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Dielectric properties of three-ring fluorinated compounds

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Four three-ring compounds, consisting of two cyclohexyl rings and one mono- or difluorinated phenyl ring, were studied using dielectric spectroscopy methods over a broad frequency range (1 kHz–3 GHz). They exhibit a nematic phase in a broad temperature interval, enriched by a smectic B phase in one case. The static and dynamic dielectric properties were analysed. It was established that the bridging CH₂CH₂ group placed between cyclohexyl and phenyl rings considerably changes the reference frame of the molecule, unlike the situation when it links two cyclohexyl rings. In the nematic and smectic B phases the motion around the short axis is a Debye process, whereas the rotation around the long axis is split into two processes: independent rotation of the whole molecule and its fluorophenyl part.

Keywords: nematic phase; dielectric anisotropy; relaxation time; dipole moment; three-ring compound

1. Introduction

The dielectric spectroscopy method is very well suited to study the rotational dynamics of molecules in liquid crystalline (LC) phases if the constituting molecules possess a dipole moment (1, 2). In the case of elongated (rod-like) molecules, two main relaxation processes can be distinguished: one is connected with the rotations around the short axes and occurs at megahertz frequencies (the low-frequency, LF, process), and the second one is connected with the much faster rotations around the long axes (the high-frequency, HF, process) (3). Such motions are otherwise referred to as molecular “tumbling” and “spinning”, respectively. Of course, both processes can be observed when non-zero projections of the dipole moment on the principal inertia moment axes occur. Besides, the internal motions of polar groups can contribute to the relaxation spectra (see, for example, Urban *et al.* (3, 4)).

Several factors influence the dielectric properties of LC materials. The value and the position of the dipole moment in the molecule, the ratio of the longitudinal to transverse dimensions of molecules, the lengths and flexibility of the terminal groups and the rigidity or an internal rotational freedom in the molecular cores seem to be the most important structural factors. In addition, the types of molecular arrangements in a LC phase (nematic or smectic) and the thermodynamic conditions are also important (first of all the temperature range of a phase). In order to investigate which factors are decisive in that respect, the dielectric properties of substances that

belong to one homologous series or those having slightly different structures, should be studied. In the present paper, results are reported for four substances having slightly different chemical structures (see Table 1). They exhibit a nematic phase in a broad temperature interval enriched by the smectic B (SmB) phase in one case. The dielectric spectra were recorded with the aid of an impedance analyser (1 kHz–30 MHz) and time domain spectroscopy (TDS, 10 MHz–3 GHz).

2. Experimental

The substances studied were synthesised in the Institute of Chemistry, Military University of Technology in Warsaw. Their chemical structures, together with the acronyms used and their phase transition temperatures, are presented in Table 1.

The dielectric relaxation spectra, $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$, in the nematic and SmB phases were recorded with the aid of a HP 4192A impedance analyser in the 1 kHz–30 MHz frequency range. The thickness of the samples was 0.7 mm. In the nematic phase the samples were oriented by a magnetic field of 0.7 T (either with perpendicular or parallel alignments). In the SmB phase the sample of 5CyCy2BF2 was not oriented as the magnetic field available in the experiment was ineffective in that respect. The temperature was stabilised within ± 0.2 K. The dielectric spectra in the isotropic phase, as well as for the perpendicular orientation of the samples in the nematic phases, were also recorded in the 10 MHz–3 GHz frequency range using TDS (5).

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Table 1. Chemical structures, acronyms used and phase sequences of the four substances studied.

Substance	Acronym	Phase sequence/°C
	3CyHeBF	Cr 59 N 150 I
	3CyCyBF2	Cr 48 N 124 I
	3Cy2CyBF2	Cr 38 N 104 I
	5CyCy2BF2	Cr 30 SmB 73 N 121 I

3. Results

Figure 1 presents the static dielectric permittivity components, ϵ_{\parallel} and ϵ_{\perp} , as a function of shifted temperature (i.e. normalised to the clearing point) of all of the four compounds studied. Below the nematic–SmB phase transition, the 5CyCy2BF2 sample could not be aligned and the permittivity dropped considerably. The dielectric anisotropy of these compounds in their nematic phase, $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, was recently analysed in terms of the order parameter, together with the results obtained by ^{13}C NMR and optical methods (6, 7). In this paper, attention will be focused on the dynamic properties of molecules in different phases.

The dielectric relaxation spectra in the isotropic phase of three substances are presented in the form of Cole–Cole plots (1, 2) in Figure 2. Due to the high temperatures of the clearing point, the spectra were

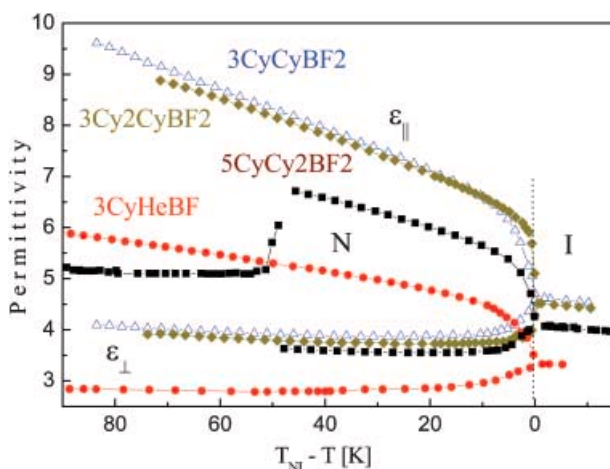


Figure 1. Permittivity components in the nematic and, in the case of 5CyCy2BF2, SmB phases of the four substances studied.

recorded at one temperature only. They were analysed as a superposition of two relaxation spectra of the Debye type:

$$\epsilon^*(\omega) - \epsilon_{\infty} = \frac{\delta\epsilon_1}{1 + i\omega\tau_1} + \frac{\delta\epsilon_2}{1 + i\omega\tau_2}, \quad (1)$$

where $\delta\epsilon_1 = \epsilon_{s1} - \epsilon_{\infty 1}$ and $\delta\epsilon_2 = \epsilon_{s2} - \epsilon_{\infty 2}$ are the dielectric increments, ϵ_s and ϵ_{∞} are the static and high-frequency permittivities, respectively, corresponding to particular relaxation processes and τ is the relaxation time.

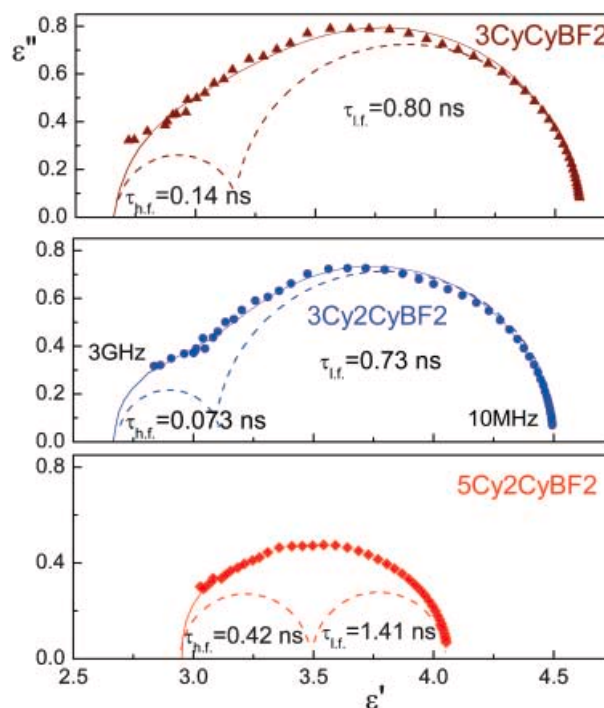


Figure 2. Cole–Cole plots for the isotropic phase of three compounds. The spectra were collected with the aid of the TDS setup at 127°C.

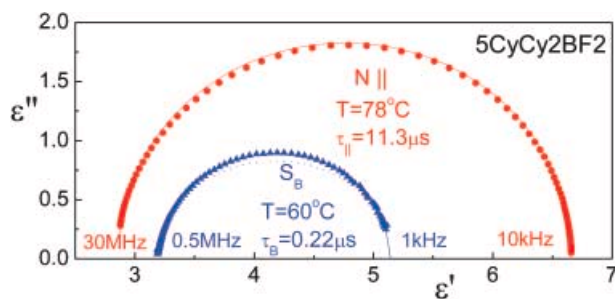


Figure 3. Cole–Cole plots from the relaxation spectra of 5CyCy2BF2 in the nematic (parallel alignment) and SmB phases.

The spectra in the nematic phase (parallel alignment) and in the SmB phase of 5CyCy2BF2 are excellently described by a single Debye equation (see Figure 3).

In contrast, the spectra measured for the perpendicular alignment of the nematic phase of 3CyCyBF2 and 3Cy2CyBF2 consisted of two processes (Figure 4), which were analysed using Equation (1). The relaxation times obtained from the analysis of the data for all the four substances investigated are presented in Figure 5 as Arrhenius plots.

4. Discussion

It can be seen from Figure 1 that the values of the permittivity components strongly depend on the chemical structure of the molecules, which affects the value and the location of the dipole moment. The permittivity values of 3CyHeBF are considerably lower than those measured for other substances. This is due to smaller value of the dipole moment (~ 2.1 D for 3CyHeBF, ~ 3.0 D for three other compounds (6, 7)). For 3CyCyBF2 and 3Cy2CyBF2 the permittivity

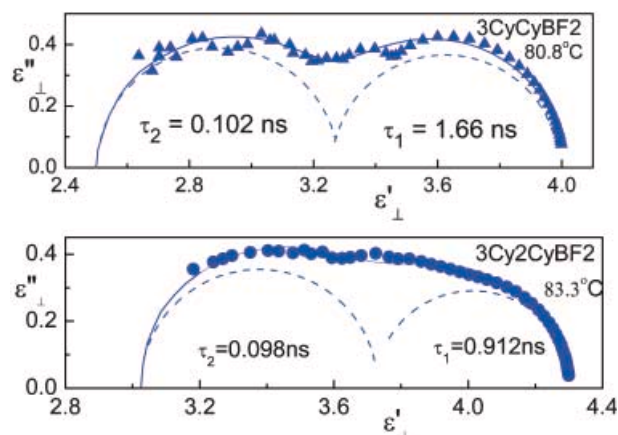


Figure 4. Cole–Cole plots from the TDS spectra of 3CyCyBF2 and 3Cy2CyBF2 in the nematic phase (perpendicular alignment).

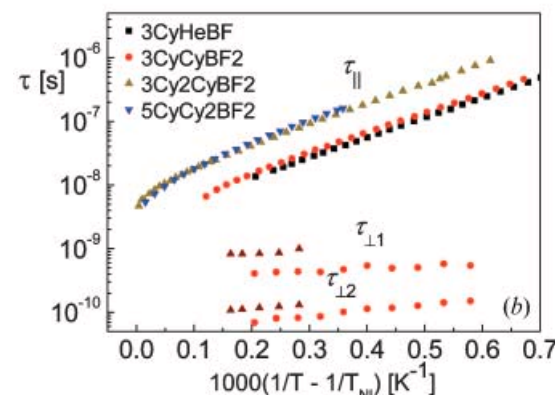
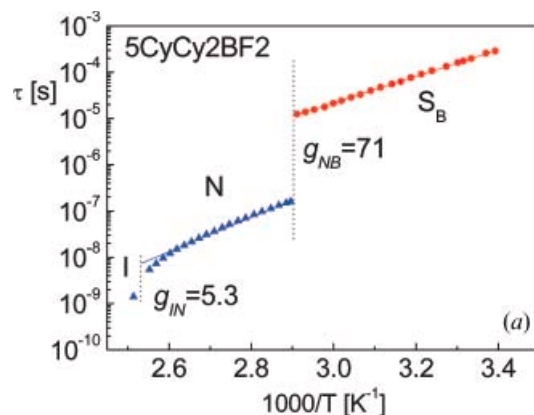


Figure 5. Arrhenius plot for the flip-flop process: (a) in the isotropic, nematic and smectic B phases of 5CyCy2BF2; (b) in the nematic phase of four substances (for the perpendicular orientation only two substances were studied). In the latter case the temperature scale was normalised to the clearing point in order to eliminate the shifts caused by different T_{NI} values.

values are practically the same in spite of the presence of the CH_2CH_2 bridging group in the latter case. On the other hand, the bridging group placed between the cyclohexyl and the fluorophenyl ring results in a marked lowering of the permittivity values for 5CyCy2BF2. To a small extent this is caused by the increase of the length of the alkyl tail (8, 9). However, the main effect must be attributed to the change of the direction of the long axis with respect to the net dipole moment characterised by the angle β . According to Maier and Meier (10) the dielectric anisotropy is given by

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} = \epsilon_o^{-1} N_0 h F \left[\Delta\alpha - F \frac{\mu^2}{2k_B T} (1 - 3 \cos^2 \beta) \right] S, \quad (2)$$

where ϵ_o is the permittivity of free space, N_0 is the number density ($= N_A \rho / M$; M = molar mass, ρ = density, N_A = Avogadro number) and S is the order parameter. The local field factors h and F are dependent upon the mean dielectric permittivity

$\langle \varepsilon \rangle = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$. In the case where the polarisability anisotropy $\Delta\alpha$ and the dipolar anisotropy differ considerably, i.e. $\Delta\alpha \ll F\mu^2/2k_B T$, as in the present case (6, 7), the increase of the β angle from 30° to 40° reduces $\Delta\varepsilon$ by a factor of 0.6.

A confirmation of this effect can be deduced from the spectra of the isotropic phase. The two relaxation processes observed (Figure 2) must be ascribed to the molecular rotations around the principal inertia axes: the low-frequency process to the rotation around the short axis, and the high-frequency one to the rotation around the long axis.

By applying the Onsager Equation (2),

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{N_0}{3\varepsilon_0} \frac{\mu^2}{3kT}, \quad (3)$$

separately to the low-frequency increment, governed by the longitudinal component μ_{\parallel} , and to the high frequency increment, governed by the transverse component μ_{\perp} , one can calculate the angle $\beta = \tan^{-1}(\mu_{\parallel}/\mu_{\perp})$. Taking into account the values of increments from the spectra presented in Figure 2 the following angles β were calculated: 30.7° for 3CyCyBF2, 28.5° for 3Cy2CyBF2 and 43.7° for 5CyCy2BF2. One can conclude therefore that the bridging group placed between the cyclohexyl and phenyl ring changes the reference frame of the molecule markedly. This means that the shape of molecules is strongly determined by the position of the bridging CH_2CH_2 group.

In the nematic phase the substances exhibit a positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$ at low frequencies (static case, see Figure 1). However, at MHz frequencies $\Delta\varepsilon$ changes its sign (Figure 6) due to the dispersion of the parallel dielectric permittivity component $\varepsilon'_{\parallel}(f)$ and a flat behaviour of the perpendicular component $\varepsilon'_{\perp}(f)$ over broad range of frequency. Such behaviour of the dielectric anisotropy has been also reported for other LC

compounds having different chemical structures (11). This effect enables a dual analysis of the displays based on these substances.

Figure 3 shows typical dielectric spectra in form of the Cole–Cole plots in the nematic (parallel alignment) and the SmB phase of 5CyCy2BF2. In both phases, only one relaxation process connected with the molecular rotation around the short molecular axis (the LF process) was observed in the frequency range covered in the experiment (1 kHz–30 MHz). In the nematic phase of other substances the same behaviour also was observed. The relaxation times in both LC phases of 5CyCy2BF2 are presented in Figure 5 a in form of the Arrhenius activation plot. As can be seen in the figure, the relaxation times are retarded at the nematic–SmB transition temperature by a factor $g_{\text{BN}} = \tau_{\text{B}}/\tau_{\text{N}} = 71$, whereas the retardation occurring at the isotropic–nematic transition is one order of magnitude smaller, i.e. $\tau_{\text{N}}/\tau_{\text{I}} = 5.3$. At the same time, the activation barrier hindering the flip-flop molecular motion is considerably smaller in the SmB phase in comparison to the nematic phase of 5Cy2CyBF2 (see Table 2). Similar behaviour has also been observed for other substances (12), and by means of ^2H NMR relaxation studies (13).

It is characteristic that the TDS spectra recorded for the perpendicular oriented samples in the nematic phase of compounds with and without the bridging group (3Cy2CyBF2 and 3CyCyBF2, respectively) exhibit two relaxation processes separated roughly by one order of magnitude in the relaxation times scale (Figures 4 and 5(b)). The poor quality of the spectra and a limited range of the frequency available (up to 3 GHz) did not allow us to analyse the observed relaxation processes exactly. However, there is no doubt that two different molecular rotations around the long axis take place in the nematic phase of both compounds. Because the probing dipole moment is given by the fluorine atoms attached to the benzene ring one can suppose that the LF part is

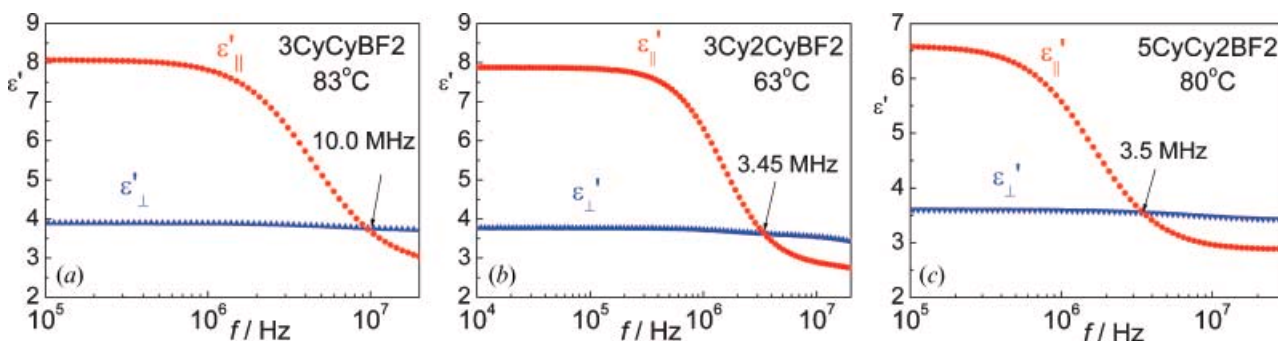


Figure 6. Dispersion spectra recorded for two alignments of 3CyCyBF2 (a), 3Cy2CyBF2 (b) and 5CyCy2BF2 (c) in the nematic phase. The chosen temperatures correspond to the same $(T_{\text{NI}} - T)$ values. The crossover frequencies are indicated by arrows.

Table 2. Activation enthalpy values calculated for the relaxation processes observed in two alignments in the nematic and in the SmB phase of the four substances studied.

Substance	Phase	$\Delta H/\text{kJ mol}^{-1}$
3CyHeBF	N	60.0
3CyCyBF2	N	60.5
3Cy2CyBF2	N	64.0
5CyCy2BF2	N	72.2
	SmB	55.4

connected with the spinning motion of the whole molecule, whereas the HF one corresponds to the faster internal rotations around the *para* axis of the phenyl ring.

Figure 5(b) presents comparisons of the relaxation times obtained for all four compounds studied in the nematic phase in the parallel, and, only for 3CyCyBF2 and 3Cy2CyBF2 samples, perpendicular orientations. The $1000(1/T - 1/T_N)$ abscissa is used in Figure 5(b) in order to avoid the shifts caused by different clearing temperatures. Clear distinction of the relaxation rates caused by the different molecular length is visible. The activation enthalpy values calculated using the Arrhenius equation $\tau = \tau_0 \exp(\Delta H/RT)$ (where R is the gas constant) for the LF process in the SmB of 5CyCy2BF2 and the nematic phase of all substances are listed in Table 2. For the HF processes in the nematic phase of 3CyCyBF2 and 3Cy2CyBF2, the estimated barrier is approximately 22 kJ mol^{-1} .

5. Conclusions

The results of dielectric studies performed for four three-ring fluorinated compounds allow us to note that:

- (1) In spite of similarity in the chemical structure, the substances studied exhibit detectably different dielectric properties.
- (2) In that respect a key role seems to be played by the position of the CH_2CH_2 bridging group: when it separates the phenyl and cyclohexyl rings the shape of the molecule, and thus the dielectric properties of the substance, changes considerably.
- (3) The angle formed by the dipole moment with the long molecular axis could be estimated from the relaxation spectra of the isotropic phase.
- (4) The low-frequency relaxation process corresponding to the molecular flip-flop rotation is a monodomain one in both the nematic and SmB phase.
- (5) In passing from the nematic to the SmB phase a marked elongation of the low-frequency relaxation time is observed, whereas the activation enthalpy becomes smaller.
- (6) The high-frequency relaxation process recorded for the perpendicularly oriented nematic phase is split into two processes indicating an independent rotation of the whole molecule and its fluorophenyl part around the long molecular axis and the *para*-axis, respectively; this indicates a weak coupling between the polar and non-polar parts of the molecules.
- (7) The substances with two fluorine substitutes change the sign of the dielectric anisotropy at MHz frequencies, which can be useful for the design of the dual addressing displays.

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