[19] For comparison: We computed the B–N bond length in hexagonal boron nitride as 1.436 Å, in cubic boron nitride as 1.547 Å. The experimental values are 1.446 and 1.565 Å, respectively (K.-H. Hellwege, A. M. Hellwege in *Landolt-Börnstein, New Series, Group III, Vol. 7, Crystal Structure Data of Inorganic Compounds, Part C*, Springer, Berlin, **1978**).

[20] For both structures, β-2-$Si_3B_3N_7$ and α-1-$Si_3B_3N_7$, the mean Si–N bond distance is 1.715 Å, with very small deviations. This is nearly exactly the same as computed for α-Si_3N_4 and β-Si_3N_4, 1.713 and 1.716 Å, respectively (experimental values: 1.738 Å (I. Kohatsu, J. W. McCauley, *Mat. Res. Bull.* **1974**, *9*, 917–920) and 1.732 Å (R. Grün, *Acta Crystallogr. Sect. B* **1979**, *35*, 800–804), respectively).

[21] There is no a priori correlation between bulk modulus and hardness. Nevertheless, for an isotropic material both values are found empirically to be proportional to each other, as long as no plastic deformations occur: R. G. Pearson, *Chemical Hardness*, WILEY-VCH, Weinheim, **1997**, chap. 6.

[22] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH, New York, **1988**.

[23] The calculation of the elastic constants for both structures revealed that they meet the Born criteria for mechanical stability (positive definite stiffness matrix). Thus, the structures are stable against strain. The actual values will be given in a full paper; they are comparable to those of β-Si_3N_4.

Modeling of Benzene Adsorption in Metal-Exchanged Zeolites by Calculation of ^{7}Li Chemical Shifts**

Dewey H. Barich, Teng Xu, Jinhua Zhang, and James F. Haw*

Metal-exchanged zeolites are important adsorbents and catalysts, and NMR spectroscopy is commonly used to determine the structure and dynamics of complexes formed between adsorbates and metal cations in zeolites, but such studies usually focus on ^{2}H or ^{13}C nuclei in the organic species. Adsorbate-induced changes in the chemical shifts have been observed for ^{133}Cs nuclei in zeolites,[1] but ^{133}Cs has an exceptionally large chemical-shift range and may not be representative. At the other extreme is lithium, which has a very modest chemical-shift range. If the ^{7}Li or ^{6}Li chemical shift were sensitive to adsorbate complexation, the effect might be generally useful, especially when quadrupolar effects can either be ignored (as for the central transition of ^{7}Li at moderate fields) or separated from the chemical shift.[2]

Magic angle spinning (MAS) ^{7}Li NMR spectra of zeolite LiZSM-5 suggest almost quantitative titration of the ^{7}Li resonance with 0.9 equivalents of benzene (Figure 1). The ^{7}Li isotropic chemical shift of the evacuated zeolite is $\delta = -0.2$ at 298 K, and adsorption of benzene results in discontinuous movement of the ^{7}Li signal to $\delta = -3.5$ ($\Delta\delta = -3.3$). The spectra appear to be in the slow-exchange regime of benzene hopping between cation sites. The ^{7}Li MAS NMR spectrum of the sample with 0.6 equivalents of benzene was recorded as a function of temperature. Coalescence of the two isotropic signals was observed in the vicinity of 493 K (not shown).

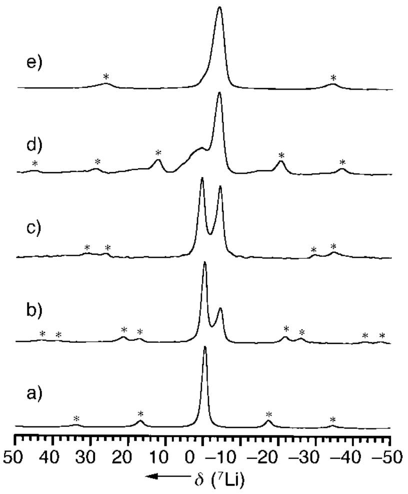

Figure 1. ^{7}Li MAS NMR spectra (116.5 MHz) of LiZSM-5 with the following benzene loadings: a) 0.0, b) 0.4, c) 0.6, d) 0.9, e) 2.0 equiv. Spinning sidebands are indicated by an asterisk.

Aromatic adsorbates such as *p*-xylene produce changes in the ^{29}Si chemical shifts of ZSM-5 zeolites by inducing a phase transition between polymorphs.[3] Here we present theoretical calculations which confirm that the changes in the ^{7}Li chemical shift above are indeed the result of 1:1 complexation between Li^+ and benzene, and not other effects.

Cation–π interactions have been studied both experimentally and theoretically, and have been recently reviewed.[4] In gas-phase calculations, Li^+ forms both 1:1 and 1:2 complexes with benzene. These are more strongly bound than analogous complexes of the other alkali metal cations. Cation–π interactions in aqueous solution have also been studied theoretically to model their roles in biochemical processes (e.g., ion-channel selectivity).[5]

We used ab initio methods to quantitatively model the experimental observations of Figure 1. We used the GIAO-MP2 method[6–8] to explore how the ^{7}Li chemical shift changes when Li^+ ions are π-complexed by benzene or when they are coordinated to various other ligands. Full geometry optimizations were performed at the MP2/6-311 + G* level (Figure 2). We used Li^+, LiH, $Li^+ \cdot H_2O$, and $Li^+ \cdot 2H_2O$ as simplified models of the uncomplexed site. Additionally, we optimized a complex of Li^+ with two benzene molecules. Because of computational costs, we did not include larger, more realistic models of Li sites, such as $Li^+ \cdot 3H_2O$.

The chemical shifts of the structures in Figure 2 were calculated at the GIAO-MP2 level (Table 1). The ^{7}Li chemical shift is relatively insensitive to the basis set on C; in each case the ^{7}Li shift moved downfield (more positive) by 0.2 ppm when the basis on C was reduced from tzp to dzp (see Experimental Section). The isotropic ^{13}C shift moved downfield by only $\Delta\delta = 3.7$ when benzene was complexed with Li^+, which is in agreement with experiment. Smaller effects were

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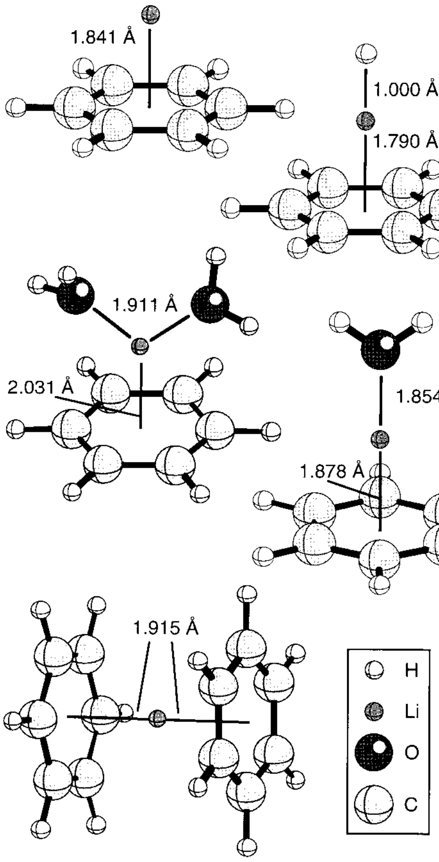

Figure 2. Theoretical structures of model compounds. All structures were optimized at the MP2/6-311 + G* level.

Table 1. Calculated ^{7}Li chemical shifts[a] of lithium–benzene model compounds.

System	C Basis	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	CSA[b]	η
$Li^+ \cdot C_6H_6$	tzp	−7.3	−0.5	−0.5	−21.0	−20.4	0.00
$LiH \cdot C_6H_6$	tzp	−6.5	2.1	2.1	−23.8	−25.9	0.00
$Li^+ \cdot H_2O \cdot C_6H_6$	tzp	−6.5	3.9	3.2	−26.5	−30.1	0.04
$Li^+ \cdot 2H_2O \cdot C_6H_6$	tzp	−4.9	6.2	−3.0	−17.9	−19.5	0.71
$C_6H_6 \cdot Li^+ \cdot C_6H_6$	dzp	−12.4	0.9	0.9	−39.1	−40.0	0.00
LiH		−0.4	2.6	2.6	−6.2	−8.8	0.00
$Li^+ \cdot H_2O$		0.5	4.2	3.7	−6.4	−10.3	0.06
$Li^+ \cdot 2H_2O$		0.9	7.5	7.5	−12.2	−19.7	0.00

[a] Chemical shifts were calculated at the GIAO-MP2 level and are reported relative to that of Li^+. The absolute shielding of Li^+ is 95.4 ppm. [b] CSA = chemical shift anisotropy.

predicted by the other models. In each case complexation shifted δ_{22} of the ^{13}C tensor downfield, but this was partially offset by upfield shifts in δ_{33}.

For the complexation of Li^+ by a single benzene molecule, $\Delta\delta(^7Li)$ ranged between −5.8 for $Li^+ \cdot 2H_2O$ and −7.3 for Li^+ (Table 1). For $Li^+ \cdot 2C_6H_6$ $\Delta\delta$ is −12.4. Not surprisingly, complexation to benzene has the most pronounced effect on δ_{33}, which lies along the axis joining the cation and the center of the benzene ring(s). The experimental $\Delta\delta(^7Li)$ value for benzene complexation in LiZSM-5 zeolite of −3.3 is several times smaller than that calculated for the 1:2 complex but only slightly smaller than that calculated for $Li^+ \cdot 2H_2O$. We conclude that the change in the ^{7}Li chemical shift reflects formation of a 1:1 complex, and the slightly smaller magnitude of the experimental $\Delta\delta$ value suggests that the zeolite channel prevents benzene from approaching Li^+ as closely as it does in the structures in Figure 2. Thus, the alkali metal nucleus is a potential source not only of dynamical but also of structural information.

Experimental Section

^{7}Li NMR spectra were recorded at 116.5 MHz on a Chemagnetics CMX-300 spectrometer with magic angle spinning, and shifts are reported relative to that for 1.0 M aqueous LiCl. Zeolite HZSM-5 (Si/Al = 19) was obtained from UOP and converted into the lithium form by repeated ion exchange. [$^{13}C_6$]Benzene was adsorbed into the zeolite by quantitative manometry and procedures described elsewhere.[9]

All geometries were optimized at the MP2/6-311 + G* level with Gaussian 94.[10] We used ACES II for all chemical shift calculations.[11] The following basis sets[12] were employed: Li: tzp {511111/1}; O: tzp {51111/311/1}; H: dz {31}. For C we used tzp {51111/311/1} and dzp {5111/31/1} basis sets for each structure, except for $Li^+ \cdot 2C_6H_6$, for which only the dzp calculation was tractable.

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