

# Localization of Adsorbed Cyclohexane in the Acid Form of Zeolite Y. A Powder Neutron Diffraction and Computational Study

Gerardo Vitale, Caroline F. Mellot, and Anthony K. Cheetham\*

Materials Research Laboratory, University of California, Santa Barbara, California 93106

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The crystal structure of the deuterated acid form of zeolite Y with adsorbed cyclohexane ( $\sim 1$  molecule/supercage) has been determined by powder neutron diffraction at 5 K. The structure was refined by the Rietveld least-squares method in the cubic space group  $Fd\bar{3}m$  [ $a = 24.711(2)$  Å,  $R_p = 3.13\%$ ,  $R_{wp} = 4.28\%$ ]. Deuterium atoms were located, in order of decreasing occupancy, on O(3)[33(3)%], O(1)[10(2)%], O(4)-[3(3)%] and O(2)[2(3)%]. Approximately half of the adsorbed cyclohexane molecules were located in the chair conformation in the 12-ring window. Energy minimization calculations predict various types of binding sites for cyclohexane in siliceous Y. One type of site is found in the 12-ring window and is in excellent agreement with the position determined from the diffraction analysis. Other binding sites in low-symmetry positions are predicted, where cyclohexane is coordinated to 4-ring and 6-ring windows; these could not be detected by the diffraction analysis. Our calculations suggest that cyclohexane molecules experience a rather flat potential surface in zeolite Y.

## Introduction

The location of benzene in Faujasite-type zeolites has been extensively investigated in a variety of structures including NaY<sup>1</sup>, H–Y<sup>2</sup>, H–SAPO-37,<sup>3</sup> CaLSX,<sup>4</sup> and NaX.<sup>5</sup> Diffraction techniques have proved to be particularly appropriate for such systems, since identifying the adsorption sites of the molecule is facilitated when high-symmetry positions arise from specific interactions between the aromatic ring and the extraframework cations. In contrast to aromatics, little work has been done on the structures of saturated hydrocarbons in zeolites. In the case of cyclohexane, for example, the less polar nature of the sorbate is expected to lead to adsorption of a nonspecific nature involving dispersive interactions with the walls of the zeolite rather than cation–sorbate interactions. In support of this difference between benzene and cyclohexane, NMR studies have shown that the diffusion of cyclohexane in NaY and NaX is more rapid than that of benzene in these systems.<sup>6,7</sup> Variations in the motional properties of benzene, *n*-hexane, and cyclohexane have also been reported in zeolite K–L,<sup>8</sup> highlighting the importance of the unsaturated nature of benzene in its adsorption behavior.

Initiation of both isomerization and cracking reactions of cyclohexane occur on zeolite H–Y at 623 K.<sup>9</sup> Although a substantial number of diffraction,<sup>10,11,12</sup> IR,<sup>13–18</sup> and computational studies<sup>19,20</sup> have investigated the structure and acidity of zeolite H–Y, no structure determination of adsorbed cyclohexane in H–Y has been reported. This paper reports the findings of a powder diffraction and a computational study of this system. Only a fraction of the adsorbed cyclohexane molecules could be located by the diffraction analysis. The computer simulations were performed to corroborate our diffraction results with the aim of yielding further insight into the nature of other binding sites. A combination of Monte Carlo packing and energy minimization calculations was used to probe adsorption sites of cyclohexane in siliceous Y. Binding-site geometries and energies are discussed in comparison with our diffraction results and experimental data for heats of adsorption.

## Experimental Section

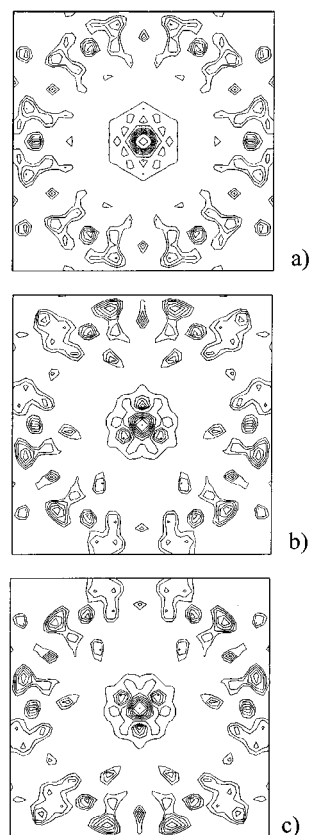
The NH<sub>4</sub>Y starting material was kindly supplied by P. D. Hopkins of Amoco Oil Company. It was synthesized from Na–Y by ion exchange with NH<sub>4</sub>NO<sub>3</sub> six times at 358 K. The chemical composition of this material in its dehydrated form is Na(NH<sub>4</sub>)<sub>55</sub>Si<sub>136</sub>Al<sub>56</sub>O<sub>384</sub>. The deuterated ammonium form of this zeolite was prepared by stirring NH<sub>4</sub>Y in a 1 M D<sub>2</sub>O solution of ND<sub>4</sub>Cl. After 24 h of stirring under a nitrogen atmosphere at room temperature, the mixture was filtered and washed several times with D<sub>2</sub>O under nitrogen, and the procedure was then repeated. The acid form D–Y was prepared by careful calcination of the ND<sub>4</sub>Y at 673 K in flowing oxygen. The thermal treatment was done under flatbed conditions with a thin film of zeolite powder. The calcination conditions were as follows: the sample was heated under flowing oxygen at a rate of 3 K/min to 573 K and held at this temperature for 4 h; it was then heated to 673 K at a rate of 3 K/min and held for 10 h at that temperature to complete the calcination process. The crystallinity of the samples after calcination was checked by X-ray diffraction.

The sample for neutron diffraction was packed into a thin-walled vanadium can and screw-sealed using indium wire. A known amount of deuterated cyclohexane for low coverage (1 molecule/supercage) was added gravimetrically to the can before sealing it. All this was done inside a nitrogen-containing glovebox. To obtain a homogeneous distribution of the sorbate, the airtight can was kept in an oven at 333 K for 2 days.

Neutron diffraction data were collected at 5 K using the powder diffractometer DUALSPEC at Chalk River Laboratories, Canada. The data were collected at  $\lambda = 1.5043$  Å, between 6° 2 $\theta$  and 120° 2 $\theta$ . The data were analyzed by Rietveld refinement<sup>21</sup> techniques using the GSAS<sup>22</sup> package. Trial structures were visualized using the MSI Catalysis software.<sup>23</sup>

The model of the D–Y parent material<sup>2</sup> was used as the starting model for this refinement. Deuterium atoms were placed at each oxygen in turn, assuming a coplanar configuration with the T–O–T atoms and an O–D bond length of 0.98 Å. Their positions, occupancies, and isotropic temperature factors were then refined. The pattern was rather poorly fitted by the model involving just the framework and the deuterium atoms.

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**Figure 1.** Difference Fourier maps perpendicular to [111]. (a) Section about  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  in the 12-ring window; (b) Section 0.4 Å below map a; (c) section 0.4 Å above map a.

At this stage, Figure 1 shows difference Fourier maps perpendicular to the [111] axis in the region of the 12-ring window. The map a is a section that has the center of reference located at  $x = y = z = 0.5$ , the center of the 12-ring window. Maps b and c show sections that are 0.4 Å below and above map a, respectively. These maps suggest the presence of cyclohexane molecules in the chair conformation adsorbed at the 12-ring window. The introduction of a cyclohexane molecule in this position, centered at  $x = y = z = 0.5$ , produced a significant improvement in the refinement. Soft constraints for the C–C (1.54 Å) and C–D (1.07 Å) bonds were imposed. The model obtained after the refinement of both coordinates and population parameters indicates that approximately 4.5 cyclohexane molecules unit-cell<sup>-1</sup> are adsorbed in the 12-ring windows. This amount is slightly more than half the value of 8 molecules unit-cell<sup>-1</sup> estimated from the experimental loading.

Separate isotropic temperature factors were refined for the framework atoms. However, a single isotropic temperature factor was refined for all four deuterium atoms. Anisotropic temperature factors were refined for the cyclohexane molecule. The lattice parameter, zero point, scale factor,  $U$ ,  $V$ ,  $W$ ,  $X$ ,  $Y$ , and  $Z$  parameters, and an asymmetry correction were refined in addition to the positional, thermal, and occupancy parameters. The refinement yielded the model presented below.

### Computational Approach

As a consequence of the partial identification of adsorption sites obtained from the diffraction analysis, a computational approach was undertaken to gain further insight into cyclohexane binding sites in zeolite Y. All our simulations were carried out on siliceous Y, circumventing the difficulty of dealing with the disordered distribution of protons. Nevertheless, the use of siliceous Y, rather than H–Y, is believed to be a good

**TABLE 1: Parameters for Short-Range and Long-Range Interactions and Hydrocarbon Internal Interactions<sup>a</sup>**

Zeolite–Hydrocarbon Short-Range Parameters <sup>28,29</sup>					
	$A_{ij}$ (eV Å <sup>12</sup> )			$B_{ij}$ (eV Å <sup>6</sup> )	
O···C (–CH <sub>2</sub> )	10539.429			17.784	
O···H (–CH <sub>2</sub> )	1158.725			6.0135	
Zeolite and Hydrocarbon Long-Range Parameters					
	atom type				
	Si	O	C(–CH <sub>2</sub> )	H <sub>axial</sub> (–CH <sub>2</sub> )	H <sub>equatorial</sub> (–CH <sub>2</sub> )
partial charge	+2.4	–1.2	–0.019	+0.017	+0.002
Hydrocarbon Internal Interactions					
two-body	$K_{ij}$ (eV Å <sup>–2</sup> )				$r_o$ (Å)
C–H	31.25				1.07
C–C	48.94				1.54
Hydrocarbon Internal Interactions					
three-body	$k_{ijk}$ (eV rad <sup>–2</sup> )				$\Theta_o$ (deg)
H–C–H	2.06				109.47
H–C–C	3.39				109.47
C–C–C	3.39				109.47
Hydrocarbon Internal Interactions					
four-body	$k_{ijkl}$ (eV)		$b_{ijkl}$		$c_{ijkl}$
H–C–C–H	0.005		3.0		1.0
H–C–C–C	0.005		3.0		1.0
C–C–C–C	0.005		3.0		1.0

<sup>a</sup> The following functional forms were used to optimize the hydrocarbon internal geometry: two-body interactions:  $E_{ij} = K_{ij}(r - r_o)^2$ ; three-body interactions,  $E_{ijk} = k_{ijk}(\Theta_{ijk} - \Theta_o)^2$ ; four-body interactions,  $E_{ijkl} = k_{ijkl}(1 + b_{ijkl} \cos(c_{ijkl}\Phi_{ijkl}))$ .

approximation for simulating the adsorption of cyclohexane, given the non polar nature of the sorbate. For probing the host–guest potential energy surface, we used a simple methodology combining the packing of a guest molecule into the zeolitic host structure followed by a fixed-lattice energy minimization of the host–guest system. This is often referred to as the Monte Carlo packing procedure; it has been successfully used for probing the binding sites of organic molecules in microporous sorbents<sup>24,25</sup> and was extended more recently to the study of cation positioning in zeolites.<sup>26,5</sup> The calculations are equivalent to 0 K calculations for a single sorbate molecule and correspond to the zero-coverage limit.

The zeolite host structure was built by using the coordinates of the Si and O atoms from the neutron diffraction refinement of the present work. The packing procedure consisted of the random selection of 20 insertion positions for one cyclohexane molecule in a unit cell of zeolite Y and the calculation of the interaction energy for the 20 host–guest systems. To avoid the generation of irrelevant insertions of cyclohexane in the  $\beta$ -cages, a dummy atom assigned with high repulsive Lennard–Jones parameters was placed at the center of each  $\beta$ -cage.

An energy minimization calculation on each structure was then performed in the triclinic space group P1 using the program DIZZY.<sup>27</sup> The guest molecule was allowed to relax and move freely within the supercell. The addition of framework relaxation during minimization calculations is known to lead to only minor stabilization energies (less than 1 kJ mol<sup>-1</sup> in the case of benzene in NaY<sup>25</sup>) when compared to fixed-lattice calculations. We therefore assumed that framework flexibility plays a negligible role in the structure and energetics of cyclohexane adsorption.

The total interaction energy between the cyclohexane molecule and the zeolite structure was modeled as the sum of a

**TABLE 2: Diffractogram Information<sup>a</sup>**

data type	neutron D–Y + cyclohexane
data collection temperature (K)	5 K
space group	<i>Fd3m</i>
<i>a</i> (Å)	24.7108(18)
Profile <i>R</i> -factor ( <i>R<sub>p</sub></i> )	0.0313
Weighted Profile <i>R</i> -factor ( <i>R<sub>wp</sub></i> )	0.0428
Structure <i>R</i> -factor ( <i>R<sub>F</sub></i> )	0.1083
Expected <i>R</i> -factor ( <i>R<sub>e</sub></i> )	0.0257
$\chi^2$	2.762
wavelength (Å)	1.5043(5)
zero correction (deg)	2.925(4)
scale factor	1207
number of reflections	622
profile function	pseudo-Voigt
asymmetry correction	2.9219
<i>U V W</i>	885(65) –1067(58) 373(18)
<i>X Y Z</i>	17(1) 0.00 0.00
background function	24 coefficient shifted Chebyshev

<sup>a</sup> Rietveld refinement was used to minimize  $\sum w_i(I_{o,i} - I_{c,i})^2$  where  $I_{o,i}$  and  $I_{c,i}$  are the observed and calculated powder diffraction intensities for the *i*th point, respectively. Weights,  $w_i$ , are  $1/I_{o,i}$ . Weighted and unweighted profile *R*-factors are defined as  $R_{wp} = \{[\sum w_i(I_{o,i} - I_{c,i})^2] / [\sum w_i(I_{o,i})^2]\}^{1/2}$  and  $R_p = \sum |I_{o,i} - I_{c,i}| / \sum I_{o,i}$ . The structure *R<sub>F</sub>* factor is defined as  $R_F = \sum (F_o - F_c)^2 / [\sum (F_o)^2]$ . The expected *R*-factor (the statistically best possible value for *R<sub>wp</sub>*) is defined as  $R_e = [(N - P) / (\sum w_i I_{o,i}^2)]^{1/2}$  where *N* is the number of observed powder diffraction data points and *P* is the number of refined parameters.  $\chi^2$  was calculated from  $(R_{wp}/R_e)^2$ .

dispersive-repulsive term using a Lennard-Jones (6-12) potential and a long-range Coulombic term:

$$E = E_{\text{Lennard-Jones}} + E_{\text{Coulombic}} \quad (1)$$

with

$$E_{\text{Lennard-Jones}} = \sum_{ij} (A_{ij}/r^{12} - B_{ij}/r^6) \quad (2)$$

and

$$E_{\text{Coulombic}} = \sum_{ij} q_i q_j / r_{ij} \quad (3)$$

Short-range interactions of the cyclohexane molecules with the zeolite were considered only with the oxygen atoms. Since silicon atoms have a smaller polarizability than oxygen atoms and are not closely accessible to adsorbed molecules, their interaction with cyclohexane was neglected. The short-range forcefield parameters were derived from the five-site model for methane<sup>28,29</sup> that has been used for simulating the adsorption of methane in various zeolites.

The zeolite charge distribution was taken from the silicate potential developed by Kramer et al.<sup>30</sup> it has partial charges, which quantum mechanical calculations on clusters have shown to be more realistic than formal charges. Cyclohexane partial charges were based on a Hartree–Fock calculation with the

6-31G\*\* basis set by fitting the electrostatic surface potential using the TURBOMOLE program package.<sup>31</sup> Although dispersive interactions are known to be predominant in such alkane/zeolite systems, including the long-range electrostatic contribution is believed to give a more realistic description of the total interaction energy.

Table 1 gives the parameters used for the short-range and long-range interactions. Since relaxation of the cyclohexane molecule was allowed during energy minimization, the functional forms and forcefield parameters adopted for the intramolecular hydrocarbon interactions are given for completeness. All calculations were carried out with a short-range term summation taken up to a cutoff radius of 12 Å, and an Ewald summation for the electrostatic contribution.

## Results and Discussion

Details of the neutron refinement are given in Table 2. Atomic parameters and anisotropic temperature factors for D–Y with cyclohexane are shown in Tables 3 and 4, respectively, and framework interatomic distances and angles in Table 5. The final observed, calculated, and difference plots for the neutron diffraction data for D–Y with cyclohexane are shown in Figure 2.

The framework structure is in line with previous studies, with T–O distances and T–O–T angles in the expected ranges. However, the O–T–O angles show a rather large spread around the tetrahedral angle; it is not clear whether this is a real effect.

Figure 3a shows the accommodation of the cyclohexane molecule in the 12-ring window, as determined from our diffraction study. Each equatorial deuterium atom is pointing toward an oxygen O(4) of the framework at a distance of 2.74 Å. Deuterium atoms of the framework were located, in order of decreasing occupancy, on O(3)[33(3)%], O(1)[10(2)%], O(4)-[3(3)%], and O(2)[2(3)%]. These values are in broad agreement with previous crystallographic studies,<sup>10–12</sup> while suggesting a slight increase in O(3) occupancy upon cyclohexane adsorption.

It was not possible to locate cyclohexane molecules in other positions using the Fourier difference maps. However, some remaining discrepancies between the experimental and the simulated patterns at low angles may indicate that there are other adsorption sites for the cyclohexane in this system, a proposal that is strongly supported by our simulation results (see below). These adsorption sites are in general positions with low-occupancy factors, thus making them difficult to pinpoint using Fourier difference maps.

Concerning our simulations, the minimized structures were analyzed in terms of the energetics and framework environments of cyclohexane. The minimized configurations converged to binding energies in the range from 55.5 to 66.4 kJ mol<sup>–1</sup>, depending on the location of cyclohexane within the supercage. The favorable binding sites identified from the minimized configurations fall into two categories: (i) sites in the plane of

**TABLE 3: Atomic Parameters for D–Y with Cyclohexane**

atom	site multiplicity	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> (Å <sup>2</sup> )	fractional occupancy
Si	192	–0.0532(4)	0.0371(5)	0.1218(5)	0.003(2)	1
O(1)	96	0.0000	–0.1069(4)	0.1069(4)	0.004(2)	1
O(2)	96	0.0006(6)	0.0006(6)	0.1355(8)	0.026(5)	1
O(3)	96	0.1754(5)	0.1754(5)	–0.0275(7)	0.019(6)	1
O(4)	96	0.1739(5)	0.1739(5)	0.3206(7)	0.0013(8)	1
D(1)	96	0.0000	–0.1349(5)	0.1349(5)	0.032(5)	0.10(2)
D(2)	96	0.02(1)	0.02(1)	0.16(2)	0.032(5)	0.02(3)
D(3)	96	0.1723(6)	0.1723(6)	0.0119(9)	0.032(5)	0.33(3)
D(4)	96	0.193(1)	0.193(1)	0.349(2)	0.032(5)	0.03(3)
C(A)	96	0.4701(1)	0.4701(1)	0.5422(2)	<i>U</i> <sub>eq</sub> = 0.065	0.28(1)
D(A1)	96	0.5840(5)	0.4617(3)	0.4617(3)	<i>U</i> <sub>eq</sub> = 0.065	0.28(1)
D(A2)	96	0.5174(7)	0.4449(2)	0.4449(2)	<i>U</i> <sub>eq</sub> = 0.065	0.28(1)

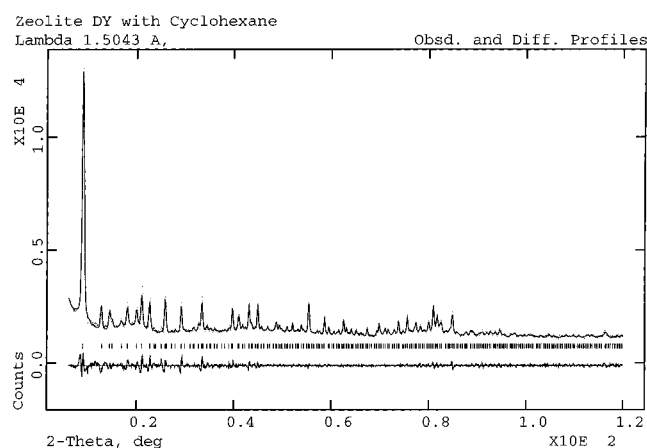
**TABLE 4: Anisotropic Temperature Factors ( $\text{\AA}^2$ ) for Cyclohexane in D-Y**

atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(A)	0.062(4)	0.062(4)	0.072(6)	-0.011(5)	0.0024(31)	0.0024(31)
D(A1)	0.0647(14)	0.0647(14)	0.0647(14)	0.0109(14)	0.0109(14)	0.0109(14)
D(A2)	0.0647(14)	0.0647(14)	0.0647(14)	0.0109(14)	0.0109(14)	0.0109(14)

**TABLE 5: Framework Interatomic Distances and Angles<sup>a</sup>**

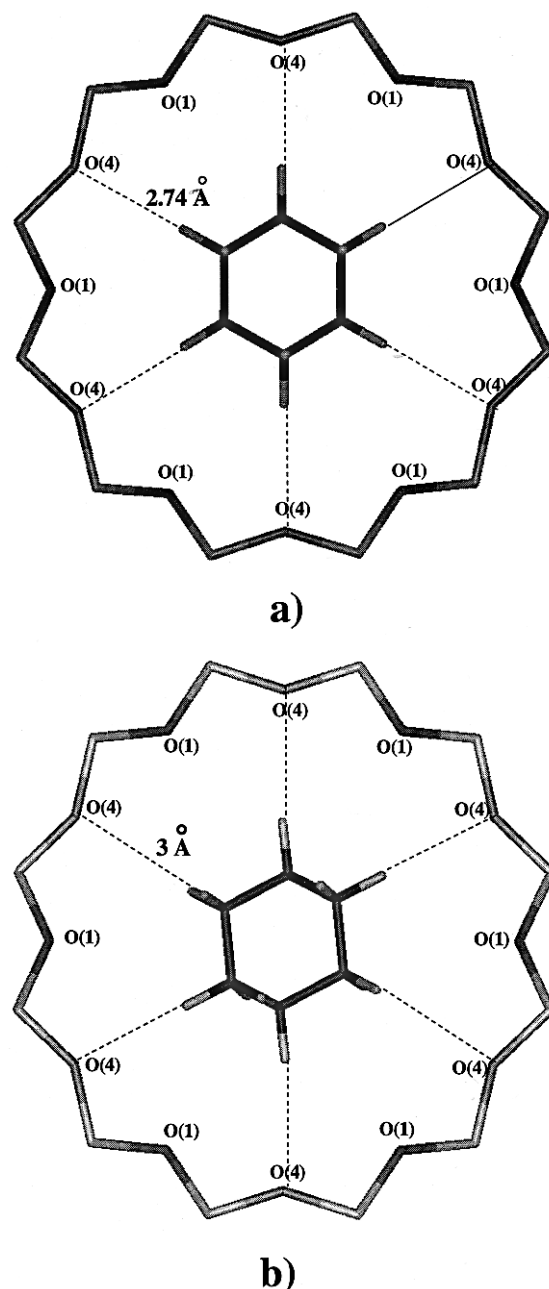
distance	D-Y + cyclohexane
T-O(1)	1.654(10)
T-O(2)	1.643(11)
T-O(3)	1.620(17)
T-O(4)	1.663(12)
average T-O	1.645(6)
angle	D-Y + cyclohexane
O(1)-T-O(2)	113.0(10)
O(1)-T-O(3)	118.1(12)
O(1)-T-O(4)	106.7(8)
O(2)-T-O(3)	98.3(11)
O(2)-T-O(4)	111.6(12)
O(3)-T-O(4)	109.2(10)
average O-T-O	109.4(4)
angle	D-Y + cyclohexane
T-O(1)-T	131.7(13)
T-O(2)-T	147.9(15)
T-O(3)-T	132.0(13)
T-O(4)-T	146.1(15)
average T-O-T	139.5(7)
distance <sup>b</sup>	D-Y + cyclohexane
C(A)-C(A)	1.540(4)
C(A)-D(A1)	1.074(8)
C(A)-D(A2)	1.073(3)
D(A1)-D(A2)	1.749(3)
angles	D-Y + cyclohexane
C(A)-C(A)-C(A)	109.8(4)
C(A)-C(A)-D(A1)	109.6(2)
C(A)-C(A)-D(A2)	109.4(3)
D(A1)-C(A)-D(A2)	109.1(7)

<sup>a</sup> Distances in angstroms, and angles degrees. <sup>b</sup> Soft constraints were used for these distances



**Figure 2.** Plot showing the observed neutron diffraction pattern of D-Y with cyclohexane (dots) overlaid with a pattern calculated from the crystal structure (solid line). The lower curve is the difference between the observed and calculated profiles. Tic marks show the Bragg peak positions.

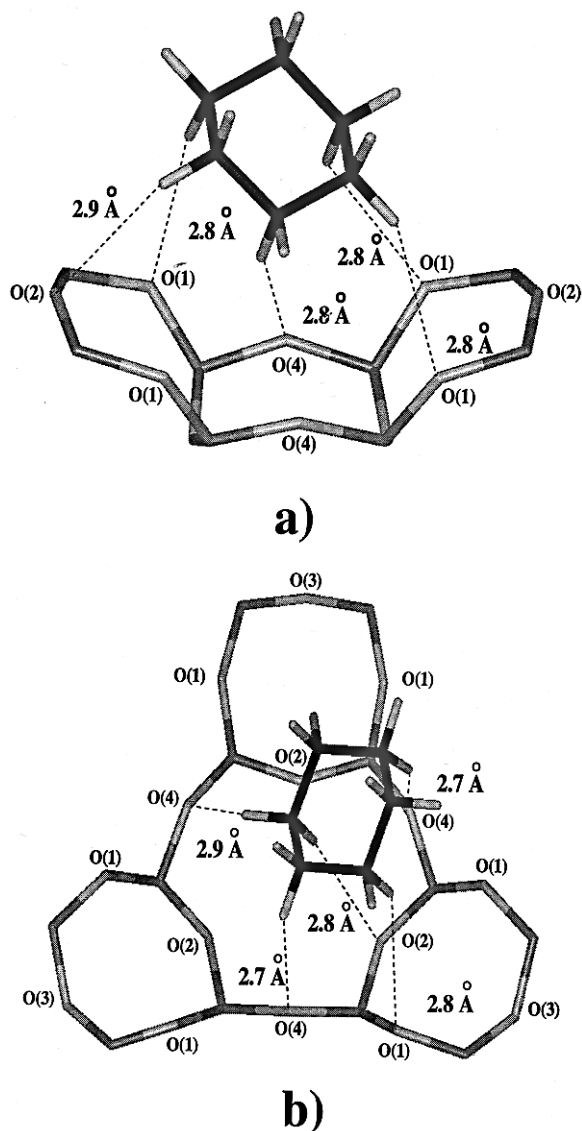
the 12-ring windows; (ii) sites close to the walls of the supercage, facing 4-ring and/or 6-ring windows. Concerning sites of type i, the simulated position is in excellent agreement with our neutron diffraction position, especially bearing in mind



**Figure 3.** Adsorbed cyclohexane at the 12-ring window in zeolite Y (a) from the diffraction analysis and (b) from the energy minimization calculations.

that the calculations were run without any symmetry constraint. The cyclohexane molecule was found in the chair conformation in the plane of the 12-ring window (Figure 3b), slightly tilted from the 3-fold symmetry position determined from the diffraction analysis. Each equatorial hydrogen is pointing toward an oxygen O(4) of the 12-ring window at a typical distance of 3 Å. The binding energy is typically around 59 kJ mol<sup>-1</sup> for these 12-ring window sites.

The second group of binding sites correspond to cyclohexane molecules located in low-symmetry positions. Two examples of these low-symmetry sites are shown in Figure 4a,b with binding energies of ~66 and ~63 kJ mol<sup>-1</sup>, respectively. The



**Figure 4.** Adsorbed cyclohexane in low-symmetry positions located from energy minimization calculations (a) facing 4-ring windows (b) facing both 6-ring and 4-ring windows.

orientation of the cyclohexane molecule toward the framework is determined by interactions between equatorial and axial hydrogens and oxygens of the 4-rings and 6-rings, with typical  $\text{H}\cdots\text{O}$  distances of 2.8 Å.

When extrapolating our computational results to the D–Y/cyclohexane system, deuterium atoms on framework oxygens O(2) and O(3), i.e., D(2) and D(3), are assumed to have a negligible influence on cyclohexane location, since they both point toward the  $\beta$ -cages. Other deuterium atoms, D(1) and D(4), which both point toward the center of the 12-ring window, may modify the geometry of the binding sites described above due to repulsive interactions. Nevertheless, since our simulations in siliceous Y accurately predict the positioning of cyclohexane in the 12-ring window, we believe that the low-symmetry positions obtained in our simulations are realistic. They reflect nonspecific interactions of the cyclohexane molecule with the walls of the zeolite, leading to a wide range of low-symmetry positions that the diffraction analysis was unable to locate.

Although the binding energies reported above are estimated from 0 K calculations, it is assumed that these favorable binding sites dominate the heat of adsorption at room temperature. We

are not aware of experimental data for the heat of adsorption of cyclohexane in H–Y or siliceous Y, but our computed values are consistent with the experimental differential heat of adsorption of 55 kJ mol<sup>−1</sup> reported by Stach et al.<sup>32</sup> from room temperature calorimetric measurements for *n*-hexane in siliceous Y. Our computational results underline the good transferability of the forcefield parameters used in this work, especially as the diffraction results and the simulations are in close agreement concerning the geometry and the framework environment of the 12-ring window site.

## Conclusions

Our powder neutron diffraction study of cyclohexane adsorbed in the acid form of zeolite Y shows that a fraction of the cyclohexane molecules ( $\sim 0.6$  molecule/supercage on average) is absorbed in the chair conformation at the 12-ring windows. In agreement with previous studies on D–Y, we find that deuterium atoms in this system are located preferentially at O(3) and O(1). Our simulations carried out on the adsorption of cyclohexane on siliceous Y give an accurate prediction of cyclohexane location in the 12-ring windows. Besides the 12-ring window site, the simulations predict low-symmetry adsorption sites facing 4-ring and 6-ring windows. These findings underline that a computational approach is especially profitable when guest molecules are adsorbed in low symmetry and disordered positions that are difficult to pinpoint by diffraction methods. From both the diffraction and simulations results, it is shown that cyclohexane molecules experience a rather flat potential energy surface when adsorbed in zeolite Y and that adsorption is driven by dispersive interactions between cyclohexane hydrogen atoms and accessible oxygen atoms of the framework.

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