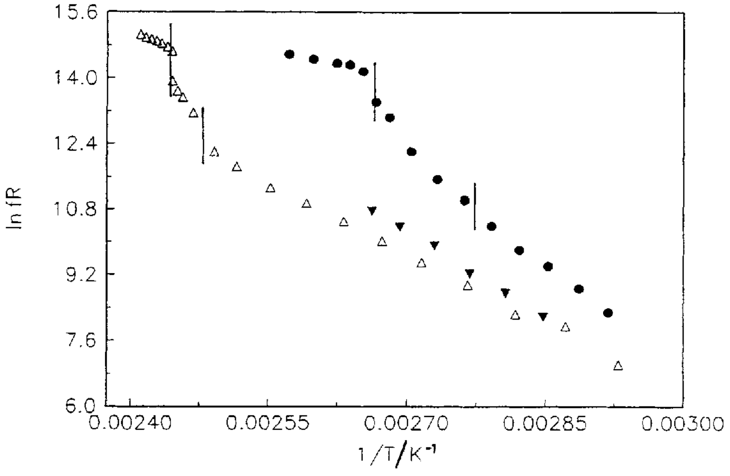

Figure 5. Arrhenius plot of the low frequency mechanism of samples **A** and **B**. The symbols are related to following samples: ● **A2**, △ **A3** and ▼ **B**. Due to the very small absorption intensity of **A1**, the data are uncertain. Phase transitions are indicated.

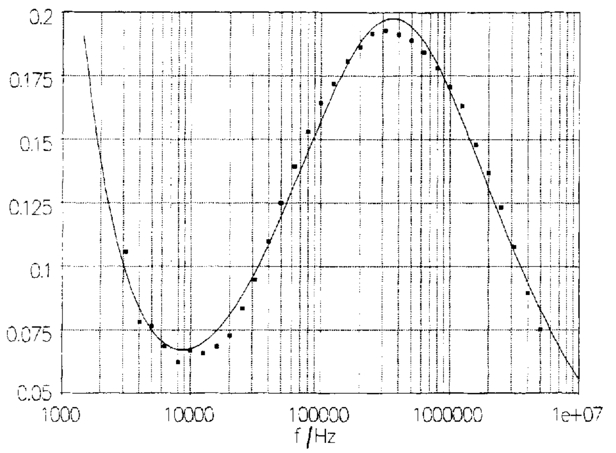

Figure 6. Experimental points for the high frequency absorption of **A2** for $\varepsilon''_{\parallel}$ at 319·4 K and the fitted curve to equation (1) with $\Delta = 0·671$, $h = 0·32$, $f_R = 0·359$ MHz, $A = 692$, $n = 1·13$.

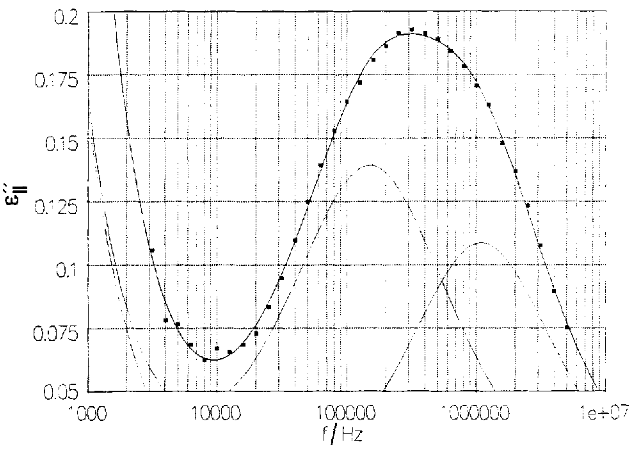

Figure 7. Experimental points for **A2** for $\varepsilon''_{\parallel}$ at 319·4 K and the fitted curves with two Cole–Cole absorption curves. $A_{1,2} = 407$, $n_{1,2} = 1·13$, $\Delta_1 = 0·364$, $h_1 = 0·17$, $f_{R1} = 0·152$ MHz, $\Delta_2 = 0·264$, $h_2 = 0·12$, $f_{R2} = 1·10$ MHz.

using an asymmetry parameter of the absorption [3], but as can easily be seen from the geometrical shape of the absorption curve in figure 6, it would be more reasonable to introduce a second absorption range of a Cole–Cole type at higher frequencies characterized by the parameters Δ_2, f_{R2}, h_2 in equation (1). The result of this procedure is shown in figure 7. This fit is much better, and therefore it may be supposed that the high frequency absorption is resolved into two processes. The same fit was carried out for different temperatures. The respective relations between the dielectric increments Δ_1 and Δ_2 are given in table 2.

Furthermore, the absorption curves for the perpendicular direction were also resolved into two processes. As shown in table 2, the absorption intensities of both high frequency processes are higher in the perpendicular than in the parallel direction. Taking into account the error of the separation procedure, one can see a relation of $(f_{R2}/f_{R1})_{\perp} \approx 7$. The intensity of the high frequency absorption 2 is about 1·5 times higher than that of the low frequency mechanism 1. In the parallel direction,

Table 2. Parameters of the MHz-relaxation for the high frequency process of **A2** estimated according to equation (1).

	HF-process 1		HF-process 2	
T/K	Δ_1	f_{R1}/MHz	Δ_2	f_{R2}/MHz
Parallel				
327·12	0·080	0·270	0·476	1·90
323·18	0·167	0·182	0·423	1·28
319·30	0·172	0·109	0·481	0·747
315·85	0·203	0·076	0·548	0·581
Perpendicular				
320·66	0·780	0·224	1·363	1·18
316·92	0·927	0·149	1·419	0·912
314·00	0·916	0·104	1·331	0·743

the intensity of the high frequency process 2 is about three times higher than that of the low frequency process.

Experimental data for the dielectric absorption measurements in the parallel direction of **A3** are presented in figure 8. The conductivity part at low frequencies was neglected. The absorptions already discussed in the kHz-range are there, and one at about 2 MHz. The last absorption again was fitted to a high (2) and a low (1) frequency Cole–Cole absorption. The sum of these three relaxation processes describes the experimental points well. From the fit, relations of the relaxation frequencies $(f_{R2}/f_{R1})_{\parallel} = 10 \pm 4$ and of the dielectric increments $(\Delta_2/\Delta_1)_{\parallel} \approx 7 \pm 3$ were calculated.

Figure 9 presents the calculated relaxation frequencies in the perpendicular direction in an Arrhenius plot. In this direction f_{R2} is about five times higher than the low frequency f_{R1}-value, and the ratio of the intensities $(\Delta_2/\Delta_1)_{\perp} \approx 1{\cdot}4 \pm 0{\cdot}2$. From figure 9 one obtains the impression that the low frequency mechanism follows the WLF equation or at least that the low frequency process exhibits a higher activation energy, and therefore the relation $(f_{R2}/f_{R1})_{\perp}$ increases with decreasing temperature.

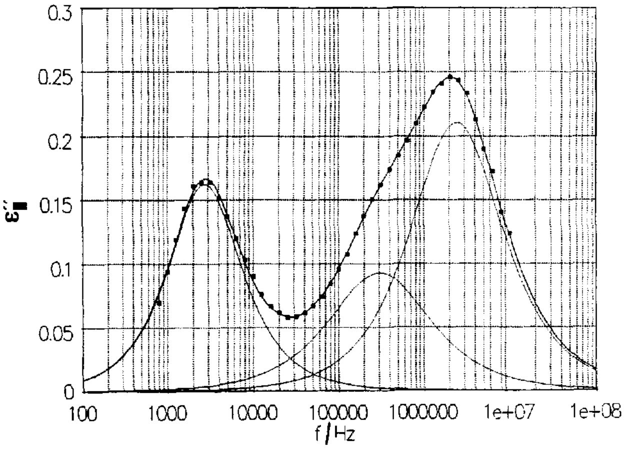

Figure 8. Dielectric data and fitted curves for **A3** at 354·9 K for $\varepsilon''_{\parallel}$. $\Delta_{\parallel 0} = 0{\cdot}291$, $f_{R0} = 2753$ Hz, $(h_0 = -0{\cdot}07)$; $\Delta_{\parallel 1} = 0{\cdot}226$, $f_{R1} = 0{\cdot}299$ MHz, $h_1 = 0{\cdot}13$; $\Delta_{\parallel 2} = 0{\cdot}474$, $f_{R2} = 2{\cdot}42$ MHz, $h_2 = 0{\cdot}07$.

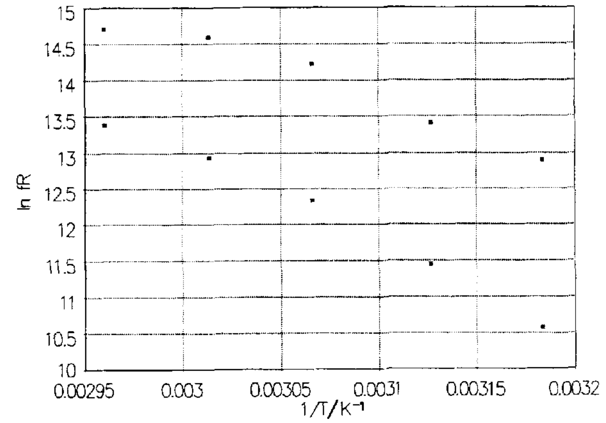

Figure 9. Arrhenius plot of the two high frequency processes of sample **A3** in the perpendicular direction.

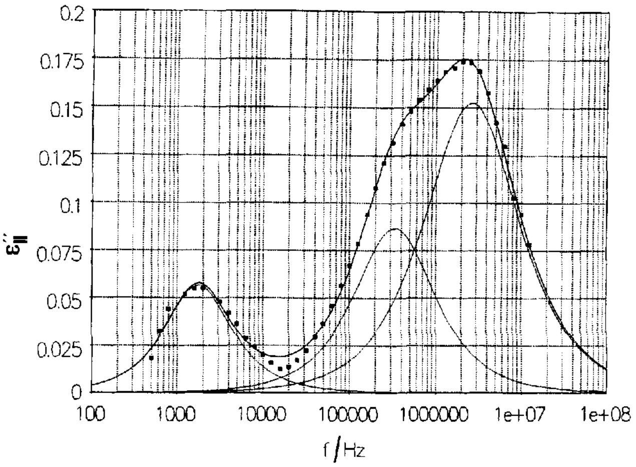

Figure 10. Dielectric data and fitted curves of **B** at 346·1 K for $\varepsilon''_{\parallel}$. $\Delta_{\parallel 0} = 0{\cdot}09$, $f_{R0} = 1780$ Hz, $(h_0 = -0{\cdot}12)$; $\Delta_{\parallel 1} = 0{\cdot}169$, $f_{R1} = 0{\cdot}334$ MHz, $(h_1 = -0{\cdot}01)$; $\Delta_{\parallel 2} = 0{\cdot}348$, $f_{R2} = 2{\cdot}63$ MHz, $h_2 = 0{\cdot}08$.

If our assumption about the different relaxation times is related to the central core and the lateral substituent, one would expect a stronger separation of both mechanisms by elongation of the spacer as was effected for sample **B**. Indeed the separation of the two mechanisms becomes better as demonstrated in figure 10. From the calculated data, the following relations could be obtained:

parallel direction

$$f_{R2}/f_{R1} \approx 15 \pm 4; \quad \Delta_2/\Delta_1 = 3{\cdot}9 \pm 1{\cdot}7$$

perpendicular direction

$$f_{R2}/f_{R1} \approx 10 \pm 5; \quad \Delta_2/\Delta_1 = 2{\cdot}0 \pm 0{\cdot}5$$

Also, in this case, the mean activation energy of the low frequency process (91 kJ mol^{-1}) is higher than that of the high frequency process (68 kJ mol^{-1}).

The static dielectric constants of **B** given in figure 11 show a pronounced step in $\varepsilon_{\perp 0}$ at the phase transition N/S$_A$. This step could not be detected in the *meta*-derivative **A2**, and seems to indicate a perpendicular dipolar correlation.

4. Discussion

From the very small absorption peak of compound **A1** in the parallel direction shown in figure 2, it was concluded that the cyano dipole—and together with it that of the lateral substituent—does not reorient together with the whole molecule. The argument that

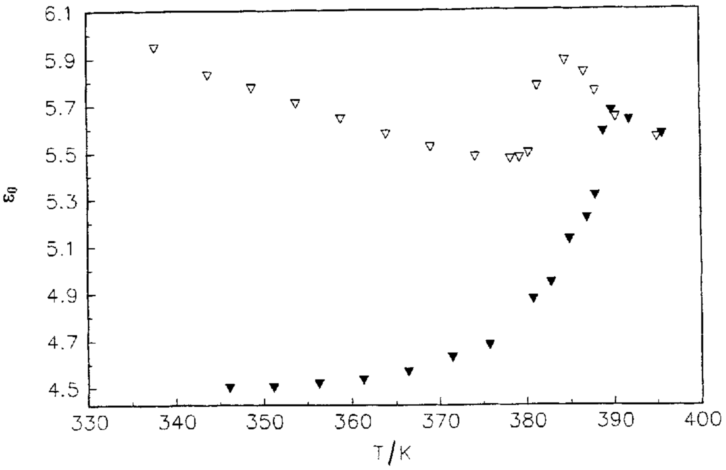

Figure 11. Static dielectric constants for sample **B**. The solid points ▼ are related to $\varepsilon_{\|0}$ and $\varepsilon_{0,\mathrm{is}}$, the open points ▽ to $\varepsilon_{\perp 0}$ and $\varepsilon_{0,\mathrm{is}}$.

the dipole of the lateral group acts exactly perpendicular to the director and therefore that one cannot see this motion in $\varepsilon_{\|0}$ cannot be accepted, because the sample exhibits a positive dielectric anisotropy $\Delta\varepsilon_0$. This can only be connected with the lateral substituent, because if this one is replaced by the nearly non-polar C_7H_{15} group, $\Delta\varepsilon_0 = -0{\cdot}88$ $(T = 0{\cdot}98\,T_{N/I})$ has been measured [9]. In contradiction to this, for the other samples, a more intensive dielectric absorption in the parallel direction was detected. In these cases one must assume a reorientation of the whole molecule around an axis perpendicular to the *para*-axis of the central core. The intensity of this absorption should be related mainly to the square value of the effective dipole moment of the lateral substituent in the direction of the *para*-axis. This dipole is difficult to estimate because a large part of the dipole moment is compensated due to antiparallel correlation (see figure 4). Especially in view of the $\varepsilon''_{\|}$-data for **A1**, it was assumed that a second part of the dipole of the lateral substituent can be related to an independent angular vibration which may be detected at higher frequencies. Indeed there are experimental arguments to fit the relaxation range at higher frequencies at least with the aid of two Cole–Cole mechanisms. Consequently one has to consider the molecular origin of this effect. One hypothesis could be the independent reorientation of the dipoles of the main part of the molecule and that of the lateral group. This is supported by the experimental result that the relation between the dielectric increments for the high (2) and low (1) frequency process after separation is different for the two main directions. In the parallel direction, the increment in the low frequency mechanism $\Delta_{\|1}$ seems to be smaller (increase of $(\Delta_2/\Delta_1)_{\|}$) especially for **A3** with the strong dipolar correlation in the parallel direction. From this it may be concluded that the low frequency mechanism is connected with independent angular vibration of the dipole of the lateral substituent, as discussed above, which can be detected in both directions. Under this assumption the high frequency process (2) should be related to the fast reorientation of the dipoles perpendicular to the *para*-axis of the central core and of the lateral substituent.

In general our experiments show that with a more complicated molecular structure and packing of the molecules in the different liquid crystalline phases, the dynamical behaviour becomes more differentiated.

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