Solid-State NMR Study of Guest Molecule Dynamics in 4-Alkyl-*tert*-butylbenzene/Thiourea Inclusion Compounds

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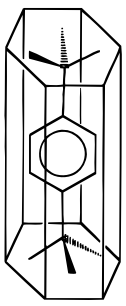
Received: July 1, 1997[⊗]

Deuterium nuclear magnetic resonance (NMR) powder spectra, deuterium spin−lattice relaxation times (T_1) and ^{13}C CP/MAS NMR spectroscopy are used to investigate guest motion in 4-alkyl-*tert*-butylbenzene/thiourea inclusion compounds (alkyl = *tert*-butyl, isopropyl, and ethyl). Differential scanning calorimetry data indicate no solid−solid phase transitions for any of the three inclusion compounds in the temperature range −100 to +200 °C. Carbon-13 CP/MAS dipolar dephasing experiments indicate that the phenyl ring of all three guests reorient rapidly about the C_1-C_4 axis at room temperature. Deuterium T_1 data for the 1,4-di-*tert*-butylbenzene-d_{18}/thiourea (DTBB-d_{18}/TU) inclusion compound display two distinct mimina. Internal methyl rotation modulates T_1 in the higher temperature region, while *tert*-butyl reorientation affects T_1 at lower temperatures. Activation energies of 12.0 (±0.5) kJ/mol and 11.3 (±0.4) kJ/mol, respectively, were determined. Low-temperature ^{2}H spectra of the DTBB-d_{18}/TU inclusion compound provide insight into the conformation of the methyl protons within the *tert*-butyl group. Deuterium NMR spectra indicate that the phenyl ring of the guest DTBB-d_4 in thiourea reorients between three positions in the host hexagonal channel. Distortions of the thiourea channel at lower temperatures affect the populations of the three sites. Deuterium T_1 data for the DTBB-d_4/TU inclusion compound allows a comparison of the rate of phenyl ring reorientation with that of *tert*-butyl motion and shows that the two motions within the same molecule are not correlated. The deuterium NMR spectra of the guest 4-isopropyl-d_6-*tert*-butylbenzene in thiourea (ITBB-d_6/TU) can be simulated using a model where six-site exchange of the isopropyl group modulates the line shape while the methyl rotation remains fast ($k > 10^8$ s^{-1}). At the temperatures investigated, ^{2}H spin−lattice relaxation times for ITBB-d_6/TU are being influenced by internal methyl rotation within the isopropyl group. An activation energy of 13.1 (±0.5) kJ/mol was calculated. Similarly, the changes in the ^{2}H spectra of the 4-ethyl-d_3-*tert*-butylbenzene/thiourea clathrate (ETBB-d_3/TU) indicate that the ethyl group also reorients between six sites in the host channel, superimposed by fast methyl rotation, which remains rapid ($>10^8$ s^{-1}) on a lowering of temperature. Again ^{2}H T_1's are being influenced by internal methyl rotation (E_a = 11.6 (±0.5) kJ/mol) over the temperature range investigated. Finally, the rate of methyl rotation within each of the three functional groups is correlated with the strength of intramolecular interactions within the respective alkyl groups.

Introduction

Thiourea is known to form channel inclusion compounds with a wide variety of organic guest molecules, such as cyclohexane derivatives, branched-chain paraffins, and some alkyl-substituted aromatic compounds.[1,2] In the presence of guest molecules, the thiourea lattice usually adopts a rhombohedral structure.[3−5] X-ray diffraction studies have shown that the thiourea molecules form a hexagonal channel, of approximately 7.0 Å diameter, in which guests of appropriate size reside.[6,7] The lattice is held together by hydrogen-bonded thiourea molecules. Calorimetric studies of thiourea clathrates often show phase transitions, which are associated with a change in the channel's size or shape.[8] The thiourea host has a repeating structure in that the thiourea molecules point directly into the center of the channel at every third level, and it is usually at this point where the guest molecule is located.[9]

A prerequisite for the understanding of the stability of these inclusion compounds is a knowledge of the dynamic behavior of the guest molecule. X-ray diffraction studies of thiourea clathrates are often unable to locate the atomic positions of the guest molecule, but rather show a smeared-out electron density resulting from fast reorientational motion of the guest.[10] Deuterium NMR studies of the guest molecular dynamics in thiourea inclusion compounds of cyclohexane,[11] ferrocene,[12] and 1,4-di-*tert*-butylbenzene[13] have recently been reported. We have chosen to continue studies of the 1,4-di-*tert*-butylbenene/thiourea (DTBB/TU) inclusion compound (**1**),in addition to examining



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the 4-isopropyl-*tert*-butylbenzene/thiourea (ITBB/TU) inclusion compound deuterated exclusively on the isopropyl methyl

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S1089-5647(97)02128-7 CCC: $14.00

groups, and the 4-ethyl-*tert*-butylbenzene/thiourea (ETBB/TU) clathrate deuterated on the ethyl CH_3 group. These studies will provide insight into the effect of steric interactions (both host−guest and intramolecular) on the dynamics of these three alkyl groups.

The dynamics of guest molecules in clathrate compounds is complex because these molecules are often only weakly held within the structure. As well as internal rotational motion, the guest may undergo reorientation and translation within the lattice formed by the host molecules. In this particular study, the following molecular reorientations must be considered: (1) motion of the methyl groups about the CH_3−C bonds; (2) motion of the *tert*-butyl, isopropyl, or ethyl group(s); (3) motion of the phenyl ring within the host lattice. Another important question to be addressed is whether the rates of molecular reorientation are primarily determined by intramolecular or guest−host interactions.

Theoretical Background

Solid-state deuterium NMR spectroscopy is one of the principal techniques used to study guest motion in inclusion compounds. In deuterium NMR spectroscopy, the spectrum is dominated by the interaction between the deuterium quadrupole moment, eQ, and the electric field gradient, whose principal component is eq_{zz}. The quadrupolar coupling constant, χ, is a measure of the strength of the quadrupolar interaction and is given by

$$\chi = \frac{e^2 q_{zz} Q}{h} \tag{1}$$

The asymmetry parameter of the electric field gradient tensor is defined as the difference between the two smaller principal components of the diagonalized electric field gradient tensor, eq_{xx} and eq_{yy}, with respect to the largest component, eq_{zz}.

$$\eta = \frac{eq_{yy} - eq_{xx}}{eq_{zz}} \tag{2}$$

In aliphatic compounds, the electric field gradient is usually axially symmetric along the C−D bond direction. For static methyl deuterons, η is usually zero and χ generally lies between 165 and 175 kHz. In that case, the spectrum from a deuterium nucleus located in a static C−D bond consists of a doublet with spacing

$$\Delta\upsilon = \frac{3e^2 q_{zz} Q}{4h}(3\cos^2\alpha - 1) \tag{3}$$

where α is the angle between the C−D bond and the static B_0 field. In powdered samples, the line shape is determined by the random distribution of the C−D bond orientations with respect to the magnetic field, yielding a Pake doublet with a characteristic splitting between peaks of $3\chi/4$ and shoulders separated by $3\chi/2$.

Molecular motion has two general effects on the deuterium powder spectrum. The motion averages the effective quadrupolar coupling constant to a value smaller than the static one. When the rate of reorientation is much less than χ, the motion has no influence, but when the rates are greater than χ, the spectra are determined by the motionally averaged quadrupole interaction. The motionally averaged spectrum may not necessarily have the axial symmetry of the static case. When the motion has less than 3-fold symmetry, the axial symmetry is lost.

In the intermediate dynamic range, when the reorientational rates are on the order of χ ($\sim 10^5$ s^{-1}), the ^{2}H powder spectra obtained by Fourier transforming the quadrupolar echo signal are severely distorted due to the very large T_2 anisotropy associated with the dynamic process.[14] In this motional regime there is a wide variation in T_2 with orientation of the axis of motion with respect to the direction of the applied magnetic field. As a consequence, crystallites with different orientations will exhibit different T_2's and will contribute in varying degrees to the echo signal and the subsequent spectrum. The deuterium spectra in the intermediate rate regime can be used as a method of determining both the type and rate of the molecular motion. Provided a suitable model for the motion is available, the spectra may be simulated.[15]

A further complicating factor in considering the motion of guest molecules is the possibility that the host cavity does not have the symmetry of the guest molecule. This can result in unequal populations of the sites taken up by the exchanging deuterium nucleus, leading to asymmetry in the powder spectrum.[16]

Enclathrated molecules may also undergo a librational motion, which can be modeled as precession of the principal symmetry axis on a cone, which may have a circular or elliptical shape.[17] This type of motion has a very small activation energy and is usually only encountered in the fast rate limit. Although the motion is best described as diffusion within a cone where the possible angles, ψ, are governed by a distribution function $g(\psi)$, a simpler model may be employed in which the molecule is allowed to precess on the surface of a cone of constant half-angle ψ.[17]

The spin−lattice relaxation time, T_1, characterizes the return of the bulk magnetization to its equilibrium state after a perturbing rf pulse. Relaxation is stimulated by time dependent nuclear spin interactions and is most efficient when these fluctuations occur at the resonance frequency of the nucleus. For deuterons, the primary source of these fluctuating fields is the time dependent part of the quadrupolar interaction.

When the reorientational motion can be described by an exponential correlation function and the temperature dependence of the correlation time follows Arrhenius behavior, the rate of relaxation may be fit to the following equations:[18]

$$\frac{1}{T_1} = K\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right) \tag{4}$$

$$\tau_c = \tau_\infty \exp\left(\frac{E_a}{RT}\right) \tag{5}$$

τ_c is the correlation time for the motion ($\tau_c \propto k^{-1}$), τ_∞ is its value at infinite temperature, and ω_0 is the Larmor precession frequency. In addition, E_a is the activation energy for the motion influencing T_1, and K depends on the strength of the dominant nuclear spin interaction (in this case χ^2) and the exact nature of the reorientational motion.[17] The form of the expression in parentheses in eq 4 assumes an exponential correlation function.

In this case, if a plot of T_1 vs inverse temperature is made, one often sees a V-shaped curve, with a T_1 minimum at $\omega_0\tau_c \approx 1$. There is, in general, considerable information to be extracted from this T_1 plot. The slope of the curve on either side of the T_1 minimum is proportional to the activation energy for the motion influencing T_1. The T_1 intercept gives a value for τ_∞, while the depth of the minimum can be used to determine a value for the effective quadrupolar coupling constant, χ. Note that knowledge of τ_∞ and E_a allows calculation of the motional rate at any temperature, through eq 5. In addition, ^{2}H spectral line shape changes are usually observed at temperatures cor-

responding to the low-temperature (ascending) side of the T_1 vs $1/T$ plot, for the particular motion influencing both the spectra and T_1's.

Usually, solid-state ^{13}C NMR is characterized by very broad resonances, but in some cases, the signals may be narrowed experimentally to a degree where chemical shifts can be resolved.[19] The dipole−dipole interactions and chemical shift anisotropy usually affect the NMR response of solid samples, but are averaged to zero in the liquid phase due to isotropic reorientation. In solids, these interactions can be removed by the combination of magic angle spinning (MAS) and high-power dipolar decoupling. In addition, cross polarization (CP) from ^1H to ^{13}C greatly increases the signal strength.

The nonquaternary suppression (NQS) pulse sequence is used to attenuate ^{13}C signals from carbons that have directly bonded protons. Experimentally, a brief delay, without proton decoupling, is inserted between the contact pulse and the free induction decay, during the normal cross polarization pulse sequence.[20] A very important exception to this rule occurs when the carbon under study undergoes rapid molecular motion. Some methyl ^{13}C resonances are difficult to attenuate entirely, because rapid methyl rotation reduces the magnitude of proton−carbon dipolar coupling. This can also apply to rapidly rotating CH or CH_2 groups. Therefore, this pulse sequence can qualitatively determine whether or not a CH group or a CH_2 group is undergoing rapid reorientation in the solid state.

Experimental Section

Deuterated samples of 1,4-di-*tert*-butylbenzene (DTBB) were prepared by Friedel−Crafts alkylation of benzene or benzene-d_6 with *tert*-butyl-d_9 chloride or *tert*-butylchloride and ferric chloride. Products were recrystallized from ethanol and were shown to be pure by high-resolution NMR and melting point. The DTBB/TU clathrate was prepared by mixing equal weights of thiourea and deuterated DTBB in enough methanol to dissolve both solids at room temperature. After slow evaporation the crystals were harvested and washed with pentane in order to remove excess DTBB. Elemental analysis showed that the DTBB/thiourea clathrate crystallized in a 1:6 complex.

4-Isopropyl-d_6-*tert*-butylbenzene was prepared by first reacting 4-*tert*-butylphenylmagnesium bromide with acetone-d_6 to give 4-*tert*-butyl-α,α-dimethyl-d_6 benzyl alcohol. The alcohol was then reduced by lithium in a liquid ammonia/tetrahydrofuran mixture at −78 °C (dry ice/acetone bath) to give nearly pure product. The product was not further purified but was selectively separated by adding the resultant liquid to 10 mL of a saturated thiourea/methanol solution. The crystalline inclusion compound was separated by filtration and air dried. The product was shown to be pure by solution NMR.

4-Ethyl-d_3-*tert*-butylbenzene was prepared by the reaction of 4-*tert*-butylbenzaldehyde and the CD_3MgI Grignard reagent, with subsequent reduction of the alcohol by the aforementioned method. The product was shown to be pure by solution NMR. It should be noted that thiourea inclusion compounds could not be made with *tert*-butylbenzene or 4-methyl-*tert*-butylbenzene as guests.

The deuterium spectra were recorded on a home-built, phase coherent pulsed NMR spectrometer operating at 44.7 MHz, using the quadrupolar echo pulse sequence: $(\pi/2)_{\pm x}-\tau_Q-(\pi/2)_y-\tau_Q-$acquire.[21] The length of the $\pi/2$ pulse was approximately 3.5 μs. At each temperature, the echo signals were collected for a τ_Q value of 40 μs. The echo signals were Fourier transformed to obtain the deuterium NMR spectra. The spectrometer was used with a 50 mm bore, 6.8 T (Bruker/Nalorac) superconducting magnet. The nuclear signal was digitized in a Nicolet Explorer digital oscilloscope, which was interfaced to an IBM PC. The computer was programmed to provide automatic temperature regulation for the sample and data acquisition. The sample probe was designed to study powder samples over a temperature range of 100−400 K. The sample chamber was surrounded by a thick-walled copper container. Cold N_2 gas was passed through channels that had been milled into the copper vessel, to cool the sample chamber. The temperature of the chamber was electronically regulated to within ±0.1 °C over the course of a measurement using a copper-constantan thermocouple to monitor the temperature and a heater would nonconductively on the copper vessel. A second separate thermocouple located near the sample itself was used to record the actual sample temperature, which was known to within ±0.5 °C.

The deuterium T_1 data were acquired using an inversion recovery pulse sequence modified for quadrupolar nuclei: $(\pi)_x-\tau-(\pi/2)_{\pm x}-\tau_Q-(\pi/2)_y-\tau_Q-$acquire.[22] Typically, 12 values of τ were used to determine T_1 at each temperature. The pulse spacing, τ_Q, for the T_1 determination was 40 μs. The time between repetitions of the pulse sequence was always greater than $10T_1$. The data were fit using a nonlinear least-squares algorithm employing an exponential fitting function to obtain the relevant relaxation time parameters. The intensity at each pulse spacing was determined from the echo integral. The T_1 values were reproducible to within 5% at a given temperature.

Quadrupolar echo spectra were simulated by standard methods using the program MXQET.[15] Simulated spectra were visually matched to experimental line shapes. The T_1 data were least-squares fit to the BPP spectral density function[23] to obtain the activation energy, E_a, the correlation time at infinite temperature, τ_∞, and the effective quadrupolar coupling constant, χ_{eff} (eqs 4 and 5).

^{13}C CP/MAS NMR spectra were recorded on a Bruker ASX 200 spectrometer at a frequency of 50.3 MHz. The ^{13}C $\pi/2$ pulses were 4.0 μs, and cross polarization times of 3 ms were used. Typically 100−150 transients were accumulated, and the recycle delay was 5 s. The samples were spun at 5 kHz, using a 7 mm Bruker MAS probe. The chemical shifts were referenced to the low-frequency signal of adamantane (29.5 ppm), and following acquisition, an exponential apodization of 10 Hz was applied before the Fourier transform.

Heat capacity measurements were performed on a Dupont Model 2910 differential scanning calorimeter. Approximately 10 mg of sample was hermetically sealed in an aluminum pan. Liquid nitrogen was used to cool the sample below room temperature, and a ramp (heating) rate of 10 K/min was employed. The reference sample was an empty aluminum pan, and indium metal was used as the standard for temperature calibration.

Results and Discussion

1,4-Di-*tert*-butylbenzene/Thiourea. The ^{13}C CP/MAS spectrum of 1,4-di-*tert*-butylbenzene in the thiourea inclusion compound, at room temperature, is shown in Figure 1. The signals in the spectrum were assigned to the carbons of the guest based on ^{13}C chemical shift correlation tables.[24] Note that there is only one signal for all six methyl carbons, which indicates that *tert*-butyl rotation is fast on the ^{13}C spectral time scale at room temperature and that the two *tert*-butyl groups occupy equivalent crystallographic sites. In addition, there is only one signal for all four unsubstituted CH atoms of the benzene ring, again implying magnetic equivalence, likely due to molecular motion. This is confirmed by the NQS experiment. The resonance corresponding to the CH phenyl carbons is not eliminated by dipolar dephasing, indicating that the phenyl ring is rotating rapidly at room temperature. The rapid reorientation

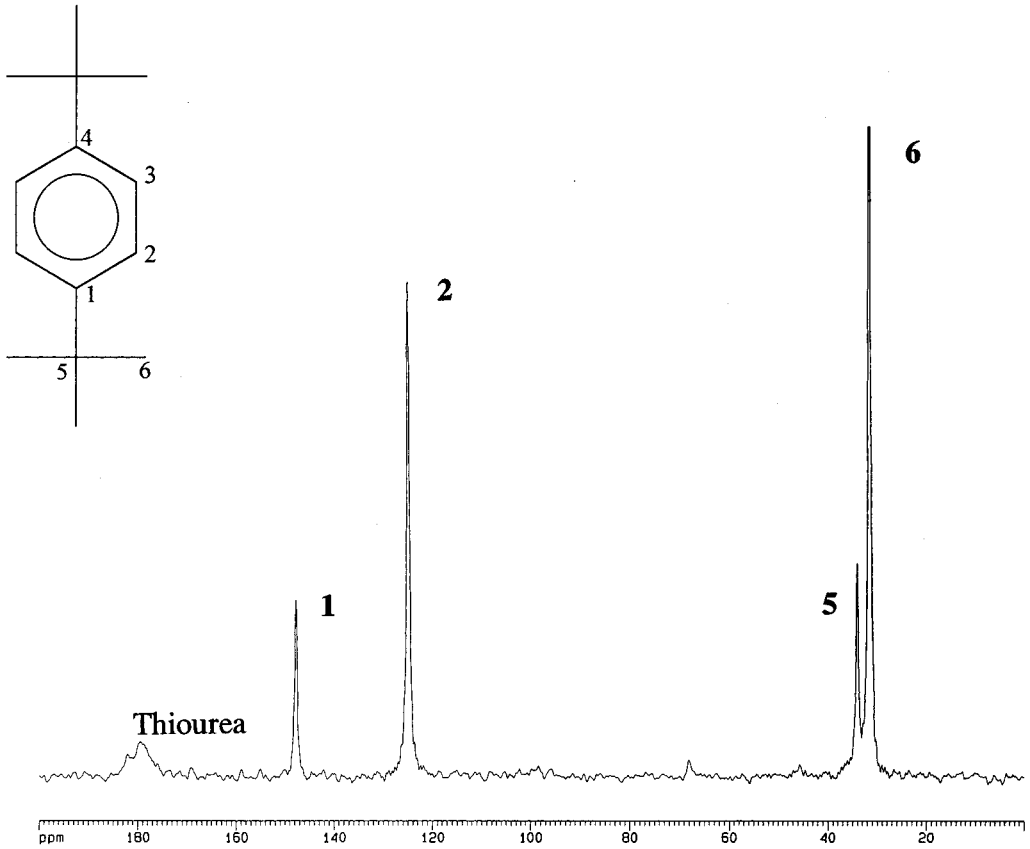


Figure 1. ^{13}C CP/MAS powder spectrum of the 1,4-di-*tert*-butylbenzene/thiourea inclusion compound, at room temperature, with signal assignments.

is confirmed by ^{2}H data for the same compound, which indicate that the motion of the phenyl ring is proceeding at a rate greater than 10^{7} s^{-1} down to 120 K.[13]

The ^{13}C CP/MAS spectrum for pure, unenclathrated solid 1,4-di-*tert*-butylbenzene, at room temperature, is depicted in Figure 2A. With the exception of a few spinning sidebands in the 40−80 ppm range, the spectrum is similar to that of 1,4-di-*tert*-butylbenzene in thiourea, showing that the resonances correspond to the same carbons as those of the DTBB guest in the thiourea clathrate. One exception is the signal corresponding to the CH ring carbons, which is split into two equal intensity peaks, suggesting that the symmetry of the phenyl ring is reduced due to a combination of crystal packing and lack of phenyl ring motion. Carbons 2 and 3 of the ring give one signal, as do carbons 5 and 6. However, carbon 2 is now magnetically inequivalent to carbon 6. The lack of phenyl ring motion is confirmed by the nonquaternary suppression pulse sequence, as the doublet described above disappears (Figure 2B). This indicates a strong heteronuclear dipolar coupling, which is not averaged by fast motion. Once more, these results agree with ^{2}H NMR data, which indicate that the phenyl ring is static at all temperatures below the melting point (349 K).[13]

From differential scanning calorimetry data, there are no phase transitions for the 1,4-di-*tert*-butylbenzene/thiourea inclusion compound, in the temperature range −100 °C (173 K) to +200 °C (473 K), other than decomposition of the inclusion compound at 178 °C and melting of the thiourea host at approximately 185 °C.

The ^{2}H T_1 data for 1,4-di-*tert*-butylbenzene-d_{18} in the thiourea inclusion compound is shown in Figure 3. Two distinct minima are apparent, each corresponding to one of the two motions of the *tert*-butyl group. From simulations of the ^{2}H spectral data, it can be clearly shown that methyl rotation slows first as the temperature decreases. The deuterium NMR spectra for DTBB-d_{18}/TU cannot be simulated using a model where *tert*-butyl reorientation slows first upon lowering of the sample temperature.[13] Both motions are in the extreme narrowing limit at room temperature ($\omega_0\tau_c \ll 1$), so the high-temperature minimum is due to changes in the rate of methyl rotation, while *tert*-butyl rotation is influencing T_1 in the low-temperature region. In addition, the ratio of relaxation times at the two T_1 minima provides further proof of this model. It can be shown that, if methyl rotation slows first as the temperature decreases, then the ratio of T_1 at the two minima should be 1.5. If *tert*-butyl rotation slows first, then the above ratio would be 9.0.[25] The measured ratio is approximately 6 ms/5 ms = 1.2. Thus, the first case is correct.

By fitting the high temperature T_1 data to eqs 4 and 5, an activation energy of 12.0 ± 0.5 kJ/mol was determined for methyl rotation, and τ_∞ was (1.4 ± 0.5) × 10^{-12} s. A similar analysis of the low-temperature region of the T_1 curve yields an activation energy for *tert*-butyl rotation of 11.3 ± 0.4 kJ/mol, while the correlation time at infinite temperature is 2.0 ± 0.7 × 10^{-14} s. Note that these two values allow calculation of the motional rate at any temperature, according to eq 5. The near equivalence of activation energies (11.3 and 12.0 kJ/mol) does not necessarily mean that rate of each motion should show the same temperature dependence, because the rate also depends on τ_∞. Indeed, τ_∞ is different by approximately 2 orders of magnitude, which then dictates that methyl rotation slows down first as the temperature is lowered. A fit of the relaxation curve yields an effective static quadrupolar coupling constant, χ, of 166.7 ± 0.8 kHz, which is typical for methyl deuterons.

In pure, solid 1,4-di-*tert*-butylbenzene, the *tert*-butyl rotation is hindered by relatively strong intermolecular interactions.[26] This results in *tert*-butyl dynamics that are almost equivalent, as far as motional rates are concerned, to the internal rotation of the methyl groups (the rate of *tert*-butyl reorientation starts to decrease from 1 × 10^{7} s^{-1} at temperatures immediately below ambient temperature).[13] In the DTBB/thiourea inclusion com-

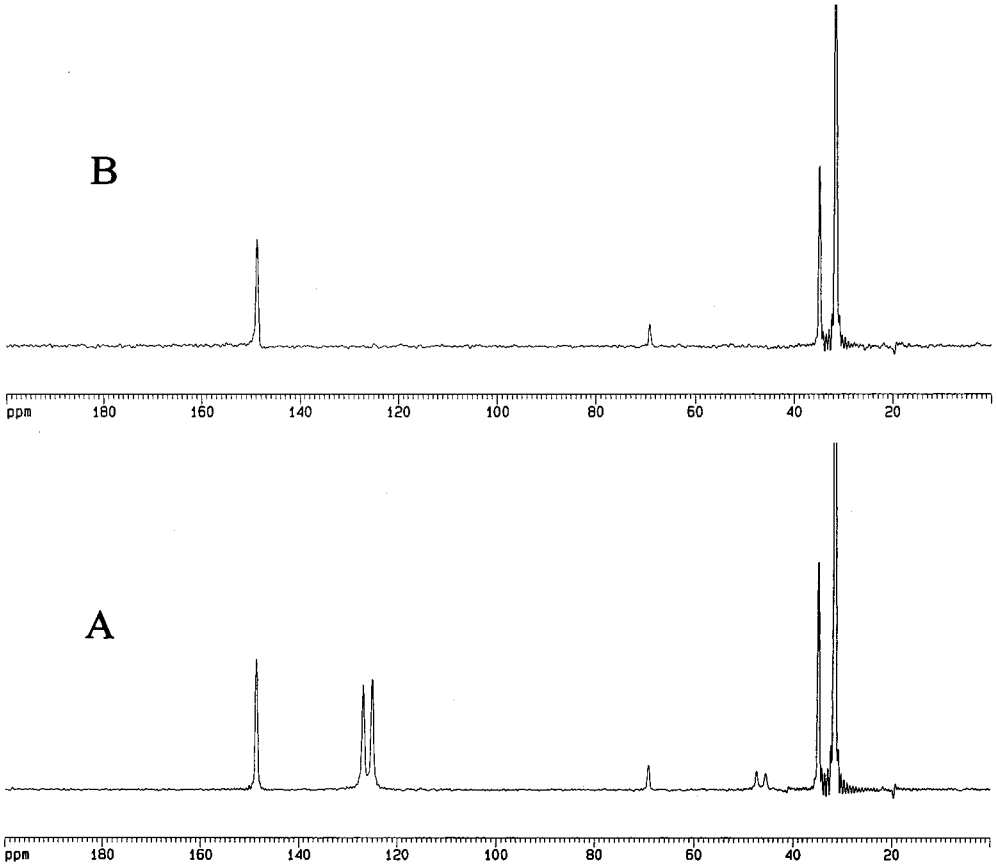


Figure 2. (A) Normal ^{13}C CP/MAS spectrum of pure, unenclathrated 1,4-di-*tert*-butylbenzene. (B) ^{13}C CP/MAS spectrum with dipolar dephasing.

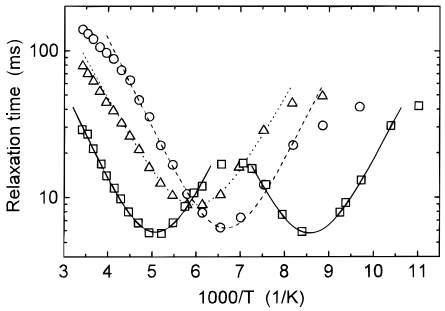
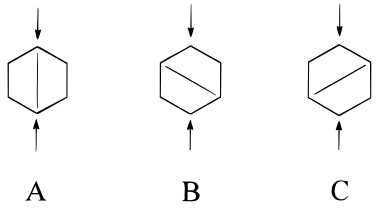


Figure 3. ^{2}H spin−lattice relaxation time data, as a function of temperature, along with best fit curves for (A) 1,4-di-*tert*-butyl-d_{18}-benzene/thiourea inclusion compound (squares), (B) 4-isopropyl-d_6-*tert*-butylbenzene/thiourea inclusion compound (triangles), and (C) 4-ethyl-d_3-*tert*-butylbenzene/thiourea inclusion compound (circles).

pound, the guest molecules are less tightly held by the thiourea host lattice. The consequence of this fact is that, as determined from deuterium spin−lattice relaxation time measurements and deuterium NMR spectra,[13] the *tert*-butyl rotation rate does not slow below 1×10^6 s^{-1}, even down to 77 K. The methyl rotation dynamics are almost the same in both compounds, because methyl rotation is dominated by intramolecular interactions within the *tert*-butyl group, which broadly speaking, do not change from the pure solid to the thiourea inclusion compound. On the other hand, intermolecular interactions between neighboring molecules, which influence *tert*-butyl rotation, are markedly different from the neat solid (stronger) to the thiourea clathrate (weaker).

The ^{2}H NMR spectra of 1,4-di-*tert*-butylbenzene-d_4 in the thiourea inclusion compound, in the higher temperature region, were previously simulated using a model where the phenyl ring takes up three sites in the hexagonal thiourea channel.[13] As the temperature is lowered below room temperature, the channel distorts from hexagonal symmetry. The easiest way to describe

SCHEME 1



the distortion is a constriction in one direction, which continuously increases as the temperature is lowered (see Scheme 1), as was also observed for the thiourea/cyclohexane inclusion compound,[11,27] the adamantane/thiourea clathrate,[28] and the *n*-$C_{16}H_{34}$/urea adduct.[29] In our case, the distortion causes the fractional population of site A to decrease, relative to sites B and C, which remain equally populated. Simulations in which the relative population of site A was larger that sites B and C gave spectra with too large an effective quadrupolar coupling constant.[13]

With the previously described model and an exchange rate of 10^8 s^{-1}, the experimental spectra from 392.0 K ($P_A = 0.312$, $P_B = 0.344$, $P_C = 0.344$) to 172.3 K (0.047, 0.476, 0.476) could be successfully simulated. As the temperature is lowered from 392 K, the asymmetry parameter η gradually increases toward 1.0 at 270.3 K. Then η decreases to essentially zero at 185.6 K. Below this temperature η increases again to about 0.4 at 121.7 K. The four ^{2}H spectra below 172.3 K could not be simulated using a model where one of the three sites is less populated than the other two.[13]

Intuitively, the simplest model for the four lowest temperature spectra would be to allow the population of site A to decrease to zero and consider a two-site exchange in which the sites are allowed to have different populations, reflecting the introduction of a more complex distortion. The ^{2}H spectra below 172.3 K were successfully simulated using this model and keeping the

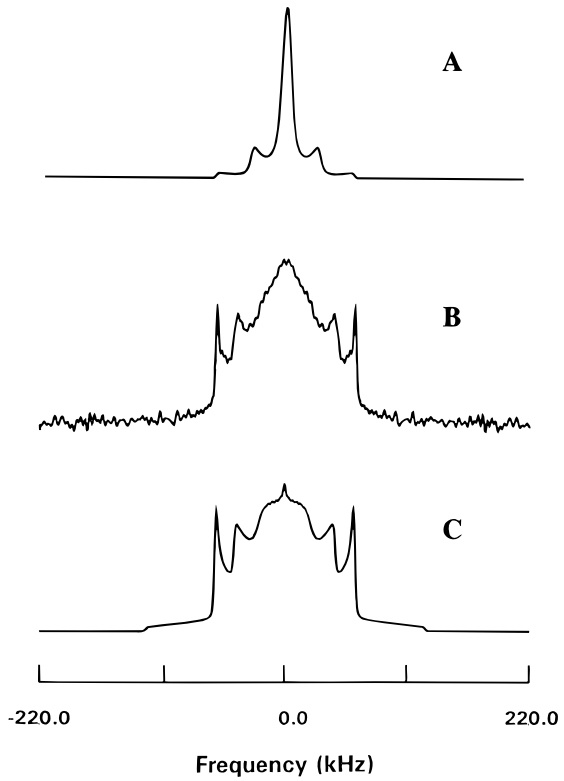


Figure 4. ^{2}H NMR powder spectrum of 1,4-di-*tert*-butylbenzene-d_{18} in thiourea, at 77 K (B), along with simulations with the axial methyl proton point toward the phenyl ring (A) and pointing away from it (C).

TABLE 1: Fractional Populations of the Three Sites Taken Up by the Phenyl Ring in the Thiourea Channel, of the 1,4-Di-*tert*-butylbenzene/Thiourea Inclusion Compound, Corresponding to Scheme 1, Based on ^{2}H Spectra

temp (K)	P_A	P_B	P_C
392.0	0.312	0.344	0.344
357.5	0.306	0.347	0.347
329.7	0.298	0.351	0.351
295.7	0.280	0.360	0.360
270.3	0.256	0.372	0.372
249.7	0.240	0.380	0.380
224.0	0.204	0.398	0.398
203.7	0.156	0.422	0.422
185.6	0.092	0.454	0.454
172.3	0.047	0.476	0.476
158.6	0	0.420	0.580
138.4	0	0.300	0.700
121.7	0	0.280	0.720
101.9	0	0.220	0.780

rate at 10^8 s^{-1}. The fractional populations of the three sites are recorded in Table 1.

Finally, the ^{2}H spectrum of the 1,4-di-*tert*-butylbenzene-d_{18}/thiourea inclusion compound, at 77 K, pictured in Figure 4B, provides insight into the conformation of the methyl deuterons. At this temperature, methyl rotation has stopped on the ^{2}H spectral time scale ($k < 1 \times 10^3$ s^{-1}), while *tert*-butyl rotation is still in the intermediate exchange region ($k' = 2 \times 10^6$ s^{-1}). There are two components to the experimental spectrum. The inner, narrower component corresponds to the 12 methyl C−D bonds that point off to the side, making an angle of approximately 70.5° with respect to the rotation axis. The outer component corresponds to the six C−D bonds that make an angle of 0° with respect to the *tert*-butyl rotation axis (the "axial" deuterons). Whether these C−D bonds point toward or away from the phenyl ring is of some question. However, simulations indicate that these C−D bonds point away from the phenyl ring (Figure 4C), not toward it (Figure 4A). This agrees with the steric argument that if they pointed toward the phenyl ring, they would be in close contact with the *ortho* protons of the benzene ring. The correct conformation for the *tert*-butyl group at 77 K is shown below (**2**).

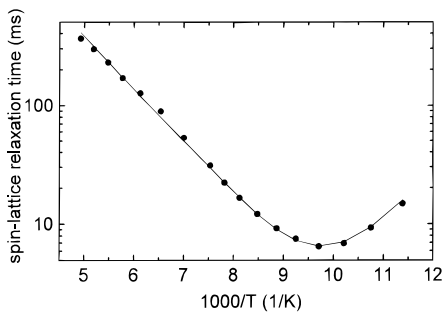
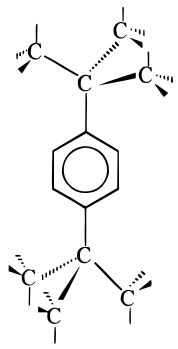


Figure 5. Deuterium spin−lattice relaxation times for 1,4-di-*tert*-butylbenzene-d_4 in the thiourea inclusion compound, as a function of inverse temperature.



2

Internal Rotation versus Molecular Rotation. Previous experimental and theoretical work on alkylbenzenes yields liquid- and gas-phase barriers to internal rotation for ethyl,[30] isopropyl,[31] and *tert*-butyl[32] groups of 4−8, 1−9, and 2−5 kJ/mol, respectively. Evidently, these barriers are not sufficiently high that the alkyl groups can be considered as locked into one position with respect to the phenyl ring. The question then arises as to whether the alkyl groups are rotating together with the rest of the molecule inside the thiourea channel. Our previous work on 1,4-di-*tert*-butylbenzene in thiourea[13] showed clearly that both the *tert*-butyl groups and the phenyl ring were rotating rapidly, even down to very low temperatures (below 100 K). If two parts of a molecule can rotate about a common axis, similar activation energies do not necessarily mean that the two groups are rotating together. The correlation times, τ_c (or rotational rates, k), may still be different, indicating that the two groups are not rotating together, if the τ_∞ (or k_∞) values are different (see eq 5).

In the previous work on the 1,4-di-*tert*-butylbenzene-d_4/thiourea inclusion compound,[13] deuterium spin−lattice relaxation time measurements showed a T_1−temperature profile that did not reach a T_1 minimum, even down to 110 K. Due to instrumental limitations, it was not possible at the time to go below this temperature. This precluded a detailed T_1 fit, to determine E_a and τ_∞, for the three-site exchange of the phenyl ring in the thiourea lattice. In this work (see Figure 5), we have acquired T_1 data for DTBB-d_4/TU down to 88 K, and the presence of a definite minimum is apparent. We found an activation energy for the three-site reorientation of 8.4 ± 0.5 kJ/mol and a correlation time at infinite temperature of (1.1 ± 0.4) × 10^{-13} s. Using these two values, along with eq 5, it is possible to find the rate of the three-site exchange of the phenyl ring, as a function of temperature. From the earlier fit of the low-temperature T_1 data for 1,4-di-*tert*-butylbenzene-d_{18}/thiourea

($E_a = 11.3$ kJ/mol and $\tau_\infty = 2.0 \times 10^{-14}$ s), corresponding to *tert*-butyl reorientation, it is possible to compare the rate of the phenyl ring rotation with the rate of rotation of the *tert*-butyl group, as a function of temperature. Equations 6 and 7 are the result of fitting the T_1 curves for DTBB-d_4/TU and DTBB-d_{18}, respectively.

$$\tau_c(\text{ring}) = 1.1 \times 10^{-13} \exp[(8400)\ \text{J mol}^{-1}/RT] \quad (6)$$

$$\tau_c(\text{butyl}) = 2.0 \times 10^{-14} \exp[(11300)\ \text{J mol}^{-1}/RT] \quad (7)$$

From these equations it is obvious that the two motions have the same rate at only one temperature, 205 ± 10 K.

Using standard bond angles, bond lengths, and elementary trigonometry, we estimate that the phenyl hydrogens of DTBB project approximately 2.15 Å from the molecular axis of rotation (which passes through C_1 and C_4 of the phenyl ring). In contrast, the *tert*-butyl hydrogens are about 2.34 Å from the same axis. This may help to explain why the activation energy for *tert*-butyl reorientation is higher than that for phenyl ring rotation. The *tert*-butyl protons are closer to the hexagonal thiourea channel and are thus likely to interact more strongly with the host, as compared to the phenyl ring protons of DTBB.

4-Isopropyl-*tert*-butylbenzene/Thiourea. The room-temperature ^{13}C CP/MAS spectrum of 4-isopropyl-*tert*-butylbenzene in thiourea is presented in Figure 6A. The resonances were assigned based on ^{13}C chemical shift correlation calculations.[24] The two *ipso* carbons are now magnetically inequivalent because two different substituents are present, as are carbons 2 and 3, in comparison to 1,4-di-*tert*-butylbenzene. The signals due to the isopropyl carbon and the *tert*-butyl methyl carbons overlap. The fact that only one signal is seen for the isopropyl methyls and the *tert*-butyl methyls (each) suggests that they are each exchanging rapidly and occupying crystallographically equivalent sites. Similarly, two signals for the four CH phenyl carbons suggest that the ring reorientation proceeds at rate greater than 10^3 Hz. This conjecture of rapid rotation is supported by the NQS experiment. In this spectrum, the CH phenyl carbons retain most of their intensity, implying a reduction in the magnitude of heteronuclear CH dipolar coupling, due to rapid reorientation.

From differential scanning calorimetry data, no phase transitions were observed for the 4-isopropyl-*tert*-butylbenzene/thiourea inclusion compound, between −100 °C (173 K) and 200 °C (473 K), other than decomposition of the clathrate at 167 °C and melting of the thiourea host at 183 °C.

To investigate the motion of the isopropyl group in the thiourea channel, ^{2}H NMR powder spectra of ITBB-d_6/TU were obtained between 273 and 153 K (Figure 7). The spectrum at the highest temperature, which has a quadrupolar splitting of 12.0 ± 0.5 kHz, and an asymmetry parameter of approximately zero, is characteristic of both fast ($>10^8$ s^{-1}) methyl rotation and fast isopropyl reorientation. The nature of the isopropyl exchange is uncertain. The projected angle between the two methyl groups is very close to 120°, so the motion must be at least 3-fold, in agreement with the axially symmetric spectrum observed at room temperature. However, one must also consider the effect of the thiourea host channel on the motion. The 6-fold symmetric hexagonal channel implies that the isopropyl group rotates through six sites. The reduction in quadrupolar splitting would be the same as a three-site jump. The six positions of the isopropyl group in the thiourea channel are depicted in Scheme 2. The isopropyl proton is not shown for clarity, but is at an angle of 120° to both methyl groups. Since this proton is so much smaller than the methyl groups, we will consider its influence to be negligible in the steric interactions between host and guest considered below. A third motion is present, which is a librational motion of the molecule, this libration spectrally manifesting itself as a slight reduction in the effective quadrupolar coupling constant.

As the temperature is changed from 273 to 15 K, the effective asymmetry parameter gradually increases from zero at 273 K to ∼0.5 at 153 K. This implies that the relative populations of the sites taken up by the isopropyl deuterons are changing as the temperature is lowered. The asymmetry cannot be within the three sites taken up by the methyl deuterons, because of the C_3 symmetry of the methyl group. It is the populations of the six sites of the isopropyl group which are becoming unequal, due to the previously mentioned distortion of the thiourea channel, from hexagonal symmetry, which gradually increases as the temperature decreases.[11,27,28] In addition, the gradual coalescence of the central dip of the spectra, as the temperature decreases, suggests that a motional rate is decreasing on the ^{2}H NMR time scale.

From our studies on 1,4-di-*tert*-butylbenzene in thiourea,[13] and various other thiourea inclusion compounds, it is understood that the host channel distorts continuously with a decrease in temperature by decreasing the length of one of the three hexagonal axes (see Scheme 2). This distortion results in a decrease in the populations of sites 2, 3, 5, and 6, while sites 1 and 4 would correspondingly increase in population, because when the isopropyl group is positioned in sites 1 and 4, there is no methyl group pointing directly into the distorted (compressed) axis. In the other four sites, one of the two methyl groups points directly into the distorted axis, where there is less space (more steric hindrance). Since the distortion is likely symmetric, one would expect sites 2, 3, 5, and 6 to decrease in population equally, while sites 1 and 4 would have equal, but larger, populations. The seven spectra were successfully simulated using this model. At 293 K the asymmetry parameter is zero, implying that all populations are equal and that the host channel has hexagonal symmetry.

As was mentioned above, the change in the depth of the central dip of the spectra indicates that a motional rate is decreasing. We attempted to simulate the deuterium powder spectra with three different models. In the first model, we held the rate of the six-site reorientation at 10^8 s^{-1}, while allowing the rate of methyl rotation to gradually decrease from the fast rate limit. Secondly, we allowed both motions to decrease from 10^8 s^{-1} in concert, as the temperature drops from ambient temperatures. Neither of these two models were able to simulate the experimental ^{2}H powder spectra. An alternative choice available to us was to hold the rate of methyl rotation at 10^8 s^{-1}, while decreasing the rate of the six-site exchange. As can be seen in Figure 7, the match between the two sets of spectra is very good. The rate of the six-site reorientation is indicated with each of the seven spectra. A least-squares fit of the rates to the Arrhenius equation ($\ln k = \ln A - E_a/RT$) gave an activation energy for this motion of 8.4 ± 1.8 kJ/mol and a ln A value of 18.5 ± 0.5. It should be noted that all ^{2}H spectra acquired at temperatures below 153 K were featureless "bumps" that provided no definite information concerning rates or types of molecular reorientation.

The ^{2}H spin−lattice relaxation time data for 4-isopropyl-d_6-*tert*-butylbenzene in thiourea are presented in Figure 3. It can be seen that a well-defined minimum is present. In the temperature range in which we performed our measurements, the rate of the six-site exchange (of the isopropyl group) was always less than 10^7 s^{-1} (as determined from ^{2}H spectra), and as T_1 is generally modulated by motion in the rate 10^8 to 10^{12} s^{-1}, the minimum is likely due to changes in the rate of methyl rotation. Indeed, when one compares the rate of six-site

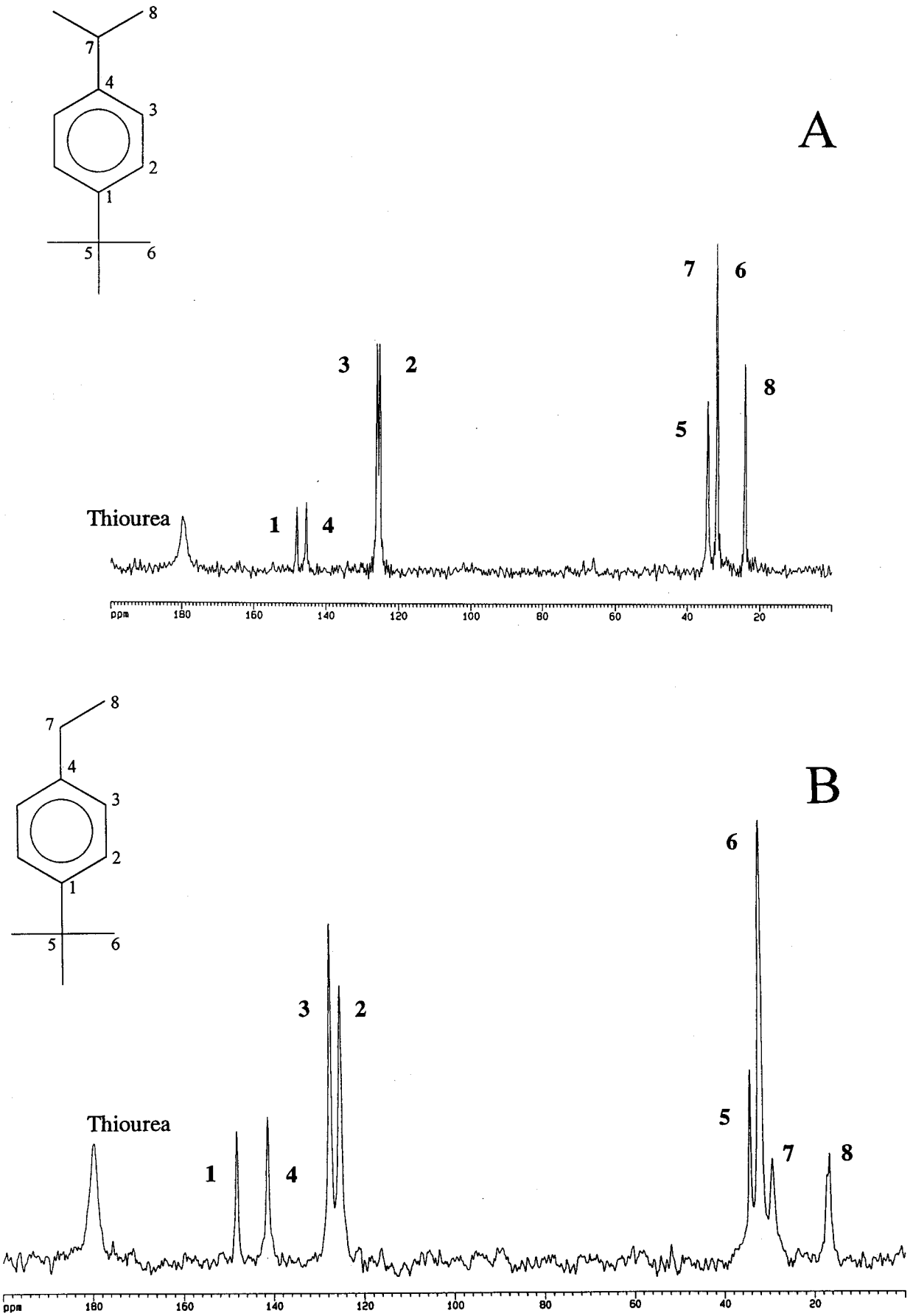


Figure 6. ^{13}C CP/MAS spectra of (A) the 4-isopropyl-*tert*-butylbenzene/thiourea inclusion compound and (B) the 4-ethyl-*tert*-butylbenzene/thiourea inclusion compound.

exchange of the isopropyl group (from ^{2}H spectra) with the rate of motion calculated from the T_1 curve, the two rates are different by approximately 3 orders of magnitude (see Figure 8). Thus the motion influencing T_1 in the observed minimum cannot possibly be the six-site exchange and therefore is assigned to methyl rotation. We attribute the decrease in T_1 at

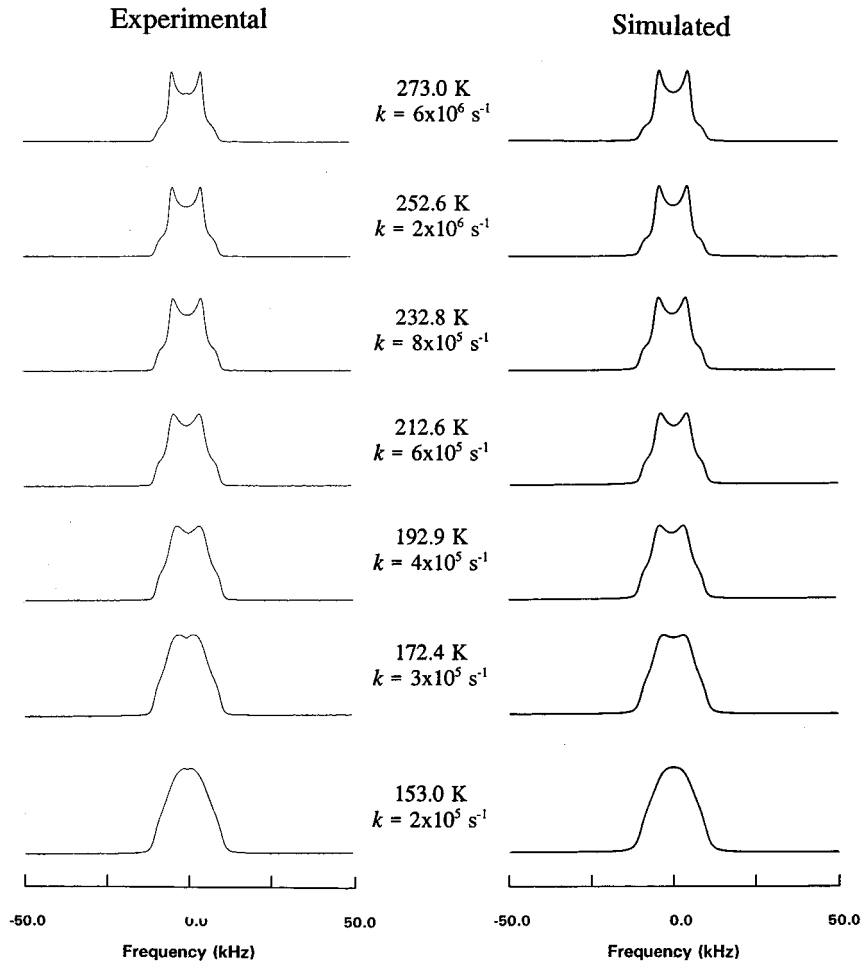
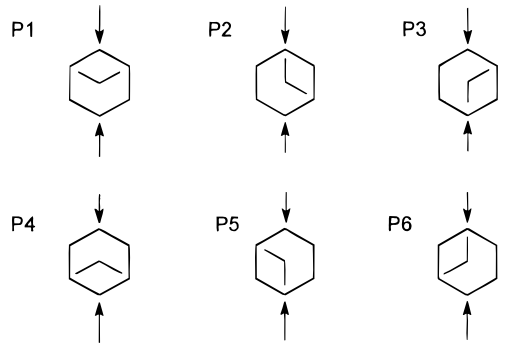


Figure 7. ^{2}H NMR powder spectra of 4-isopropyl-d_6-*tert*-butylbenzene in the thiourea inclusion compound along with best fit simulations, at the temperatures indicated. The rate of six-site exchange of the isopropyl group within the host channel is listed with each pair of spectra.

SCHEME 2



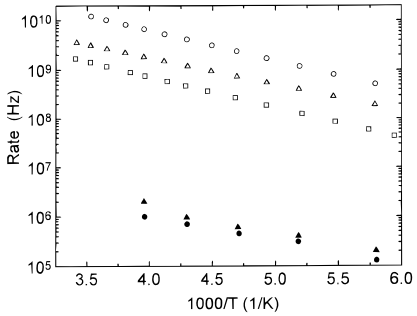


Figure 8. Plot of reorientational rate, as a function of temperature, for the rate of six-site exchange of the isopropyl group (in ITBB/TU) and six-site exchange of the ethyl group (in ETBB/TU), both calculated from ^{2}H NMR spectra. In addition, we have included the rate of internal methyl rotation, determined from deuterium spin−lattice relaxation times, for all three inclusion compounds. Filled triangles: six-site, ITBB/TU. Filled circles: six-site, ETBB/TU. Empty circles: methyl rotation, DTBB/TU. Empty triangles: methyl rotation, ITBB/TU. Empty squares: methyl rotation, ETBB/TU.

low temperatures to rotation of the phenyl ring. At these low temperatures both the isopropyl group and the two methyl groups are rotating too slowly ($k < 10^6$ s^{-1}), but the phenyl ring rotation is reorienting at a rate comparable to the spectrometer frequency ($k \approx 10^7$ s^{-1}). The deuterons are most likely relaxing via a ^{2}H−^{1}H dipole−dipole mechanism. When the phenyl ring and a methyl group are coplanar, the dipolar coupling is several kilohertz. The small deviation from the fitted curve at higher temperatures is most probably due to changes in the rate of six-site exchange of the isopropyl group, which dominates the ^{2}H T_1 time scale only at temperatures above room temperature.

By fitting the T_1 data (Figure 3, triangles) of the central minimum, we determined the correlation time at infinite temperature to be $(4.9 \pm 2.0) \times 10^{-13}$ s, and the activation energy for methyl rotation to be 13.1 ± 0.5 kJ/mol. This compares to an activation energy, for internal methyl rotation, of 14.2 kJ/mol for pure isopropylbenzene, as determined from proton spin−lattice relaxation time measurements,[33] 14 kJ/mol for pure 1,4-diisopropylbenzene[34] and 13 kJ/mol for 1,3,5-triisopropylbenzene.[35] In pure isopropylbenzene the rate of isopropyl group reorientation is slow on the ^{1}H inverse Larmor frequency time scale. This is likely because of the lack of symmetry of the isopropyl group, as compared to the C_3 symmetry of the *tert*-butyl groups of 1,4-di-*tert*-butylbenzene (the three-site exchange of the *tert*-butyl group in pure DTBB is fast on the ^{2}H spectral time scale at room temperature[13]). However, in the case of the ITBB/thiourea inclusion compound,

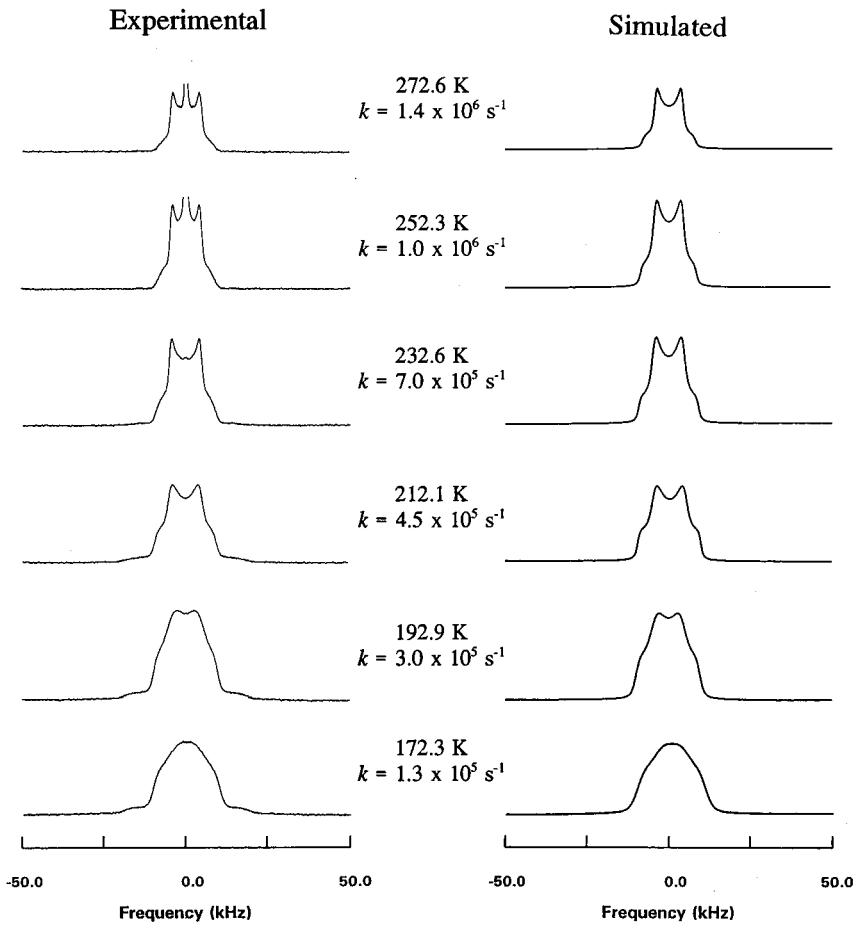


Figure 9. ^{2}H NMR powder spectra of the 4-ethyl-d_3-*tert*-butylbenzene/thiourea inclusion compound, deuterated on the CH_3 ethyl group, along with best fit simulations and the rate of six-site exchange of the ethyl group at each temperature.

there is a six-site symmetry imposed by the hexagonal host channel. This, together with the relatively weak guest−host interaction, results in isopropyl group reorientation that reaches the fast rate limit at ambient temperature.

4-Ethyl-*tert*-butylbenzene/Thiourea. The ^{13}C CP/MAS room-temperature spectrum of 4-ethyl-*tert*-butylbenzene/thiourea is presented in Figure 6B. The resonances were assigned based on ^{13}C chemical shift correlation calculations.[24] The signals in the low-field region are similar to those of 4-isopropyl-*tert*-butylbenzene/thiourea, as carbons 2 and 3 (along with carbons 1 and 4) are inequivalent. In the dipolar dephasing experiment, carbons 2, 3, and 7 retain most of their intensity, indicating that both the phenyl ring and the ethyl CH_2 group are reorienting at a rate greater than 10^3 Hz at room temperature.

From differential scanning calorimetry data, no phase transitions were found for the 4-ethyl-*tert*-butylbenzene/thiourea inclusion, other than decomposition of the inclusion compound at 117 °C and melting of the thiourea at 181 °C.

Deuterium powder NMR spectra of the 4-ethyl-d_3-*tert*-butylbenzene/thiourea (ETBB-d_3/TU) inclusion compound, along with simulations, appear in Figure 9. The spectrum at 272.6 K is a Pake doublet, with an effective quadrupolar coupling constant $\chi_{eff} = 34.3 \pm 0.5$ kHz. This value is indicative of fast ($k > 10^8$ s^{-1}) methyl rotation and fast six-site exchange of the ethyl group through six positions in the hexagonal thiourea channel. At this temperature, the populations of the six sites are equal, suggesting that the host channel is not appreciably distorted. As the temperature is decreased, the ^{2}H spectrum coalesces and forms a featureless line shape at 172.3 K. The shape of the spectrum does not then change appreciably on going down in temperature to 85 K. The simulations indicate that the populations of two of the six sites continually decrease with the drop in temperature, representing, again, a compression along one of the axes of the hexagonal channel. The spectra also indicate that the six-site reorientation slows down first, while methyl rotation proceeds at a rate greater than 10^8 s^{-1}, even down to 172 K. As with ITBB-d_6/TU, we were unable to simulate the ^{2}H powder spectra using any other feasible model of reorientation. From the deuterium spectra, we determined the rate of the six-site exchange as a function of temperature (see Figure 8). From a least-squares fit to the six data points, we determined an activation energy for the six-site exchange of 9.0 ± 0.1 kJ/mol and a value of 18.1 ± 0.1 for ln A. This compares to 8.4 ± 1.8 kJ/mol for the six-site exchange of the isopropyl group in ITBB/TU and 11.3 ± 0.4 kJ/mol for the three-site exchange of the *tert*-butyl group in DTBB/TU. Again, as was the case with ITBB/TU, all ^{2}H spectra acquired at temperatures below 172 K were featureless and provided little information about the reorientation of the guest's ethyl group. The narrow central peak at higher temperatures and the broad shoulders observed at lower temperatures are due to a small amount of liquid ethylbenzene-d_3 in the sample.

In Figure 3, a temperature profile of the deuterium spin−lattice relaxation time for the ETBB-d_3/TU inclusion compound, deuterated on the ethyl CH_3 group, is presented. In the central region there is a broad minimum, which, as in the case of ITBB/TU-d_6, we attribute to the methyl group rotation.

By fitting the T_1 data, an activation energy for this motion of 11.6 ± 0.5 kJ/mol was found. The constant K (see eq 4) is 3.1×10^{10} s^{-2}, while the correlation time at infinite temperature is approximately $(2.0 \pm 0.8) \times 10^{-13}$ s. This compares to an activation energy, for internal methyl rotation, of 13.2 kJ/mol in pure ethylbenzene, 15 kJ/mol in 1,3-diethylbenzene, and 12 kJ/mol in 1,2-diethylbenzene.[35] As in the case of ITBB/TU

(see Figure 3, triangles), there are downward deviations from the fitted curve at both high and low temperatures (see Figure 3, circles).

It is interesting to compare the rate of internal methyl rotation for each of the three inclusion compounds studied here. The rate of this motion, as a function of inverse temperature, calculated from ^{2}H spin−lattice relaxation time measurements, is shown in Figure 8. Not only does it confirm that, for ITBB/TU and ETBB/TU, the six-site exchange does not determine T_1 in the temperature range investigated it also provides information about steric interactions within the three functional groups. Intuitively, one would expect intramolecular interactions within the alkyl group to be weakest within an ethyl group, intermediate for an isopropyl group, and strongest for a *tert*-butyl functionality. At any given temperature, the rate of methyl rotation is fastest for ETBB/TU, intermediate for ITBB/TU, and slowest for DTBB/TU. Therefore, the rate of methyl rotation and the strength of these steric interactions correlate very well.

Summary

We have shown that the guest molecules 1,4-di-*tert*-butylbenzene, 4-isopropyl-*tert*-butylbenzene, and 4-ethyl-*tert*-butylbenzene, when enclathrated in the channels of thiourea, execute a number of motional modes. The slowest mode is the reorientation of the alkyl groups. As a consequence of their lower symmetry, the rotation of the isopropyl and ethyl groups is slower than that of the *tert*-butyl group. The methyl substituents that make up these groups rotate faster, and their rates follow the sequence $k_{\text{ethyl}} > k_{\text{isopropyl}} > k_{t\text{-butyl}}$. It is further shown that in the 1,4-di-*tert*-butylbenzene inclusion compound the ring and the *tert*-butyl group are not reorienting at the same rate and that the activation energy for ring rotation is smaller than that for *tert*-butyl rotation.

Acknowledgment. We would like to thank NSERC Canada for financial support. We are grateful to Sandy Smith for assistance with the differential scanning calorimeter and Patrik Nechala for a synthesis of ETBB.

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