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Molecular self-diffusion in a columnar liquid crystalline phase determined by deuterium NMR

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We report translational diffusion coefficients in a columnar phase of a discotic liquid crystal formed by a triphenylene-based compound. The experiments were performed using ^{2}H stimulated-echo-type pulsed-field-gradient spin-echo NMR applied to a chain-deuterated sample. The diffusion coefficients were found in the range of 1×10^{-14}–4×10^{-14} m^2/s, three orders of magnitude lower than in the isotopic phase of the same compound. This, together with the high activation energy obtained in columnar phase, indicates that the diffusion is dominated by solidlike jump processes.

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Compounds consisting of disklike molecules with symmetrically attached side chains often exhibit one or several liquid crystalline phases [1]. These mesophases of discotic molecules are usually columnar with the molecules stacked into aggregates, which in turn are arranged in two-dimensional arrays with various symmetries. Investigations of the molecular dynamics in columnar phases have recently attracted considerable attention. Whereas the molecular reorientation [2–5] and chain conformational dynamics [6–9] is relatively well understood there is only scarce information on the translational motion in columnar phases. This latter information, however, is important for understanding the anisotropic properties and the molecular ordering of the phase. Previously, several studies of the diffusive transport in columnar discotic phases [10–19] have been reported. Optical microscopy measurements [10–13] monitor the transport of optically active impurities and provide, therefore, no direct information on the diffusion of the solvent molecules. Neutron quasielastic scattering investigation reports short-range (in-cage) diffusion coefficient, which was estimated to 10^{-10} m^2/s [14]. Similarly, nuclear spin relaxation is most sensitive to short-scale molecular diffusion (yielding $D\sim10^{-10}$ m^2/s [15]) and its interpretation is, moreover, model dependent.

In the present work we report diffusion coefficients in the columnar phase of a deuterated discotic liquid crystal by ^{2}H stimulated-echo-type pulsed-field-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR). This direct method has recently been tested in thermotropic calamitic liquid crystals, where diffusion coefficients down to 4×10^{-12} m^2/s were accurately measured [20]. Proton PGSE NMR has already provided reliable diffusion data of the order of 10^{-11} m^2/s in the isotropic phase of discotic materials [16,18,19]. Since PGSE NMR experiments are more difficult to perform in anisotropic systems such as liquid crystals [20–24], there is only one detailed investigation by PGSE NMR performed on the residual protons in deuterated discotic samples [17]. The experiments reported in that study yielded diffusion coefficients in the range of $(2-6)\times10^{-11}$ m^2/s in the columnar phase. This number, although attributed to liquidlike clusters or domains in the mesophase [16,19], is frequently referred in the literature as characteristic of the diffusion coefficient in the columnar phase.

Here, the measurements were performed on a chain perdeuterated discotic liquid crystal hexa-(pentyloxy)-triphenylene (THE5) (Fig. 1). This compound forms a columnar mesophase (D_{ho}, whhere ho refers to hexagonal ordered phase structure) in the temperature range 69–122 °C. The phase transition temperatures estimated from the NMR spectra were in agreement with the literature values [25]. The sample, prepared by slow cooling from the isotropic phase in the magnetic field of the NMR spectrometer (4.6 T), consists of domains of columns oriented with their director in the plane perpendicular to the magnetic field. In addition, measurements of translational diffusion were carried out in an unoriented columnar phase formed by truxene hexadodecanoate (TxHA11). The compounds were synthesized by the procedures described in Refs. [26–28].

The NMR experiments were carried out on a Bruker DMX-200 spectrometer, operating at 31 MHz for ^{2}H. For diffusion measurements a wide-bore ^{1}H/^{2}H gradient probe (Bruker) with gradient strength up to 900 G/cm was used. The length of a 90° rf pulse for deuterium was 7.0 μs. Three different PGSE NMR techniques were used for the determination of molecular diffusion: (i) a stimulated-echo-

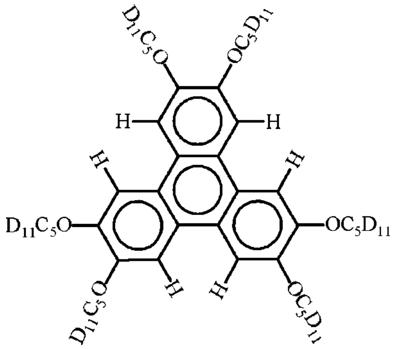

FIG. 1. Molecular structure of the disckotic mesogen, chain perdeuterated hexa-(pentyloxy)-triphenylene (THE5).

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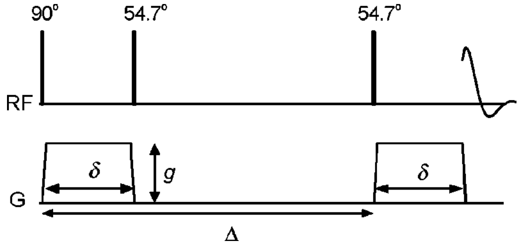

FIG. 2. The basic pulse sequence for diffusion measurement by deuterium PGSTE NMR sequence. The quadrupolar modulation of the echo signal is suppressed by setting the flip angles of the second and third pulses to magic angle value 54.7° and by phase cycling [20]. The details (additional radio-frequency pulses) of the PGSTE experiment extended with magic echo during the coherence evolution periods (PGSTE-ME) and of the PGSTE experiment where the gradient encoding/decoding is performed on double-quantum coherences (PGSTE-DQ) are given in Refs. [20,29] and [30], respectively.

type experiment with encoding/decoding of single-quantum coherences (PGSTE) (Fig. 2) [20], (ii) the same experiment extended with magic echo decoupling (PGSTE-ME) [20,29], and (iii) a stimulated-echo-type experiment with encoding/decoding of double-quantum coherences (PGSTE-DQ) [30]. The diffusion in the *isotropic* phase was measured by conventional PGSE NMR [31].

Deuterium NMR spectrum of THE5 collected at 390 K is shown in Fig. 3. The central doublet (see the inset in Fig. 3) corresponds to the signal from the methyl group. Methyl deuterons, on which all measurements were performed, show quadrupolar splitting of less than 100 Hz and have favorable relaxation times $T_1 \simeq 0.63$ s and $T_2 \simeq 11$ ms at this temperature. This is the result of fast side-chain dynamics that averages efficiently the quadrupolar coupling of the methyl deuterons. The relatively long T_2 time allows for inserting long ($\delta \sim 10$ ms) gradient pulses in the PGSTE experiment. Hence, in spite of low magnetogyric ratio for deuterons compared to protons, efficient gradient encoding is provided, thus allowing for detecting very slow molecular diffusion. With the available maximum gradient and with the diffusion time $\Delta \sim 1$ s (limited by the relaxation time T_1) the diffusion coefficient of the order of 10^{-14} m^2/s can be measured. The PGSTE-ME experiment provides somewhat better signal-to-noise ratio since it effectively prolongs the decay time of the single-quantum coherences to $T_{2ME} \simeq 20$ ms, which results in less signal decay during the gradient pulses [20]. The PGSTE-DQ experiment could, in principle, allow a further increase of the gradient encoding efficiency by a factor of two [32,33]. In the present sample, however, this gain is reduced because of the short decay time for the double-quantum coherences ($T_{2DQ} \simeq 6.5$ ms at 390 K). Notably, the three different techniques produced consistent results (see below).

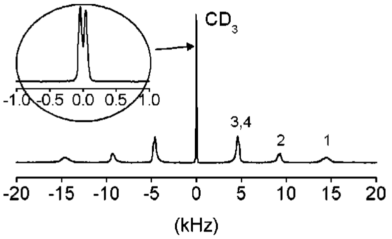

FIG. 3. ^{2}H NMR spectrum of chain deuterated THE5 measured at 390 K. The methylene deuterons are numbered starting with the α-CD$_2$. The signal from the methyl group is shown in the inset.

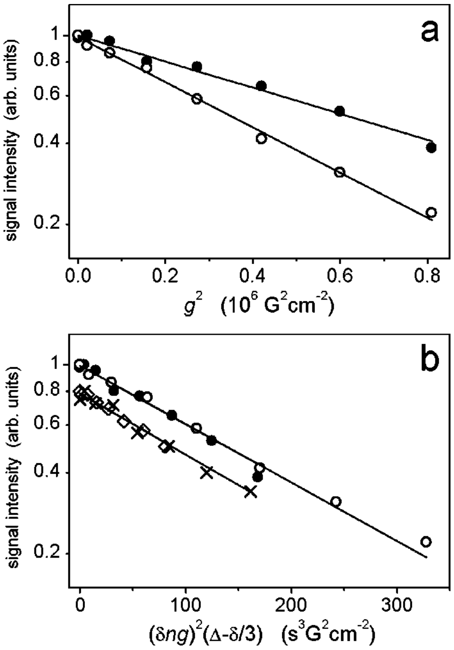

FIG. 4. The signal decays in ^{2}H PGSTE NMR diffusion experiments in THE5 at 390 K. (a) The PGSTE-ME experiment applied with: $\delta = 14.47$ ms, $\Delta = 1$ s (●) and $\delta = 16.47$ ms, $\Delta = 1.5$ s (○). (b) The $(\delta n g)^2(\Delta\text{-}\delta/3)$ dependence of the signal [see Eq. (1)]. Symbols (●,○) are as in (a). Data from the PGSTE-DQ experiment are shifted for clarity [$\delta = 5.0$ ms, and $\Delta = 1$ (◇) and $\Delta = 2$ s (×)]. Lines are fits to Eq. (1).

The echo decay, observed in a PGSTE experiment is given by [31]

$$A(g,\delta,\Delta) \propto \exp[-(\gamma n g \delta)^2(\Delta - \delta/3)D], \qquad (1)$$

where γ is the magnetogyric ratio, n the coherence order, g the magnetic field gradient, δ the total length of the encoding (and thereby also the decoding) gradient pulses during the coherence evolution periods, Δ denotes the diffusion delay, and D the molecular diffusion coefficient. In Fig. 4(a) the experimental echo decays obtained for two different sets of parameters are displayed. As expected for the diffusion dephasing effect, the signal attenuation becomes stronger with increasing gradient time δ and/or diffusion delay Δ. In Fig. 4(b) the data, including those from DQ experiments, were replotted as a function of $(n\delta g)^2$ $(\Delta - \delta/3)$ that yields a common slope. From this slope the diffusion coefficient is estimated to $(3.1 \pm 0.2) \times 10^{-14}$ m^2/s. In the isotropic phase of the same compound the diffusion is much faster. Just above the phase transition (395 K) the diffusion coefficient $D = (2.4 \pm 0.2) \times 10^{-11}$ m^2/s was obtained.

Diffusion coefficients at several temperatures, determined using different experimental techniques, are collected in

TABLE I. Diffusion coefficients in THE5 measured by different versions of the ^{2}H PGSE NMR experiment.

Temperature (K)	Diffusion coefficient ($\times 10^{-14}$ m^2/s)
391	3.8 ± 0.4 [a]
	3.9 ± 0.4 [b]
390	3.1 ± 0.2 [b]
	3.3 ± 0.4 [c]
385	1.9 ± 0.2 [b]
	1.8 ± 0.3 [a]
380	1.2 ± 0.2 [b]

[a] Stimulated-echo-type experiment with encoding/decoding of single-quantum coherences (PGSTE) [20].

[b] The PGSTE experiment extended with magic echo decoupling (PGSTE-ME) [20,29].

[c] The PGSTE experiment with encoding/decoding of double-quantum coherences (PGSTE-DQ) [30].

Table I. The results are consistent within the experimental error. At decreasing temperature the diffusion decay slows down and at temperatures below 370 K no attenuation of the signal is detected. Since the obtained diffusion data are close to the setup sensitivity limit, attention must be paid to experimental artifacts. Nonequivalence of gradient pulses during encoding/decoding periods would lead to additional signal decay, thus resulting in faster apparent diffusion. This effect was practically suppressed by running the experiment with several dummy gradient pulses and by setting the delay between successive gradient pulses equal to diffusion delay Δ, so that saturation equilibrium of the gradient current amplifier is achieved. Furthermore, the eddy current effect after strong gradient pulses was removed by appropriately adjusted longitudinal eddy current delay [34]. With these precautions we observed no decay in diffusion experiment with the maximum gradient and delay lengths at low temperatures (below 370 K), where the effect of diffusion is below the detection limit.

The diffusion measured in the direction of the magnetic field corresponds to molecular transport perpendicular to the columns, which, as a result of the discotic molecular shape, is expected to be faster than the diffusion parallel to the column. For measuring diffusion in the latter direction the gradient orientation perpendicular to the magnetic field is required, which was not possible in the present experimental setup. The observed diffusion in the columnar phase decreases drastically with decreasing temperature. The apparent activation energy can be estimated to $E_a \simeq 115$ kJ/mol. Such high activation energy cannot be ascribed to simple liquidlike diffusion of individual molecules. However, similar values of E_a are typical of some smectic mesophases, where the diffusion is described by solidlike jump motion [21]. Collective processes involving large number of molecules, such as defects rearrangements or annealing, may also result in high activation energy.

Our results differ by about three orders of magnitude from those of Ref. [17], where the diffusion in a similar deuterated compound was measured via the ^{1}H NMR signal. Those data were analyzed under the assumption that the ^{1}H signal arises exclusively from the residual protons of the mesogenic molecule. The values reported in Ref. [17] [$(2-6)\times 10^{-11}$ m^2/s] could be easily measured with our experimental setup. We also measured the diffusion by observing the ^{1}H signal at the frequency of methyl group, thus repeating the experiment used in Ref. [17] on our sample. The observed decay was non-Gaussian, indicating several diffusion processes taking place. Forced fit to a Gaussian function [see Eq. (1)] produced $D(^1\mathrm{H}) = 1.4\times 10^{-13}$ m^2/s at 390 K, which is a factor of four higher than obtained by ^{2}H NMR, but still more than two orders of magnitude lower than the previous result [17]. We also performed preliminary diffusion measurements by the ^{2}H NMR methods of this work in some other discotic liquid crystals. In all cases, the diffusion coefficients were below 10^{-13} m^2/s; for instance, $D = 1.6\times 10^{-14}$ m^2/s in a sample of TxHA11 in an unoriented columnar phase at 380 K. Based on these observations, we propose two explanations to the discrepancy between the earlier [17] and the present results. First, the residual ^{1}H NMR signal could contain a large contribution from rapidly diffusing small-molecular impurities. Second, isotropic clusters (or domains) may be present in the liquid crystal [35]. Since the diffusion coefficient in the isotropic phase is high ($D_{iso} = 2.4\times 10^{-11}$ m^2/s just above the phase transition point, which is in rough agreement with the results of Ref. [17]), the fast diffusion observed in Ref. [17] could originate from those isotropic clusters. Although such clusters may persist much below the clearing point [16,19,35], their contribution at our temperatures is limited to less than a few percent of the total sample volume. This is verified by the absence of any observable isotropic signal in the middle of the ^{2}H spectrum (Fig. 3). In principle, a combination of these two explanations is also possible.

The present results suggest that translational self-diffusion in the columnar phase of a discotic liquid crystal is extremely slow. Moreover, the diffusion coefficient decreases by about three orders of magnitude at the phase transition from isotropic liquid to columnar phase. This drastic change is more typical of a liquid-solid transition. In contrast, the isotropic-nematic or isotropic-smectic phase transitions in calamitic thermotropics are commonly assumed to be liquid-liquid like, which is based, among other observations, on diffusion coefficients of comparable magnitude across the phase transition [20–22,24].

Clearly, more experimental data are required for interpretation of observed diffusion behavior in columnar phase. Other NMR methods (diffusion in a static fringe field gradient) would allow measuring even slower diffusion. Measuring the diffusion anisotropy requires either a gradient field perpendicular to the applied magnetic field or a monodomain sample whose director can be set at different angles to magnetic field or both. The work along these lines is now in progress.

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