Melting of Low Molecular Weight Compounds in Confinement Observed by ^2H -Solid State NMR: Biphenyl, a Case Study

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Dedicated to Professor Hans Wolfgang Spiess on the occasion of his 70th birthday

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The ^2H -NMR solid echo spectra of biphenyl molecules as guests in the mesopores of neat and silylated SBA-15 have been measured as a function of temperature. At low temperatures typical ^2H -Pake patterns with parameters of ($Q_{zz} = 132$ kHz, corresponding to $Q_{cc} = 176$ kHz) and ($\eta = 0.04$) are observed. All samples exhibit a strong reduction of the melting point from the bulk value of 342.4 K to values between 222 K and 229 K, depending on both the pore diameter and the surface state and a glass like behavior of the biphenyl molecules in the melting regime. Employing the Roessler *two-phase model* of the modeling of glass-transitions by ^2H -solid state NMR the distribution of activation energies for the rotational motions has been determined. At temperatures closely below the glass-transition temperature deviations from a static Pake pattern of an aromatic deuteron are observed, which indicate a pre-melting motion of biphenyl, which could be caused by C_2 -ring flips of the phenyl rings.

1. Introduction

Despite considerable progress in the theoretical modeling of small guest molecules confined in porous solid hosts [1–5] it is still difficult to predict the behavior of specific molecules when pore and molecular diameters are of the same order. In this case, the guests cannot be treated as homogenous phase nor can the molecular structure of the pore walls be neglected.

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A salient step in the understanding of the behavior of molecular guests inside porous hosts is a detailed study of the melting process. Here it is important to note that already below the melting temperature molecules can exhibit considerable molecular dynamics. An experimental analysis of these initial steps of the melting process can provide valuable data material for gauging molecular dynamics simulations of the behavior of small molecules inside the pores. ^2H solid-state NMR spectroscopy is an experimental technique, which is well-suited to study these dynamic processes.

Periodic mesoporous silica materials with pore diameters in the nanometer-range, originally envisioned by Beck *et al.* [6], are particularly suited for the study of confinement effects on low-molecular weight organic materials [7–15], since they provide a controlled environment with defined pore-diameters and chemically modifiable surface [2,16–24]. Owing to this versatility they are also employed as controlled drug delivery carriers [25–27], gas adsorbents [28], molecular sieves [29], as matrix for fine chemical synthesis [30], their use in separation techniques for functional food ingredients [31] or in heterogeneous catalysis [32–35]. The main difference between the synthesis of zeolites (see for example [36] and references therein) and that of M41S-type materials resides in the templating mechanism employed to control their morphology. Here, the self-aggregation of structure directing surfactant molecules to micelles of specific shapes and eventually liquid crystals in aqueous solution determines their structure [37]. Hexagonal, cubic and lamellar templating phases generate M41S mesoporous materials of the families MCM-41, MCM-48, and MCM-50, respectively. MCM-41 has cylindrical pores arranged in hexagonal array and exhibits a narrow pore size distribution in the range from 2 to 10 nm. The pore diameter is determined by the diameter of the micelles in the template solution, which in turn is determined by the length of the alkyl-chains of the tenside molecules.

MCM-41 exhibits a high specific surface area. Its Brunauer, Emmett, Teller (BET [38]) surface area is of the order of $1000\text{ m}^2/\text{g}$ and the specific pore volume is approximately $1\text{ cm}^3/\text{g}$. The large surface area allows us to directly observe the interaction between molecules adsorbed on the surface and the surface to which they are attached using solid state NMR [39], where often sensitivity problems are encountered. Other interesting characteristics of MCM-41 include its smooth pore surface [40,41], high porosity, controllable and narrowly distributed pore sizes, high thermal stability [39] and the possibility of modifying and functionalizing the pore surface [42].

The organization and physico-chemical properties of guest molecules confined in the restricted volume of nanometer pores can differ considerably from their behavior in bulk. A striking effect of such a confinement is a drastic lowering of the melting point or glass transition temperature [10,43–51]. For example, benzene confined inside mesoporous silica exhibits different phases, which can be identified as a glass-like amorphous surface phase and an inner crystalline phase with properties close to solid bulk benzene [10,13]. Studies of iso-butyric acid confined in mesoporous silica materials [14,19] revealed the formation of different motional phases. Inside the mesopores of MCM-41 and SBA-15 a liquid-like phase; a solid phase exhibiting rotation of the methyl group and a solid phase with no rotational motion on the time scale of the NMR experiment were observed. Thus, these materials are of considerable interest in the investigation of basic interactions between surfaces and substrates [46–53].

Fig. 1. Structure and torsional ring flip between two configurations of biphenyl.

The change of the melting point is often discussed in terms of the Gibbs-Thomson equation [54], which predicts a linear dependence of the melting point depression ΔT_m on the inverse pore radius $1/R$,

$$\Delta T_m = T_{m(\text{bulk})} - T_{m(\text{pore})} = \frac{2V_m T_{m(\text{bulk})}(\gamma_{cw} - \gamma_{lw})}{\Delta H_m R}, \quad (1)$$

where $T_{m(\text{bulk})}$ is the bulk melting temperature, V_m the molar volume of the liquid phase, ΔH_m the molar enthalpy of melting and $(\gamma_{cw} - \gamma_{lw})$ the difference of the surface free energies crystal-wall and liquid-wall, which for the case of complete wetting of the pore walls by the liquid is given by the crystal/liquid interfacial free energy γ_{el} [2].

In both cases described above a common feature is that the guest molecule has no internal degree of freedom with activation energies which are on the same scale as the typical intermolecular interactions. For this reason we decided to study biphenyl (Fig. 1), which consists of two phenyl rings connected by a single C-C bond. Because of this single bond, biphenyl exhibits an internal torsional ring flip between two configurations as illustrated in Fig. 1.

For biphenyl in the gas phase there are opposing interactions which determine its equilibrium structure, namely the steric hindrance of the central hydrogen atoms, which tends to twist the two phenyl planes into a perpendicular conformation ($\alpha = 90^\circ$) and the conjugation interaction of the π -electrons which favors a planar structure ($\alpha = 0^\circ$) of the molecule. The resulting torsional angle and the torsional angular motion depends strongly on the environment. In the gas phase Almenningen *et al.* [55] found an equilibrium angle of $(44.4-1.2)^\circ$ for biphenyl- h_{10} and $(45.5-1.2)^\circ$ for biphenyl- d_{10} . The two configurations in Fig. 1 are degenerate in the gas phase, and the corresponding rotational barrier heights were found to be (6.0 ± 2.1) kJ/mol at 0° and (6.5 ± 2.0) kJ/mol at 90° for the protonated isotopolog. For the deuterated isotopolog 9.9 kJ/mol respectively 9.2 kJ/mol have been found. For solutions of biphenyl in CCl_4 Szymoszek *et al.* [56] calculated by molecular dynamics simulations an equilibrium angle of 28° . Employing NMR relaxation methods and infra-red spectroscopy Akiyama *et al.* [57] reported an equilibrium angle of 37° , a value of 4.8 kJ/mol for the barrier around 0° and of 14.7 kJ/mol for the barrier around 90° for biphenyl in a CS_2 solution.

In the solid state the situation is much more complex, since already neat biphenyl forms different phases. In the room temperature phase I the two phenyl rings are planar (Fig. 2a) or disordered, at least on average. By contrast, at low temperature structural transitions into phases II and III take place at 42 and 17 K in biphenyl and at 38 and 24 K in biphenyl- d_{10} , respectively, where the biphenyl molecules become non-planar [58]. The structure of biphenyl- d_{10} derived using neutron diffraction by Cailleau *et al.* [59] indicates a torsional angle of about 10° as illustrated in Fig. 2. Moreover mo-

Fig. 2. Neutron crystal structure of solid biphenyl-d₁₀ projected along the *c*-axis. **a** Room temperature structure. **b** Approximate “basic” low-temperature structure to which approximate H positions have been added here. Adapted from Cailleau *et al.* [59,60].

lecular jumps into neighboring sites along the *b*-axis require 10° flips of both phenyl rings, whereas jumps along the *a*-axis are associated with 90° reorientations of the whole molecule. However this structure was shown later to be approximate as both phases II and III were found to be incommensurate [60]. From these results an effective double well potential of biphenyl in the solid was suggested which leads to molecular motions [61]. Molecular dynamics studies of biphenyl [62] calculated that the free energy of biphenyl in the solid is substantially reduced if some molecules have a low torsion angle (0–2°) and others have a higher torsion angle of *ca.* 22° and a relatively flat potential curve in this range of torsional angles [63].

Owing to this interesting phase behavior the Haebleren group has performed a series of single crystal solid state ²H NMR studies of bulk deuterated biphenyl in all three phases [64–68]. These authors found evidence for C2-flips in the room-temperature phase I exhibiting an activation energy of 75 kJ/mol [65]. This process is illustrated in Fig. 3. Furthermore, information about the structure and motions in the incommensurate low-temperature phases II and III were obtained.

Fig. 3. C2 or 180° angle flips in the room-temperature phase I of solid biphenyl. Adapted from Cailleau *et al.* [59,60]. For clarity only one of each inequivalent deuteron is shown.

In our study we have applied solid state ^2H NMR methods to characterize the rotations of biphenyl- d_{10} in MCM-41 below and in the neighborhood of the melting point where we expected also C2 ring flips of essentially planar molecules according to Fig. 3. Thus, we did not search for more complicated motions typical for the incommensurate low-temperature phases.

The C2 ring flips lead to a change of the quadrupole coupling tensor by rotations of the CD-bond directions. As illustrated in Fig. 3, in the planar configuration, only the *ortho*- and *meta*-deuterons move in space during a 180° or C2 flip, but not the *para*-deuteron. Owing to the molecular symmetry, this process is degenerate or quasi-degenerate in the solid, and characterized by the same forward and backward rate constant k_{180° .

In the following, after an Experimental Section, our results are presented and discussed.

2. Experimental part

2.1 ^2H NMR solid state NMR spectroscopy

Following the seminal work of Spiess and coworkers on ^2H -Fourier Transform NMR spectroscopy, the analysis of line-shape changes in one [69] and two-dimensional ^2H -NMR spectra [70–73] has become the tool of choice for the analysis of molecular motions and reorientations in solid organic materials.

The theory of the simulation of ^2H -solid state NMR spectra in the presence of molecular motions is well known (see text-books [74,75]). The quadrupole coupling determines the positions of the two spin-transitions of an individual deuteron

$$\begin{aligned} \nu_Q(\vartheta, \varphi) &= \pm \frac{3}{4} \frac{eQeq}{h} \frac{1}{2} (3 \cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2\varphi) \\ &= Q_{zz} \frac{1}{2} (3 \cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2\varphi) \end{aligned} \quad (2)$$

Here eQ is the electric quadrupole moment, eq represents the principle component of the EFG tensor, η is the asymmetry parameter, which gives information about the shape of the electric field gradient, and Q_{zz} is a measure for the strength of the quadrupolar interaction; ϕ and ϑ are the azimuth- and polar angles of the quadrupolar PAS with respect to the external magnetic field B_0 .

The quadrupolar coupling Q_{cc} constant is obtained from the experiment as

$$Q_{cc} = \frac{eQeq}{h} = \frac{4}{3}Q_{zz} \quad (3)$$

In a non-oriented powder sample the average over all possible orientations has to be calculated by integration over the polar angles ϑ and ϕ , yielding the well-known Pake-pattern. This line shape changes when the orientations of the quadrupolar interaction tensors change on the time-scale of the NMR-experiment. The actual line shape depends strongly on the type of the molecular motions or exchange processes present in the sample, and hence on the corresponding exchange rate constant k : In the fast limit $k \gg Q_{cc}$ a motionally averaged spectrum results; in the intermediate exchange regime relatively complicated line-shapes are expected, which contain detailed information about the geometry of the underlying motional process [75]. Numerical modeling of the ^2H -NMR spectra thus enables us to develop quantitative models of the melting process. This modeling is performed employing the stochastic Liouville von Neumann equation [73].

In this modeling, the molecular reorientations are modeled as a stochastic exchange between a set of discrete molecular orientations with different quadrupolar interaction tensors. This reduces strongly the computational costs of simulating the spectra.

In the case of the isotropic melting, suitable sets of orientations are given for example by the Platonic solids: tetrahedron, cube, octahedron, dodecahedron and icosahedron. They are all regular convex polyhedra, whose faces are congruent regular polygons. The vector starting at the center of gravity of the Platonic solid and ending at one of its vertexes is regarded as the axis of a chemical bond, which corresponds to the main component of the Principal Axis System of the Electric Field Gradient (EFG) tensor around the deuterium nucleus. This vector is randomly jumping between the different edges of the platonic solid. In the case of restricted (anisotropic) motions, a different suitable set of angles, which mimics the motional geometry, has to be chosen. Here, C_n -rotations are of particular simplicity.

2.2 Synthesis of MCM-41

MCM-41 was produced exhibiting two different pore diameters, 2.5 nm and 2.9 nm. The only difference in the whole procedure is the starting template molecule, *i.e.* dodecyltrimethylammonium bromide (C12TAB) for the former and tetradecyltrimethylammonium bromide (C14TAB) for the latter. The methods proposed by Gruen *et al.* [76] and Liu *et al.* [77] were followed. The surfactant salt (C12TAB, Fluka, 2.1 g, or C14TAB, Aldrich, 2.4 g) was dissolved in ammonia (9.5 g, 25%). Tetraethoxysilane (Aldrich, 10 g) was added under stirring and the solution kept at 80 °C for 72 h. The precipitated product is filtered, dried and calcined.

Nitrogen isotherm curves of the MCM-41 samples studied were measured using a Gemini 2375 instrument from Micromeritics. The BET specific surface area [38] calculated from the initial rise of the isotherm were found to be 1002 m²/g and 1292 m²/g (for C12TAB and C14TAB respectively). The pore diameters, determined from the relative pressure at the steep rise of volume adsorption according to the Dollimore & Heal formalism [78], were 2.5 nm and 2.9 nm respectively. The adsorbed volume when the

pores are completely filled gave the pore volumes, $0.48 \text{ cm}^3/\text{g}$ and $0.76 \text{ cm}^3/\text{g}$ respectively. Part of the material had its surface hydroxyl groups silylated [79] by stirring the powder silica overnight with chlorotrimethylsilane (Aldrich) using 1 : 5 mass ratio in benzene at room temperature. For the silylated samples a reduction of ca 3% of the specific pore volume was estimated. The resulting solution was filtered and dried.

2.3 Sample preparation

Before samples were prepared, the MCM-41 was dried overnight on a vacuum line at 10^{-5} bar and 140°C in a Young NMR tube. After drying, biphenyl was added under an inert atmosphere in amounts corresponding to less than 90% of the nominal pore volume to avoid extraporous biphenyl. Employing the density of bulk biphenyl- d_8 (1.06 g/cm^3) and the 3% reduction of the pore volume by silylation, the following nominal pore filling factors were obtained (S1: 87%; S2: 83%; S3: 89%; S4: 85%). Then the tube was flame sealed. The samples were kept overnight at ca 70°C to ensure that all biphenyl enters the pores. Four samples corresponding to the possible combinations between silylated and non-silylated MCM-41, and MCM-41 with larger ($29 \text{ \AA}$) and smaller ($25 \text{ \AA}$) pore diameters were prepared in this way.

2.4 Low-temperature ^2H solid state NMR

All ^2H NMR spectra of the samples were measured in a home-built 7-Tesla solid state NMR spectrometer described previously [80]. A standard Oxford wide bore magnet (89 mm) equipped with a room temperature shim unit was used. ^2H -NMR pulses were generated employing a 1 kW class AB amplifier from Dressler Hochfrequenz Technik, Stolberg. A pulse width of typically $3 \mu\text{s}$ for the ^2H nuclei was used. All experiments were performed using a home-built 5 mm NMR probe, which was placed in a dynamic Oxford CF1200 helium flow cryostat. The sample temperature was controlled by an Oxford ITC 503 temperature controller. During data acquisition the temperature was directly controlled *via* a Cernox sensor (Lakeshore, Westerville) placed in the direct vicinity of the sample. The temperature was stabilized over long periods (hours) before data acquisition started. All spectra were recorded using the solid echo technique with an echo spacing of $30 \mu\text{s}$ and a full 32-step phase cycle. The number of accumulations was between 1024 and 4096 scans per spectrum. Before Fourier transforming the echo-signal, the phase was corrected and the imaginary part zeroed to give fully symmetric spectra.

3. Results

Figure 4 shows a selection of experimental ^2H -NMR spectra of sample S1 which is composed of biphenyl- d_{10} in MCM-41 (pore diameter 2.5 nm and pore load *ca.* 90%, pore wall silylated). At low temperatures typical ^2H -Pake patterns [69] with parameters of ($Q_{zz} = 132 \text{ kHz}$, corresponding to $Q_{cc} = 176 \text{ kHz}$) and ($\eta = 0.04$) are observed. This quadrupolar parameters are typical for aromatic deuterons in a relatively rigid environment without substantial librations [81,82].

Fig. 4. Experimental ^2H -NMR spectra of sample S1 (biphenyl- d_{10} inside silylated pores of MCM-41 with 2.5 nm pore diameter).

Fig. 5. Experimental ^2H -NMR spectra of samples S2–S4.

At high temperatures the spectra change *via* an intermediate line-shape into the typical Lorentzian line shape, which indicates that the molecules perform isotropic reorientations which finally result in the normal melting to a liquid phase. A closer inspection of the line-shapes below the melting region reveals that the temperature dependence of the line-shape changes can be divided into two different regimes, namely a low-temperature regime, where only relatively small changes of the line-shape are observable and a high-temperature regime where the typical melting to isotropic reorientation is observed. This is a clear indication of a pre-melting behavior in the low-temperature regime, which will be discussed below in detail. Similar changes are also visible in the spectra of the other three samples (Fig. 5), however at slightly different temperatures.

4. Discussion

The temperature dependent spectra were analyzed employing laboratory written MATLAB code for the simulation of the spectra. In this analysis two different models were considered, namely using (a) the assumption that molecules inside the pores have a very narrow distribution of activation energies for their rotational motions (*narrow distribution model*) and (b) the assumption that a broad distribution of activation energies (*two-phase model*) is present, as typically found in glass-like cases.

In the case of the *narrow distribution model* the spectrum exhibits typical features in the transition from slow jumps ($k \ll Q_{cc}$) to fast jumps ($k \gg Q_{cc}$) which depend on the geometry of the jump process.

In the case of a very broad distribution the spectra represent a weighted superposition of the line shapes for slow and fast jumps [83], which for simplicity we call *two-phase model*. This model implies the coexistence of two phases (slow jump and fast jump regime without an intermediate jump regime) with individual quadrupolar coupling constants and varying relative intensities of each phase. In this case Roessler *et al.* developed in their seminal work [83] the following expression for the relative concentrations of the two phases.

$$c_A(T) = \int_0^T \frac{1}{\sqrt{2\pi\Delta T^2}} \exp\left(-\frac{(T-T_0)^2}{2\Delta T^2}\right) dT$$

$$= \frac{1}{2} \operatorname{erf}\left(\frac{1}{\sqrt{2}\Delta T}(T-T_0)\right) + \frac{1}{2} \operatorname{erf}\left(\frac{1}{\sqrt{2}\Delta T}T_0\right) \quad (4)$$

This is simply a shifted Gauss error-function, which is zero at low temperatures and one at high temperatures. As was also shown by Roessler *et al.* [83] it is possible to determine the distribution of activation energies in temperature units from concentration by differentiation,

$$g(T) = \frac{d}{dT} c_A(T) = \frac{1}{\sqrt{2\pi\Delta T}} \exp\left(-\frac{(T-T_0)^2}{2\Delta T^2}\right) \quad (5)$$

An approximate conversion between temperature and energy is done assuming an Arrhenius dependence between the characteristic activation energy, the temperature and

Fig. 6. Experimental and simulated ^2H -NMR spectra of the melting process of biphenyl- d_{10} inside silylated pores of MCM-41 (2.5 nm pore diameter) employing the two-phase model.

the correlation times of the jump process:

$$E(T) = \ln \left(\frac{\tau(T)}{\tau_{\infty}} \right) k_B T = \alpha T. \quad (6)$$

For the evaluation of the experimental data the value of α has to be estimated, which implies the estimation of the values of the correlation times $\tau(T^*)$ and τ_{∞} . Since only the logarithm of their ratio is used, which varies only weakly with its argument, we can assume a typical vibrational correlation time of $\tau_{\infty} = 1 \times 10^{-13}$ s for the latter [83]. For $\tau(T^*)$ we choose a value which is in the middle of the intermediate exchange regime, namely $\tau(T^*) = 3 \times 10^{-6}$ s. With these values the following relation between $E(T)$ and T is found

$$E(T) = \ln \left(\frac{\tau(T^*)}{\tau_{\infty}} \right) k_B T = 17.2 k_B T. \quad (7)$$

In principle, both the *two-phase* and the *narrow distribution model* are capable of reproducing the experimental data. However, the width of the transitions indicates that the *two-phase model* is physically more realistic than the *narrow distribution model*. This result is similar to our previous studies of iso-butyric acid inside silica [19], where we have performed a detailed quantitative comparison of the two models. For these reasons the following discussion will be based on the *two-phase* model and the *narrow distribution* model will not be considered further.

From the temperature dependence of the spectra it is evident that both the pore diameter and the surface structure influence the phase behavior of the biphenyl molecules inside the pores. For a quantitative evaluation we fitted the temperature

Fig. 7. Relative concentrations of the liquid- and the solid-like contributions of the four different samples (a: S3, b: S4, c: S1, d: S2) and their simulation employing Eq. (4).

Table 1. Parameters from the fitting of the temperature dependence of the concentration of liquid and the solid-like contributions of the four different samples employing Eq. (4).

Nr.	Sample	T_{mid}/K	$\Delta T/\text{K}$
S1	2.5 nm silylated	225.5 ± 0.4	9.5 ± 0.6
S2	2.9 nm silylated	228.9 ± 0.3	4.3 ± 0.4
S3	2.5 nm non-sil.	221.9 ± 0.4	6.5 ± 0.6
S4	2.9 nm non-sil.	221.8 ± 0.1	4.2 ± 0.15

dependent spectra as the superposition of a Pake spectrum representing the solid contribution and a Lorentzian function representing the liquid-like contribution. Figure 6 displays as example the results of the fitting of sample S1.

The relative areas of these two line shapes are measures of the relative concentration of the two phases. Figure 7 displays the temperature dependence of the two concentrations and their modeling employing Eq. (4). The corresponding parameters are shown in Table 1.

The resulting fits show on the one hand that the temperature regime of the transition from a solid-like to a liquid-like spectrum is broader for the samples with the

Fig. 8. Distribution of the phase transition temperatures (and activation energies) for the isotropic motion (melting) of biphenyl- d_{10} in SBA-15 as calculated by Eqs. (4) and (6).

narrow diameter (2.5 nm) as compared to the 2.9 nm samples. On the other hand, the phase-transition temperatures of the silylated samples occur at higher temperatures as compared to the non-silylated samples. It is interesting to compare these transition temperatures with the melting point of neat biphenyl, which is 69.2°C , *i.e.* 342.4 K. Thus the melting point of the molecules inside the pores is reduced by 110–120 K, depending on the diameter and surface structure of the samples.

Employing Eqs. (5) and (7) the distribution of the phase transition temperatures and activation energies of the melting process can be determined. The resulting curves are shown in Fig. 8. From the graphs it is evident that the narrower pores have a broader distribution of activation energies of the melting process than the larger pores.

Thus, enlarging the pore diameter changes the distribution of activation energies of the molecules towards higher average melting activation energies. This may be interpreted through the fact that larger pores eventually allow a more ordered packing of the guest molecules. The latter results in less packing defects and less unoccupied space, characteristics that explain much of the motional profile observed in those samples. A better packing hinders motion and increases its activation energy.

Fig. 9. Cartoon of the possible motional modes, which are able to explain the observed line-shape changes in the pre-melting region of the confined biphenyl. a) 180° -rotation of the whole biphenyl molecule; b) 180° -ring flip of a single phenyl ring according to Fig. 3a.

Fig. 10. Simulated deuteron NMR line shapes for a C_2 -flip of the biphenyl. a) full spectrum; b) sub-spectrum of para-deuterons; c) sub-spectrum of ortho- and meso-deuterons. Flip rates are from bottom to top (0 kHz; 1 kHz; 2 kHz; 3 kHz; 4 kHz; 5 kHz; 6 kHz; 7 kHz; 8 kHz; 10 kHz; 20 kHz; 50 kHz; 100 kHz; 200 kHz; 500 kHz; 1000 kHz; 2 MHz; 5 MHz; 10 MHz; 20 MHz; 50 MHz).

It is surprising that the transition temperature distributions in Fig. 8 are narrower than those found for the melting of benzene inside SBA-15 silica (Ref. [10], 15 K) and iso-butyric acid inside MCM-41 and SBA-15 (Ref. [19], 13 K respectively 26 K), despite the less favorable steric structure of the biphenyl.

As mentioned above there are some small deviations from the pure Pake line-shape already at temperatures well below the melting point, which are an indication of a pre-melting behavior.

From the geometry of the biphenyl molecule with its two-fold (C_2) axis it is tempting to model the first process at lower temperatures as a C_2 -rotational jump (180° flip) of the molecule respectively a phenyl-ring flip (Fig. 9). Both motions result in a C_2 -jump of the main principle axis of the quadrupolar tensors of the *o*, *m*- and the *o'*, *m'*

^2H -nuclei, exhibiting a flip angle of 120° . The main axis of the p, p' ^2H -nuclei is not affected. To study these possibilities we simulated the deuteron spectral line shape as a function of the C_2 -jump rate (Fig. 10). The simulations of the spectra with flip rates in the range of 100 kHz to 1 MHz resemble the experimental spectra at temperatures around 200 K, whereas the spectra around 150 K exhibit only small flip rates. This is confirmed by the similarity of the value of $Q_{zz} = 132$ kHz with the corresponding value of 133 kHz found previously for rigid benzene- d_6 [10,81]. If we tentatively assign these flip rates to a temperature activated Arrhenius process with a pre-exponential factor of 10^{13} s^{-1} we can estimate that the activation energy of the flip is in the range of (7–13) kJ/mol. Since these values are close to the values reported for the C_2 -flip of a single ring (see introduction), we take these results as a hint that C_2 -flips contribute substantially to the pre-melting behavior of the biphenyl.

A detailed study of the pre-melting behavior would necessitate the application of the one- and two-dimensional solid state NMR methods developed over the years by the Spiess group for phenyl-group dynamics (see for example refs [84–89]), preferably on selectively ^2H or ^{13}C -labeled biphenyl, which is beyond the scope of the present paper.

5. Summary and conclusion

The temperature dependence of the ^2H -NMR solid echo spectra of biphenyl molecules as guests in the mesopores of neat and silylated SBA-15 where measured. A strong reduction of the melting point of the biphenyl molecules by 110–120 K, depending on the diameter and surface structure of the samples, is observed. The line-shape changes in the melting region exhibit the typical glass-like behavior, observed also for other low-molecular weight organic molecules in confinement. This is indicative for a relatively broad distribution of rotational correlation times for the isotropic reorientation of the biphenyl molecules. This distribution of correlation times can be attributed to a broad distribution of activation energies for the rotational motions, which is characteristic for a glass-like amorphous phase. Employing the Roessler *two-phase* model and assuming an Arrhenius relation between correlation times and activation energies and a Gaussian distribution of activation energies, it is possible to elucidate the centers of gravity and the widths of these activation energy distributions from the experimental data. Finally at temperatures closely below the glass-transition temperature characteristic deviations from a static Pake pattern of an aromatic deuteron are observed, which are indicative for a pre-melting of the biphenyl. A more detailed analysis of this phase behavior would necessitate calorimetric measurements, which are beyond the scope of the present paper.

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