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Dielectric studies of two liquid crystalline benzoates with coupled and decoupled CN groups

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The results of dielectric studies performed in a broad frequency range for two compounds, 4-cyanophenyl 4-*n*-heptylbenzoate (7BBCN) and 4-(4-cyanobutyloxy)phenyl 4-*n*-heptylbenzoate (7BB4CN), are compared. They have the same molecular core whereas the strongly polar CN group is attached to the benzene ring in 7BBCN or is separated from it by the butyloxy chain in 7BB4CN. 7BBCN has a nematic phase, whereas 7BB4CN exhibits a monotropic nematic and smectic A_2 polymorphism. Large differences in the dielectric properties of the two substances were found. The analysis of the results led to the conclusion that the antiparallel dipole–dipole associations are considerably stronger in the substance with a decoupled CN group.

1. Introduction

Typical liquid crystalline (LC) substances of rod-like shape consist of a rigid core and flexible tail(s). Usually the polar groups, active in dielectric spectroscopy, are attached to the core [1]. Dielectric relaxation studies can therefore yield information on the rotational motions of whole molecules around their principal inertia axes. A large moment of inertia for the motion about the short axis means that even in the isotropic phase the corresponding relaxation process falls in the MHz frequency range (low frequency, l.f., relaxation process). This becomes additionally slowed down when passing into a LC phase due to the anisotropy of the interaction potential. The rotational motion around the long axis is less hindered and is observed in the hundreds of MHz or even in the GHz frequency range (high frequency, h.f., relaxation process), e.g. [2, 3].

In cases where the dipolar group is incorporated in flexible parts of a molecule, the relaxation spectrum becomes more complex due to the conformational motions. The aim of this paper is to compare the results of dielectric studies of two benzoates having the same molecular core, whereas the strongly polar CN group is either attached to the benzene ring or is separated from it by a butyloxy chain. Their chemical structures, the acronyms used, and their phase sequences as observed in the dielectric studies (cooling) and DSC measurements (heating) are presented in table 1. Both substances have already been studied by dielectric spectroscopy methods [4–6]. However, in [5] only the nematic (N) phase was observed over a narrow temperature range for 7BB4CN, whereas we were able to study the additional monotropic smectic A (SmA) phase down to *c.* 37°C below the clearing point. In the case of 7BBCN the present studies were extended to distinctly broader temperature ranges in the isotropic (I) and N phases than those examined in [6].

7BB4CN is closely related to substances synthesized by the Strasbourg group [7–10] which exhibit SmA_2 polymorphism. One of them, CN-4.O8, is shown in

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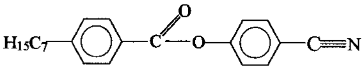
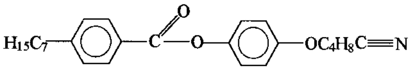
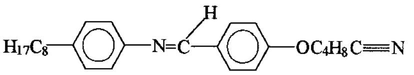
Table 1. Chemical structures, acronyms and phases sequences of the substances studied.

Substance	Acronym	Phase sequence[a]
 4-Cyanophenyl 4-*n*-heptylbenzoate	7BBCN	I–56.5°C–N–31°C–Cr Cr–44.0°C–N–56.3°C–I
 4-(4-Cyanobutyloxy)phenyl 4-*n*-heptylbenzoate	7BB4CN	I–(47.6°C–N–45.8°C–SmA–<10°C)–Cr[b] Cr–61.7°C–I
 4-(4-Cyanobutyloxy)benzylidene-4′-octylaniline	CN-4.O8	I–85.3°C–SmA_2–60.5°C–SmB_2–(40°C)–Cr

[a] For both 7BBCN and 7BB4CN, the phase sequences on cooling are from the dielectric studies and on heating by DSC.
[b] Observation by polarizing microscopy revealed the transition N–SmA_2 at 34°C.

table 1. The close similarity of the chemical structures and the textures observed by polarizing optical microscopy [8] suggest that the monotropic smectic phase observed for 7BB4CN has also a bilayered structure due to antiparallel coupling of the cyano end groups. This possibility needs experimental confirmation by X-ray which is a difficult task, however, because of the monotropic character of the phase.

2. Experimental

The substances 4-(4-cyanobutyloxy)phenyl 4-*n*-heptylbenzoate (7BB4CN) and 4-cyanophenyl 4-*n*-heptylbenzoate (7BBCN) were synthesized in the Institute of Chemistry, the Military University of Technology, Warsaw. The observations by polarizing microscopy of the monotropic phases of 7BB4CN obtained by slow cooling of the liquid revealed the transition to the nematic phase at 47.1°C. The nematic texture was hardly observed however due to the almost complete homeotropic alignment of the sample by wall effects. At *c.* 34°C the transition was visible to a smectic phase with a focal-conic texture typical for the SmA phase. By analogy with similar substances with the Schiff's base linkage [8] referred to above, we suppose that one is dealing with a bilayer SmA_2 molecular arrangement.

The measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, were performed with the aid of two sets of apparatus. In the frequency range 10 kHz–13 MHz, a HP 4192A impedance analyser was used. The plane capacitor ($C_o \sim 50$ pF) has gold covered plates. Noticeable conductance effects were observed below *c.* 10 kHz in the I and N phases of 7BBC4CN. In the N phase the samples were oriented by means of a magnetic ($\mathbf{B} = 0.8$ T, $\varepsilon_\perp^*$) or an electric ($\mathbf{E} = 3500$ V cm^{-1}, $\varepsilon_\parallel^*$) field. In spite of several attempts, in the N phase of 7BB4CN the parallel aligned orientation could only be kept to *c.* 2.5°C below the clearing temperature, whereas the perpendicular orientation could never be obtained. In most cooling runs, immediately below the nematic phase the permittivity dropped considerably, indicating the transition to the SmA phase, see figure 1 (*b*). In three runs the monotropic smectic phase could be supercooled down to *c.* 10°C. After heating the sample to *c.* 30°C an abrupt transition to the solid phase occurred. The nematic phase of 7BBCN could be supercooled to *c.* 30°C.

To study the high frequency processes taking place in both substances, the time domain spectrometer (TDS) at Uppsala University was used to cover the frequency range 20 MHz–3 GHz. In the isotropic phase two time windows, 10 and 50 ns, were used and then the spectra were spliced [11]. In the nematic and smectic phases only the 10 ns time window was used.

3. Results

The static permittivities measured for the isotropic and LC phases of both compounds are presented in figure 1. Application of a d.c. orienting electric field in the N phase of 7BBCN resulted in markedly higher $\varepsilon_\parallel$ values in comparison with previous results [4–6], where a magnetic field was used.

Figures 2–4 present typical relaxation spectra collected for different phases of particular substances in the form of Cole–Cole diagrams resulting from the well known equation

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau)^{1-\alpha}} \qquad (1)$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, and α characterizes a distribution of the relaxation times τ. When necessary the conductivity term was added to equation (1).

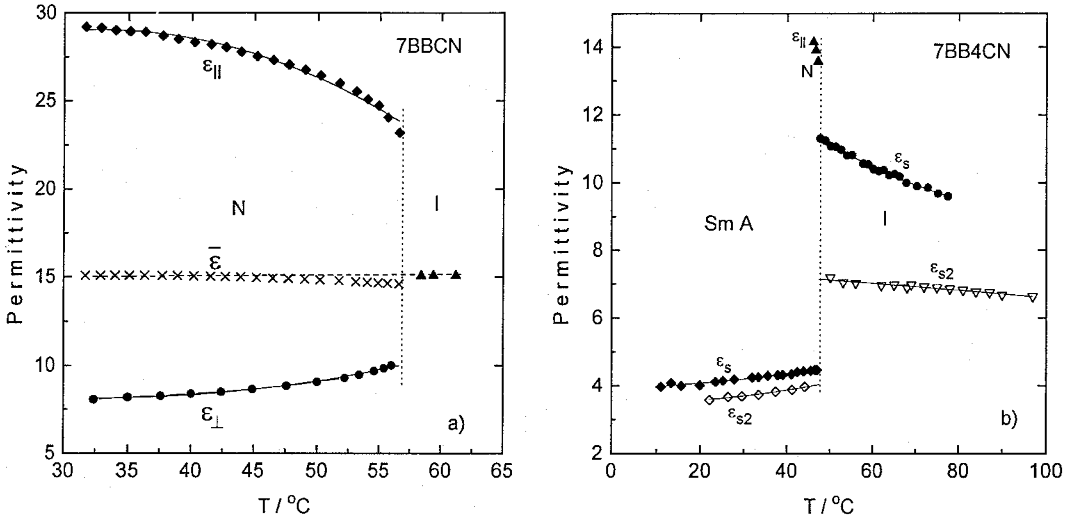


Figure 1. Static permittivities versus temperature in the isotropic and LC phases of (*a*) 7BBCN and (*b*) 7BB4CN. Full and open symbols correspond to the data measured with the aid of the HP and TDS set-ups, respectively. The same convention is used in other figures.

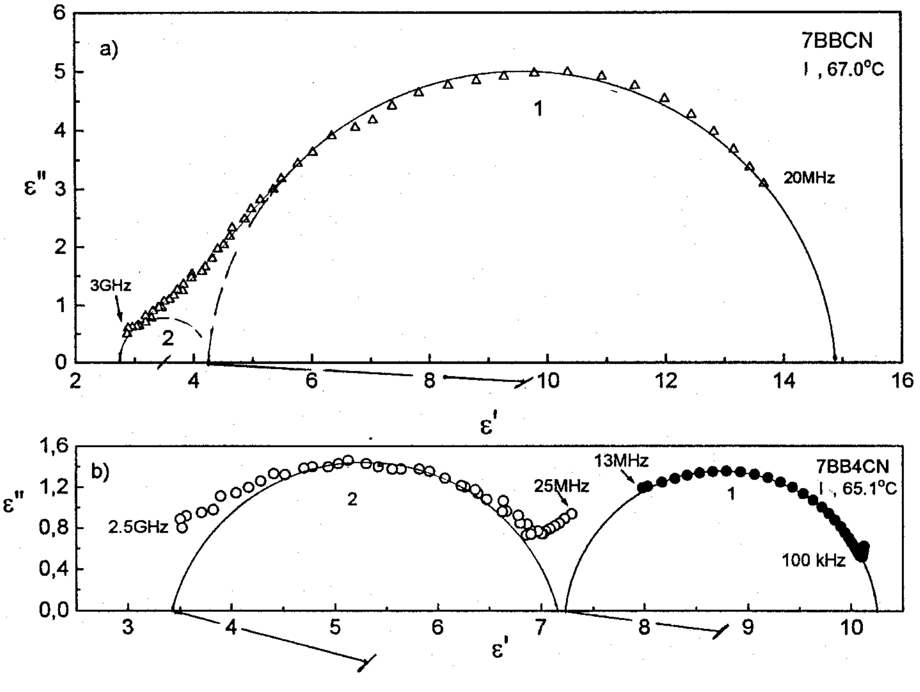


Figure 2. Cole–Cole plots for the isotropic phases of (*a*) 7BBCN and (*b*) 7BB4CN. The fitting parameters are: (*a*) $\delta_1 = 9.90$, $\tau_1 = 5.34$ ns, $\alpha_1 = 0.07$, $\delta_2 = 1.20$, $\tau_2 = 0.22$ ns, $\alpha_2 = 0$; (*b*) $\delta_1 = 3.10$, $\tau_1 = 22.7$ ns, $\alpha_1 = 0.08$, $\delta_2 = 3.90$, $\tau_2 = 0.25$ ns, $\alpha_2 = 0.18$.

The spectra in the isotropic phases of both substances differ considerably (figure 2). For 7BBCN the spectrum is dominated by the l.f. relaxation process with a large dielectric increment $\varepsilon_s - \varepsilon_\infty$ resulting from the large longitudinal dipole moment μ_l given by the CN group (~4.5 D). The high frequency process, having a distinctly smaller increment, is connected with the transverse component of the dipole moment μ_t determined by the central COO group (1.9 D). The corresponding relaxation times can be calculated by fitting the spectrum to a model function assuming two relaxation processes

$$\varepsilon^* - \varepsilon_\infty = \frac{\delta_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\delta_2}{1 + (i\omega\tau_2)^{1-\alpha_2}} \qquad (2)$$

where $\delta_1 = \varepsilon_s - \varepsilon_{s2}$ and $\delta_2 = \varepsilon_{s2} - \varepsilon_\infty$ are the strengths (increments) of the two relaxation processes. τ values corresponding to both processes observed differ by a

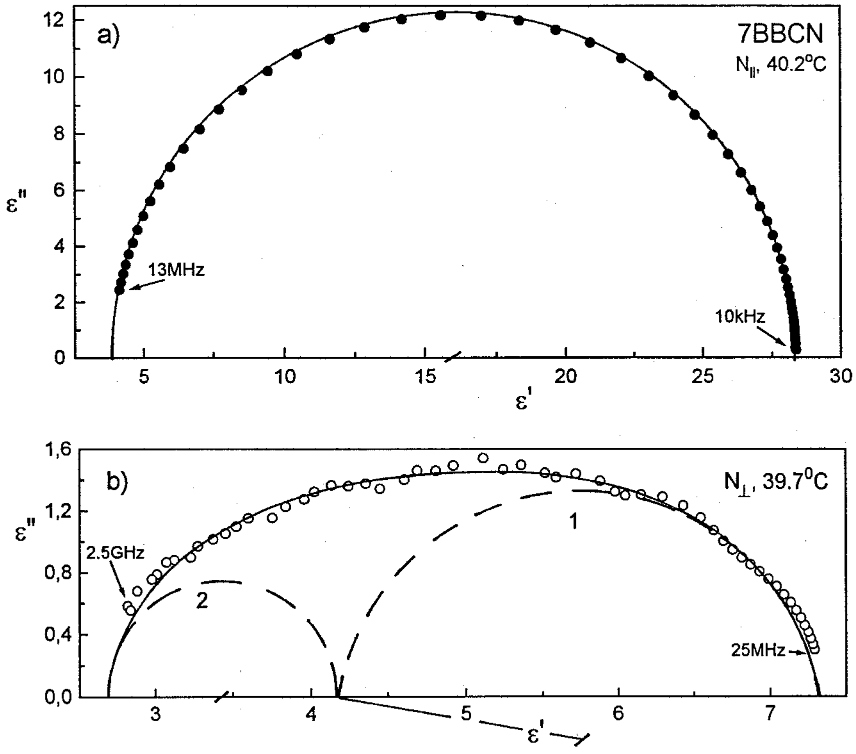


Figure 3. Cole–Cole plots for two orientations of the nematic phase of 7BBCN. The fitting parameters are: (*a*) $\delta = 25.5$, $\tau = 16.6$ ns, $\alpha = 0$; (*b*) $\delta_1 = 3.25$, $\tau_1 = 4.97$ ns, $\alpha_1 = 0.18$, $\delta_2 = 1.34$, $\tau_2 = 0.64$ ns, $\alpha_2 = 0$.

factor of *c.* 25, see figure 5(*a*). The activation enthalpy for the l.f. process (see table 2) is similar to those obtained for other two-ring compounds in the isotropic phase [11–13]. Such a dielectric property of the isotropic phase is typical for LC substances having a strong polar group (CN or NCS) attached to the rigid core [6, 12, 13].

In the case of 7BB4CN the situation is drastically different. There are two well separated relaxation bands characterized by comparable dielectric increments, and each

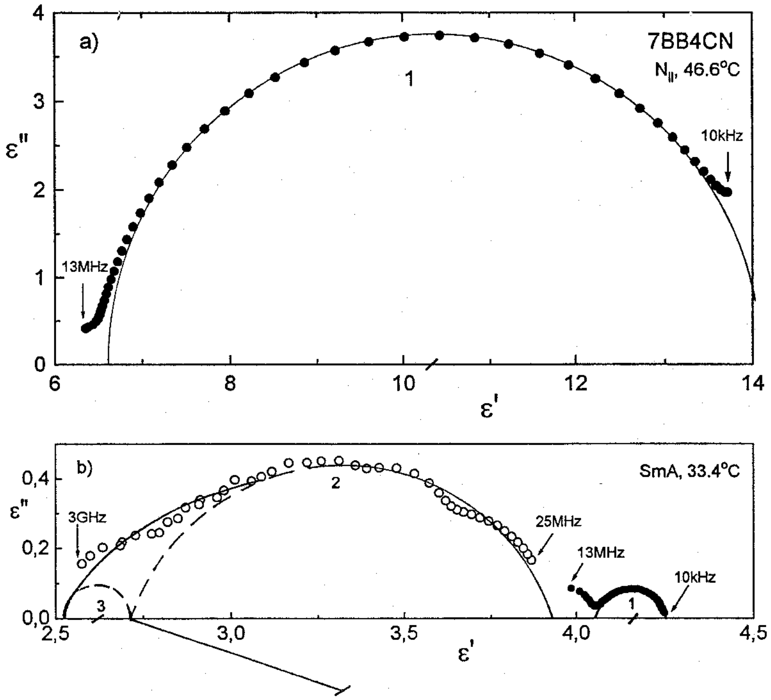


Figure 4. Cole–Cole plots for the (*a*) nematic and (*b*) smectic A phases of 7BB4CN. The fitting parameters are: (*a*) $\delta_1 = 7.70$, $\tau_1 = 334$ ns, $\alpha_1 = 0$; (*b*) $\delta_1 = 0.20$, $\tau_1 = 870$ ns, $\alpha_1 = 0$, $\delta_2 = 1.13$, $\tau_2 = 0.81$ ns, $\alpha_2 = 0.20$, $\delta_3 = 0.16$, $\tau_3 = 0.04$ ns, $\alpha_3 = 0$.

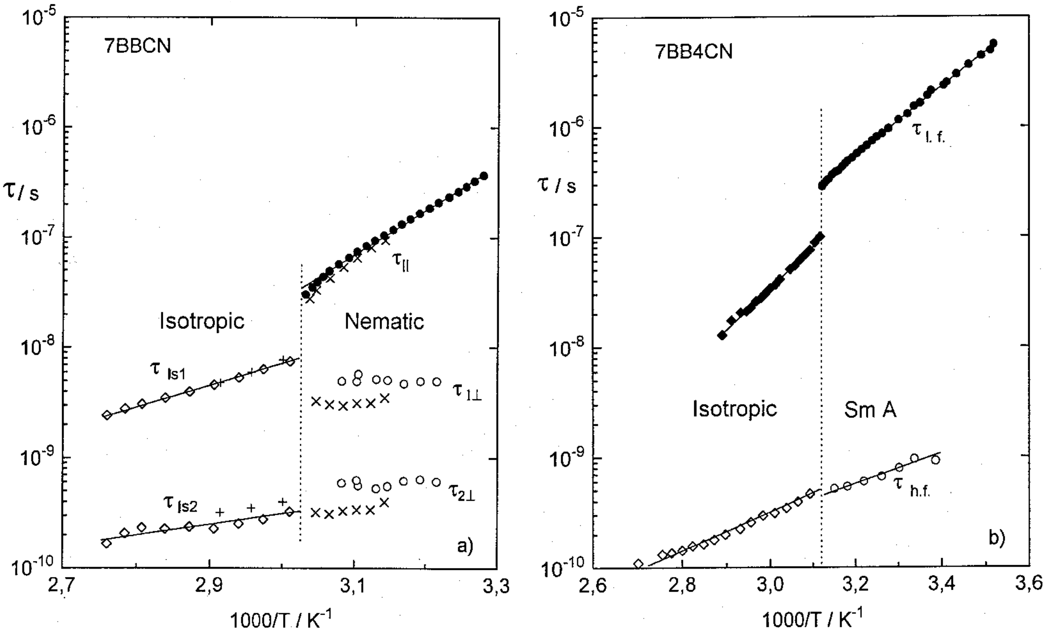


Figure 5. Arrhenius plots for (*a*) 7BBCN and (*b*) 7BB4CN. In (*a*) the data marked by × and + are taken from [6] with changed numbering of the relaxation processes for the perpendicular orientation of the N phase.

Table 2. The activation enthalpy $\Delta H(\mathrm{kJ\,mol^{-1}}) = R(\partial \ln \tau / \partial T^{-1})$ for the l.f. and h.f. processes in the isotropic and LC phases of 7BB4CN and 7BBCN.

Phase	Substance 7BBCN	 7BB4CN
Isotropic		
l.f.	36.6 ± 2, 46 ± 2 [6]	72.0 ± 2
h.f.	17 ± 5, 21 ± 2 [6]	30.3 ± 3
Nematic		
E∥**n**	75.4 ± 2, 84 [5], 91 ± 2 [6]	155 [5]
E⊥**n**		
band 1	~0	
band 2	~0	
SmA		
l.f.		60.7 ± 1
h.f.		26.7 ± 3

of them can be analysed separately using equation (1), see figure 2(*b*). The relaxation times obtained now differ by a factor of about 90, see figure 5(*b*). The corresponding activation enthalpies are distinctly larger than those for 7BBCN (table 2).

In the nematic phase of 7BBCN the l.f. process measured for parallel orientation obeys excellently the Debye equation—equation (1) with $\alpha = 0$, figure 3(*a*). In the case of the perpendicular orientation, the TDS spectra can be described by a superposition of two relaxation processes, figure 3(*b*). In [6] yet another process was observed at low frequencies, just below our limiting frequency of 25 MHz.

The spectrum of the N phase of 7BB4CN, figure 4(*a*), resembles that shown in figure 3(*a*), although its increment is considerably smaller (7.7 in comparison with 25.5; similar values are reported in [5]). A large ε_{∞} value (*c*. 6.5) indicates the presence of an additional h.f. relaxation process. However, in the TDS measurements below the clearing point, the SmA phase was always obtained. Two relaxation processes are evident in the SmA phase of 7BB4CN, figure 4(*b*). They are separated in the frequency scale by three orders of magnitude and could be analysed independently. The l.f. process is of the Debye-type, whereas the h.f. process exhibits a large distribution of the relaxation times ($\alpha \approx 0.20$). The l.f. and h.f. processes in the SmA phase do not match because the samples in both experiments were ‘polycrystalline’ and perhaps did not fill the sample holders completely. This influences the permittivity values, but not the frequency dependence of the spectra. It is seen clearly in figure 5(*b*) where the points corresponding to the l.f. process in the SmA phase coming from three independent runs are presented. In spite of slightly different ε' and ε'' values in particular runs, the τ values were excellently consistent. Besides, yet another process with a rather small increment and very short relaxation time can be separated from the TDS spectra—left small circle in figure 4(*b*). However, the analysis of all spectra collected gave no consistent temperature variation of the increments and relaxation times for this process.

As one can see in figure 5, the l.f. relaxation times are increased at the clearing point of both substances, whereas the h.f. relaxation times behave rather smoothly at the transitions.

4. Discussion

Two striking features may be pointed out when the dielectric properties of both substances studied are compared: (*i*) a large reduction of the static permittivity in the isotropic and nematic phases of 7BB4CN in comparison with 7BBCN, and (*ii*) an evident difference in the relaxation spectra measured for the two substances. This must be attributed to the different positions of the CN group in the molecules.

The relaxation process observed for the $\mathbf{E}\|\mathbf{n}$ geometry in the N phase of 7BBCN is undoubtedly connected with molecular rotation around the molecular short axes. The values of the relaxation times and the activation barrier are similar to those obtained for several two-ring compounds, e.g. [2, 3, 11–14]. This motion is also responsible for the l.f. process in the isotropic phase. The present activation enthalpy values are markedly lower than those given in earlier data (table 2), but they seem to be better established, as the relaxation times were measured within distinctly broader temperature ranges in the N and I phases of 7BBCN.

The second principal molecular motion, the rotation around the long axes, must be visible in the spectra measured for the $\mathbf{E}\perp\mathbf{n}$ geometry if the dipole moment has a non-zero transverse component. The 7BBCN molecule has two polar parts: the COO bridging group and the cyanophenyl moiety. Both of them contribute to μ_t, in particular CN, because the *para*-axis of the phenyl is inclined from the lowest inertia moment axis of the molecule due to conformational motions of the alkyl tail. There is experimental evidence [14] that intramolecular rotation around the CO–O bond can lead to the dielectric relaxation process visible in the perpendicularly oriented nematic phase. Thus, the two relaxation bands observed in figure 3 (*b*) may be ascribed to the whole molecule rotating around the long axis—slower process characterised by $\tau_{1\perp}$ in figure 5 (*a*)—and the independent rotation of the alkyl–phenyl–CO–moiety—faster process with $\tau_{2\perp}$ in figure 5 (*a*). This interpretation differs from that proposed by Jadżyn *et al.* [6]. These authors ascribed the h.f. process—their domain 3, in figure 5 (*a*) points close to the $\tau_{2\perp}$ values—to the molecular rotation around the long axis; but the l.f. process—their domain 2, in figure 5 (*a*) points close to the $\tau_{1\perp}$ values—is ascribed to the stochastic precessional movements and/or fluctuations of the molecular long axis with respect to the director. The latter prescription especially seems to be doubtful.

The 7BB4CN molecule has one additional polar component, viz. the butyloxy group separating the CN dipole from the benzene ring (table 1). In spite of that, the static permittivity in the isotropic phase is markedly lower than in the case of 7BBCN (figure 1). Such an effect is commonly attributed to antiparallel dipole–dipole association between molecules and can be analysed with the help of the Onsager equation,

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{N_0 \mu_{\text{app}}^2}{3\varepsilon_0 3k_B T} \tag{3}$$

where the apparent dipole moment μ_{app} is introduced to account for dipole correlation. The relation between μ_{app} and the dipole moment value μ of the isolated molecule is expressed by the Kirkwood correlation factor $g = \mu_{\text{app}}^2/\mu^2$. The antiparallel associations are present in the isotropic and LC phases of all cyano compounds [11, 15] giving $g < 1$. However, in the case of 7BB4CN they seem to be more pronounced than in 7BBCN. This conclusion is additionally corroborated when the parallel permittivity components in the N phase of both substances are compared. Although the nematic range observed for 7BB4CN is narrow, figure 1 (*b*), there is no doubt that the $\varepsilon_\|$ values differ considerably for the two substances ($\sim$23 and $\sim$14 at similar distances from the clearing points, figure 1). This means that the antiparallel associations play a much more important role in the substance with a decoupled cyano group, as also happens for other similar compounds [7–10]. One can suppose that these associations also exist in the smectic phase of 7BB4CN and should lead to the double-layered smectic structure, the SmA_2 phase [16].

The dielectric increment characterizing a given relaxation process reflects the strength of the dipole moment taking part in the corresponding molecular motion: $\delta \sim \mu^2$. Looking at the spectra in figure 2 and the dipolar structure of the molecules (table 1) one can say that the relations between δ_1 and δ_2 correspond roughly with the ratio μ_t^2/μ_l^2 for 7BBCN, but not for 7BB4CN. The fact that $\delta_1 < \delta_2$, figure 2 (*b*), indicates that the CN dipole is considerably inclined from the molecular long axis due to the flexible butoxy group separating it from the benzene ring. Taking the experimental permittivity values and inferring equation (3), we could estimate the angle β formed by the total dipole moment with the long axis: $\tan^2\beta = \mu_t^2/\mu_l^2$. This gives $\beta \approx 47°$, in good agreement with the value of 45° obtained from the Kerr constant [5].

Looking at the spectra presented in figures 2 (*b*) and 4 (*b*), one can note a large reduction of the increments for both relaxation processes observed in the smectic phase in comparison with the isotropic phase. This is certainly caused by a lack of orientation of the smectic phase in both experiments. In spite of that, one can note the Debye-type l.f. relaxation process and a very broad relaxation spectrum at high frequencies. The former process can be ascribed to the movement of the whole molecule around the short axis, whereas the latter process certainly consists of several motions of the whole molecule and its parts around the long axis, including conformational and/or rotational motions of the cyanobutyloxy group. The activation barriers (table 2) are similar to those determined for other substances in the smectic A phase [13].

The l.f. relaxation process is retarded at the clearing point by similar factors: $g_{\mathrm{l.f.}} = \tau_{\mathrm{N}}/\tau_{\mathrm{Is}} = 4.3$ for 7BBCN and $g_{\mathrm{l.f.}} = \tau_{\mathrm{Sm}}/\tau_{\mathrm{Is}} = 3.1$ for 7BB4CN, whereas the h.f. relaxation times pass smoothly through the clearing point in both cases. Such behaviour is typical for LC substances, e.g. [3, 12, 13]. Surprisingly, the activation enthalpy for the l.f. process is markedly larger in the isotropic than in the smectic phase of 7BB4CN (figure 5, table 2)! This is the first such finding for LC substances.

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