

# Solid State NMR Studies of the Bromocyclohexane/Thiourea Inclusion Compound

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**Abstract.** Solid state  $^{13}\text{C}$ -MAS and  $^2\text{H}$ -NMR investigations have been performed on the bromocyclohexane/thiourea inclusion compound. The main objective of this study was the evaluation of the molecular features of the guest molecules and their changes over a large temperature range ( $100\text{ K} < T < 350\text{ K}$ ). Particular emphasis was placed on the molecular behaviour in the vicinity of a solid–solid phase transition at  $T = 237\text{ K}$  and in the low temperature phase, which was hitherto unknown. The  $^2\text{H}$ -NMR lineshape and relaxation studies reveal that, in the low temperature phase, restricted but fast overall motions (MHz to GHz region) of the guest molecules are dominant and reflect the distorted symmetry of the thiourea channels. On heating above the solid–solid phase transition almost unrestricted overall motions appear, together with a large degree of orientational disorder at higher temperature. Furthermore, the ring interconversion process presents a major relaxation process in the MHz region. The conformational order is unusual in the sense that the axial conformational state of the guest molecules is stabilized in the thiourea channels. It turns out that this unique property is also preserved in the low temperature phase.

**Key words:** thiourea inclusion compounds,  $^2\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, solid state NMR.

## 1. Introduction

It is well known that thiourea and urea form inclusion compounds in the presence of suitable organic guest molecules like cycloalkanes or *n*-alkanes [1, 2]. X-ray diffraction studies have shown that at room temperature both systems build up one-dimensional, channel-like structures with typical hexagonal cross-sections (Figure 1), stabilized by hydrogen bonds, and which can be distinguished by their diameter [3–8]. The urea channel appears to be rather ‘homogeneous’ having an almost constant inner diameter of 5.5–5.8 Å along the channel. Due to the rather small cross-sectional area of the urea channels only linear and branched or functionalized hydrocarbons can be incorporated [1]. The amount and type of branching, however, is limited by the channel diameter. Typical substituents in such alkane chains are methyl and ethyl groups or halogen atoms. In contrast, the thiourea channels are appropriate for storing bulky molecules such as substituted cycloalkanes [2, 9]. Their channel diameters vary between about 5.8 and 7.1 Å, which is a direct consequence of the special arrangement of the host molecules. In most systems investigated so far the thiourea lattice at room temperature (space group:  $R\bar{3}c$ )

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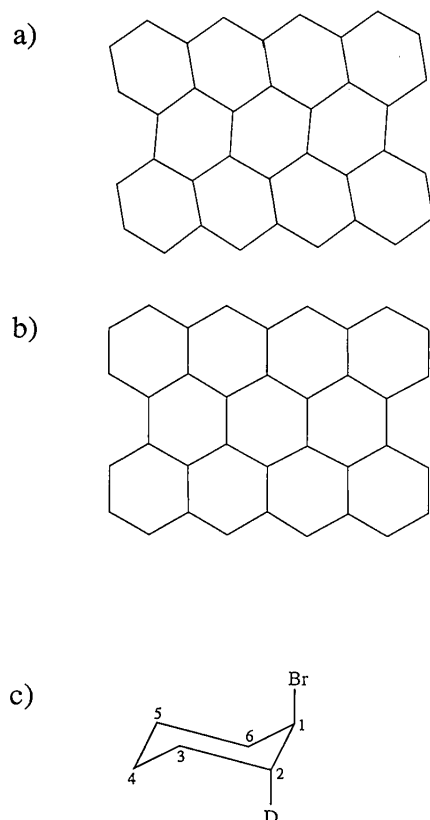


Figure 1. Sketch of the host lattice structure in thiourea inclusion compounds: low (a) and high (b) temperature phase (after [39]). Chemical structure of the selectively deuterated bromocyclohexane (c).

exhibits positions which are surrounded by three sulfur atoms at  $c/4$  and  $3/4c$  (diameter 7.1 Å) and  $\text{NH}_2$  groups at  $c/2$  and  $c$  (diameter 5.8 Å).

X-ray, NMR and differential scanning calorimetry (DSC) investigations have revealed that thiourea and urea inclusion compounds undergo solid-solid phase transitions below room temperature. These are connected with changes in the host lattice structure and have an impact on the molecular properties of the guest molecules [10–14]. In the low temperature phase a superstructure can often be detected [10] which is in line with an order–disorder phase transition.

Detailed studies have been performed, using a variety of experimental techniques, to obtain information about the structural and dynamic characteristics of the guest molecules within the host channels. For example the cyclohexane/thiourea inclusion compound has been studied extensively by thermochemistry [14–16], X-ray diffraction [3, 15–18],  $^{14}\text{N}$ -Nuclear Quadrupole Relaxation [15, 19], broadband  $^1\text{H}$ -NMR and relaxation measurements [18, 19] and solid-state  $^2\text{H}$ -NMR techniques [20, 21]. In particular, the latter studies have evaluated three different types

of motions for the guest molecules. In the low temperature phase with a monoclinic host lattice [18] the cyclohexane molecules are allowed to reorient only around their  $C_3$  symmetry axes which for their part are fixed within the host lattice. At the order–disorder phase transition the host lattice changes to a rhombohedral structure. This gives rise to additional motions of the cyclohexane molecules which have been assigned to a reorientational process of the guest molecules within the hexagonal channels. Eventually, at elevated temperatures the ring interconversion of the cyclohexane molecules becomes the most important relaxation process of the cyclohexane guests in these inclusion compounds. It was possible to show that the host lattice has almost no impact on the ring interconversion dynamics of the guest molecules [21].

Another well studied system with an order–disorder transition is the ferrocene/thiourea inclusion compound. In the low temperature phase two groups of ferrocene molecules can be assigned [22, 23]. Each group consists of three molecules having the molecular axis perpendicular to the channel axis or tilted by an angle of  $17^\circ$  with respect to the channel long axis, respectively. Above the phase transition the molecules start to exchange their positions within each group and at higher temperatures they also undergo exchange between the positions of the two different groups, which results in a net exchange between all six possible sites.

To put such order–disorder transitions on a broader basis we have carried out solid state  $^{13}\text{C}$ - and  $^2\text{H}$ -NMR experiments on bromocyclohexane in thiourea. Bromocyclohexane is different from the guest molecules mentioned above since it exhibits only a plane of symmetry. Such monosubstituted cyclohexanes are very well known as guests in thiourea inclusion compounds and have been investigated in detail by  $^{13}\text{C}$ -NMR, FT-IR and Raman spectroscopy [24–30]. The most prominent result of these studies was the observation of an unusual stabilization of the axial conformations of monosubstituted cyclohexanes bearing polar substituents. Likewise, the conformational dynamics between about 220 K and room temperature has been determined via variable temperature  $^{13}\text{C}$  magic angle spinning (MAS) NMR experiments [27–30]. These latter investigations gave further evidence of the presence of additional, most probably overall, motions of the guest molecules, a point which is not pursued further here. Complementary DSC studies for thiourea inclusion compounds with guest molecules like bromo- or chlorocyclohexane revealed a low temperature solid–solid phase transition [30]. The main objective of the present contribution is to obtain further insight into the specific molecular features of the bromocyclohexane molecules in the thiourea inclusion compound. Particular emphasis is placed on the behaviour in the vicinity of the solid–solid phase transition at  $T = 237$  K and in the low temperature phase, for which no experimental studies have previously been reported.

## 2. Experimental

Samples of thiourea inclusion compounds were prepared from a methanolic solution of thiourea and the desired guest molecule, as described elsewhere [2]. The selectively deuterated *trans*-bromocyclohexane-2-*d*<sub>1</sub> (Figure 1) was prepared by the reaction of cyclohexene with acetyl bromide, acetic anhydride and D<sub>2</sub>O by the method of Fahey *et al.* [31]. The purity of the compound was evaluated by high resolution <sup>13</sup>C- and <sup>1</sup>H-NMR spectroscopy and <sup>2</sup>H-NMR spectroscopy of a liquid crystalline solution [32]. Calorimetric studies were carried out with a Netzsch DSC 200 differential scanning calorimeter.

NMR measurements were performed on a basic Bruker CXP 300 spectrometer which was equipped with a Tecmag control unit and which operates at a frequency of 46.07 MHz for deuterium and 75.47 MHz for carbon, respectively. The <sup>2</sup>H-NMR spectra were obtained using a 5 mm home-built probe employing the quadrupole echo sequence  $(\pi/2)_x-\tau-(\pi/2)_y-\tau$  with  $\pi/2$  pulses of 2.0–2.2  $\mu$ s width and a time interval between the pulses of 20  $\mu$ s. The number of scans varied between 256 and 1024. The same pulse sequence could be used for the determination of spin–spin relaxation times ( $T_2$ ). Spin–lattice relaxation times ( $T_1$ ) were measured by the inversion recovery method using the quadrupole echo sequence for signal detection. In these experiments composite pulses were used instead of the inversion  $\pi$  pulse [33] consisting of the train  $[\pi/2]_\phi[\pi/2]_{\phi\pm\pi/2}[\pi/2]_\phi$ , with appropriate phase cycling ( $\phi = 0, \pi/2, \pi$  and  $3\pi/4$ ). The sample temperature during the variable temperature experiments was controlled with a Bruker BVT 1000 temperature control unit. Generally the temperature stability was maintained within  $\pm 1$  K.

For the <sup>13</sup>C-MAS-NMR investigations a Bruker 4 mm MAS probe was used. The experiments were carried out with the cross polarization technique (contact time 5 ms) or single pulse excitation ( $\pi/2$  pulse width 4  $\mu$ s) followed by high power proton decoupling. The recycle delay for these experiments was 12 s and the number of scans was between 256 and 512. The <sup>13</sup>C- $T_1$  measurements were done using the pulse sequence CP- $(\pi/2)$ - $\tau$ - $(\pi/2)$  as proposed by Torchia [34]. Here, CP means cross polarization and  $\tau$  refers to the variable delay.

Magnetization transfer spectra were obtained by the sequence CP- $\Delta$ - $(\pi/2)$ - $\tau$ - $(\pi/2)$  according to Szeverenyi *et al.* [35]. During this experiment the carrier frequency is set halfway between the peaks undergoing magnetization transfer. The delay  $\Delta$  is given by  $\Delta = 1/4\delta$  which ensures that at its end the two magnetizations are in antiphase to each other.  $\delta$  is the chemical shift difference of the two peaks in Hz and  $\tau$  is the variable delay.

Experimental data processing and analysis was done on a Sun Sparc 10 workstation with the NMR1 and Sybyl/Triad (Tripos/St. Louis) software packages. Lineshape simulations have been performed with suitable FORTRAN simulation programs. Details of the underlying procedures will be published elsewhere [36].

### 3. Results and Discussion

Variable temperature solid state NMR experiments have been performed on the bromocyclohexane/thiourea inclusion compound. To begin with, we discuss the results of the  $^{13}\text{C}$ -MAS-NMR experiments performed with the non-deuterated sample. A detailed study of the high temperature phase between 240 and 300 K has been published previously [30]. In that study it was shown that bromocyclohexane, like other mono- and disubstituted cyclohexanes [28–30, 37], undergoes ring interconversion with kinetic parameters very close to those evaluated from kinetic studies in solution. The most prominent result was the strong preference for the axial conformational state (population of the axial conformer:  $p_a = 0.95$ ) of bromocyclohexane, which is in line with the observations for other monosubstituted cyclohexanes bearing polar substituents. During the course of those  $^{13}\text{C}$ -MAS experiments it was shown further that the cross polarization technique [38] is rather inefficient. These findings have been related to a general high mobility of the cyclohexane derivatives in the thiourea channels which causes a reduction of all anisotropic magnetic interactions, such as the  $^{13}\text{C}$ - $^1\text{H}$  dipolar coupling or  $^{13}\text{C}$  chemical shift anisotropy. The latter motional reduction of the chemical shift anisotropy is also responsible for the observation that even for a slowly spinning sample (spinning frequency 1 kHz) no spinning sidebands are detectable.

The results discussed so far refer to the high temperature phase, which exists around room temperature. DSC investigations on the bromocyclohexane/thiourea inclusion compound revealed a low temperature solid–solid phase transition at  $T = 237$  K, which also exists for other systems [30]. During the  $^{13}\text{C}$ -MAS investigations of the present study several interesting observations were made upon cooling below the solid–solid phase transition: (i) the cross polarization becomes more efficient; (ii) small carbon signals show up at 28.8, 40.2 and 51.0 ppm; (iii) a splitting of some of the carbon signals is visible (carbons 2 and 6 by 0.8 ppm, carbons 3 and 5 by 0.5 ppm) (see Figure 2).

The improved cross polarization between protons and carbons can be related to a reduction of the overall mobility of the guest molecules in the low temperature phase. Thus, the heteronuclear carbon–proton dipolar coupling is stronger than in the high temperature phase, which is a prerequisite for an efficient polarization transfer. The additional weak signals are due to the equatorial bromocyclohexane conformer [39] with a relative amount of only 2% as derived from the integrated signal intensities. In contrast to the high temperature phase where, immediately above the phase transition, the ring interconversion gives rise to a significant broadening and merging of all NMR lines, now the ring interconversion dynamics of the bromocyclohexane guests is completely frozen on the NMR time scale. Well separated NMR lines can thus be observed for the axial and equatorial conformers. The relative amount of the two conformers is very close to the value found from the lineshape analysis of the variable temperature  $^{13}\text{C}$ -NMR experiments in the high temperature phase [28–30]. This implies that the conformational equilibrium

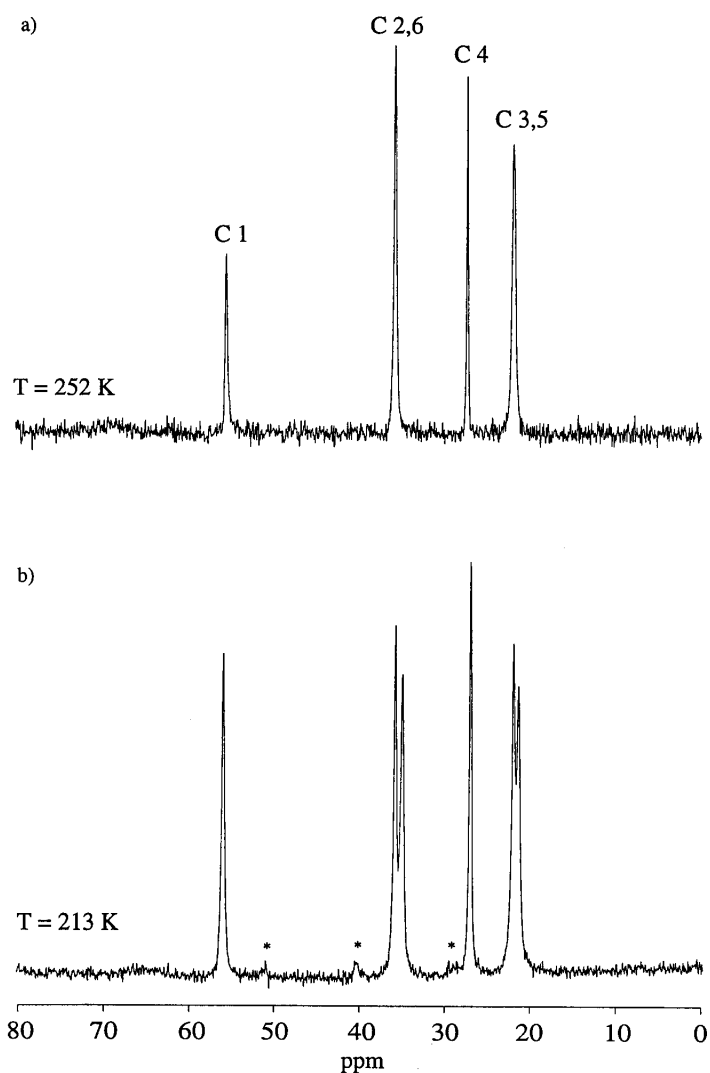


Figure 2.  $^{13}\text{C}$ -MAS-NMR spectra of the bromocyclohexane/thiourea inclusion compound in the high (a) and low (b) temperature phase. The spectra were taken at a sample spinning rate of 4.1 kHz. Asterisks indicate the  $^{13}\text{C}$ -NMR signals due to the equatorial conformer.

is almost unaffected at the solid–solid phase transition. The unusual stabilization of the axial conformer, which is still not completely understood on a molecular level, is obviously preserved in the low temperature phase. It should be noted that a theoretical model has recently been applied to the chlorocyclohexane/thiourea inclusion compound [40]. The authors were able to show that the preferred axial conformation of the guest species can be understood on the basis of a commensurate behaviour of the guest and host substructures. It might be possible that this model

is also adequate to explain the conformational equilibrium of bromocyclohexane in thiourea. Further work along this line is in progress.

$^{13}\text{C}$   $T_1$ -relaxation measurements and magnetization transfer experiments have been performed to obtain further insight into the nature of the splitting of some carbon signals in the low temperature phase. Thus, it is expected that different types of molecules are distinguishable by their  $T_1$  relaxation behaviour. As a result, the two lines within each signal pair of the carbons 2,6 and 3,5, respectively, should relax differently if they originate from two species within the channel. However, as can be seen from Figure 3, the carbon signals within each pair exhibit the same experimental  $T_1$  relaxation time (for carbons 2, 6:  $T_1 = 450$  ms); i.e. the two types of molecules, if they are present at all, are indistinguishable on the basis of the  $T_1$  relaxation data. The magnetization transfer experiment can give information about exchange processes between two molecular species on a time scale comparable with the variable delay  $\tau$  (see Section 2). Representative magnetization transfer spectra of bromocyclohexane in thiourea are given in Figure 3. The delay  $\Delta$  has been chosen so that the lines of the signal pair for carbons 2,6 are in antiphase to each other. From the experimental spectra there is no evidence of an exchange process which would give rise to a fast decay of the two signals in antiphase. Rather, the signal decay is determined by the  $T_1$  relaxation, as can be seen from a comparison with the partially relaxed  $^{13}\text{C}$   $T_1$  spectra.

On the basis of these experiments it is very unlikely that the observed splitting of the strong (and also of the weak)  $^{13}\text{C}$ -NMR signals for carbons 2,6 and 3,5 are due to two different types of guest molecules, i.e. two types of molecules which are distinguished by their locations within the thiourea channels. In that case one would also expect an additional splitting of the signals for carbons 1 and 4, which is in contrast to the present observations. Rather, we have to deal with a single type of guest molecule in the low temperature phase where the carbons of the two wings of the molecules – which are related by the molecular plane of symmetry – lose their magnetic equivalence. On the average the two wings of the bromocyclohexane molecules experience a different chemical environment which supports the assumption of motionally restricted guest species. It should be noted that the above interpretation holds for both the axial (relative amount 98%) and equatorial conformational state (2%) of the bromocyclohexane guests.

Information about the exact location or orientation of the guest molecules that could help in the interpretation of these findings cannot be obtained from the present investigations. Although there is no X-ray structure available for the low temperature phase of the compound examined here, it is reasonable to assume that the host lattice is distorted – similar to the observations for the inclusion compounds with cyclohexane, ferrocene or 1,5-cyclooctadiene [19, 41, 42].

Here, a severe steric hindrance of the guest species is expected and should cause the observed reduction of the guest mobility. In fact, in a recent X-ray investigation of the chlorocyclohexane/thiourea inclusion compound, the host lattice structure of both the high and low temperature phase has been determined. For the high

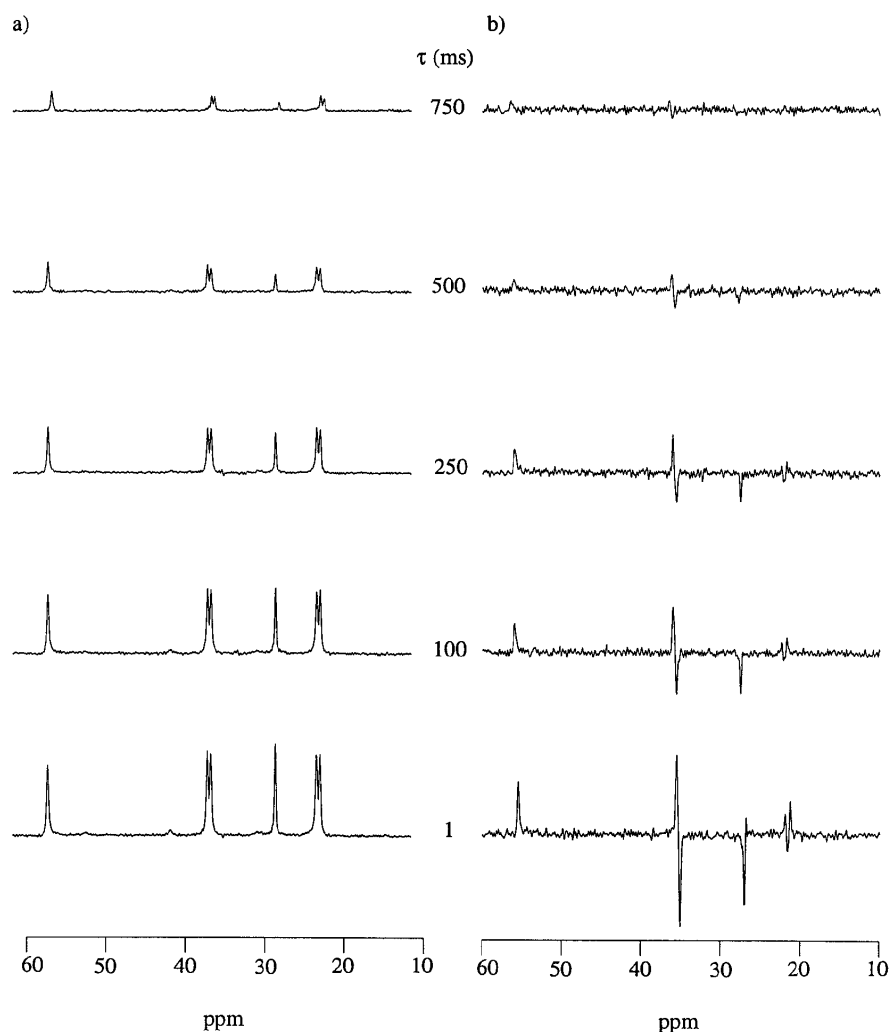


Figure 3. (a)  $^{13}\text{C}$ -CP/MAS spectra of bromocyclohexane in thiourea obtained during  $T_1$  relaxation experiments at the intervals  $\tau$  given in the spectra. (b)  $^{13}\text{C}$  magnetization transfer spectra of the same compound at various intervals  $\tau$ . All spectra were recorded at  $T = 213\text{ K}$ .

temperature phase the host lattice is again found to be rhombohedral with hexagonal host channels, while for the low temperature phase a monoclinic structure with distorted hexagonal channels has been derived [43].

In this X-ray study the authors offer the opinion that, as a result of the Rietveld refinement routines, the chlorocyclohexane guests might exist in an 'envelope'-like conformation. It is mentioned, however, that a final proof of this proposed structure is not possible with the available experimental X-ray data. Our present  $^{13}\text{C}$ -NMR spectra demonstrate that such a conformation for bromocyclohexane in thiourea



Table I.  $^{13}\text{C}$  chemical shift values for bromocyclohexane in the thiourea inclusion compound and in solution.

	Chemical shift (ppm)				
	C-1	C-2,6	C-3,5	C-4	
(a) <i>Thiourea</i>					
High temperature phase ( $T = 252\text{ K}$ )	55.4	35.7	21.9	27.4	
Low temperature phase ( $T = 213\text{ K}$ )	<i>ax</i>	55.9	35.0	21.5	27.0
			35.8	22.0	
	<i>eq</i>	51.0	40.2	28.8	–
(b) <i>Solution</i> *					
	<i>ax</i>	55.2	34.9	21.2	26.0
	<i>eq</i>	52.2	38.9	28.0	25.2

\* Data taken from H.-J. Schneider and V. Hoppen: *Tetrahedron Lett.* **7**, 579 (1975).

is rather unlikely. The ‘envelope’-like conformation should cause a considerable change of the chemical shift values for all carbons, which is not found in the system examined here. On the contrary, the observed chemical shift values in the low temperature phase are still very close to the values reported for isotropic solution (see Table I) where the guest species adopt the common chair configuration.

To obtain additional information about the behaviour of the guest molecules in the two solid phases, and particularly in the vicinity of the phase transition, we have performed  $^2\text{H}$ -NMR investigations of bromocyclohexane which was selectively deuterated at carbon 2. Dynamic  $^2\text{H}$ -NMR spectroscopy is a well established technique to evaluate the motional and structural characteristics on a molecular level. In recent years this technique has shown its particular potential during the characterization of such quite different chemical systems as liquid crystals, polymers, biological membranes or inclusion compounds [44–49]. Taking into consideration the various experimental techniques available, dynamic  $^2\text{H}$ -NMR spectroscopy can be used to study molecular processes over several orders of magnitude. First of all, the  $^2\text{H}$ -NMR lineshapes are dominated by the quadrupolar interaction with the main interaction axis along the C— $^2\text{H}$  bond. The corresponding  $^2\text{H}$ -NMR spectra and the spin–spin relaxation times,  $T_2$ , are sensitive to molecular processes with rate constants of the order of the quadrupole coupling constant, i.e. between  $10^4$  and  $10^8\text{ s}^{-1}$ . Likewise, spin–lattice relaxation measurements can be used to study very fast motions with rate constants between  $10^8$  and  $10^{11}\text{ s}^{-1}$ . Very slow motions (rate constants  $10^{-1}$ – $10^2\text{ s}^{-1}$ ) are accessible employing 2D exchange [50] and hole burning experiments [51].

Figure 4 shows a representative series of variable temperature  $^2\text{H}$ -NMR spectra of this compound for both the low and high temperature phase. At low temperatures,

$T < 110$  K, a typical 'rigid limit' spectrum, characteristic of an immobile sample, is observed with a quadrupolar splitting between the perpendicular singularities of about 120 kHz. The spectra change significantly on heating. Eventually, close to the phase transition at  $T = 213$  K, a motionally narrowed, biaxial spectrum shows up with a splitting of about 16 kHz. The spectrum is further narrowed at the solid–solid phase transition. Just above the transition at  $T = 253$  K the spectral splitting is found to be 4.4 kHz. Note the different spectral widths for the low and high temperature phase spectra. Further temperature increase finally results in a single, almost isotropic line at  $T = 333$  K.

These spectra clearly indicate that the guest molecules possess some motional freedom, even in the low temperature phase. Although we are not at present able to perform a satisfactory lineshape simulation for the whole temperature range examined experimentally, the  $^2\text{H}$ -NMR lineshapes of the low temperature phase imply the existence of rather fast overall molecular motions of the guest molecules. It is most likely that they can be assigned to reorientational motions of the guests around their equilibrium positions which, however, are restricted by the distorted thiourea host channels.

Various motional models have been examined for a description of the experimental  $^2\text{H}$ -NMR spectra of the low temperature phase. We started by taking into account three-site (jump angle  $120^\circ$ ) or six-site (jump angle  $60^\circ$ ) nearest neighbour jumps around a symmetry axis. The distorted channel was considered by the assumption of unequally populated sites. Model calculations have been done on the basis of these approaches by varying the rate constants and the populations of the sites. However, the agreement between theory and experiment was rather poor.

Another approach was a tumbling motion of the guest molecules within the anisotropic channel matrix. This model was proposed earlier by Greenfield et al. [52] as a seven- or 19-site jump model in which the molecules are able to undergo nearest neighbour jumps along a sector of a sphere. Calculated quadrupole echo spectra ( $\tau = 20 \mu\text{s}$ ) obtained using the 19-site model with the same rate constant of  $k = 10^9 \text{ s}^{-1}$  (fast exchange limit) are shown in Figure 5. Again, the distortion of the hexagonal symmetry of the channel is considered by a highly unequal population of the various sites. For these simulations the population of the sites was kept constant while the opening angle  $\Theta$  was varied as given in the figure. The angle  $2\Theta$  describes the section of the sphere along which the molecules can reorient. Inspection of these spectra reveals that at least the experimental high temperature spectra between 200 and 235 K can be described assuming this model. However, the spectra at lower temperatures cannot be reproduced satisfactorily. At present, we follow this line by taking more complex motional modes into account, as, for example, superpositions of restricted reorientational and rotational motions.

In the high temperature phase the molecular constraints imposed by the host lattice are significantly reduced, which results in the observed narrowing of the experimental  $^2\text{H}$ -NMR spectra. The guest molecules are motionally and orientationally disordered, i.e. they undergo fast anisotropic reorientational motions within

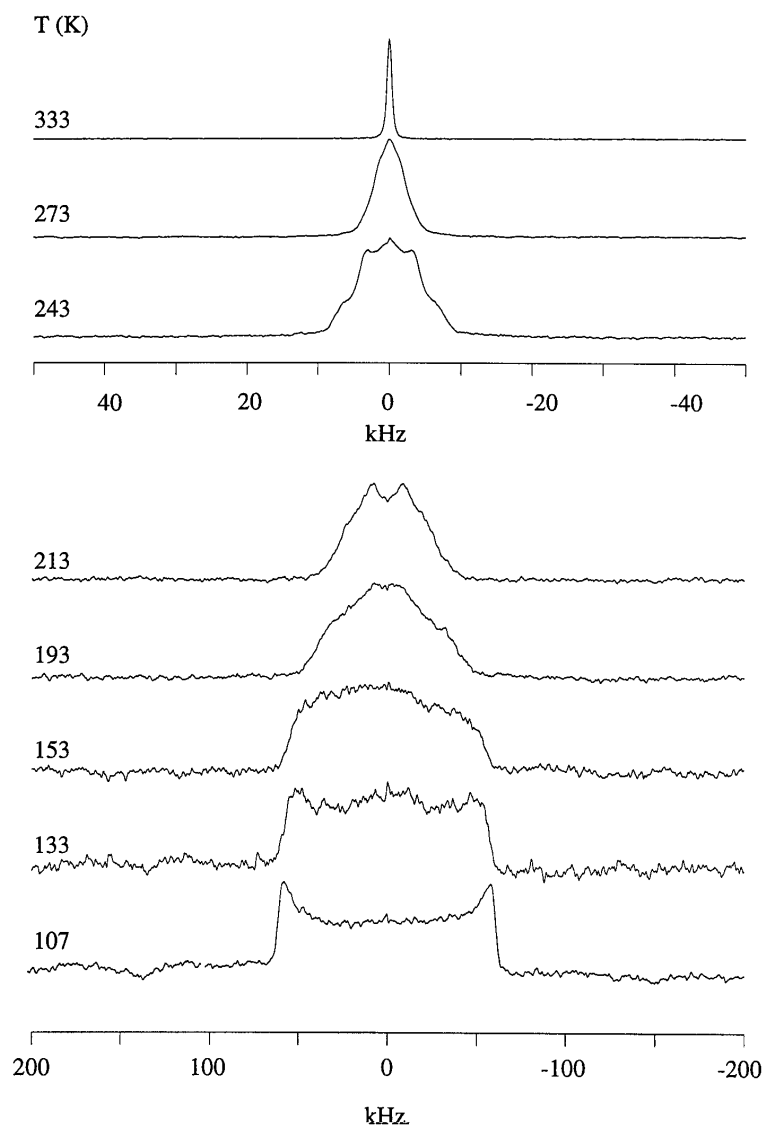


Figure 4.  $^2\text{H}$ -NMR spectra (quadrupole echo experiment:  $\tau = 20 \mu\text{s}$ ) of selectively deuterated bromocyclohexane in thiourea at the temperatures given in the figure. Note the different scaling for the upper and lower series of spectra.

the hexagonal potential of the host lattice. The latter also is reflected by the axial symmetric spectra found just above the phase transition. At higher temperatures the spectra accidentally change to a single, almost isotropic line (linewidth around 1 kHz) which arises from a further decrease in the orientational order and presumably from a change of the orientation of the motional symmetry axis of the bromocyclohexane molecules. Similar  $^2\text{H}$ -NMR experiments on the chlorocyclo-

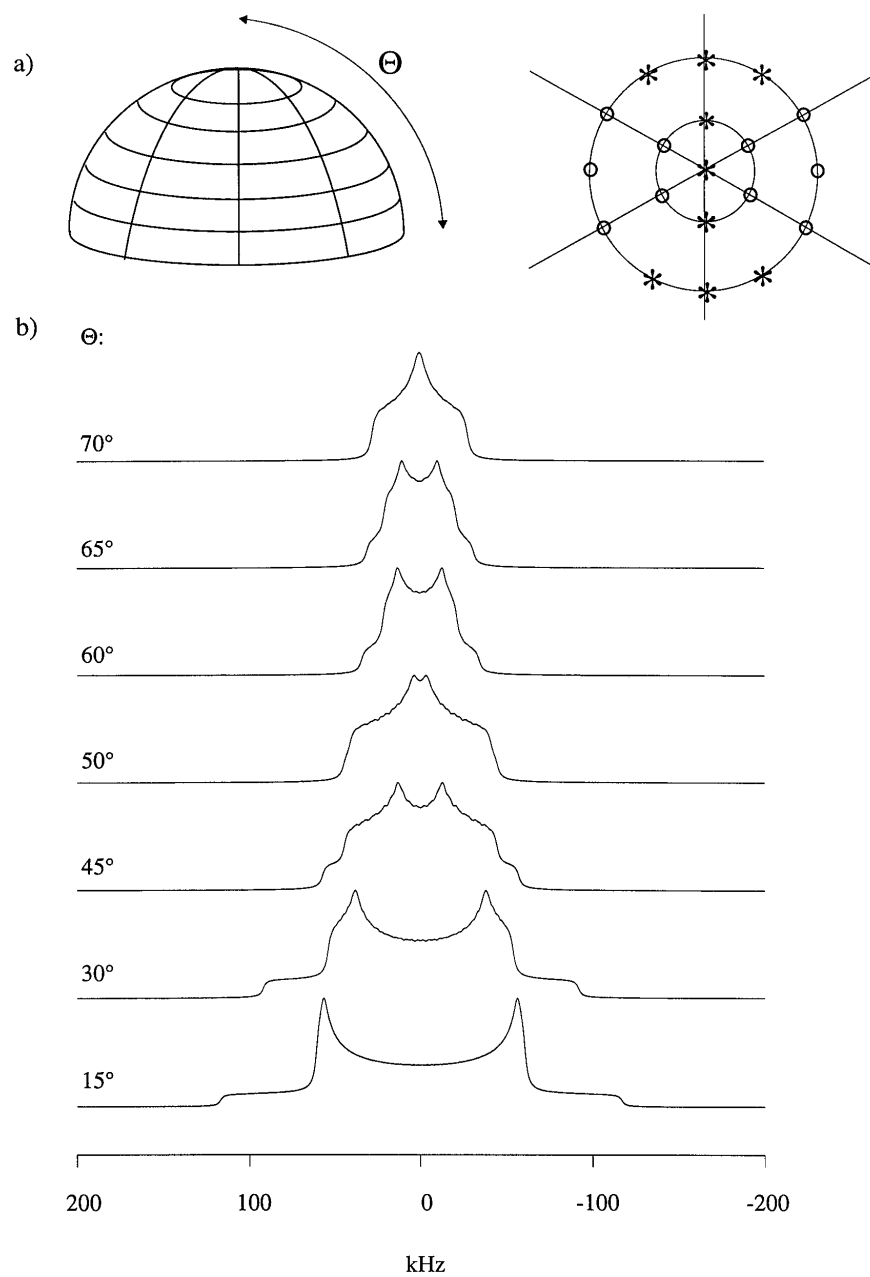


Figure 5. (a) Sketch of the 19-site model assuming a molecular reorientation of the molecules on a sector of a sphere. The symbols \* and ○ indicate sites which are distinguished by their population. (b) Simulated  $^2\text{H}$ -NMR quadrupole echo spectra ( $\tau = 20 \mu\text{s}$ ) using the 19-site model in the fast exchange limit ( $k = 10^9 \text{ s}^{-1}$ ). Other simulation parameters: quadrupole coupling constant:  $e^2qQ/h = 168 \text{ kHz}$ ; residual linewidth: 1 kHz; site populations:  $p(*)/p(\circ) = 10/1$ .

hexane/thiourea inclusion compound show motionally narrowed, axially symmetric lineshapes in the high temperature phase too, which remain up to the decomposition temperature of the sample. In this respect the thiourea host lattice behaves like a liquid crystalline solvent where the  $^2\text{H}$ -NMR spectra of a deuterated solute reflect the symmetry of the liquid crystalline environment and likewise the inherent molecular disorder of the sample [53].

Figures 6–8 display the results from the spin–spin and the spin–lattice relaxation experiments obtained for the selectively deuterated bromocyclohexane. In Figure 6 the  $T_1$  and  $T_2$  data are given as functions of the reciprocal temperature while representative partially relaxed spectra at two selected temperatures are shown in Figures 7 and 8. The  $T_1$  and  $T_2$  values refer to powder values which have been derived from the amplitudes of the corresponding free induction decays (FID). Although the partially relaxed  $T_1$  spectra show a typical  $T_1$  anisotropy across the spectrum (see below), the FID amplitudes were found to decay exponentially. For the quadrupole echo decay curves an exponential behaviour could again be used, although, in general, a non-exponentiality is expected for the intermediate regime [54]. As seen from Figure 6, in the high temperature phase the  $T_2$  values run through a shallow minimum at about 260 K, which reflects the contribution to the spin–spin relaxation from the ring interconversion process. At the minimum, this process has a rate constant of about  $10^5 \text{ s}^{-1}$  which is very close to the value obtained from an analysis of previous variable temperature  $^{13}\text{C}$ -MAS investigations [30]. In the low temperature phase the  $T_2$ -values gradually increase with temperature and continuously pass through the solid–solid phase transition.

The gradual increase of the  $T_2$  values in the low temperature phase is related to an increase in motional mobility, which is thermally activated and is also reflected in the  $^2\text{H}$ -NMR lineshapes, as discussed above. Again, it is assumed that a tumbling motion of the guest molecules within the asymmetric potential of the distorted host channels is responsible for the spin–spin relaxation. This interpretation is supported by the partially relaxed spectra [55] given in Figure 7, which were obtained from the quadrupole echo experiment and which are plotted to equal intensity to emphasize the  $T_2$  anisotropy across the spectrum. For longer pulse spacings ( $\tau > 75 \mu\text{s}$ ) it is found that the centre of the spectrum relaxes faster than the outer spectral regions. Simulations of the partially relaxed  $^2\text{H}$ -NMR spectra on the basis of the motional 19-site model presented above show a behaviour in the  $T_2$  relaxation that is quite similar to the experimental spectra. However, a quantitative fit deserves further refinements of the motional model, as mentioned earlier during the discussion of the NMR lineshapes.

It is interesting to note that no  $T_2$  minimum is observed in the low temperature phase. This is related to the fact that the relevant molecular motions are already beyond the  $T_2$  minimum, i.e. close to the fast exchange limit (see also next paragraph). Thus, the main contribution to the changes in  $T_2$  in the low temperature phase stems from the increase in spatial freedom which also is reflected by the narrowing of the  $^2\text{H}$ -NMR spectra.

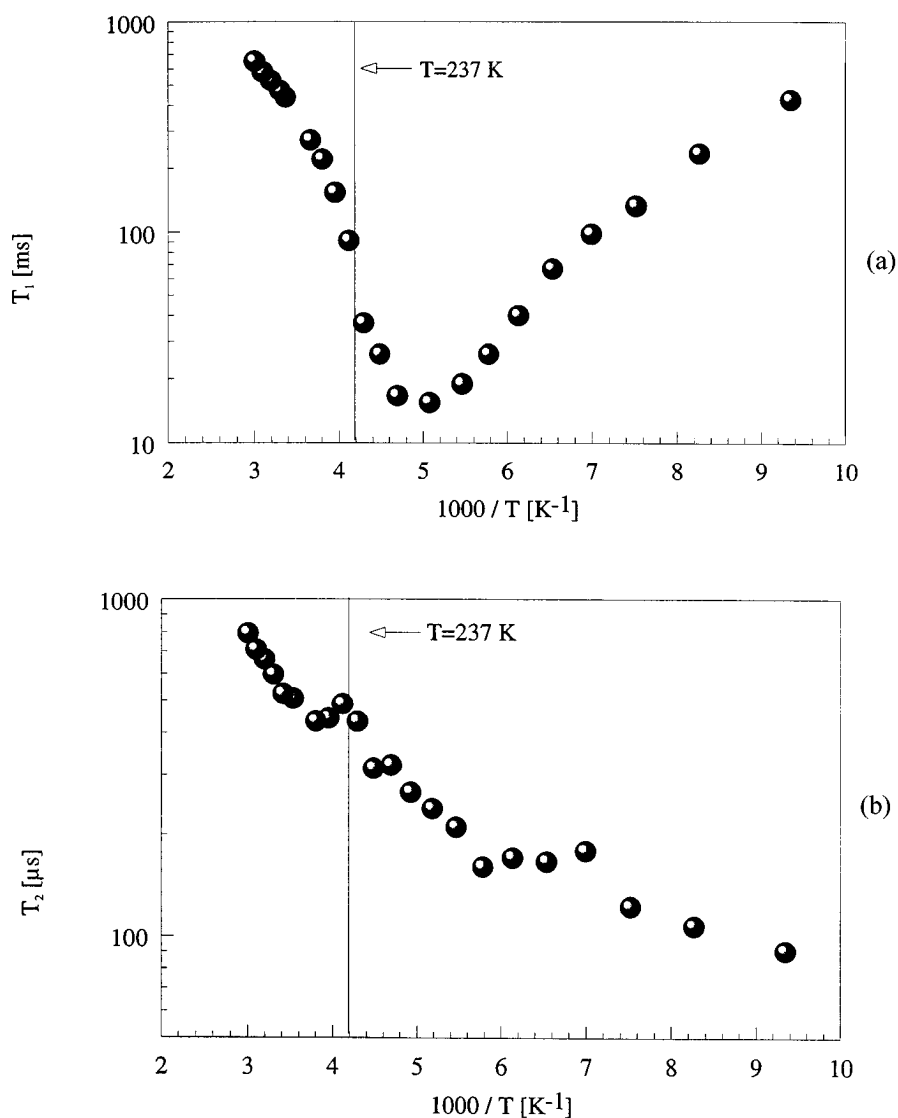


Figure 6. Experimental  $T_1$  and  $T_2$  relaxation data for deuterated bromocyclohexane in thiourea in the low and high temperature phases.

A further interesting behaviour is evident from the  $T_1$  relaxation data given in Figure 6. Here, a significant  $T_1$  minimum at around 200 K with an absolute  $T_1$  value of 15 ms can be found, which clearly proves the presence of a rapid motional process with a rate constant of the order of about  $10^9$  s<sup>-1</sup>, the experimental Larmor frequency. Further information about the underlying process might be obtained from the partially relaxed spectra, which are given in Figure 8 and which are plotted with equal intensity (i.e. not scaled). Again, a pronounced  $T_1$  anisotropy is

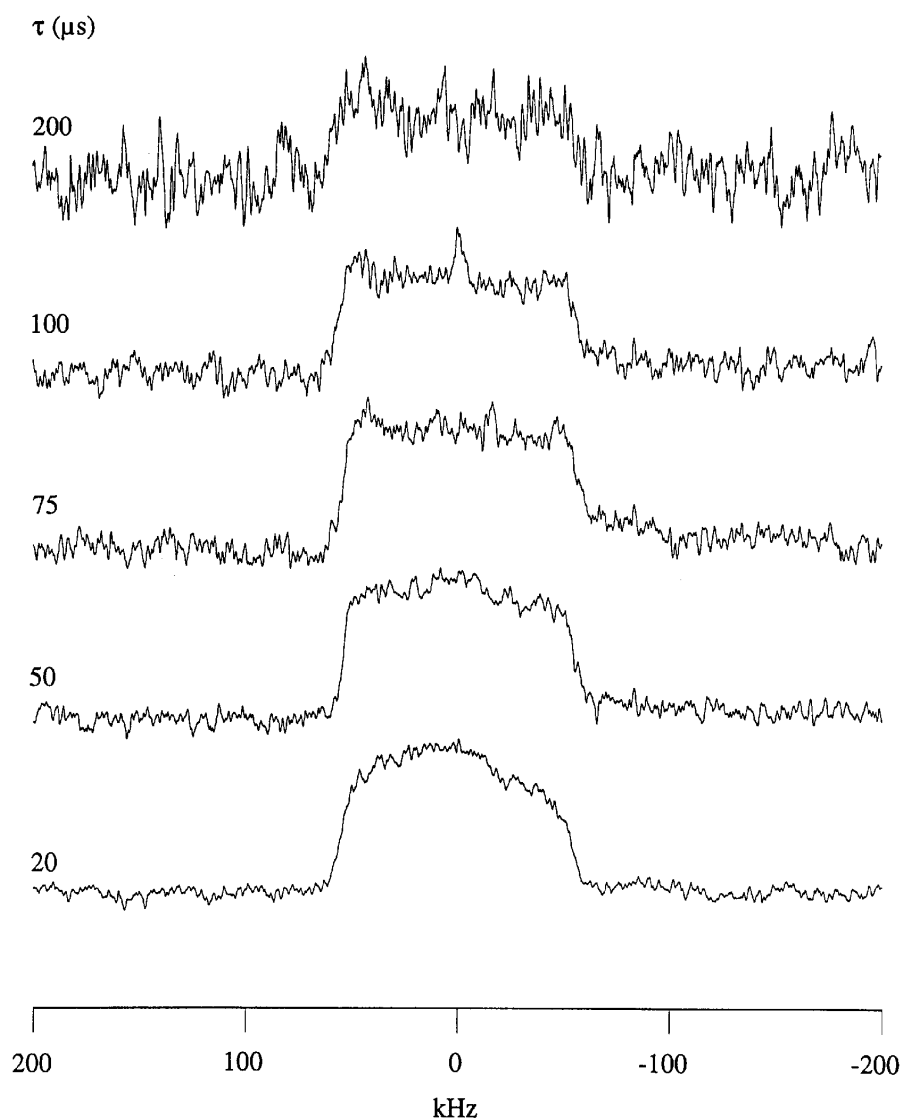


Figure 7. Experimental partially relaxed  $^2\text{H}$ -NMR spectra (quadrupole echo experiment) of selectively deuterated bromocyclohexane in thiourea in the low temperature phase at  $T = 153$  K. The pulse spacings used for the various experiments are given in the figure. All spectra are plotted with equal intensity (not scaled, see text).

observed, which indicates the presence of a very rapid restricted motional process [56]. Whether the underlying process is the same tumbling motion as proposed above, or whether an additional process is dominant here, cannot be answered finally.

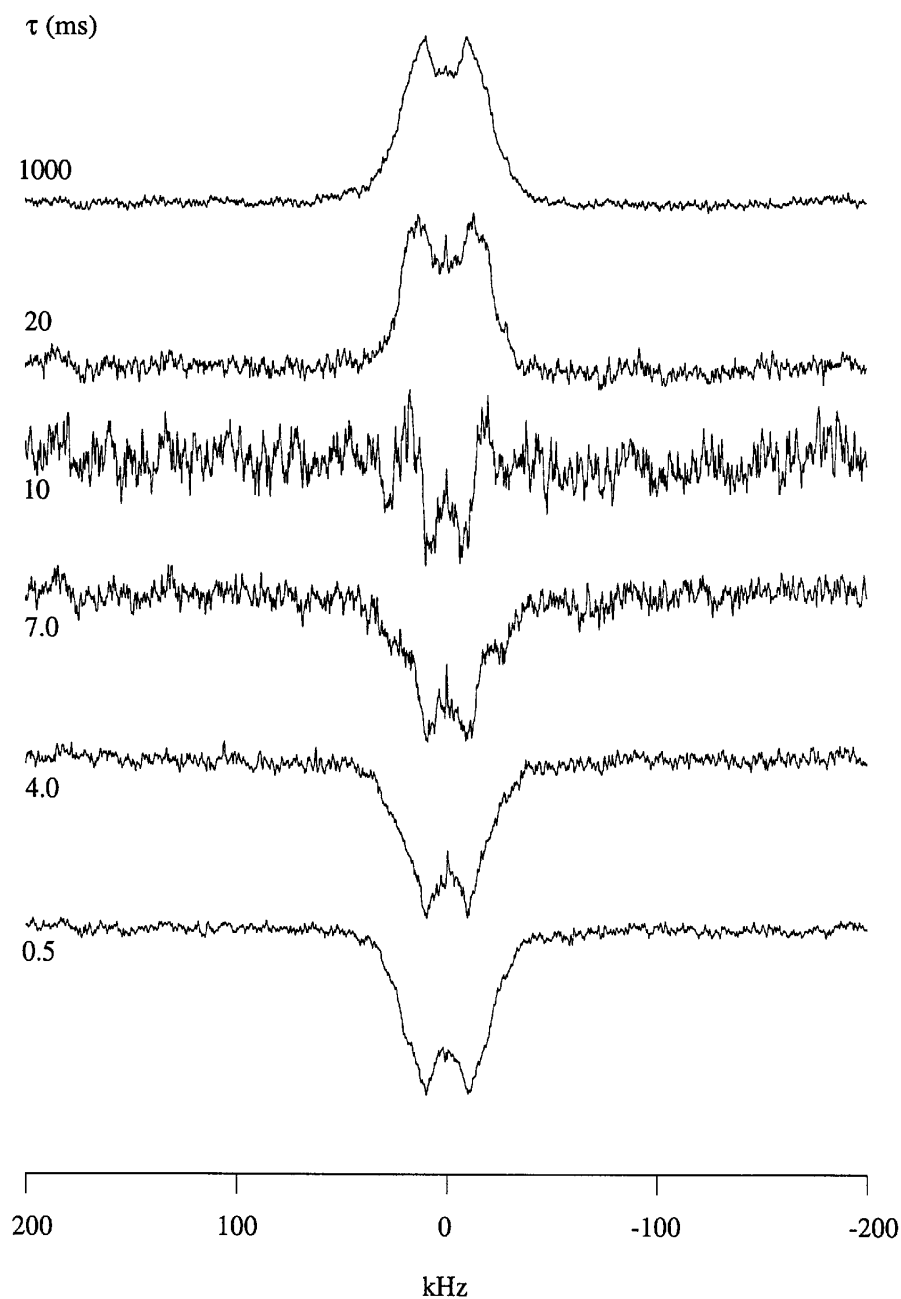


Figure 8. Experimental partially relaxed  $^2\text{H}$ -NMR spectra (inversion recovery experiment) of selectively deuterated bromocyclohexane in thiourea in the low temperature phase at  $T = 223\text{ K}$ . The pulse spacings used for the various experiments are given in the figure. All spectra are plotted with equal intensity (not scaled, see text).



A further hint about the motional behaviour can be obtained from the slopes of the  $T_1$  curve. As seen from Figure 6, there are changes in the slope of the  $T_1$  curve which indicate various contributions to the  $T_1$  relaxation. To begin with, the phase transition is accompanied by a discontinuity in the  $T_1$  curve reflecting an abrupt change of the overall molecular motions. Furthermore, the change in the slope of the  $T_1$  curve above the phase transition is most probably caused by the additional contribution from the ring interconversion process. In the low temperature phase the slope decreases below 150 K, which suggests the presence of a second motional contribution and which is also expected from the lineshape simulations. Further experiments using other selectively deuterated compounds as well as the development of a suitable  $T_1$  simulation program are in progress. Nevertheless, we can state that a very rapid overall motional contribution exists in the low temperature phase. From the slope of the  $T_1$  curve in the extreme narrowing limit (in the vicinity of the  $T_1$  minimum), an activation energy of about 15 kJ/mol can be derived, which is a reasonable value for such overall motional processes. For example, activation energies of about 10 kJ/mol have been found for the rotational motion of cyclohexane in inclusion compounds [21, 57].

The present  $^2\text{H}$ -NMR investigations, comprising lineshape studies and  $T_2$  and  $T_1$  relaxation experiments, gave information about the dynamics of the bromocyclohexane guests in the low and high temperature phase in the thiourea inclusion compound. Although the experimental data are still not fully understood, insights into the rather complex motional behaviour of monosubstituted cyclohexanes in thiourea inclusion compounds, in particular for the low temperature phase, have been achieved for the first time. Comparable  $^2\text{H}$ -NMR investigations have previously been performed on highly symmetric molecules like cyclohexane and ferrocene in thiourea or trioxane in urea inclusion compounds [20–23, 58]. In this context, the investigations on *n*-alkanes in urea should also be mentioned [59]. For the former group of systems low temperature solid–solid phase transitions have been reported which had a strong impact on the molecular dynamics of the guest species. These systems, however, after all appear to be much simpler since the guest molecules exhibit a higher molecular symmetry. Thus, in their low temperature phases all overall motions have usually been frozen, except for the rotational motions around the  $C_3$  symmetry axis, which is otherwise fixed in the host lattice. Additional reorientational motions and ring interconversions take place in the high temperature phase, which result in a large degree of orientational disorder. The solid–solid phase transitions for these systems can therefore be well understood as order–disorder transitions.

The same is true for hexadecane in urea. Here, a recent  $^2\text{H}$ -NMR study showed that the low temperature phase can be characterized by a very rapid restricted rotation of the alkane chains around their long axis in the GHz region [60]. The rotational angle increases linearly with temperature. Above the solid–solid phase transition this motion again is replaced by an almost free rotation of the alkane chains. This latter motion is well known from previous studies of the high tempera-

ture phase of other urea inclusion compounds and gives rise to a rotational disorder [59].

Likewise, the low temperature phase of the system examined here is characterized by restricted overall motions, most probably reorientational motions (tumbling) of the molecules around their equilibrium positions. The  $T_2$  and  $T_1$  relaxation experiments clearly show that the timescale of these processes are in the MHz to GHz region. In the high temperature phase the overall motions become much less restricted, which causes a large orientational disorder of the guest species. As for the systems mentioned above, the solid–solid phase transition can thus be ascribed to a dynamic order–disorder transition.

#### 4. Conclusions

Solid state NMR investigations employing  $^{13}\text{C}$ -MAS and  $^2\text{H}$ -NMR techniques have been performed on the bromocyclohexane/thiourea inclusion compound. It has been shown that the high temperature phase is characterized by a high degree of orientational disorder. This stems from the high mobility of the guest molecules in the hexagonal channels which are anisotropic reorientational motions within the symmetric thiourea channels. Furthermore, the ring interconversion process has to be taken into account as it presents a significant contribution to the  $T_2$  relaxation behaviour in the high temperature phase. With respect to the conformational order, a strong preference for the axial conformational state has been derived.

In the low temperature phase all overall motions, although highly restricted, still show up on a rather fast timescale. Reducing the temperature to about 100 K eventually results in a freezing of all overall motional modes. Upon heating above the solid–solid phase transition these restricted processes are replaced by almost unrestricted overall reorientational motions of the high temperature phase, as mentioned above. Thus, on the molecular level the phase transition is primarily expressed by the build-up of hexagonal thiourea channels, along with an increase in motional mobility which causes motional or orientational disorder. That is, we have to deal with a dynamic order–disorder transition. So far, an absolute determination of the various motional modes together with a complete evaluation of the corresponding kinetic parameters is not possible. Further work along this line is in progress, taking into account other selectively deuterated bromocyclohexanes as well as other guest molecules.

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