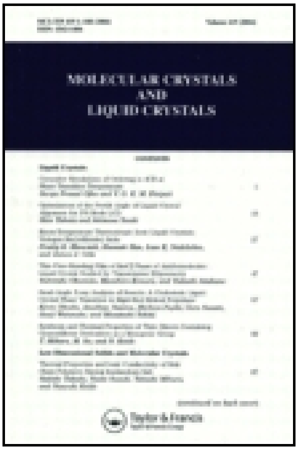

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Dielectric and X-ray Studies of Substances with the Smectic B phase

Stanisław Urban [a] , Joanna Czub [a] , Jan Przedmojski [b] , Roman Dąbrowski [c] & Marco Geppi [d]

[a] Institute of Physics, Jagiellonian University, Reymonta, Kraków, Poland

[b] Physics Department, Warsaw University of Technology, Warsaw, Poland

[c] Institute of Chemistry, Military University of Technology, Warsaw, Poland

[d] Department of Chemistry and Industrial Chemistry, University of Pisa, Italy

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Dielectric and X-ray Studies of Substances with the Smectic B phase

Stanisław Urban
Joanna Czub
Institute of Physics, Jagiellonian University, Reymonta, Kraków, Poland

Jan Przedmojski
Physics Department, Warsaw University of Technology, Warsaw, Poland

Roman Dąbrowski
Institute of Chemistry, Military University of Technology, Warsaw, Poland

Marco Geppi
Department of Chemistry and Industrial Chemistry, University of Pisa, Italy

Several substances of different chemical structures exhibiting the smectic B polymorphism in a wide temperature range [accompanied by the nematic (N) phase in few cases] were studied with the aid of the dielectric relaxation and X-ray methods. The dielectric relaxation time $\tau_{\|}$ *connected with the end-over-end rotations of molecules was determined. It elongates considerably at the N–B transition whereas the activation barrier hindering the flip–flop motion* decreases. *The parameters of the hexagonal unit cell were determined as functions of temperature. The packing parameter,* $p = ZV_{mol}/V_{u.c.}$, *was calculated which exceeds value of c. 0.6, thus is typical for the plastic crystals. The dynamical properties of molecules are discussed in relation to their packing in the smectic layers. The applicability of the Arrhenius equation to calculation of the activation barrier from the temperature dependence of* $\tau_{\|}$ *in the B phase seems to be doubtful in view of the experimental data collected. It was concluded that all examined substances have rather the hexatic than the crystalline B phase.*

Keywords: dielectric relaxation; nematic; smectic B; X-ray diffraction

Address correspondence to Stanisław Urban, Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland. E-mail: ufurban@cyf-kr.edu.pl

1. INTRODUCTION

Liquid crystalline (LC) substances form variety of smectic phases characterized by the layer structures [1,2]. The *liquid*-like phases with no order of molecular centers of mass in the layers (S_A, S_C) can be distinguished from the *crystal*-like phases where such arrangements within the layers (and probably between the layers) are present (S_B, S_E, $S_G, \ldots$). In particular, the S_B phase is characterized by the hexagonal arrangement of molecules which are orthogonal to the layer planes. However, one can distinguish between the hexatic B (S_{Bhex}) phase exhibiting a long range *bond orientational* order, and the crystalline B (S_{Bcr}) phase exhibiting a long range *translational* order [3–6]. The packing of molecules may be described by a herringbone structure without or with the 3-dimensional correlations, respectively. Obviously, such a situation has to differentiate the molecular dynamics in particular types of the B phase. Especially the rotational motions of molecules around the short axes should be affected by the subtle differences between the structures. The dielectric spectroscopy is a powerful tool for studying such motions provided that the molecules possess the longitudinal dipole moment. The most comfortable situation for that purpose would be studying a substance which has two B phases appearing subsequently with changing temperature. Such a phase sequence has been observed by Górecka *et al.* [7,8] for several materials with the intramolecular hydrogen bonds, but the studies of the dynamical properties of molecules by means of the EPR method were limited to the fast rotational motions around the long axes only [9].

The dielectric studies of compounds forming the B phase were carried out by several groups [10–17]. The relaxation process in the kHz region was observed for all cases except for one [15]. It has been attributed to the molecular rotations around the short axes (end-over-end relaxation of the longitudinal component of the dipole moment). Two common features of the process have to be pointed out: a drastic slowing down of the molecular motion around the short axis when a liquid-like phase passes into the S_B phase, and only a slight change of the corresponding activation barrier. However, it seems that the problem of mutual relations between the dynamics of molecules and their arrangements in different types of the B phase has not been yet well recognized.

In the dielectric studies of smectic B phases by Kresse *et al*. [10–13] the main criterion for distinguishing between the S_{Bhex} and S_{Bcr} phases was based on the retardation of the longitudinal relaxation time $\tau_{\|}$ at the transition from the nematic N to B phase. The retardation factor $g = \tau_B/\tau_N$ determined for several substances [13] amounts from 30 up to 2000. At the same time the activation barrier hindering the flip-flop motions in both phases does not increase at the transition $N \rightarrow S_B$. The entropy change at the N/S_B transition is large (between 8 and 16 J mol^{-1} K^{-1}) and no correlation with the *g*-value is noted [13]. On that basis Kresse *et al.* concluded that all studied B–phases were the S_{Bcr} ones. On the other hand, Gouda *et al.* [15] found that in the chiral smectic B^*_{Cr} phase the molecular rotation around the short axis was frozen whereas the rotation around the long axis persisted.

In the present work we applied the following experimental strategy: Several substances of different chemical structures which showed the smectic B polymorphism in a wide temperature range were chosen. In some of them the B phase was accompanied by a nematic phase. The dynamic behavior of molecules studied by the dielectric spectroscopy method was confronted with the X-ray observations yielding the information about the molecular packing in the smectic layers.

2. EXPERIMENTAL

The names of compounds studied together with transition temperatures and acronyms used are listed in Table 1. All of them were synthesized in the Institute of Chemistry, Military University of Technology, Warsaw.

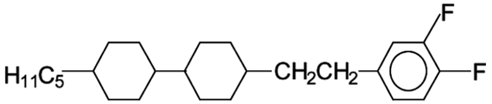
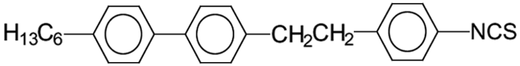
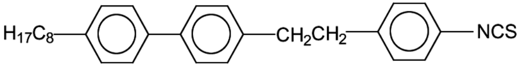
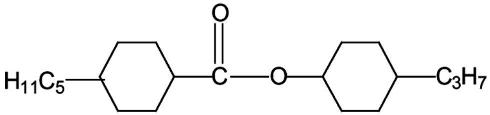
The dielectric relaxation spectra, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, were recorded by means of an impedance analyzer HP 4192 A in the frequency range 100 Hz–30 MHz. The samples in the N phase were oriented by a magnetic field of 0.8 T. Two experimental geometries were applied: $E||B$ and $E\perp B$, which enabled to measure the $\varepsilon_{||}$ and $\varepsilon_{\perp}$ permittivity tensor components, respectively. The thickness of the samples were 0.7 mm. The temperature was stabilized within ±0.2 K.

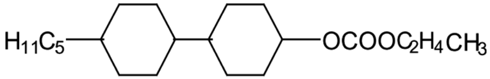
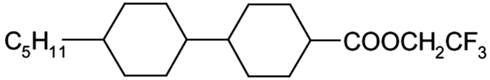
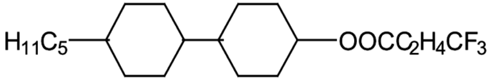
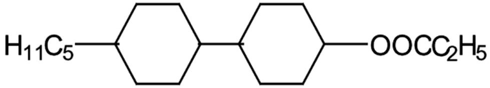
The X'Pert (PHILIPS) diffractometer equipped with the Cu radiation monochromatized by an absorption Ni filter and a proportional counter was used. The intensity of diffracted beam was measured by changing the scattering angle step by step while temperature was constant within ±0.1 K. Guinier camera used had 114 mm diameter. The diffracted rays were focused symmetrically. The sample was placed in holes of the net of 0.5 mm thick.

3. RESULTS

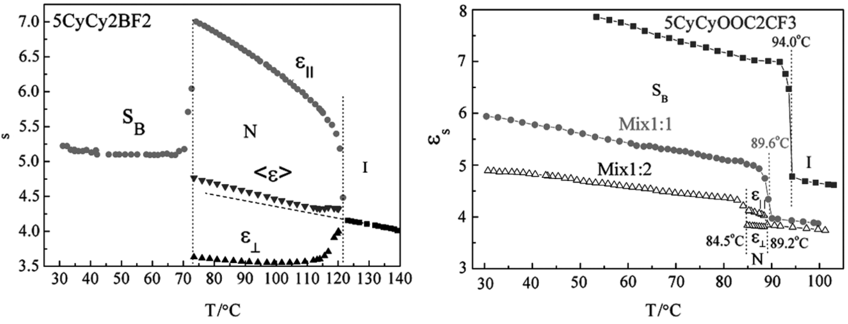
a) Dielectric measurements. A typical temperature dependence of the static permittivity tensor components for substances with the N and B polymorphism and those with the B phase alone are shown in

TABLE 1 Chemical Structure, Acronym Used and Phase Sequence of Substances Studied

	Substance	Acronym	Phase sequence
1		5CyCy2BF2	Cr ~ 25°C–S_B–73.3°C–N–121.3°C–I
2		6BB2B-NCS	Cr–70°C–S_B–100°C–N–132°C–I
3		8BB2B-NCS	Cr–60°C–S_B–104°C–N–130°C–I
4		5CyCOOCy3	Cr–25°C–S_B–37.2°C–N–52.7°C–I

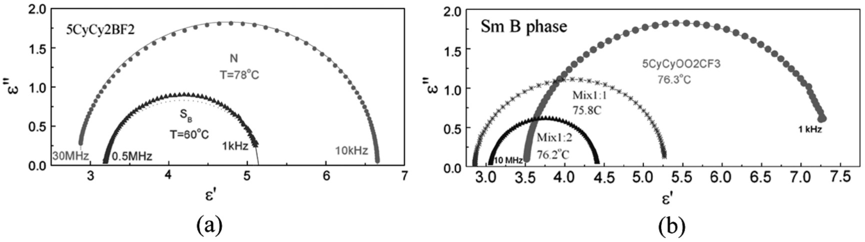
5		5CyCyOCOO3	Cr–38.9°C–S_B–63°C–N–80.2°C–I
6		5CyCyCOO1CF3	Cr–38.5°C–S_B–42°C–I
7		5CyCyOOC2CF3	Cr–60°C–S_B–94°C–I
8		5CyCyOOC2	Cr–72.5°C–N–90.1°C–I
9	5CyCyOOC2CF3:5CyCyOOC2 1:1	Mix 1:1	Cr ~ 30°–S_B–89.6°C–I
10	5CyCyOOC2CF3:5CyCyOOC2 1:2	Mix 1:2	Cr–50°C–S_B–84.5°C–N–89.2°C–I

Figures 1a, b. All measurements were carried out with a step-wise decreasing of temperature starting always from the isotropic phase. In this way the B phase could be supercooled considerably (sometimes by 40 K). For 8BB2B-NCS a bi-phase region was observed in which the N and B phases coexisted even by a few day period. In the case of 5CyCyOOC2CF3 and its mixture with 5CyCyOOC2 in 1:1 molar proportion (Mix 1:1) the permittivity increases at the Is – B phase transition indicating some parallel order of the sample in the B phase due to, perhaps, an influence of a capacitor's walls (**E** and **B** fields did not change the permittivity in the B phase). For the 1:2 mixture (Mix 1:2) a nematic phase appears in a narrow range of temperature (see Table 1). The parallel orientation of the N phase persisted to the B phase as well. The permittivity values in the isotropic phase increase considerably when the CH_3 group is replaced by the CF_3 group indicating the increase of the dipole moment of the molecules (according to the well known Onsager equation $\varepsilon_s \sim \mu^2$). For other samples the transition from the oriented N to the B phase resulted in "averaging" of the permittivity values as is shown in Figure 1a. The relaxation spectra are presented in the form of the Cole–Cole plots in Figure 2 that can nicely be described by semicircles. It means that in all LC phases the relaxation process can be considered as a mono-domain or Debye-type process characterized by the longitudinal relaxation time $\tau_\parallel$. Using the Arrhenius equation, $\tau_\parallel = \tau_0 \exp(\Delta H/RT)$, the activation enthalpy ΔH was calculated. Figures 3 and 4 present the Arrhenius plots for particular substances, whereas the ΔH values are gathered in Table 2. In cases when the B phase exists in broad temperature ranges the Arrhenius plots can be divided into two parts



(a) (b)

FIGURE 1 Static dielectric permittivity vs. temperature for (a) 5CyCy2BF2, and (b) for 5CyCyOOC2F3 and its two mixtures with 5CyCyOOC2.



(a) (b)

FIGURE 2 Cole-Cole plots for 5CyCy2BF2 in the N and B phases (a), and for a neat 5CyCyOOC2F3 and its two mixtures with 5CyCyOOC2 in the B phase (b).

with different slopes of the fitted lines (Figs. 3b and 4a). The low temperature part shows a reduced slope in relation to the high temperature one which indicates a lowering of the activation barrier–see Table 2. A similar effect was observed by Schacht *et al*. [18] in the case

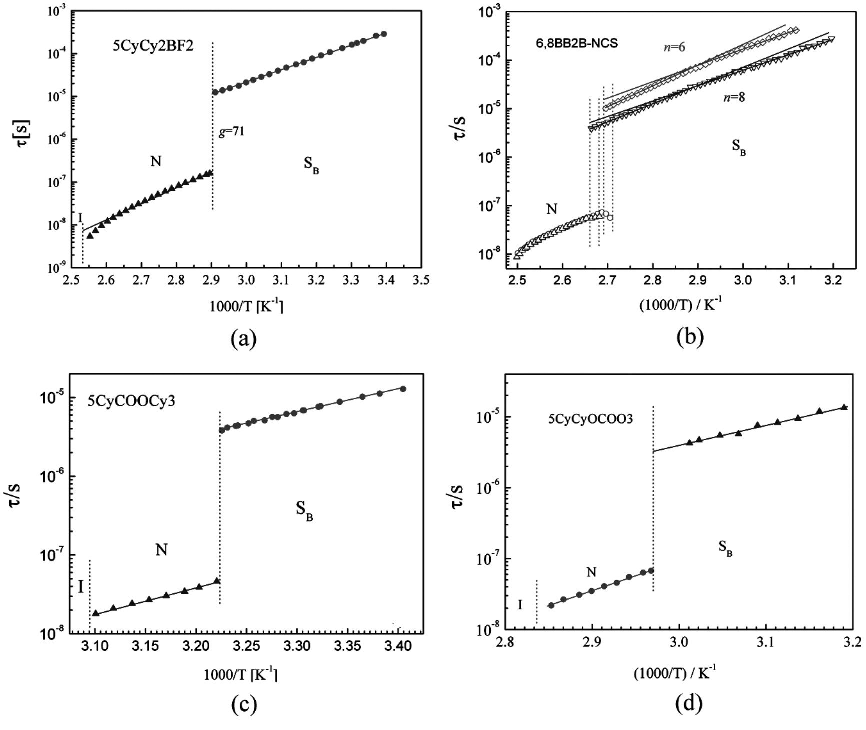
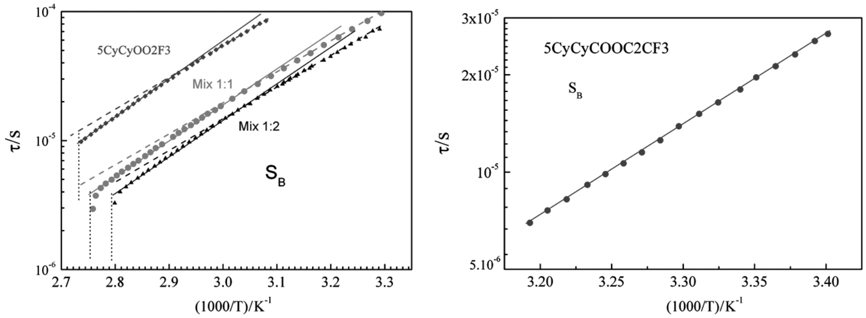


FIGURE 3 Arrhenius plots for substances with the N and S_B polymorphism.



(a) (b)

FIGURE 4 Arrhenius plots for substances with the S_B polymorphism. In the case of Mix 1:2 the N phase exists in a narrow temperature range and the relaxation time shows a strong temperature dependence due to pretransitional effects and was not displayed in (a).

of dielectric relaxation in the crystal E phase. We expected that the X-ray studies can throw more light on that unusual behavior.

b) X-ray measurements. A typical X-ray pattern recorded in the B phase is presented in Figure 5 for 5CyCy2BF2. The indexing of the peaks is based on the orthorhombic unit cell with $a = 2b \cos 30^\circ$ resulting from the hexagonal unit cell. A strong (001) Bragg reflection allowed us to determine the layer thickness d in the B phase of particular substances with a good accuracy (±0.01 Å or better). Figure 6a shows the d-values versus temperature for 6BB2B-NCS and 8BB2B-NCS

TABLE 2 The Retardation Factor g and the Activation Enthalpy ΔH (in kJ/mol) Calculated from the Data Presented in Figs. 3a–3f. The Errors in ΔH Values are c. 5% for the N Phase and c. 3% for the B phase

			Smectic B		
Substance	$g_{BN} = \tau_B/\tau_N$	Nematic	Average	Low T	High T
5CyCy2BF2	71	72	55		
6BB2B-NCS	150	74	74	65	79
8BB2B-NCS	75	83	66	61	72
5CyCOOCy3	84	64	55	–	–
5CyCyOCOO3	46	81	54	–	–
5CyCyCOO1CF3	–	–	54	–	–
5CyCyOOC2F3	–	–	53	49	56
Mix 1:1	–	–	51	46	54
Mix 1:2	317	–	50	46	55

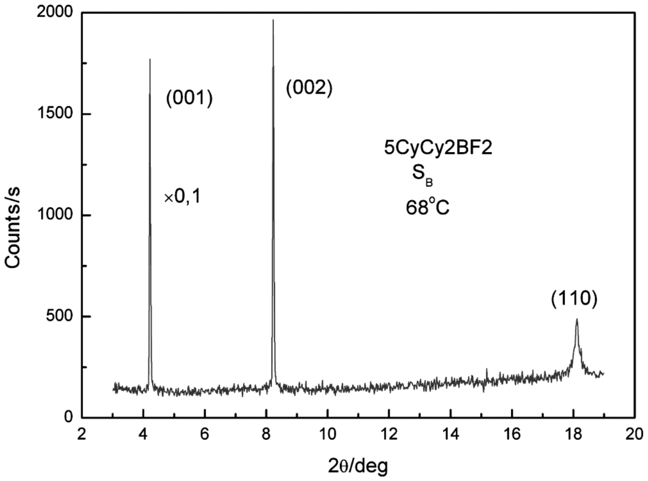


FIGURE 5 Diffractogram of 5CyCy2BF2 in the B phase.

obtained in the cooling run. The *d(T)* plots show changes at temperatures corresponding roughly to the melting points of both substances. The effect is more pronounced for the longer homologue. It is seen better when the ratio $d(T)/d_m$ is plotted (Fig. 6b), with d_m values

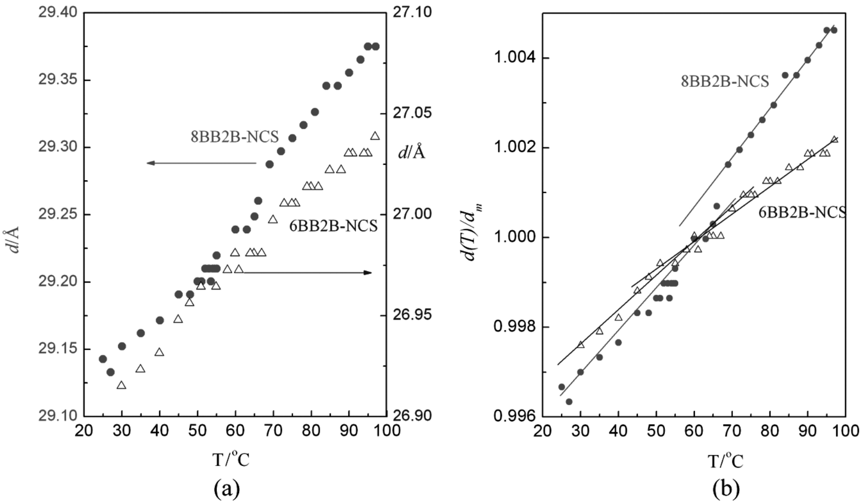


FIGURE 6 The layer thickness d (a) and the ratio of d/d_m (b) for 6BB2B-NCS and 8BB2B-NCS (d_m was taken at the melting point).

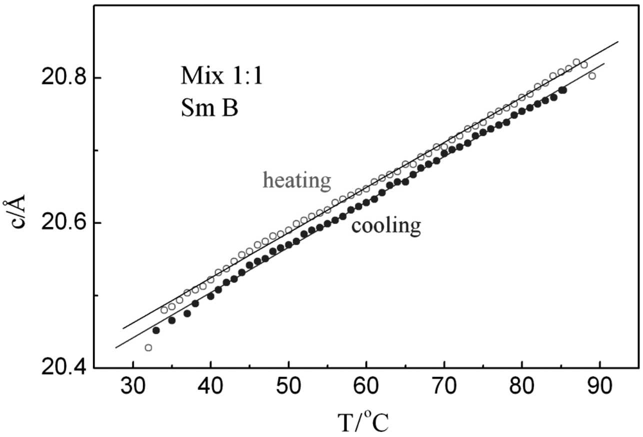


FIGURE 7 The layer thickness versus temperature for Mix 1:1.

taken at the points where the straight lines cross in Figure 3b. It seems therefore that a small change of the molecular packing takes place at these points which might influence the molecular dynamics (compare Figs. 3b and 6b). However, no change was observed in the *d(T)* behavior for the Mix 1:1, Figure 7, which could explain the bend in the Arrhenius plot shown in Figure 4a. The unit cell parameters for the neat 5CyCyOOC2F3 as well as for the Mix 1:1 were determined in broad temperature intervals (Fig. 8). All parameters as well as the unit cell volumes change smoothly with temperature. It can be noticed that a dilution of the 5CyCyOOC2F3 molecule in the slightly shorter 5CyCyOOC2 matrices results in shortening of all lattice constants. The unit cell parameters were also determined for three other substances in the B phase. They are gathered in Table 3. Using the Cerius program the volume V_m and the length l of molecules were calculated for the most extended conformation of the alkyl tails. Assuming two molecules in the cell the packing parameter $p = 2V_m/V_{uc}$ was calculated for particular substances (which characterizes the free volume the molecules have in the cell).

3. DISCUSSION

As it was said, the aim of the work was to search for the relationships between the dynamical properties of molecules and their arrangements in the smectic B phase. In spite of very different chemical structures of molecules (see Table 1) one can note several common features of the

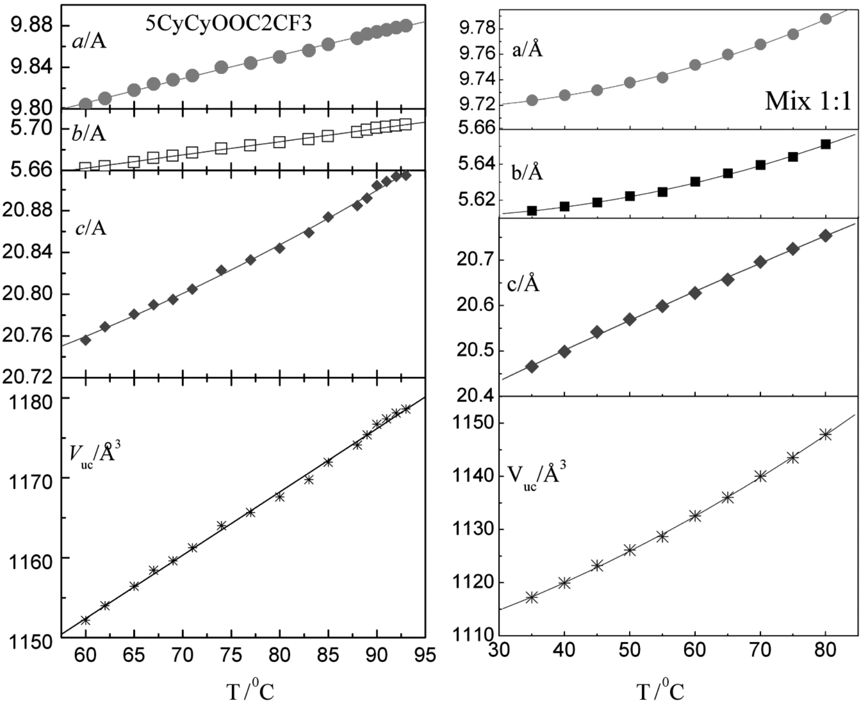


FIGURE 8 Lattice constants and the volume of the unit cell as functions of temperature in the B phase of 5CyCyOOC2CF3 and Mix 1:1.

TABLE 3 Unit Cell Parameters, the Volume of Unit Cell V_{uc}, Volumes of Molecules V_m Calculated with the Aid of the Cerius Program, and the Packing Parameter p for Particular Substances

Substance	5CyCy2BF2	6BBAB	8BBAB	5CyCyOOC2F3	Mix 1:1
a [Å]	9,87	9,02	9,02	9,84	9,75
b [Å]	5,70	5,21	5,21	5,68	5,64
c [Å]	22,04	27,3	29,5	20,8	20,6
l [Å]	22,4	25,6	28,3	21.3	21.3[a]
V_{uc} [Å^3]	1240	1269	1377	1163	1133
V_m[Å^3]	380,38	380,33	418,0	355,12	338,19[b]
$p = 2V_m/V_{uc}$	0,614	0,600	0,607	0,611	0,597

[a] for shorter member of the mixture $l = 19{,}5$ Å.

[b] mean value of the two components.

results obtained (known also in other cases as well [10–17]): *i*) the low frequency process is a monodispersive one; *ii*) in the case of the N–B polymorphism no systematic behavior of the retardation factor $g_{NB} = \tau_B/\tau_N$ can be noticed; and *iii*) the activation enthalpy for the flip-flop motion of molecules is usually greater in the liquid-like N than in the crystal-like B phase. A new feature observed in the present study concerns the division of the activation plot into two parts when the B phase exists in a broad temperature range (Figs. 3b, 4a). It is characteristic that the activation barrier for the flip-flop motion is smaller for the low temperature part, hence for a more ordered part of the phase. From the point of view of molecular dynamics one can suppose that two different B phases exist in the mentioned above cases. In the case of two members of *n*BB2B-NCS series a small discontinuity of the *d(T)* plots (Fig. 6) might indicate some changes in the molecular packing. However, for the Mix 1:1 no changes was detected in the *d(T)*, Figure 7, as well as in the intensity and the full with at half maximum of the (001) reflection for neither cooling nor heating runs.

The problem of identification of the B phases seems to be rather difficult due to a very limited number of the Bragg reflections observed [usually only (001), (002) and (110) reflections are recorded – see Fig. 5]. The measurements of the extent of the in-plane positional correlations in respect to the interlayer correlations can be decisive in that case [3–5,7,8]. Unfortunately, such measurements could not be done in the present studies. Therefore we tried to select those features of the X-ray and dynamical results which could be helpful to identification of the type of B phase in the substances studied.

Many efforts were undertaken in order to detect possible differences between the high and the low temperature parts of the B phase and/or to establish with which B phase one deals in particular substances. The measurements were made using the Guinnier camera, the diffractometer and the polarizing microscope. Unfortunately, no evident origin of the observed effects could be found although small changes in the textures within another orthogonal phase, the E phase, were already recorded [18]. However, the fact that the observed Bragg reflections are placed on an incoherent background (especially at higher scattering angles) may indicate rather limited long-range ordering of the molecular centers of mass in the "lattice".

Table 3 contains the X-ray data for the B phase of five substances. In all cases the *c*-values (the layer thickness) are comparable with the molecular lengths for the most extended conformation of terminal groups. The values of the *b*-parameters are typical of substances with aromatic cores [6,22] and should correspond to the molecular diameters. If so, the lattice constant a characterizes the intermolecular distance in the cell. The ratio $a/l \sim 0{,}32 \div 0{,}46$ seems to indicate how large fluctuation of the molecular positions has to occur in order to create a sufficient space for the molecular flip-flop motion. Another measure of the necessary volume fluctuation comes from the high pressure studies of the low frequency relaxation process in the LC phases [25,26]. The so-called activation volume exceeds *c*. 20% of the molar volume.

It is characteristic that the packing parameter values, $p \sim 0.60$, are typical for the plastic crystalline (ODIC) phases [19,20]. On the other hand these values are smaller than those calculated for other compounds in the crystalline E phase [21,22] in which the molecular rotations around the short axes are also present ($p \sim 0.63$–0.67).

The above mentioned facts, as well as relatively small retardation of the molecular rotation around the short axes (Table 2), let us suggest that all examined substances have the hexatic rather than the crystalline B phase.

It is interesting to note that the packing parameter for the Mix 1:1 is smaller than for the neat 5CyCyOOC2F3 substance which well correlates with a slight lowering of the activation barriers (Table 2). Also the relaxation times become markedly shorter after dilution of the polar molecules in non-polar solvent (Fig. 4a). Similar effects were observed for other mixtures as well [23,24].

4. SUMMARY

Common studies of the molecular dynamics connected with the end-over-end rotations of rod-like molecules and their packing in the crystalline B phase allow us to better understand of the relationship between both factors. The molecules in the B phase are arranged in the hexagonal structure but due to relatively weak intermolecular interactions they form rather loosely packed system – only c. 60% of the unit cells are occupied by the molecular bodies. It facilitates the long-range fluctuations of the molecular centres of mass which creates a space necessary for the voluminous flip-flop jumps of molecules. A large number of the "lattice" defects, typical for the ODIC phases [14,19,20], is a favorable factor in that respect.

However, two facts have to be pointed out once more: at the N–B transition the relaxation times *elongates* considerably whereas the activation barrier hindering the flip-flop motion *decreases*. Moreover, in the low temperature part of the B phase the barrier hindering this motion is smaller than in the high temperature part. Thus, the question might be put forward: is the Arrhenius-type equation applicable for the activation process governed by the strong rotation – translation coupling taking place in the crystal-like smectic phases?

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