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^{2}H NMR and X-Ray Studies of a Substance Exhibiting Crystal-Like Smectic Phases

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^{2}H NMR and X-Ray Studies of a Substance Exhibiting Crystal-Like Smectic Phases

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DSC, polarizing optical microscopy and X-ray diffractometry were used to investigate the mesomorphic behaviour of 4-n-butyl-4′-acetyl-biphenyl, which resulted to exhibit a smectic E and, possibly, a smectic K phase. Additionally, ^{2}H NMR spectroscopy was applied on a selectively deuterated sample to study the properties of alignment of the mesophases within a magnetic field, as well as to characterize molecular dynamics. Two motional processes were found to be active in the smectic E phase, namely fast π-flips of the benzene rings and molecular self-diffusion about the herringbone bidimensional lattice of the layers. No molecular overall diffusional motions were observed by either ^{2}H NMR spectroscopy or dielectric relaxation measurements.

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INTRODUCTION

Substances having rod-like shape of molecules are able to form many calamitic liquid crystalline (LC) phases that differ by the degree of the orientational and/or translational order of the molecules. In some cases a small difference in the chemical structure of compounds results in a very different phase behavior. For example, two well known alkyl-biphenyl homologous series, nCB and nBT, differing in the terminal substitute only (CN and NCS, respectively), form substantially different mesophases for small n values: a nematic in the first case and a crystal-like smectic E phase in the latter case [1]. Therefore, it seemed valuable to test how the phase behaviour would change if a different terminal group was attached to the alkyl-biphenyl moiety. In this work we studied a molecule having the $COCH_3$ terminal group and $n = 4$ (4-*n*-butyl-4′-acetyl-biphenyl). Several experimental methods were employed to characterize its physical properties: DSC, polarizing optical microscopy and X-ray diffractometry gave information on the mesomorphic behaviour, while ^2H NMR and dielectric spectroscopies were used to get insights into molecular dynamics.

EXPERIMENTAL

4-*n*-butyl-4′-acetyl-biphenyl-d_4 (**1**), selectively deuterated as shown in Figure 1, was synthesized according to the route described in [2]. 4-*n*-butyl-4′-acetyl-biphenyl is a by-product in the synthesis of the 4-*n*-butyl-4′-isothiocyanato-biphenyl (4BT), which exhibits a crystal E phase.

X-ray measurements were performed as reported in references [3,4].

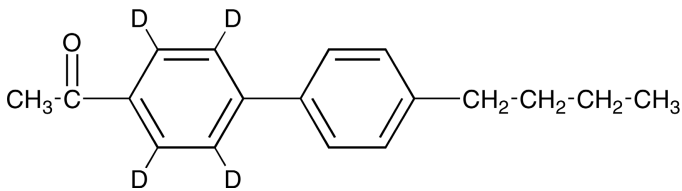

FIGURE 1 Molecular structure of **1**.

^2H NMR experiments were carried out on a Varian Infinity Plus 400 spectrometer, working at 61.4 MHz for deuterium, equipped with a goniometric T3 probe. The quadrupolar echo sequence was used, with an echo delay of 12 μs, a 90° pulse of 3.0 μs and a relaxation delay of 1 s. Temperature was controlled within 0.1°C. Angular orientation of the sample with respect to the external magnetic field was set with a precision of 0.07°.

RESULTS AND DISCUSSION

The DSC traces of **1** exhibit two peaks on the heating run (see Fig. 2) corresponding to a first phase transition at 88.4°C (5.40 kJ/mol) and the clearing point at 93.1°C (13.75 kJ/mol). However, on cooling the sample, the high-temperature phase supercools down to 72.6°C.

The textures of the two phases, as obtained by polarizing optical microscopy, are shown in Figure 3, and they do not seem typical of crystalline phases.

In order to identify the observed phases, X-ray measurements were performed: typical patterns are shown in Figure 4.

The Bragg reflections observed in the high-temperature phase (Fig. 4a) correspond to a orthorhombic unit cell with the lattice parameters displayed in the inset. Therefore, this phase can be identified with a crystal-like smectic E phase; this attribution was additionally confirmed by a miscibility test using 4BT as reference sample. The X-ray pattern of the

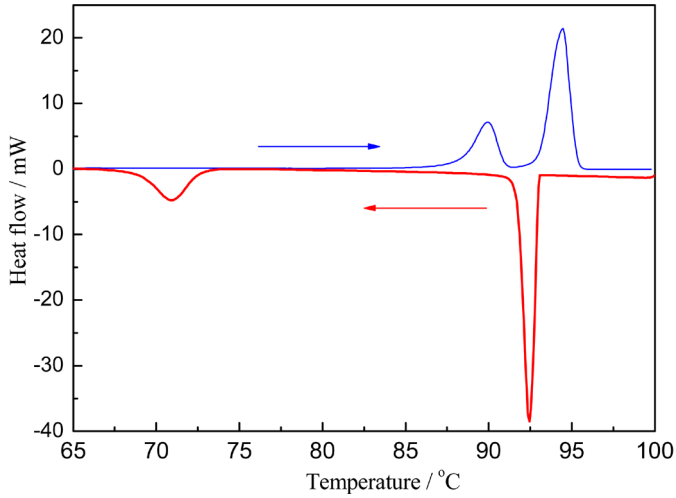

FIGURE 2 DSC traces of **1** obtained with a 5°C/min scan rate. (See COLOR PLATE VII)

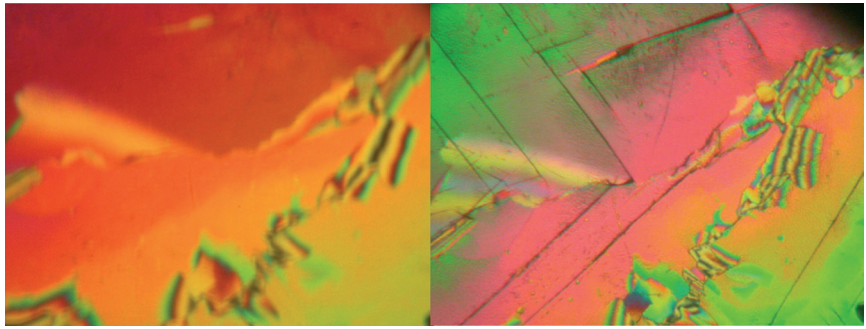

FIGURE 3 Textures of **1** in the high- (left, 90°C) and low-temperature (right, 65°C) phases. (See COLOR PLATE VIII)

low-temperature phase (Fig. 4b) is very similar to that recorded for the smectic E phase, but all the reflections are slightly shifted towards larger angles. Slow cooling of the sample led to a biphasic region of about 5

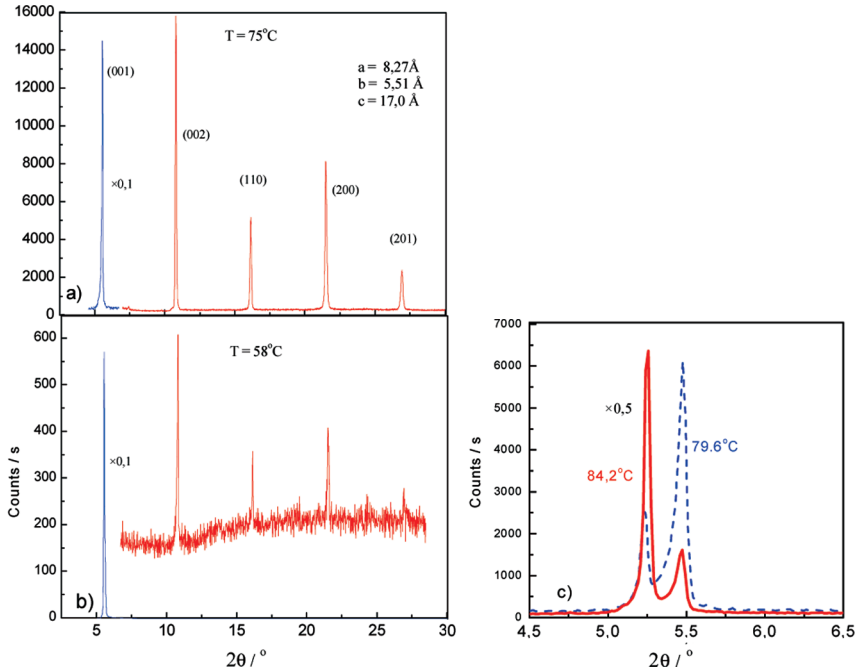

FIGURE 4 X-ray patterns recorded in the high- (a) and low-temperature (b) phases of **1**. (c) Detail of the first reflection in a biphasic region recorded on a slow cooling run. (See COLOR PLATE IX)

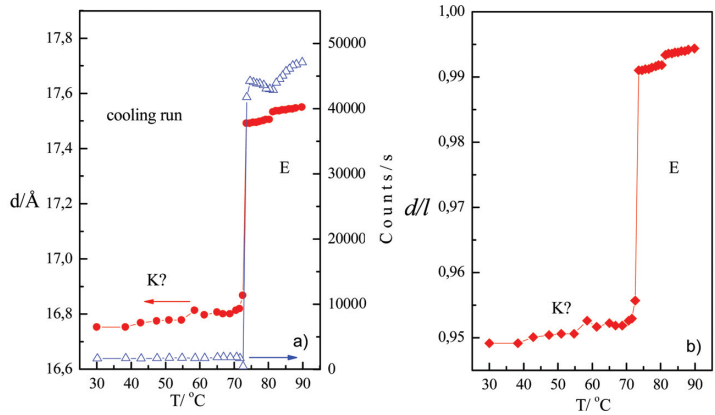

FIGURE 5 Temperature dependence of (a) layer thickness and intensity of the (001) reflection, and (b) ratio between the layer thickness d and the molecular length l. (See COLOR PLATE X)

degrees, in which both sets of reflections were seen (Fig. 4c). The X-ray pattern of the low-temperature phase did not change after keeping the sample several hours at room temperature. Special attention was paid to the temperature dependence of the layer thickness d and the intensity of the (001) reflection (see Fig. 5a). Within the smectic E phase a small discontinuity in both quantities was detected, which may be associated to a slight change in the molecular arrangement, like that observed in another substance exhibiting the same phase [5]. A jump-wise decrease of both quantities accompanies the phase transition. Taking into account the molecular length l (estimated using the HyperChem Release 7.5 program) the ratio d/l was calculated (see Fig. 5b). In the smectic E phase the layer thickness is substantially equal to the molecular length, whereas in the low-temperature phase the molecules must be tilted by an angle of about 18° with respect to the layer normal. Therefore, this phase can be tentatively identified with a crystal-like smectic K phase.

The unit cell parameters of **1** give a unit cell volume $V_{u.c} = 774.7\,\text{Å}^3$, whereas a value of $828.8\,\text{Å}^3$ was previously obtained for the isothiocyanato analogue 4BT. The volumes of the molecules V_{mol}, calculated using Cerius2 (Accelrys) are equal to $246.51\,\text{Å}^3$ and $264.07\,\text{Å}^3$ for **1** and 4BT, respectively. Assuming that two molecules are present per unit cell, an identical value of 0.64 for the packing parameter $p = 2V_{mol}/V_{u.c.}$ is obtained for the two substances in their smectic E phase. This indicates that the molecules have relatively large free space to perform overall reorientational motions.

Therefore, in order to get insights into the dynamic behavior of **1**, we performed both dielectric relaxation and ^{2}H NMR measurements. The dielectric measurements were carried out in the frequency range 100 Hz–1 MHz. At the transition between the isotropic and smectic E phases, the permittivity value measured at 100 Hz dropped from 8.3 to 3.4. The latter value is typical for a phase in which the dipole rotation is frozen out. The collected spectra did not reveal any relaxation process in both the mesophases. This result is quite surprising taking into account that in other substances exhibiting smectic E and K phases the relaxation process connected with the molecular rotations around the short axes has been observed [2,6]. On the other hand, it must be noticed that the short members (n = 4,3,2) of the nBT homologous series exhibited a dramatic slowing down of this motion on entering the smectic E phase [2]. Therefore, we could suppose that this relaxation process could be observed in a sub-hertz region for our sample, thus below the accessible frequency range. On the other hand, an experiment exploring the sub-hertz region might be strongly disturbed by the ionic conductivity [6], which makes a separation of the relaxation and conductivity components difficult or even impossible.

These observations are compatible with the results obtained from the few ^{2}H NMR studies on smectic E phases reported in the literature [7–9]. Indeed, the analysis of deuterium spectra recorded on magneto-aligned samples has revealed that overall rotational diffusive motions are strongly hindered, whereas aromatic ring π-flips and self-diffusion of the molecules about the herringbone lattice of the smectic E phase ("α-jumps") occur in the frequency region affecting deuterium lineshape [8]. In order to confirm these results for our sample, we attempted its alignment within the magnetic field on cooling from the isotropic phase. Unfortunately, no uniform alignment of the sample was obtained in a field of 9.4 T, even using very slow cooling rates (0.1°C every 20 minutes), because of the absence of less ordered phases in between the smectic E and the isotropic phase. Examples of ^{2}H NMR spectra recorded at 86°C after different thermal treatments of the sample are reported in Figure 6. It is possible to notice that the spectrum obtained by abruptly cooling the sample from the isotropic phase within the magnetic field (Fig. 6b) is quite similar, but not identical, to that recorded after heating a poly-crystalline sample obtained by quenching the isotropic liquid in liquid nitrogen outside the magnetic field in order to guarantee an isotropic distribution of the molecules ("powder" spectrum, Fig. 6a).

This suggests that by fast cooling the sample to the Smectic E phase the presence of the magnetic field only slightly perturbs the distribution of phase directors (normal to the smectic layers), which

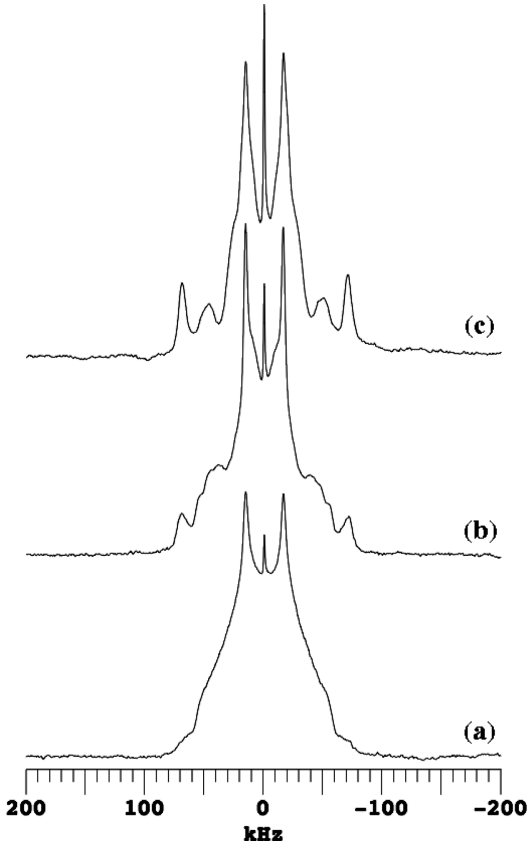

FIGURE 6 ^2H NMR spectra of **1** recorded at 86°C after different thermal treatments: (a) on heating a poly-crystalline sample; (b) abruptly cooling the sample from the isotropic phase; (c) slowly cooling the sample (0.1°C every 20 minutes) from the isotropic phase.

therefore results to be nearly isotropic like in powder samples. This observation is further confirmed by ^2H NMR spectra recorded at different orientations of the sample with respect to the magnetic field direction (results not shown): all these spectra are very similar, confirming the substantial absence of preferential directions of alignment for the molecules. On the contrary, the spectrum recorded at 86°C after a very slow cooling of the sample from the isotropic phase (Fig. 6c) exhibits much more noticeable differences with respect to the "powder" spectrum; in particular, increased intensities appear in correspondence of the spectral discontinuities. The complex spectral

shape indicates the absence of a uniform alignment of the phase directors towards the magnetic field direction, which would indeed give rise to a typical quadrupolar doublet in the ^{2}H NMR spectrum. On the other hand, a similar behavior has been previously observed for the high temperature phase of a class of discotic compounds [10] and it is ascribable to the simultaneous presence of multi-domains and of a partial degree of alignment of the molecules. The occurrence of a partial alignment has been confirmed by the remarkable changes in the spectral features observed by changing the sample orientation with respect to the magnetic field (see Fig. 7).

Given the impossibility of getting easily interpretable deuterium spectra on uniformly aligned samples, we decided to record ^{2}H NMR spectra on completely unaligned samples whose line shapes would be sensitive to molecular motions in the frequency region between 10^4 and $10^7\,s^{-1}$. Spectra were therefore acquired at different temperatures on heating a poly-crystalline sample within the magnetic field, starting from -50°C; a selection of spectra is reported in Figures 8 and 6a.

At -50°C the spectrum exhibits a rigid solid pattern corresponding to a quadrupolar splitting constant $\nu_Q = 3e^2qQ/4h = 131.5\,kHz$. With increasing the temperature up to 60°C typical dynamic features of two site jumps appear leading to a spectrum of an average biaxial quadrupole coupling tensor with $\langle\nu_Q\rangle = 82.5\,kHz$ and $\langle\eta\rangle = 0.6$. This fast exchange limit spectrum is characteristic of a two site jump process in which the unique principal direction of the deuterium quadrupole interaction tensor rapidly flips by $\pm 60^\circ$ about an average direction [11]; such spectrum is therefore expected for deuteria in a benzene ring undergoing rapid π-flips about its *para* axis. A detailed analysis of the spectra, involving comparison with spectra calculated in terms of theoretical models for this motion [12,13] was therefore performed in order to get insights into the dynamic behavior of **1**. The analysis revealed that the spectral line shape evolution observed on heating from 0 to 60°C can be satisfactorily reproduced (see Fig. 8) with a combination of two spectral components both ascribable to deuteria on benzene rings undergoing π-flips, but with flip rates differing by about two orders of magnitude, indicating a heterogeneous molecular dynamics in this temperature range. The first component has the same $\langle\nu_Q\rangle$ and $\langle\eta\rangle$ as determined for the spectrum at 60°C, thus corresponding to rapid π-flips of the benzene rings (the flip rate k is set to $4{\cdot}10^6\ s^{-1}$ in the simulation). The second one is characteristic of much slower π-flips ($k = 5{\cdot}10^4\ s^{-1}$ in the simulation). The contribution of the fast component increases on heating as reported in the caption of Figure 8, reaching 100% at 60°C. At higher temperatures the spectral

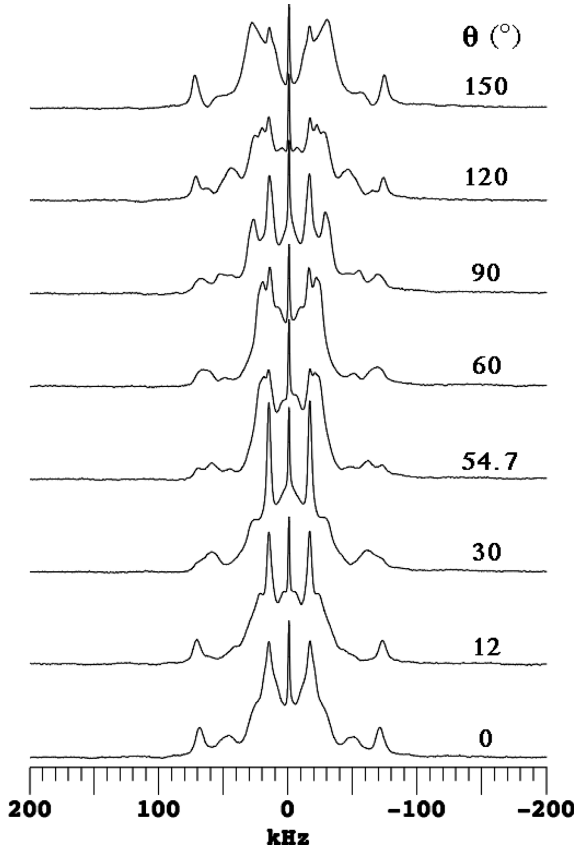

FIGURE 7 ^{2}H NMR spectra of **1** recorded at 86°C after slowly cooling the sample (0.1°C every 20 minutes) from the isotropic phase, after rotating the sample about a direction perpendicular to the magnetic field by different angles θ.

line shape slightly changes up to 76°C and, then, it remains the same up to the clearing point (see Figure 6a); the parameters characterizing the average quadrupolar tensor become $\langle \nu_Q \rangle = 74\,\text{kHz}$ and $\langle \eta \rangle = 0.51$, indicating that another rapid dynamic process occurs in the smectic E phase in addition to benzene π-flips. On the basis of the $\langle \nu_Q \rangle$ and $\langle \eta \rangle$ values we can identify this motion as the self-diffusion of molecules about the herringbone bidimensional lattice of the smectic layers which provides discrete jumps of the benzene rings between four equally probable sites, as described by Vaz *et al.* [8]. In our case, the α angle characteristic for this motion is found to be 14° (with $\nu_Q = 131.5\,\text{kHz}$ and $\eta = 0.04$).

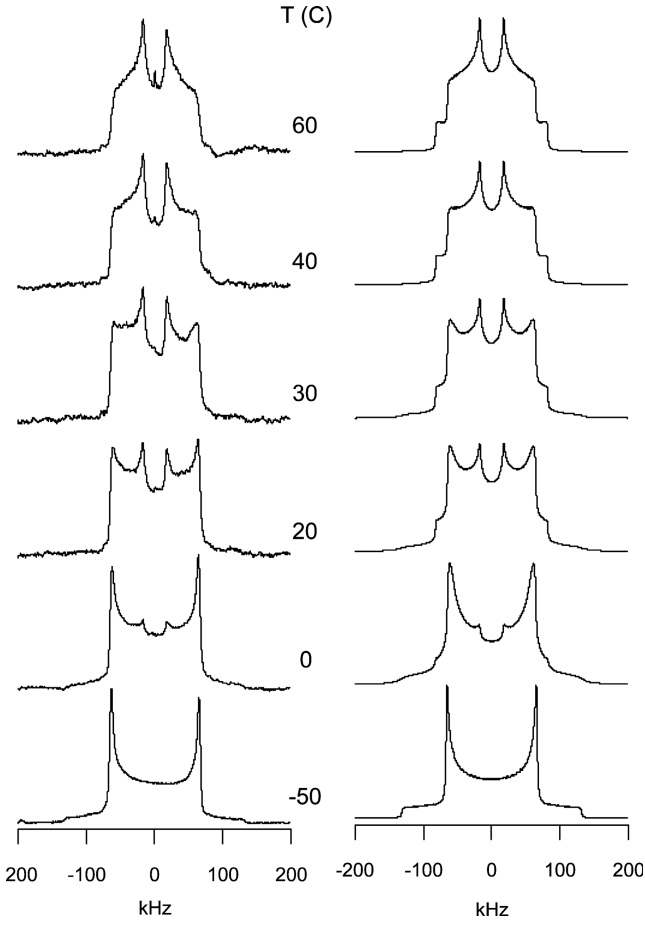

FIGURE 8 Left: ^{2}H NMR spectra of **1** recorded at the indicated temperature on heating a poly-crystalline sample. Right: simulated spectra with $\nu_0 = 131.5\,\text{kHz}$, $\eta = 0.04$ and line width $1/T_2 = 700\,\text{s}^{-1}$. The spectrum at -50°C was calculated with a rate constant k of $1{\cdot}10^3\,\text{s}^{-1}$ for the ring π-flip motion. Spectra at higher temperatures were obtained as the superposition of two components characterized by $k = 5{\cdot}10^4\,\text{s}^{-1}$ and $k = 4{\cdot}10^6\,\text{s}^{-1}$, respectively. The contribution of the fast component to the spectrum is 0, 55, 70, 90 and 100% at 0, 20, 30, 40, and 60°C, respectively.

CONCLUSIONS

No substantial differences in the mesomorphic behavior have been observed between 4-*n*-butyl-4′-acetyl-biphenyl (**1**) and 4-*n*-butyl-4′-isothiocyanato-biphenyl (4BT), two calamitic mesogens differing only in

the terminal group ($COCH_3$ instead of NCS). In fact, both substances exhibit a smectic E phase below the isotropic one. However, in the case of 4BT the smectic E phase hardly transforms into the crystal phase on cooling [14], whereas the smectic E phase of **1** transforms into another metastable crystal-like smectic phase with a very similar molecular arrangement (most probably a K phase), which can be kept unchanged for long time at room temperature. Dielectric relaxation measurements indicate that molecular rotations around the short axis do not occur or are shifted towards very low frequencies (sub-hertz) in both the smectic E and K phases of **1**. ^2H NMR spectroscopy investigations confirm that no overall longitudinal or transversal molecular rotational diffusion motions are present at frequencies higher than $10^3\,s^{-1}$, whereas fast π-flips of the benzene rings and self-diffusion of the molecules about the herringbone bidimensional lattice of the layers occur in the smectic E phase, and only π-flips are detected at lower temperatures. Side chain internal motions could also be present in these phases [14], but selective deuteration of the *n*-butyl moiety would be necessary in order to verify this hypothesis.

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