

Conformational Properties of Monosubstituted Cyclohexane Guest Molecules Constrained within Zeolitic Host Materials

A Solid-state NMR Investigation

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The conformational properties of monosubstituted cyclohexane guest molecules ($C_6H_{11}X$ with $X = CH_3$, OH, Cl, Br and I) included within microporous solid host materials (silicalite-I, H-ZSM-5, NH_4 -mordenite and zeolite NH_4 -Y) have been elucidated *via* high-resolution solid-state ^{13}C NMR spectroscopy. For all of the inclusion compounds investigated, the fraction of monosubstituted cyclohexane molecules in the equatorial conformation is similar to that in solution, suggesting that these host materials do not impose any significant constraints upon the conformational properties of the monosubstituted cyclohexane guest molecules. For the monohalogenocyclohexane guest molecules ($C_6H_{11}X$ with $X = Cl$, Br and I), this result is in marked contrast to the situation for the same guest molecules in the thiourea host structure, for which the conformational properties of the guest molecules are substantially different from those of the same molecules in solution. For cyclohexanol ($C_6H_{11}OH$) in H-ZSM-5, some amount of dicyclohexyl ether ($C_6H_{11}OC_6H_{11}$) is observed, and is analogous to the proposed production of dimethyl ether in the first stage of methanol-to-gasoline conversion on this zeolite. The comparatively low temperature (ambient temperature) at which this conversion from cyclohexanol to dicyclohexyl ether occurs is noteworthy. In addition to our high-resolution solid-state ^{13}C NMR studies of these materials, 1H MAS and ^{27}Al MAS NMR spectra have also been recorded, and are discussed.

One major impetus underlying current research on solid inclusion compounds is the desire to investigate the properties that may be conferred upon an organic 'guest' molecule by virtue of embedding it within a crystalline 'host' material and to understand the extent to which the properties of the guest molecule may be altered from those of the same molecule in dispersed phases or in its 'pure' crystalline phase. Many solid host materials are known, encompassing aluminosilicates, aluminophosphates, organic solids and many other classes of material. These host materials possess a wide variety of different inclusion topologies,^{1,2} such as linear tunnels, isolated cages, networks of intersecting tunnels and/or cages, and two-dimensional regions within layered hosts.

Monohalogenocyclohexanes ($C_6H_{11}X$, with $X = Cl$, Br, I) generally exist as an equilibrium between axial and equatorial conformations (with a chair conformation of the cyclohexane ring). In the liquid and vapour phases there is a considerable excess of the equatorial conformer,^{3–5} whereas in the solid state it has been reported⁶ that only the equatorial conformation exists. However, when included as guest molecules within the thiourea host structure (the inclusion topology of which comprises uni-directional tunnels⁷), $C_6H_{11}Cl$, $C_6H_{11}Br$ and $C_6H_{11}I$ have been shown to exist predominantly in the axial conformation. These results have been established from IR,⁸ Raman⁹ and high-resolution solid-state ^{13}C NMR^{10,11} techniques.

High-resolution solid-state ^{13}C NMR investigations¹¹ of thiourea inclusion compounds containing monosubstituted cyclohexane guest molecules ($C_6H_{11}X$) have shown that these guest molecules can be subdivided into two classes: those with $X = Cl$, Br and I have a predominance of the axial conformer (fraction of equatorial conformer *ca.* 0.05–0.15), whereas those with $X = CH_3$, NH_2 , and OH have a predominance of the equatorial conformer (fraction of equatorial conformer *ca.* 0.82–0.97). The fact that the conformational properties of the $C_6H_{11}X$ guest molecules within their thiourea inclusion compounds depend critically upon the identity

of the substituent X reflects the fine and subtle energetic balances that exist for these inclusion compounds, and important insights into the reasons underlying the preference for the axial conformation of the $C_6H_{11}Cl$ guest molecules in thiourea have been obtained¹² from the application of a theoretical approach that has been developed for the prediction and rationalization of structural properties of one-dimensional inclusion compounds.

In this paper, we have extended our studies of the conformational properties of organic guest molecules in constrained solid-state environments to encompass monosubstituted cyclohexane guest molecules within several crystalline zeolitic host materials. From the results, direct comparisons can be drawn between the inclusion compounds of these microporous hosts and the inclusion compounds containing the same guest molecules within the thiourea host structure. Such comparisons are particularly interesting in view of the prospect that the thiourea inclusion compounds (and other solid organic inclusion compounds) may, in many respects, represent model systems for structurally similar (*i.e.* possessing uni-directional tunnel topologies) zeolitic host materials.

In this work, the following microporous host materials have been considered: silicalite-I, H-ZSM-5, NH_4 -mordenite and zeolite NH_4 -Y. ZSM-5 is a medium-pore zeolite, the structure of which consists of a set of sinusoidal tunnels intersecting a set of straight tunnels, each with 10-membered ring openings. The diameter of the straight tunnels is *ca.* 5.3–5.6 Å, and the diameter of the sinusoidal tunnels is *ca.* 5.1–5.5 Å. The framework structure of silicalite-I is the same as that of ZSM-5, and can therefore be regarded as the purely siliceous version of ZSM-5. Zeolite Y has 12-membered rings of *ca.* 7.4 Å diameter leading to a supercage with diameter *ca.* 13 Å, whereas mordenite has 12-membered rings forming one-dimensional tunnels with diameter *ca.* 6.5–7.0 Å.

The conformational properties of monosubstituted cyclohexane guest molecules ($C_6H_{11}X$ with $X = CH_3$, OH, Cl, Br and I) included within these host materials have been investigated *via* high-resolution solid-state ^{13}C NMR spectroscopy.

The results are discussed in the light of our previous studies¹¹ of the conformational properties of the same guest molecules included within the thiourea host tunnel structure and in the solution state.

Experimental

The following host materials were used in this work: silicalite-I, H-ZSM-5 (Laporte Inorganics, RD1136/88), NH₄-mordenite (Si/Al = 10.1), and zeolite NH₄-Y (Strem Chemicals, Inc.). All of these samples were calcined in a muffle furnace at 773 K for at least 24 h before use. The monosubstituted cyclohexanes were obtained commercially and were used without further purification, with the exception of C₆H₁₁Cl which was distilled at 415 K before use.

Two different methods for including the guest molecules within the host materials were considered. In method A, the monosubstituted cyclohexanes were adsorbed into the host materials by contacting about 5 cm³ of the liquid monosubstituted cyclohexane with ca. 0.6–1.0 g of the powdered host material in a round-bottomed flask under vacuum for ca. 3 days. After this period, the excess liquid was removed under vacuum and the solid allowed to dry. The flask was sealed and removed to a dry box, in which the solid was transferred to the rotor to be used in the solid-state NMR experiments. In method B, the host material was exposed to the liquid monosubstituted cyclohexane for ca. 20–40 h in an ultrasonic bath at ca. 303 K. After this treatment, the excess liquid was removed and the solid washed with 2,2,4-trimethylpentane and then allowed to dry. The solid was packed into the NMR rotor in the open laboratory (*i.e.* not in a dry box). It is clear that the amount of water present within the host materials may be higher for those materials prepared *via* method B.

In order to confirm that the monosubstituted cyclohexanes were adsorbed on the internal (rather than the external) surfaces of the host materials, a control experiment was carried out by subjecting a sample of quartz to the same preparation procedures (with C₆H₁₁Cl as the potential adsorbate). High-resolution solid-state ¹³C NMR spectra of the samples of quartz recovered following these preparation procedures revealed no detectable amounts of C₆H₁₁Cl (which, if present, would necessarily have been adsorbed on the external surfaces of the quartz). On the basis of the results of these control experiments, it was concluded that the amounts of monosubstituted cyclohexanes on the external surfaces of the host materials, subjected to the same preparation procedure, would be insignificant, and that any detected amounts of these molecules must be adsorbed on the internal surfaces of the host materials.

Solid-state ¹H, ¹³C and ²⁷Al NMR spectra were recorded at 500.13, 125.76 and 130.32 MHz, respectively, on a Bruker MSL500 spectrometer using a standard Bruker magic-angle sample spinning (MAS) probe with double-bearing rotation mechanism. The samples were studied as polycrystalline powders in zirconia rotors (4 mm external diameter) and MAS frequencies between 2 and 12 kHz (with stability better than ca. ±10 Hz) were used. Single-pulse and cross-polarization (CP) techniques were used to record the ¹³C NMR spectra, under conditions of MAS and with inverse-gated ¹H decoupling applied during acquisition. Although the CP technique is intrinsically non-quantitative (since the efficiency of polarization transfer may vary from one carbon environment to another), our experiments have shown that single-pulse and CP (contact time = 1 ms) techniques give the same relative intensities for the resonance lines for the cyclohexane derivatives at room temperature. ¹³C and ¹H chemical shifts are given relative to tetra-

methylsilane and ²⁷Al chemical shifts are given relative to the signal assigned to Al(H₂O)₆³⁺ in the sample. The stability and accuracy of the temperature controller (Bruker B-VT1000) were ca. ±2 K.

Results and Discussion

Fig. 1 shows ¹³C CP-MAS NMR spectra of C₆H₁₁Br/H-ZSM-5 (prepared by method A), recorded at 293 and 200 K. At 200 K, there are two sets of signals with approximate integrated intensity ratio 4:1. The ¹³C NMR resonance lines with chemical shifts 39.4, 25.0 and 27.9 ppm are assigned as carbons C(2), C(3) and C(4) in the equatorial conformer and the resonance lines at 34.7 and 21.1 ppm are assigned as carbons C(2) and C(3) in the axial conformer. These chemical shifts are in close agreement with those found for the C₆H₁₁Br/thiourea inclusion compound.¹¹ The resonance line for C(1) is broad (particularly at low temperature), and it is possible that second-order quadrupolar effects from bromine contribute to this broadening.¹³

The ¹³C CP-MAS NMR spectrum of C₆H₁₁Cl/H-ZSM-5 (prepared by method A) recorded at 200 K also contains two sets of signals, assigned to equatorial [$\delta_{C(2)} = 38.2$ ppm; $\delta_{C(3)} = 24.8$ ppm; $\delta_{C(4)} = 27.1$ ppm] and axial [$\delta_{C(2)} = 34.7$

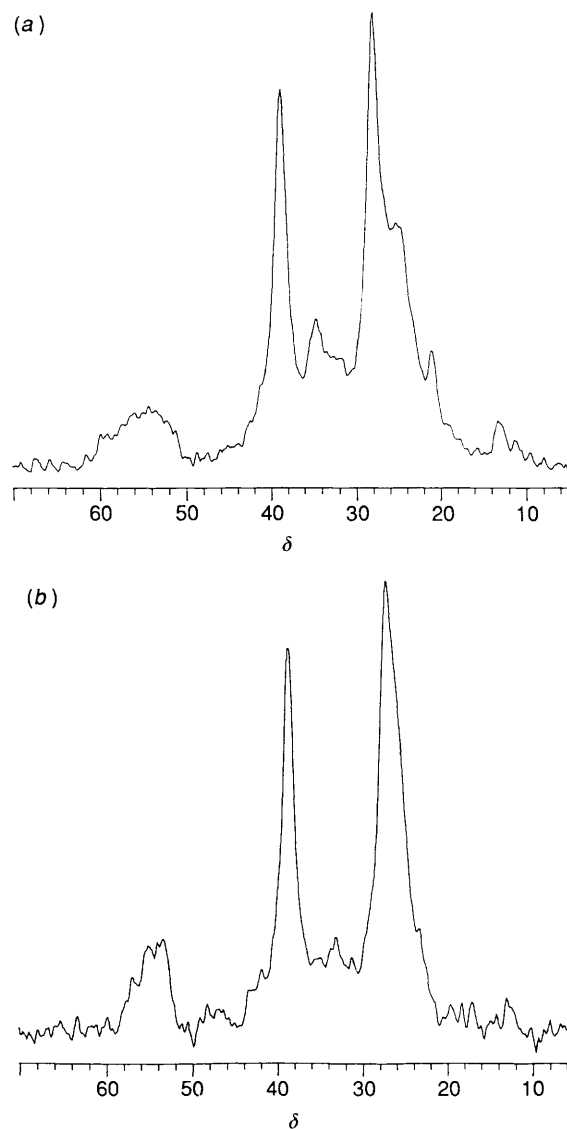


Fig. 1 ¹³C CP-MAS NMR spectra of C₆H₁₁Br/H-ZSM-5 (prepared using method A) recorded (a) at 200 K and (b) at 293 K

ppm; $\delta_{C(3)} = 20.7$ ppm] conformers, with approximate integrated intensity ratio 4:1. As in the case of $C_6H_{11}Br/H-ZSM-5$, the resonance line for C(1) is broad (particularly at low temperature), and it is possible that second-order quadrupolar effects from chlorine contribute to this broadening.¹³

Although such low-temperature ^{13}C NMR spectra provide direct identification of the axial and equatorial conformers, the low loadings of guest molecules within the host materials and the fact that the resonance lines are comparatively broad (as discussed in more detail below) complicate considerably the application of ^{13}C NMR for an accurate study of the conformational properties of the guest molecules in these inclusion compounds. To determine the relative proportions of equatorial and axial conformers at ambient temperature, we have employed a technique which considers NMR parameters averaged by the axial-equatorial exchange. This technique has been applied successfully to study conformational equilibria for substituted cyclohexanes and other systems from solution-state NMR data.¹⁴ For the conformational equilibrium between the axial and equatorial conformers in monosubstituted cyclohexanes (*i.e.* a simple two-site exchange process), the fraction (p_{eq}) of molecules in the equatorial conformation is determined from:

$$p_{eq} = \frac{\langle \delta \rangle - \delta_{ax}}{\delta_{eq} - \delta_{ax}} \quad (1)$$

where δ_{eq} and δ_{ax} are the chemical shifts for a given carbon in the equatorial and axial conformers, respectively, and $\langle \delta \rangle$ is the averaged chemical shift observed for the same carbon in the measured spectrum (recorded under fast-exchange conditions), see Table 1. Although this approach requires the intrinsic temperature dependence of the chemical shifts for the axial and equatorial conformations to be known, it has been shown¹⁴ that this technique provides acceptable results for the C(2) and C(3) carbons in monosubstituted cyclohexanes in the solution state; furthermore, the temperature dependence of the isotropic chemical shifts for these molecules in the solid host materials considered here may be expected to be less than in solution, in view of the comparatively small coefficients for thermal expansion of these materials. For the C(2) carbon of the $C_6H_{11}X$ guest molecules considered here, the ^{13}C NMR chemical shift can be determined with an accuracy of *ca.* ± 0.2 ppm, leading to a percentage error of *ca.* 10% in the estimate of p_{eq} ; although this error is comparatively large, the results obtained by this method are nevertheless sufficiently accurate to distinguish whether the conformational properties of the guest molecules

in these host materials resemble those of the same molecules in the thiourea host structure or in solution. Using this technique, the values of p_{eq} for $C_6H_{11}Cl/H-ZSM-5$ and for $C_6H_{11}Br/H-ZSM-5$ were estimated [from the chemical shift values for C(2)] to be *ca.* 0.8 in both cases.

Values of p_{eq} for $C_6H_{11}Cl/H-ZSM-5$ and for $C_6H_{11}Br/H-ZSM-5$ have also been determined directly from the integrated intensity ratios for the peaks due to C(2) in the ^{13}C CP-MAS NMR spectra recorded at 200 K, and it is interesting to note that these values are in close agreement (see Table 2) with those determined at 293 K *via* the method described above. It should be noted that our assessment of p_{eq} from integrated peak areas in the ^{13}C CP-MAS NMR spectra recorded at 200 K is based upon the assumption that the CP efficiency for a given carbon environment [specifically C(2)] is the same in the axial and equatorial conformations. This assumption is reasonable in view of the fact that the protons directly bonded to carbon will dominate the polarization transfer from protons to carbon in the CP experiment, together with the fact that the geometry of the CH_2 group is essentially the same for the axial and equatorial conformations.

For all the other inclusion compounds studied in this

Table 2 Fraction (p_{eq}) of equatorial conformer, as a function of temperature, for monosubstituted cyclohexane ($C_6H_{11}X$) molecules in solid host materials and in solution

X	environment	T/K	p_{eq}
CH ₃	thiourea	208	0.97
	solution	200	0.99
	H-ZSM-5	293	1
OH	thiourea	198	0.82
	solution	200	0.96
	H-ZSM-5	303	0.9
I	thiourea	177	0.15
	solution	220	0.76
	H-ZSM-5	293	0.8
Br	thiourea	208	0.05
	solution	200	0.75
	H-ZSM-5	200	0.83
Cl	H-ZSM-5	293	0.8
	thiourea	200	0.08
	solution	200	0.81
	H-ZSM-5	200	0.76
	H-ZSM-5	293	0.8
	silicalite-I	293	0.8
	NH ₄ -mordenite	293	0.8
	NH ₄ -Y	293	0.8

Table 1 ^{13}C NMR chemical shifts for monosubstituted cyclohexane ($C_6H_{11}X$) guest molecules within microporous host materials

X	host material	T/K	δ				
			C(1)	C(2)/(6)	C(3)/(5)	C(4)	CH ₃
CH ₃	H-ZSM-5	293	33.5	36.3	27	27	21.1
OH	H-ZSM-5	293	72.5	36.4	25	25	
I	H-ZSM-5	293	34	40.9	25.0	29.0	
Br	H-ZSM-5	293	53	38.6	27	27	
Br	H-ZSM-5	200	*	39.4 (eq)	25.0 (eq)	27.9 (eq)	
			*	34.7 (ax)	21.1 (ax)	*	
Cl	H-ZSM-5	293	60	37.5	26	26	
Cl	H-ZSM-5	200	*	38.2 (eq)	24.8 (eq)	27.1 (eq)	
			*	34.7 (ax)	20.7 (ax)	*	
Cl	silicalite-I	293	60	37.5	26	26	
Cl	NH ₄ -mordenite	293	63	37.6	26	26	
Cl	NH ₄ -Y	293	63	37.6	25.5	27.0	

Data for the equatorial and axial conformations are indicated by (eq) and (ax), respectively; entries marked * in the table refer to data that cannot be established from the spectra.

paper, the boundary values for δ_{eq} and δ_{ax} in eqn. (1) were taken as the values determined from the low-temperature high-resolution solid-state ^{13}C NMR spectrum of the appropriate $\text{C}_6\text{H}_{11}\text{X}$ /thiourea inclusion compound.¹¹ The values of p_{eq} determined *via* this approach are presented in Table 2, which also contains the corresponding data (taken from ref. 11) for the $\text{C}_6\text{H}_{11}\text{X}$ /thiourea inclusion compounds and for $\text{C}_6\text{H}_{11}\text{X}$ in solution. From Table 2, the proportion of molecules in the equatorial conformation is greater than *ca.* 0.8 for all $\text{C}_6\text{H}_{11}\text{X}$ guest molecules in the zeolitic host materials at ambient temperature, and the conformational properties of the $\text{C}_6\text{H}_{11}\text{X}$ guest molecules in these inclusion compounds are thus very similar to those of the same molecules in solution. The uncharacteristic conformational behaviour found for the $\text{C}_6\text{H}_{11}\text{X}$ guest molecules with $\text{X} = \text{Cl}$, Br and I in their thiourea inclusion compounds is not reproduced for these guest molecules in the zeolitic host materials investigated here.

Fig. 2 shows ^{13}C CP-MAS NMR spectra, recorded at 293 K, of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ prepared by method A [Fig. 2(a)] and by method B [Fig. 2(b)]. The linewidths of the resonances are in the range 180–400 Hz, and the chemical shifts (Table 1) are in good agreement with those expected for the equatorial conformer of $\text{C}_6\text{H}_{11}\text{Cl}$ (on the basis of substituent chemical shift parameters for the Cl substituent determined from low-temperature solution state ^{13}C NMR studies^{11,13,14} and from low-temperature solid-state ^{13}C NMR studies of the $\text{C}_6\text{H}_{11}\text{Cl}$ /thiourea inclusion compound¹¹). These linewidths are larger than those (16–27 Hz) observed previously¹¹ for the $\text{C}_6\text{H}_{11}\text{Cl}$ /thiourea inclusion compound at 293 K. The linewidth of the resonance (at *ca.* 60 ppm) due to the C(1) carbon (directly bonded to Cl) is particularly large in comparison with the other resonances. For the other inclusion compounds studied in this paper, the ^{13}C NMR linewidths are also larger than for the same guest molecule in its thiourea inclusion compound. There are several possible explanations for this observation. One possible explanation is that each broad resonance line observed in the ^{13}C CP-MAS NMR spectra of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ comprises a superposition of several isotropic peaks (with different isotropic chemical shifts), each representing $\text{C}_6\text{H}_{11}\text{X}$ guest molecules in a different environment with respect to the H-ZSM-5 host structure. The non-Lorentzian lineshape observed (Fig. 2) for the C(1) carbon in $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ is consistent with this proposal. Specifically, the signal due to the C(1) carbon in Fig. 2(a) and (b) can be considered as a superposition of at least two components: a 'broad' component at higher frequency and a 'narrow' component at lower frequency. In samples prepared by the two different methods, the ratio of the 'broad' and 'narrow' components is different, resulting in the different lineshapes for this signal in Fig. 2(a) and (b).

For $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ (prepared by method B) and $\text{C}_6\text{H}_{11}\text{Br}/\text{H-ZSM-5}$ (prepared by method B), a weak signal was detected at *ca.* 73.1 ppm in the ^{13}C NMR spectrum [Fig. 2(b)]; this signal is assigned to the C(1) carbon of $\text{C}_6\text{H}_{11}\text{OH}$ (with $\text{C}_6\text{H}_{11}\text{X} : \text{C}_6\text{H}_{11}\text{OH} \approx 7$ for $\text{X} = \text{Cl}$ and Br). A signal at *ca.* 74.5 ppm was also detected for $\text{C}_6\text{H}_{11}\text{Cl}/\text{NH}_4\text{-Y}$, and is also assigned to the C(1) carbon of $\text{C}_6\text{H}_{11}\text{OH}$ (with $\text{C}_6\text{H}_{11}\text{Cl} : \text{C}_6\text{H}_{11}\text{OH} \approx 2$). The presence of $\text{C}_6\text{H}_{11}\text{OH}$ is attributed to the occurrence of a hydration reaction of $\text{C}_6\text{H}_{11}\text{Cl}$ and $\text{C}_6\text{H}_{11}\text{Br}$ within the H-ZSM-5 and $\text{NH}_4\text{-Y}$ host materials. In this regard, it should be recalled that the amount of water present within the host materials is likely to be higher for those materials prepared *via* method B. This assignment of the signal at *ca.* 73–75 ppm in the ^{13}C NMR spectra of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$, $\text{C}_6\text{H}_{11}\text{Br}/\text{H-ZSM-5}$ and $\text{C}_6\text{H}_{11}\text{Cl}/\text{NH}_4\text{-Y}$ samples was confirmed by recording the

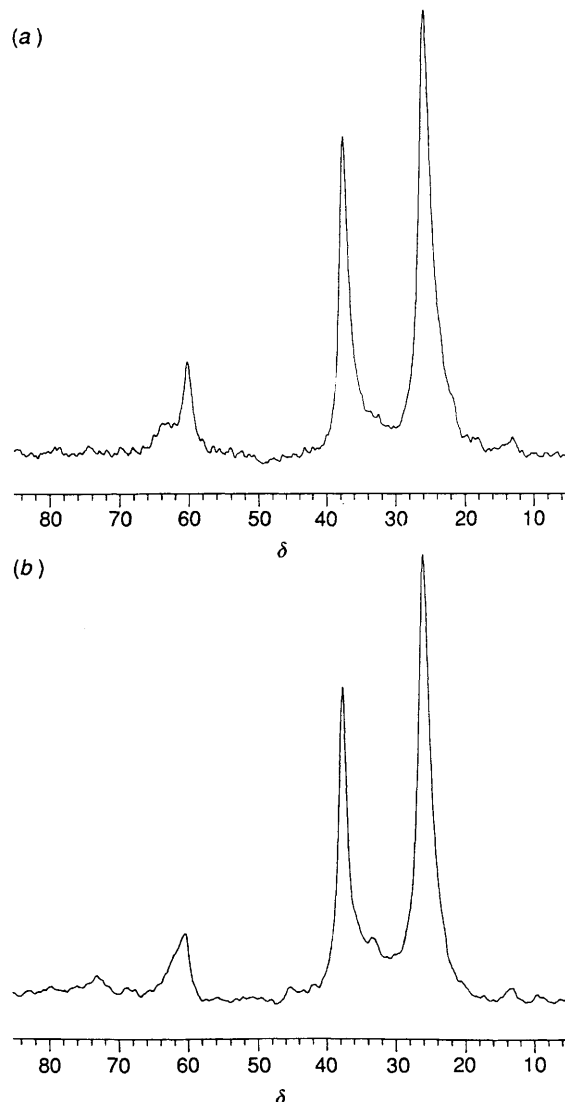


Fig. 2 ^{13}C CP-MAS NMR spectra of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ recorded at 293 K: (a) for the sample prepared using method A and (b) for the sample prepared using method B

^{13}C NMR spectra for $\text{C}_6\text{H}_{11}\text{OH}/\text{H-ZSM-5}$ samples prepared using methods A and B [Fig. 3(a) and (b)]; in these spectra, the chemical shift for the C(1) carbon is 73.2 ppm. For $\text{C}_6\text{H}_{11}\text{OH}/\text{H-ZSM-5}$, however, there is an additional signal at 79.2 ppm in the ^{13}C NMR spectrum. This signal is assigned as the C(1) carbon of dicyclohexyl ether ($\text{C}_6\text{H}_{11}\text{OC}_6\text{H}_{11}$), with $\text{C}_6\text{H}_{11}\text{OH} : \text{C}_6\text{H}_{11}\text{OC}_6\text{H}_{11} \approx 4$ for the sample prepared by method A and 1.3 for the sample prepared by method B. ^{13}C NMR chemical shift increments reported¹⁵ for alkyl groups R in ethers $\text{C}_6\text{H}_{11}\text{OR}$ corroborate our assignment of this signal to the C(1) carbon of $\text{C}_6\text{H}_{11}\text{OC}_6\text{H}_{11}$. Other signals [C(2), C(3) and C(4)] for $\text{C}_6\text{H}_{11}\text{OC}_6\text{H}_{11}$ are in the region 24–36 ppm and overlap the signals due to $\text{C}_6\text{H}_{11}\text{OH}$. It is interesting to note that an analogous conversion of methanol into dimethyl ether has been proposed as the first stage of methanol-to-gasoline conversion on H-ZSM-5.¹⁶

As for $\text{C}_6\text{H}_{11}\text{X}$ /thiourea inclusion compounds,¹¹ there is substantial line narrowing in the ^1H MAS NMR spectra of $\text{C}_6\text{H}_{11}\text{X}/\text{H-ZSM-5}$ inclusion compounds. Analogous line narrowing has also been observed for zeolite and cyclophosphazene inclusion compounds containing various substituted benzenes as the guest species.^{17,18} It has been suggested¹⁷ that, for such systems, all the dipolar interaction tensors have their principal axes in the same direction, either

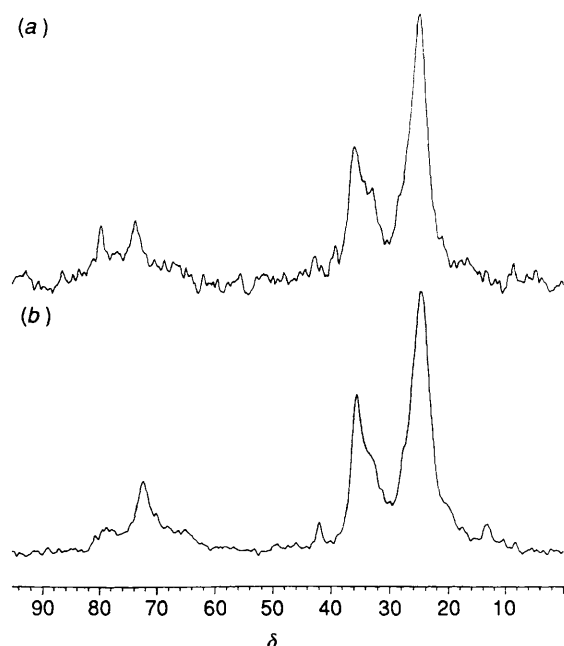


Fig. 3 ^{13}C CP-MAS NMR spectra of $\text{C}_6\text{H}_{11}\text{OH}/\text{H-ZSM-5}$ recorded at 293 K: (a) for the sample prepared using method B; (b) for the sample prepared using method A

because of special features of the crystal structure,¹⁹ or because the whole molecule performs rotational motions which substantially average the intermolecular dipolar interactions.¹⁸ In the case of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$, the narrow ^1H NMR resonance lines observed for the guest molecules (Fig. 4) suggest that ^1H - ^1H dipole-dipole interactions (including the intermolecular dipole-dipole interactions between the ^1H of the host and the ^1H of the guest) are averaged substantially as a result of high conformational, rotational and translational mobility of the guest molecules at room temperature. For $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$, ^1H NMR resonances at $\delta = 1.7$ ppm [linewidth at half-height $\Delta\nu_{1/2} \approx 0.6$

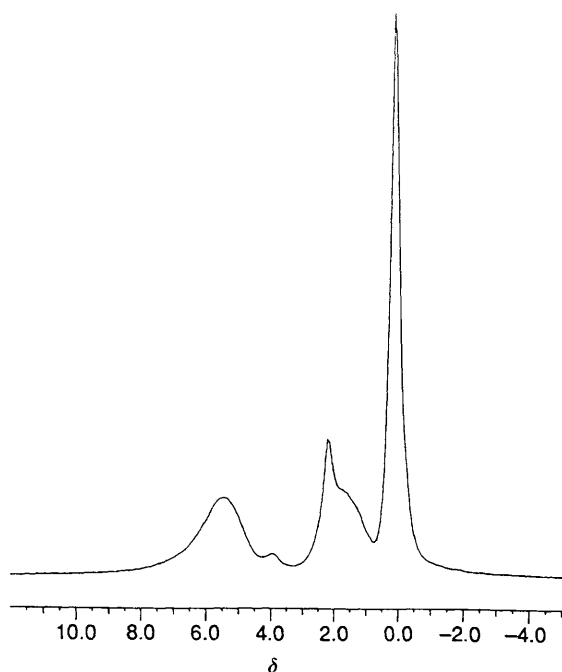


Fig. 4 ^1H MAS NMR spectrum of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ (prepared using method B) recorded at 293 K (MAS frequency = 9.3 kHz). The sharp signal at 0.2 ppm is due to tetrakis(trimethylsilyl)silane (added as an internal standard); this signal does not overlap with any signals from $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$.

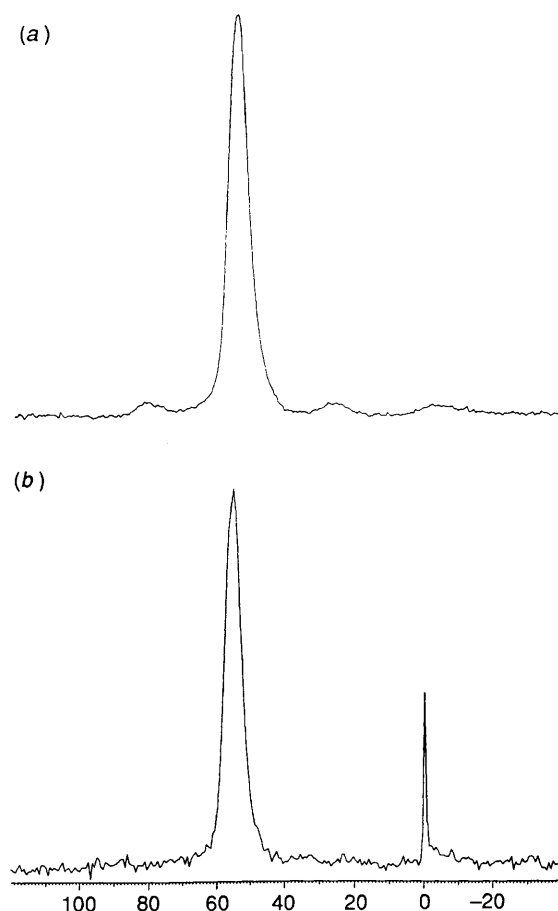


Fig. 5 ^{27}Al MAS NMR spectra of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ (prepared using method A) recorded (a) at 200 and (b) at 293 K

kHz; assigned as H(2), H(3) and H(4) of $\text{C}_6\text{H}_{11}\text{Cl}$], $\delta = 4.0$ ppm [$\Delta\nu_{1/2} \approx 0.4$ kHz; assigned as H(1) of $\text{C}_6\text{H}_{11}\text{Cl}$], $\delta = 2.2$ ppm ($\Delta\nu_{1/2} \approx 0.3$ kHz; assigned as ^1H in H-ZSM-5) and $\delta = 5.6$ ppm ($\Delta\nu_{1/2} \approx 0.7$ kHz; assigned as ^1H in H-ZSM-5) are observed in the ^1H MAS NMR spectrum recorded at 293 K (Fig. 4). For unloaded zeolites,²⁰ the line at 2.2 ppm can be assigned to the non-acidic OH groups (*e.g.* terminal OH groups at the outer surface of the zeolite or at structural defects). The line at 5.6 ppm can be assigned to the acidic bridging OH groups in the zeolite framework and/or to water molecules present within the structure; the comparatively large linewidth may arise from the presence of both of these types of OH group.

^{27}Al MAS NMR spectra were also obtained for the inclusion compounds with H-ZSM-5 as the host material. Fig. 5 shows ^{27}Al MAS NMR spectra of $\text{C}_6\text{H}_{11}\text{Cl}/\text{H-ZSM-5}$ recorded at 293 and 200 K. The broad line at 54.9 ppm ($\Delta\nu_{1/2} \approx 690$ Hz at 293 K and $\Delta\nu_{1/2} \approx 860$ Hz at 200 K) is assigned to the four-coordinated aluminium in the host framework. The narrow line at 0 ppm ($\Delta\nu_{1/2} \approx 60$ Hz) in the spectrum recorded at 293 K is assigned to the six-coordinated aluminium in $\text{Al}(\text{H}_2\text{O})_6^{3+}$.²¹ The line at 0 ppm is considerably broader at 200 K ($\Delta\nu_{1/2} \approx 1$ kHz) than at 293 K, consistent with the suggestion that the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ has less motional freedom at low temperature.

Concluding Remarks

The high-resolution solid-state ^{13}C NMR results reported here suggest that the solid host materials silicalite-I, H-ZSM-5, NH_4 -mordenite, and zeolite NH_4 -Y do not impose any major constraints upon the conformational properties of the monosubstituted cyclohexane guest molecules studied

($C_6H_{11}X$ with $X = CH_3, OH, Cl, Br$ and I); the relative proportions of the axial and equatorial conformations of these guest molecules are the same, within experimental error, as those of the same molecules in solution (at the same temperature).

It is interesting to speculate on the reasons underlying the difference in behaviour for the $C_6H_{11}X$ guest molecules with $X = Cl, Br$ and I in the thiourea host structure (for which the axial conformation predominates) compared with the zeolitic host structures considered here (for which the equatorial conformation predominates). One major difference concerns the effective loading of guest molecules within these host structures. For thiourea inclusion compounds, the host structure is stable only when there is a dense packing of guest molecules within the tunnels, and this tunnel structure collapses to a more compact structure if the guest molecules are removed; thus, the thiourea inclusion compound containing a particular type of guest is known at only one specific guest: host ratio (corresponding to 'saturation'). Zeolitic hosts, on the other hand, generally remain stable if the guest molecules are removed, and, as a consequence, inclusion compounds can be formed between a particular zeolitic host and a particular guest species with a range of guest concentrations [ranging from zero ('empty' host) to some maximum value (corresponding to saturation)]. For the preparation methods employed in this work, the loading of guest molecules is actually rather low [in the range 0.1–1.0 guest molecules per 1000 \AA^3 of the host material, determined from elemental analysis (carbon percentage) results], which is considerably lower than saturation. It is, therefore, reasonable to assume that, in the zeolitic inclusion compounds investigated in this paper, the guest molecules are essentially 'isolated' from each other.

As discussed in detail elsewhere,²² there are major fundamental differences in considering the optimum structural properties of guest molecules for cases (such as the thiourea inclusion compounds) in which the inclusion compound can exist with only one specific guest: host ratio (corresponding to saturation), in comparison with those cases (such as the zeolitic inclusion compounds) in which the guest: host ratio is an experimental variable. If the inclusion compound is of the former type, and if the host structure is a strictly one-dimensional tunnel structure, it is possible to predict and rationalize the structural properties of the inclusion compound by applying a theoretical approach that has been developed recently.^{22–24} For the inclusion compounds with zeolitic hosts (that can be prepared with essentially arbitrary guest: host ratio), on the other hand, this theoretical approach is not valid. Furthermore, the question of predicting and rationalizing the structural properties of the guest molecules on the basis of computed potential-energy functions would, in any case, become considerably more difficult for host structures (such as ZSM-5) that do not consist of independent one-dimensional tunnels, and the methodology (analogous to that developed previously for the strictly one-dimensional inclusion compounds) required for such systems has not yet been developed. Nevertheless, for zeolitic hosts containing low loadings of guest molecules, it is qualitatively clear that the host–guest interaction energy and the intramolecular potential energy of the guest molecule are the major determinants of the structural and conformational properties of the guest molecules (since the guest molecules in the inclusion compounds with low loadings of guest probably behave as essentially isolated molecules, the guest–guest interaction can be considered negligible). The constraints imposed upon the guest molecules by the host environment (quantified by a consideration of the host–guest interaction) could have a crucial influence in controlling the conformational properties

of the guest molecules, and could, in principle, outweigh the effect of the intramolecular potential energy in dictating the observed conformational behaviour of the guest molecules.

The presence of $C_6H_{11}OC_6H_{11}$ in the inclusion compound formed between $C_6H_{11}OH$ and H-ZSM-5 is interesting, particularly in view of the proposal that the corresponding ether (dimethyl ether) is produced in the first stage of methanol-to-gasoline conversion on this zeolite. It is particularly interesting that, in the case of $C_6H_{11}OH/H$ -ZSM-5, significant amounts of $C_6H_{11}OC_6H_{11}$ are produced even at ambient temperature. Control experiments were performed to prove that the $C_6H_{11}OC_6H_{11}$ is produced within the zeolite, and not in the liquid $C_6H_{11}OH$ phase during preparation of the inclusion compound (i.e. during adsorption of $C_6H_{11}OH$ from the liquid phase). It is interesting that the relative amount of $C_6H_{11}OC_6H_{11}$ produced is higher for the inclusion compound prepared by method B than for the inclusion compound prepared by method A, although the exact reasons underlying this fact remain to be investigated in detail.

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