Dielectric studies of tolane derivatives exhibiting the E and K phases

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Results of dielectric studies for three tolane derivatives containing the isothiocyanato (NCS) and alkyl or alkoxy groups in the terminal positions are presented. A relaxation process associated with molecular rotations around the short axes has been observed in the crystal-like smectic phases (B, E, K). The K phase was characterized for the first time by dielectric spectroscopy. The results are discussed by taking into account the dielectric relaxation data obtained recently for the biphenyl analogues in the E phase. The available X-ray data allow us to calculate the so-called packing parameter which characterizes the free volume of the molecules in the unit cells.

1. Introduction

Dielectric spectroscopy is a useful tool with which to study the molecular dynamics of polar molecules in liquid crystalline (LC) phases [1–5]. Two main rotational motions can be distinguished which dominate the relaxation spectra measured in the low frequency range (up to *c.* 10 MHz) and at high frequencies (above 100 MHz): rotation around the short molecular axes and around the long molecular axes, respectively. The relaxation time characterizing the higher frequency process, $\tau_{h.f.}$, essentially does not change at phase transitions separating LC phases or at the clearing point [5–9]. By contrast, the relaxation time $\tau_{l.f.}$, characterizing the low frequency process, is very sensitive to phase changes [1–5, 7–12]. The transitions between the liquid-like phases (I, N, SmA, SmC) are accompanied by changes of $\tau_{l.f.}$ within one order of magnitude, whereas each transition to a crystal-like phase (for example B, E, …) is accompanied by a more pronounced slowing of the motion. Substances having strong longitudinal dipole moments are especially interesting for studying the low frequency process in different phases as it appears as a separate process in all LC phases.

Recently several isothiocyanatotolanes were synthesized which exhibit the crystal smectic phases B, E and K [13, 14]. Three of them, one with a terminal butyl tail and two others containing hexyloxy and heptyloxy groups (see table 1), were chosen for the present studies.
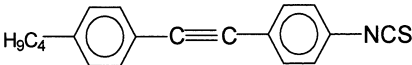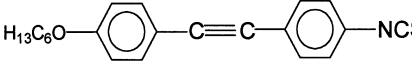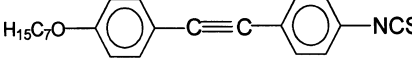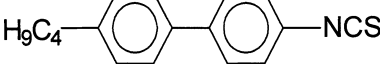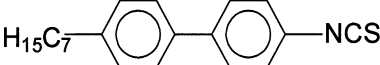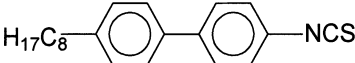
They exhibit crystal-like smectic phases in broad temperature intervals. The results of dielectric studies are compared with those obtained recently [12] for the isothiocyanato-biphenyls, *n*BTs, having exclusively the E phase. Additionally, the discussion of the dielectric results can be enriched by taking the X-ray results into account [14].

The aim of these studies is to determine how a change in the structure of the molecular core (biphenyl ↔tolane) is reflected in the determined quantities: the permittivity, the relaxation time and the activation enthalpy for the low frequency process. Therefore, the properties of substances with *n*-alkoxy groups are related to those with (*n*+1)-alkyl groups. The relaxation studies concerning the tilted (monoclinic [14]) K phase, are reported here for the first time.

The crystal-like smectic B, E and K phases show three-dimensional quasi-long range positional order [1, 14, 15]. In the B phase each molecule is surrounded by six nearest neighbours which form a hexagon. The hexagonal layers may stack with bilayer, trilayer or no interlayer correlations. The E phase has orthorhombic symmetry, but the elementary cell is more or less similar to the hexagonal cell (pseudo-hexagonal molecular packing) [14]. The K phase has a monoclinic structure which arises from the tilting of the *c*-axis of the pseudo-hexagon towards the edge [14]. X-ray patterns show strong diffuse scattering indicating the presence of considerable disorder, probably associated with very soft transverse modes involving relative displacement of layers [15].

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Table 1. Compounds studied, acronyms used and the phase sequences.

Compound	Acronym	Phase transitions/°C
H₉C₄—⟨⟩—C≡C—⟨⟩—NCS	4TOLT	Cr 44.0 K 70.5 E 86.9 I
H₁₃C₆O—⟨⟩—C≡C—⟨⟩—NCS	6OTOLT	Cr 58.4 E 112.7 N 113.6 I
H₁₅C₇O—⟨⟩—C≡C—⟨⟩—NCS	7OTOLT	Cr 60.3 E 111.6 B 112.7 SmA 112.9 I
H₉C₄—⟨⟩—⟨⟩—NCS	4BT	E 82.5 I[a]
H₁₅C₇—⟨⟩—⟨⟩—NCS	7BT	Cr 57.8 E 72.4 I
H₁₇C₈—⟨⟩—⟨⟩—NCS	8BT	Cr 30.4 E 69.4 I

[a]No clear melting point.

2. Experimental

The substances studied are shown in table 1, along with the acronyms used and the transition temperatures obtained from DSC [13, 14]. Current measurements were made using cooling runs only, which meant that the freezing point was often shifted to lower temperatures. Nematic (6OTOLT) or SmA (7OTOLT) phases with narrow temperature ranges were not observed in the present studies. However, in the middle of the B phase of 7OTOLT, the temperature could be successfully stabilized and the measurement made.

The dielectric relaxation spectra, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, were recorded with the aid of a HP4192A and a Solatron Schlumberger SI1260 impedance analyser. The samples were unoriented as the magnetic or electric fields available were ineffective in these phases. The spectra of the isotropic phase of 4TOLT were obtained with a time domain spectrometer (TDS) [16].

3. Results

Typical relaxation spectra measured for particular substances are presented in figures 1–4. They were analysed with the Cole–Cole equation with the addition (if necessary) of terms responsible for conductivity and the double layer effects [17]:

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} - \frac{iA}{f^M} + \frac{B}{f^N} \qquad (1)$$

where $\omega = 2\pi f$ (f = frequency), ε_o and ε_∞ are the low and high frequency limits of the permittivity, respectively, $\tau = 1/2\pi f_m$ is the relaxation time, f_m is called the critical

frequency corresponding to the maximum of losses and α describes a distribution of the relaxation times. The second term accounts for the d.c. conductivity, whereas the third term accounts for the capacitance of the double layer. A, B, M and N are the fitting parameters. Because the spectra of 4TOLT are concentrated on rather low frequencies their analyses were difficult, especially in the K phase (figure 2). However, the fitting procedure gave consistent results over a broad range of temperatures (compare with figure 5). In the E phase of all substances, the relaxation process observed may be considered as Debye-type because the α parameter is low (0.02–0.06). The calculated relaxation times are compared with those obtained recently for appropriately chosen nBTs [12] (see § 1). The activation enthalpy
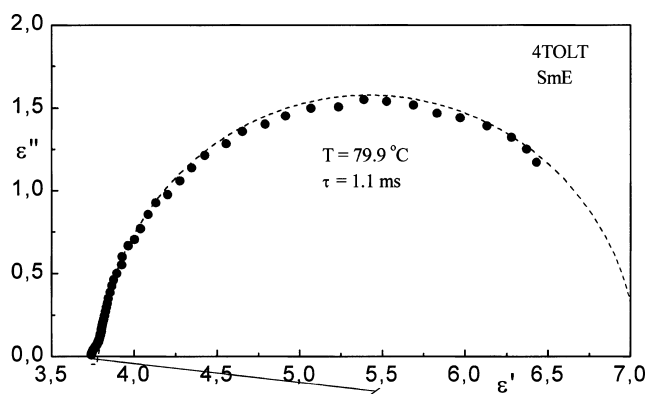

Figure 1. Cole–Cole plot for the E phase of 4TOLT. The measurement was carried out in the frequency range 100 Hz–1 MHz.
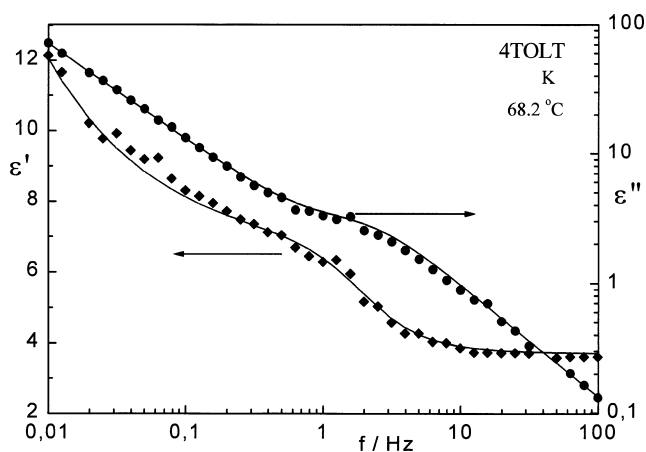
Figure 2. Dispersion and absorption spectra of 4TOLT in the K phase. The lines are fits of the real and the imaginary parts of equation (1).
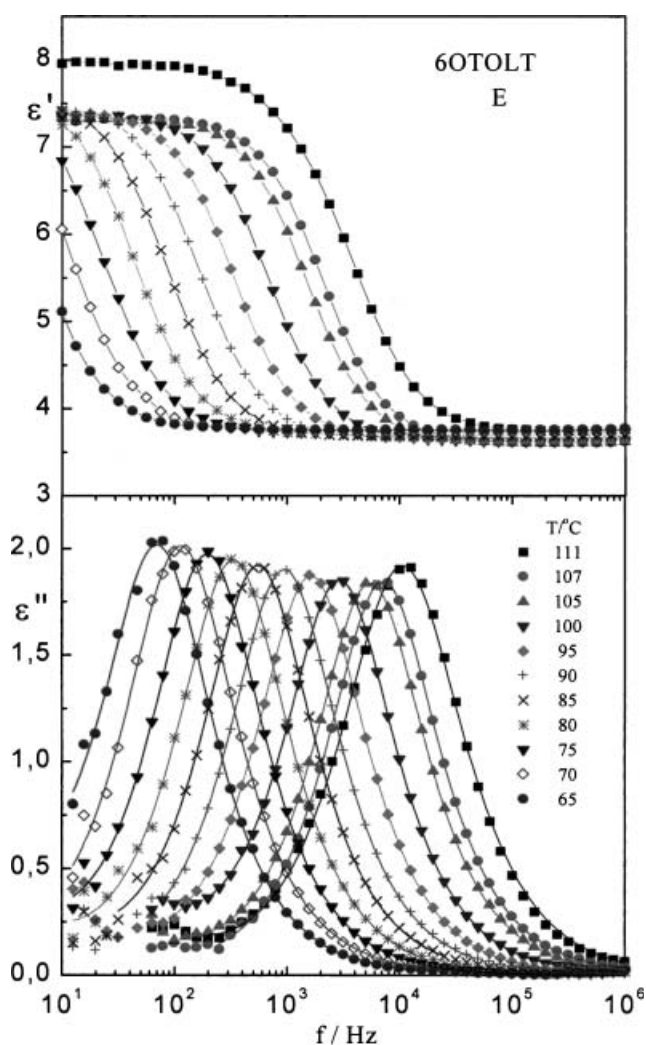

Figure 3. Dispersion and absorption spectra of 6OTOLT in the E phase.
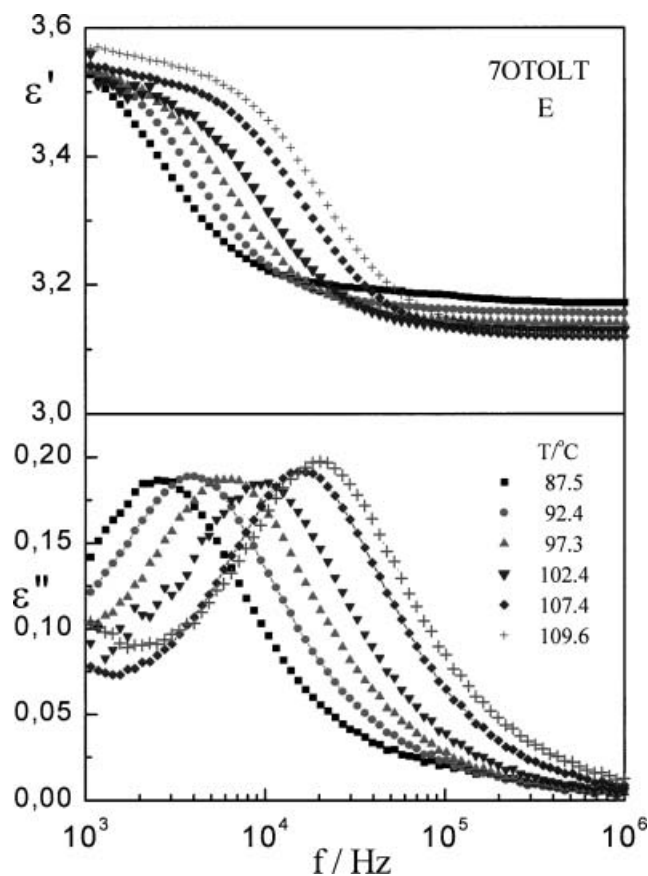
Figure 4. Dispersion and absorption spectra of 7OTOLT in the E phase.

$\Delta H = R(\partial \ln \tau / \partial T^{-1})$ (R = gas constant) calculated for particular substances are listed in table 2.

4. Discussion

As in previous studies [8, 11, 12] the transition from the isotropic or liquid-like phases to crystal-like phases is accompanied by a reduction of the static permittivity values. This is due to a lack of alignment of the sample; therefore, only the isotropic values can be compared. For the pairs of molecules listed in table 1 we have the following relations between the permittivity values measured at the clearing point: 6.88/6.32 for 4BT/4TOLT, 6.07/6.49 for 7BT/6OTOLT, and 5.90/6.41 for 8BT/7OTOLT. Of course, only the first pair is useful for the discussion of the influence of the molecular core on the static permittivity in the isotropic phase, because both molecules have the same electronic structures. In the other cases the alkoxy group increases the net dipole moment resulting in an increase of ε_{is} of 6OTOLT and 7OTOLT with respect to the nBTs. One may conclude that in reducing ε_{is} the bridging C≡C group plays a

Figure 5.   Arrhenius plots of the logarithm of the relaxation times characterizing the molecular reorientation about the short axes in crystal-like phases of biphenyl and tolane derivatives.
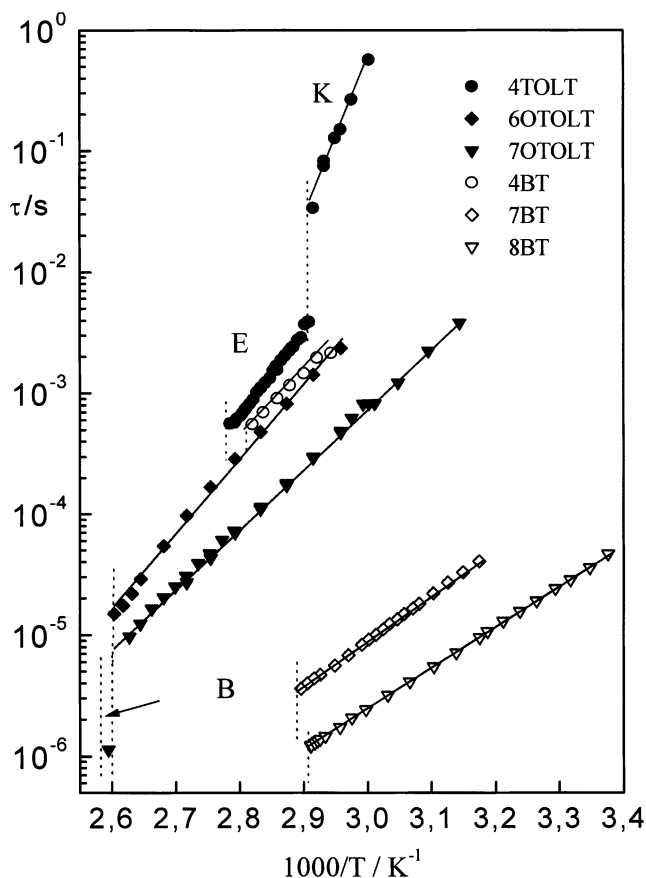

Figure 6.   Low frequency relaxation times for molecular reorientation about the short axes in the isotropic and LC phases of 4BT and 4TOLT.

similar role as two CH_2 groups in the alkyl chain of *n*BTs [12].

The relaxation times characterizing the molecular rotations around the short axes change considerably when going from the isotropic to the E phase; see figure 6. (Two other substances were not studied by TDS due to their high clearing points; however, it would be expected that the retardation of motion would exceed at least two order of magnitude, as for 7BT and 8BT [12]). The changes in the low frequency relaxation time $\tau_{l.f.}$ at the transition points between the different crystal-like phases are much less, and equal to a factor 8.6 at

B–E (7OTOLT) and 19.4 at E–K (4TOLT) transitions. Certainly, the slowing of the motion must be greater if the transition occurs between the orthogonal E and tilted K phase than between the two orthogonal B and E phases.

The activation barrier hindering the molecular rotations around their short axes in the crystal-like smectic phases is considerably larger for the tolane derivatives than for the biphenyls (table 2). The transition from the orthogonal E to the tilted K phase in 4TOLT is accompanied by a doubling of the activation barrier. Thus, both the size of the rigid core and the molecular

Table 2.   Activation enthalpy (in $kJ\,mol^{-1}$) for the low frequency relaxation process in the solid-like phases of the compounds studied.

Phase	Substance					
	4TOLT	4BT	6OTOLT	7BT	7OTOLT	8BT
E	135 ± 3	95	120 ± 3	73	95 ± 3	65
K	254 ± 10	—	—	—	—	—

Table 3. Data on the volume per molecule in the unit cell [14], the volume of molecules and packing parameter determined for the smectic phases of substances studied and for crystalline phase of two cyanobiphenyls [19]. The existence of flip-flop molecular motions is marked in the last column.

Substance	Phase	$V_{\mathrm{u.c.}}/2/\text{Å}^3$	$V_{\mathrm{mol}}/\text{Å}^3$	p	Molecular rotation
4BT	E	414.4	264.07	0.637	yes
4TOLT	E	441.4	290.00	0.657	yes
6OTOLT	E	480.2	334.75	0.672	yes
7OTOLT	B	552.4	351.87	0.637	yes
	E	524.6		0.671	yes
6CB	Cr	382.4	279.56	0.731	no
7CB	Cr	411.5	297.56	0.724	no

arrangement in the layers, determine the energy barrier hindering the flip-flop molecular motions.

Some new light on molecular freedom in the crystal-like smectic phases may be shed by taking into account the results of X-ray studies of the substances under consideration [14]. These studies enabled the determination of the unit cell parameters and the number of molecules Z in the unit cell, thus giving information about the volume per molecule in the cell. If the volume of the molecule itself is known one can discuss how much room is occupied by a molecule in the cell. The analyses carried out for many plastic-crystalline (ODIC) compounds revealed that the rotational freedom of molecules depends upon the ratio $p = V_{\mathrm{mol}}/(V_{\mathrm{u.c.}}/Z)$ which is called the *packing* parameter [18, 19]. For molecules having spherical (globular) shapes molecular rotations (overall or uniaxial) were observed if $p \leqslant 0.65$. It seems interesting therefore to see whether such analysis is applicable to LC substances having strongly asymmetric molecular shapes.

Table 3 lists the data on the unit cell volume per molecule determined from X-ray studies [14]; the volumes of molecules calculated with the aid of the HyperChem 7.0 program using the model of interpenetrating spheres; and the ratio of the two volumes giving the packing parameter p. It is also noted whether a molecular rotation about the short axis does indeed occur. From the fifth column of the table it can be seen that the molecules occupy less than 67% of the space in the crystal smectic phases and markedly more in the crystalline phase. Unfortunately, the crystallographic data for the crystalline phase of the tolane derivatives are unavailable and we have taken for comparison purposes crystallographic data on substances which do not have a smectic phase (6CB and 7CB [20]). Notwithstanding, it seems justified to conclude that, as in the ODIC phases, there is a limiting value of the p-parameter (~ 0.67) which would allow us to distinguish between the phases with a rotational freedom of molecules around the short axes and phases where such rotation is frozen out. (As was mentioned in §1 the

molecular rotations around the long axes are not disturbed at the phase transitions). Taking into account pressure–volume–temperature (pVT) studies [21, 22], one can clarify why such voluminous motion becomes considerably slower at the phase transitions between the isotropic or liquid-like LC phases to the crystal-like phases (figure 6, [1, 5, 7, 10–12]). PVT measurements of 8BT have shown that a change in the specific volume is ten times greater for the N–E than for the N–I transition [21]. A molecule in the crystal-like phase must wait a much longer time for the free volume required to overcome the energy barrier separating two potential wells. In other words, there is a strong rotational–translational coupling of molecules in a lattice.

5. Summary

Dielectric results obtained for several compounds that exhibit crystal-like smectic phases revealed that molecular rotations around the short axes are present in all the LC phases. The crystal-like K phase was characterized for the first time by the dielectric method. The replacement of the biphenyl core by tolane results in a reduction in permittivity of the isotropic phase. This is equivalent to the addition of the two CH_2 groups in the alkyl chain of the isothiocyanato-biphenyl series. The activation barrier hindering the flip-flop molecular motions in crystal-like phases depends on the molecular core size, as well as on the molecular arrangements in the layers. The packing parameter reaches a limiting value, enabling us to distinguish between the crystalline and crystal-like smectic phases in which the molecular rotations around the principal inertia axes are present.

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