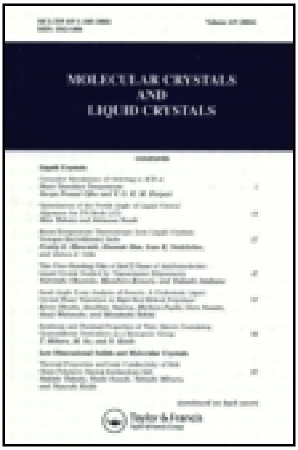

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DIELECTRIC STUDIES OF BICYCLOHEXYLCARBONITRILE NEMATOGENS WITH LARGE NEGATIVE DIELECTRIC ANISOTROPY

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Molecular dynamics of a homologous series of trans, trans-4,4′-dialkyl-(1α,1′-bicyclohexyl)-4β-carbonitrile(CCNs) with a lateral cyano group has been studied by dielectric relaxation spectroscopy. The high frequency relaxation process connected with the molecular reorientation around the long molecular axis was investigated in the isotropic and nematic phases. Due to the negligible value of the longitudinal dipole moment, the relaxation process around the short axis is inactive in dielectric spectroscopy. The dielectric relaxation time changes smoothly at the phase transition isotropic/nematic. The activation energy obtained ($E_A \sim 30\,\mathrm{kJ\,mol^{-1}}$) is typical for a relaxation process around the molecular long axis. For planar alignment the high frequency limit of the dielectric permittivity $\varepsilon_{\perp\infty}$ is distinctly higher than n_o^2. The difference $\varepsilon_{\perp\infty} - n_o^2 \approx 1.2$ is most probably connected with Poley absorption due to librational motion of molecules around the long axis.

INTRODUCTION

Nematic liquid crystals with large negative dielectric anisotropy are rare and of special interest for displays based on the dichroic dyes [1]. The investigated CCN-compounds (see Fig. 1) exhibit an axial cyano group, which is responsible for the large negative dielectric anisotropy [2] of about −9. It was proved by X-ray [3] and NMR [4] studies that the permanent dipole moment of the cyano group is situated perpendicular to the molecular long axis.

The contribution of the molecular dipole moment to the dielectric constant in the nematic phase can be expressed by the modified Maier-Meier equations [5] (1a and 1b).

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*Corresponding author.

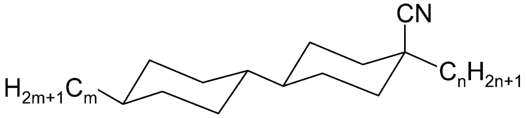

FIGURE 1 Chemical structure of the CCN-mn compounds.

$$(\varepsilon_\perp - \varepsilon_{\perp\infty}) = \frac{N_0F^2hg_\perp}{3k_BT\varepsilon_0}\left[\mu_l^2(1-S) + \mu_t^2(1+\frac{1}{2}S)\right] \tag{1a}$$

$$(\varepsilon_\| - \varepsilon_{\|\infty}) = \frac{N_0F^2hg_\|}{3k_BT\varepsilon_0}[\mu_l^2(1+2S) + \mu_t^2(1-S)] \tag{1b}$$

$$\varepsilon_{\perp\infty} = 1.05\cdot n_o^2 + N_0\frac{\mu_t^2}{\bar{v}_L^2 I_L} \tag{1c}$$

where N_0 is the number density, F and h are the Onsager local field factors, $g_\perp$and $g_\|$ are the Kirkwood correlation factors, μ_l and μ_t are the longitudinal and transversal dipole moments, S is the scalar order parameter. Equation (1c) is a contribution to the high frequency dielectric permittivity coming from the libratory motion of the molecule around its long axis. $n_o{}^2$ is the refractive index for the ordinary ray, $\bar{v}_L^2$ is the librational frequency of the molecule around its long axis, I_L is the smallest principal value of the inertia tensor of the molecule. One should explain that the contribution from the librational motion in case of the parallel component is distinctly smaller.

If the molecule possesses only a transverse component of the dipole moment ($\mu_l = 0$) one contribution exists for both principal alignments. This class of compounds give then an opportunity to study the dielectric spectra coming from only one strong dipolar group having the permanent dipole moment perpendicular to the long molecular axis (Fig. 1). One should explain that two similar compounds with an axial cyano group have recently been investigated by Urban *et al.* [6].

Theoretical models of molecular dielectric relaxation predict four relaxation processes in uniaxial systems, described by four autocorrelation functions: ϕ_{11}^1(t) and ϕ_{10}^1(t) for the planar, and ϕ_{00}^1(t) and ϕ_{01}^1(t) for the homeotropic alignment of a nematic phase [7,8], respectively. However, using the dielectric relaxation method only the relaxation process around the short axes, i.e. ϕ_{00}^1 process, can be separated from the other processes due to the retardation of the molecular reorientation around the short axis by the nematic potential. In the case of molecules without a longitudinal dipole moment component ($\mu_l = 0$) only the reorientation process around the long axis and the precessional motion around the director, described by ϕ_{11}^1 and ϕ_{01}^1, respectively, can contribute to the dielectric relaxation spectra. But up to now it has not been clearly demonstrated and discussed, whether it is possible to detect a separate model ϕ^1_{11}- process for planar and ϕ^1_{01}-process for homeotropic alignment, respectively. Additionally, due to a huge transverse dipole moment there could be a contribution to $\varepsilon_{\perp\infty}$ coming from the librational motion of the molecule around its long axis, the so-called Poley absorption [9,10]. Usually such librational relaxation process is observed in the infrared frequency range [11].

To sum up one should say that in the case of the substances studied the following contribution to the principle dielectric permittivities should be taken into account:

1° The ϕ^1_{11}-process connected with the molecular reorientation around the long axis coupled with the precession about the director;
2° The ϕ^1_{01}-process coming from the reorientation around the long axis disturbed by fluctuations of the director in the nematic potential.
3° The librational motion of molecules in the nematic potential.

It is obvious that due to the director fluctuations as well as coupling between the molecular reorientation around the long axis and the precessional motion (the ϕ^1_{11}-process) one can hardly isolate two separate model processes in the case bicyclohexylcarbonitriles studied in this work. It is interesting to point out here that in the case of cyanobiphenyls the ϕ^1_{00}-process separates from the complex dielectric spectrum due to the nematic potential. In this case one can speak of a single Debye-type dielectric relaxation process.

In the framework of this paper the compounds CCN-33, *CCN*-35, *CCN*-46, *CCN*-55 and *CCN*-38 were studied. The compounds were synthesised by the E. Merck company [4]. The phase sequence and phase transition temperatures (after [2]) are gathered in Table 1. All compounds except CCN-33 exhibit an enantiotropic nematic phase. As known from the literature[4] the birefringence of all CCNs in the nematic phase is very small ($\Delta n = +0.03$). Dielectric spectroscopy allows one to investigate temperature dependencies of the relaxation times, activation energies and discuss

TABLE 1 Phase Transition Temperatures in [°C] of the Investigated CCNs (Taken from [2])

Acronym	Cr	SmB	N	I		
CCN-33	●	33.6	–	–	(● 17.1)	●
CCN-35	●	38.4	–	–	● 45	●
CCN-38	●	41	(●	23)	● 49.5	●
CCN-46	●	30	(●	26)	● 54.7	●
CCN-55	●	25	●	30	● 66.4	●

such problems as dipole-dipole correlation. It would of special interest to compare the results of this work with the data of other nematic compounds with a longitudinal or transverse dipole moment of cyano group.

EXPERIMENTAL

The real and imaginary parts of the complex principal dielectric permittivities:

$$\varepsilon_{\perp}^{*}(\omega) = \varepsilon_{\perp}'(\omega) - i\varepsilon_{\perp}''(\omega) \tag{2a}$$

$$\varepsilon_{\|}^{*}(\omega) = \varepsilon_{\|}'(\omega) - i\varepsilon_{\|}''(\omega) \tag{2b}$$

were measured in the frequency range 10 Hz–1 GHz versus temperature for the substances studied.

Depending on the frequency, two impedance-analysers HP4192A (10 Hz–13 MHz) and HP4191A (1 MHz–1 GHz) were used. The measuring cell was a specially designed capacitor at the end of the coaxial line [12] similar to that used in the microwave frequency range by Gestblom *et al.* [13]. To obtain the experimental values of $\varepsilon_{\|}{}^{*}(\omega)$ ($\mathbf{n} \| \mathbf{E}_{\mathrm{m}}$, $\mathbf{E}_{\mathrm{m}}$ being electric measuring field) the sample was partially aligned by means of the magnetic field being parallel to the electrodes, see Figure 2. Due to the negative diamagnetic anisotropy [2] of the substance studied the director **n**, i.e. the average orientation of the long molecular axis, aligns at least in part perpendicularly to the electrodes, i.e. the electric measuring field $\mathbf{E}_{\mathrm{m}} | \mathbf{n}$. For perpendicular alignment ($\mathbf{E}_{\mathrm{m}} \perp \mathbf{n}$) a bias field of 0.1 MVm^{-1} was used (Fig. 2). Due to the negative dielectric anisotropy the director aligns parallel to the electrodes, i.e. $\mathbf{E}_{\mathrm{m}} \perp \mathbf{n}$. One should explain that the anchoring forces may play a crucial role in these alignment processes. Maybe it was a reason why the planar alignment was sometimes impossible for CCN-46 whereas in the case of CCN-38 only partial order was obtained. The

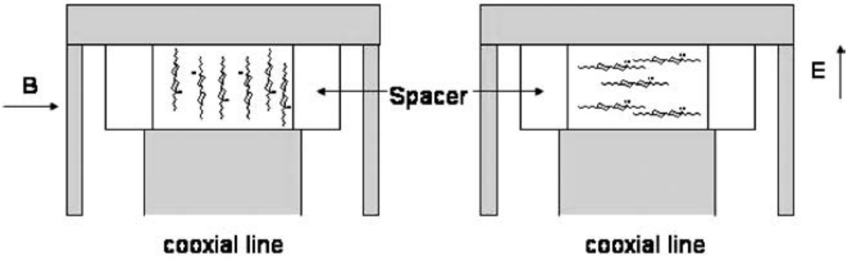

FIGURE 2 Homeotropic (left) and planar (right) alignment of the nematic phase of CCNs.

accuracy of the results was better than 3% for ε' and 6% for ε''. The temperature of the sample remained stable within ±0.1 K.

Up to our knowledge the best alignment was obtained for CCN-55, so the dielectric data acquired for this compound shall be mostly used in further discussion.

The dielectric data were analyzed by fitting the semi-empirical Cole-Cole function [14] (3).

$$\varepsilon_{\|}^{*}(\omega) = 1.05 \cdot n_e^2 + \Delta\varepsilon_{\|P} + \frac{\varepsilon_{\|0} - \varepsilon_{\|\infty}}{1 + (i\omega\tau_{\|})^{1-\alpha_{\|}}}, \tag{3a}$$

$$\varepsilon_{\perp}^{*}(\omega) = 1.05 \cdot n_o^2 + \Delta\varepsilon_{\perp P} + \frac{\varepsilon_{\perp 0} - \varepsilon_{\perp\infty}}{1 + (i\omega\tau_{\perp})^{1-\alpha_{\perp_{\|}}}} \tag{3b}$$

n_e and n_o represent the extraordinary and the ordinary refractive index, $\Delta\varepsilon_{iP}$ is the Poley absorption contribution, ε_{i0} represents the quasi-static dielectric constant; τ_i is the relaxation time and α_i is a distribution parameter. $\Delta\varepsilon_i = \varepsilon_{i0} - \varepsilon_{i\infty}$ is the dielectric strength of the i-th dielectric relaxation process. It is worth pointing out that ca. 5% of the high frequency dielectric permittivity comes from the atomic polarisation [9,15].

RESULTS

Figure 3 shows a combined dielectric spectra of *CCN*-55 in the frequency range 100 Hz–1 GHz at 26°C measured without any external aligning field. As seen a relaxation process with a relaxation frequency around 100 MHz can be detected. For both principal alignments (planar and homeotropic) only one relaxation process in this frequency range was found (Figure 4) which shows a symmetric distribution of the relaxation times ($\alpha \approx 0.1$). As seen below 1 kHz an increase of ε'' can be observed, which is due to DC conductivity.

In Fig. 4 the Cole-Cole plots for CCN-55 in the isotropic and nematic phases are shown, the fitting parameters and temperatures are indicated. For all plots the experimental points can be fitted with only one Cole-Cole function (3a or 3b). As can be interpreted the librational motions of the molecules contribute to both $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ as well as to the ε_{iso}. However, the contribution to the perpendicular component is the largest (Fig. 4b). The distribution parameter α is between 0.06 and 0.08 which is larger than the expected value for a single Debye-type dielectric relaxation process ($\alpha = 0$). This result fully agrees with the measurements on other compounds with a longitudinal cyano group [16,17]. It can be seen that

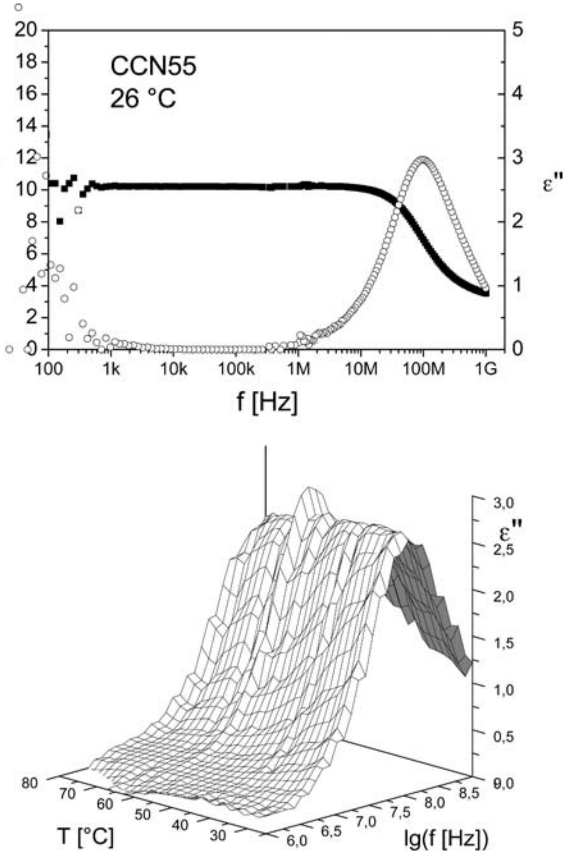

FIGURE 3 a) Real- and imaginary part of the dielectric constant in the frequency range 100 Hz–1 GHz of CCN-55 (T = 26°C, 0 BIAS) b) corresponding 3D plot.

ε_∞ in the isotropic phase is just in-between the values for the planar and homeotropic alignments. This can be explained by the high frequency polar relaxation processes connected with the librational movement of the molecules [9,10,15] around their long axes.

The temperature dependencies of the quasi-static dielectric constant are illustrated in Figure 5. In the isotropic phase the dielectric constant increases with decreasing temperature as predicted by the Onsager theory [18]. It was found that a planar alignment can be obtained in the nematic phase using a bias field of 0.1 V/μm. The influence of the bias field can be seen by the distinct increase of the dielectric constant at the nematic-isotropic phase transition. As attained in this work the magnetic field applied of 1.5 T can stabilize a homeotropic alignment. This was clearly

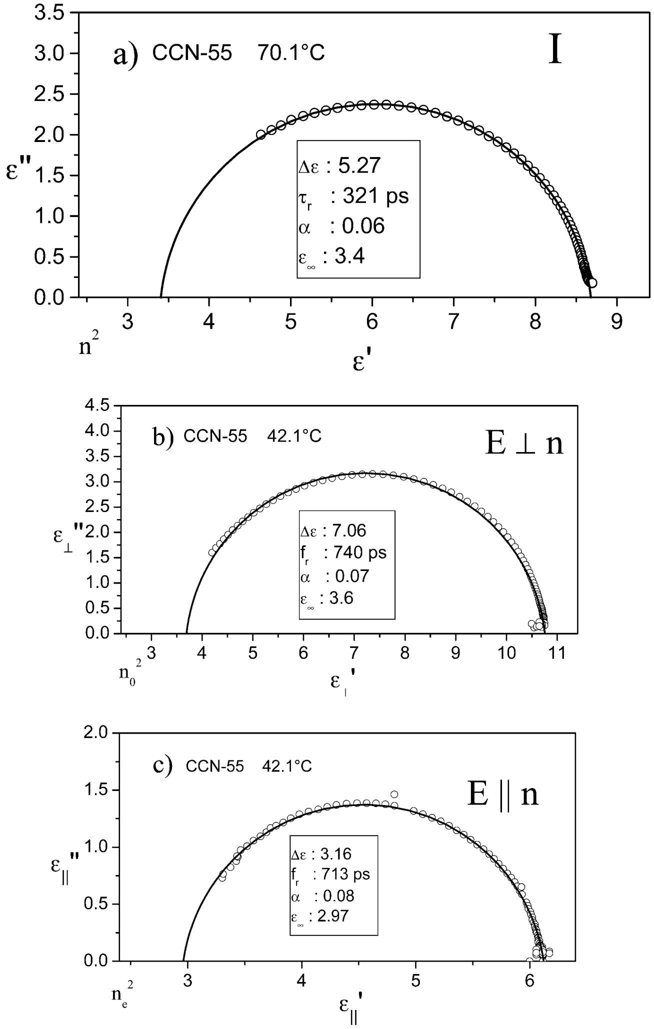

FIGURE 4 Cole-Cole plots for CCN-55 in the isotropic phase a), in the planar b) and homeotropic c) nematic phase alignments. Temperature and fitting parameters are indicated.

shown by a strong decrease of the dielectric constant at the isotropic-nematic phase transition in the presence of the magnetic field (Fig. 5). In this case at least partial homeotropic alignment was obtained. In one paper [2] lower values of the $\varepsilon_{\parallel 0}$ dielectric constant were reported for the compounds; this might mean that in our case the alignment is not complete.

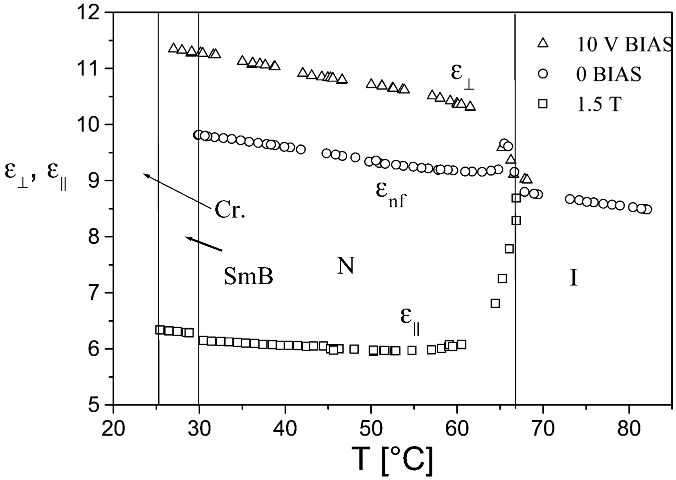

FIGURE 5 Quasi-static dielectric constants of CCN-55 for different alignments: without aligning field (circles), with bias field of 0.1 V/μm (triangles), and with magnetic field of 1.5 T (squares). ε_{nf}–measured without any alignment.

It is interesting that without external aligning fields the dielectric permittivity, measured for the nematic phase, corresponds quite well with the extrapolated values from the isotropic phase.

Figure 6 illustrates the temperature dependence of the relaxation times obtained for CCN-55 for the isotropic phase and for two principal alignments of the nematic phase. As seen – from the macroscopic point of view - two relaxation processes were found, but the relaxation time of the reorientation around the long molecular axis, $\tau_{|}$ ($\equiv \tau^{1}_{01}$), seems to be slightly smaller than the dielectric relaxation time $\tau_{\perp}$ ($\equiv \tau^{1}_{11}$) connected the rotation around the molecular long axis coupled with the precessional motion about the director. However, due to the distribution of the relaxation times ($\alpha \approx 0.1$) we are not entitled to conclude that one observes here two model relaxation processes. In other words one can not isolate two separate relaxation processes directly related to the model relaxation times: τ^{1}_{01} and τ^{1}_{11}. The small differences in temperature dependencies may indicate that the $\tau_{\perp}$, and $\tau_{|}$ dielectric relaxation processes are just the same, i.e. related to the reorientation around the long molecular axis. As one can see the relaxation time shows no stepwise change at the phase transition temperature isotropic-nematic but a very smooth temperature dependence. The activation energies calculated in the isotropic and the nematic phases differ therefore only slightly. Thus, one can conclude that the reorientation around the long molecular axis is not influenced in this case by the nematic potential.

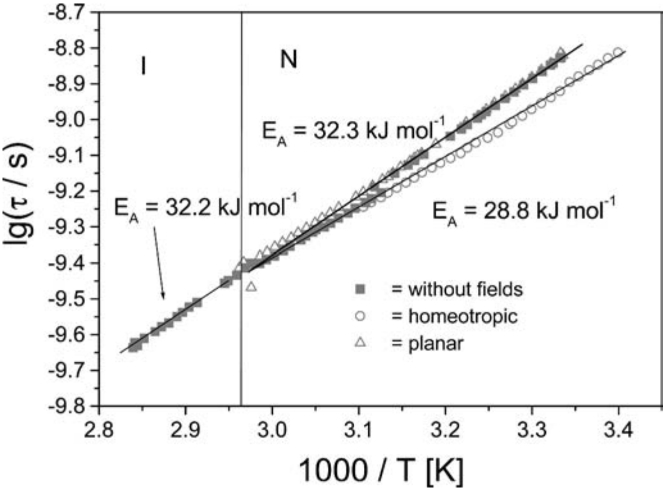

FIGURE 6 Arrhenius diagram for the relaxation time of CCN-55 at different orientations.

One can notice that the dielectric investigations under the influence of a magnetic field ($\mathbf{B}\perp\mathbf{E}_{\mathrm{m}}$) show slightly smaller relaxation times and also a smaller activation energy of $E_A = 28.8\,\mathrm{kJmol}^{-1}$. But the difference is still in the range of the experimental error limits of $\pm 2\,\mathrm{kJmol}^{-1}$, so it is safe to speak of an almost identical temperature dependence of the relaxation times.

Theoretical considerations [19] of the dependence of dipolar relaxation processes on the order parameter (theoretically at fixed temperature) can come to similar results. Depending on the anisotropy of the rotational diffusion constant τ^1_{01}/τ_0 can decrease faster than τ^1_{11}/τ_0 with increasing order parameter. With the overall temperature dependence of τ_0 in the isotropic phase a smaller activation energy of τ^1_{01}can be attained.

The dielectric investigation on the other compounds (CCN-33, CCN-38, CCN-46 and CCN-35) showed similar results. The enantiotropic nematic phase of the CCN-compounds was clearly seen at the temperatures given in Table 1. The monotropic nematic phase of CCN-33 was not observed and only the isotropic phase could be supercooled down to 3°C. An expected jump of the dielectric constant at the transition to the SmB phase was not observed.

The dielectric results of the investigated CCN-compounds are summarized in Table 2. The relaxation frequency f_r was extrapolated from the isotropic phase to room temperature for a better comparison. The activation energy E_A is given for the isotropic phase and the different orientations in

TABLE 2 Activation Energies and Relaxation Frequencies Obtained for the Investigated CCN- Compounds

Acronym	CCN-33	CCN-55	CCN-46	CCN-38	CCN-35
E_A [kJ mol^{-1}]					
iso. phase	35.2	32.2	33.4	32.2	31.4
planar	–	32.3	32.8	32.3	30.4
homeotropic	–	28.8	–	31.4	27.0
lg (f_r/Hz) at 25°C	8.15	8.0	8.04	7.98	8.12

the nematic phase. Unfortunately, a homeotropic alignment of CCN-46 could not be obtained.

CONCLUSIONS

The relaxation frequencies measured for the investigated CCN-compounds are in the same frequency range as those found for the relaxation process around the long molecular axis for other cyano compounds (nCB [16,17,20], PCHn [21], CCH-n [22]). Dielectric studies on the dielectrically negative nematic liquid crystals (*6BAP(F)* and *7CP5BOC* [23–25] as well as 7BBC6 and 8BBC4 [6]) demonstrate similar results. From this study it has been proved that the rotation around the short molecular axis of the CCN-compound is dielectrically inactive due to the perpendicular position of the cyano group dipole moment. Additional intra-molecular relaxation processes as described by other groups [16,21,25] were not observed for the CCNs in this work. However, a symmetric distribution of the relaxation times was found for both principal alignments and for the isotropic phase as well.

According to the theoretical models of the dielectric relaxation in uniaxial systems [7,26,27] two relaxation processes in the nematic phase of CCNs are expected – one for each principal alignment. It was found that the relaxation time and the calculated activation energy are slightly smaller for the macroscopic $\tau_{\|}$ process observed for homeotropic alignment as compared with the $\tau_{\perp}$ process found for planar alignment. Theoretical considerations [19] of the dependence of dipolar relaxation processes on the order parameter (theoretically at fixed temperature) lead to similar results. The mean activation energy obtained is $E_A = 31\,\mathrm{kJ\,mol^{-1}}$, and the variance is in the range of the experimental error of $\pm 2\,\mathrm{kJ\,mol^{-1}}$. This is in good agreement with the activation energies of the dielectrically negative nematic liquid crystals, like 6*BAP(F)* and 7*CP*5*BOC* showing the activation energy for a reorientation around the molecular long axis in the isotropic phase [23–25] of 29–30 kJ mol^{-1}. The activation energy of 8CHBT is

21 kJ mol^{-1}, i.e. distinctly smaller [16], which might be connected with some intra-molecular motion.

In comparison with the dielectric results on CCH-n [22] a continuous increase of the dielectric constant with decreasing temperature was found in the isotropic phase. CCH-n exhibits a critical behaviour with a maxima, which was interpreted as the formation of dimers (local antiferroelectric correlation) [22]. A strong increase of the static dielectric permittivity with decreasing temperature as well as the absence of this critical behaviour for the CCN-compounds lead to the conclusion that the CCNs do not form dimeric associations. Therefore the dielectric investigations are in agreement with the X-ray measurements for the crystalline phase [3].

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