Modeled Influence of a Structure Directing Agent on Al Siting Energetics: 
N,N,N-trimethyl-1-adamantyl ammonium (TMAda$^+$) in Chabazite

Xiaoyu Wang,$^\dagger$ Yujia Wang,$^\ddagger$ Ahmad Moini,$^\|$ Rajamani Gounder,$^\S$ Edward J. Maginn,$^\dagger$ and William F. Schneider$^{*,\dagger,\|}$

$^\dagger$Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA
$^\ddagger$Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA
$^\|$BASF Corporation, Iselin, New Jersey 08830, USA
$^\S$Charles D. Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
$^{\|}$Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556 USA

E-mail: wschneider@nd.edu

Abstract

While organic structure directing agents (OSDAs) are well known to have a directional influence on the topology of a crystallizing zeolite, the relationship between OSDA charge and siting of aliovalent ions on a primarily siliceous framework is unclear. Here, we explore the relationship between OSDA orientation, Al$^{3+}$ siting, and
lattice energy, taking as a model system CHA zeolite occluded with N,N,N-trimethyl-1-adamantyl ammonium (TMAda+) at an Si/Al ratio of 11/1. We use density functional theory calculations to parametrize a fixed-charge classical model describing van der Waals and electrostatic interactions between framework and OSDA. We enumerate and explore all possible combinations of OSDA orientation and Al location (attending to Löwenstein’s rule) within a 36 T-site supercell. We find that interaction energies vary over 60 kJ/double-six-ring-unit (d6r). Further, analysis of configurations reveals that energies are sensitive to Al−Al proximity, such that low energies are associated with Al$^{3+}$ pairs in 8-membered rings and higher energies associated with Al$^{3+}$ pairs in smaller 6- and 4-membered rings. Comparisons with Al siting inferred from CHA zeolite crystallized with TMAda$^+$ suggests that these computed interaction energies are useful reporters of observed Al siting in CHA synthesized with TMAda$^+$.

1 Introduction

Zeolites comprise a large class of microporous and crystalline aluminosilicates constructed primarily of silicon-centered and corner-sharing oxygen tetrahedra. Specific zeolite topologies are often accessed synthetically through co-crystallization of amorphous phases and gels with organic and/or inorganic structure directing agents (SDAs). Organic structure
directing agents (OSDAs) are believed to guide zeolites toward particular crystal structures through favorable interactions between the OSDA and the forming framework. The computed interaction energy between a preformed framework and an occluded OSDA has been successfully used as a reporter of the potential for an OSDA to crystallize a particular framework. This relationship has been exploited to create new zeolites and to crystallize zeolites with cages tailored to accommodate the transition state of a target reaction.

While purely siliceous zeolites are known, the large majority of zeolites contain some amount of aliovalent Al\(^{3+}\) substitution onto the Si\(^{4+}\) lattice, introducing a net charge onto the zeolite framework. Compensation of that charge by protons generates Brønsted acid sites useful for various hydrocarbon transformations. Further, the relative proximity of those Brønsted sites within a framework can influence chemical and catalytic properties. The Al\(^{3+}\) centers can also serve as coordination sites for extra lattice metal ions. Here too the proximity of centers can have an influence on metal ion speciation, nuclearity, and reactivity.

Experimental evidence indicates that synthesis conditions can influence the Al\(^{3+}\) siting preferences in zeolites. In zeolites that possess more than one type of symmetry-distinct tetrahedral (T-)site, those conditions can bias Al\(^{3+}\) away from or towards particular T-site types, for instance in MFI and FER. These effects can be rationalized based on the relative access of charge compensating ions during synthesis to T-sites of distinct environment. On frameworks constructed from a single symmetry-distinct T-site, such as CHA, these influences are manifested in differences in the proximity of Al\(^{3+}\) sites. CHA is formed from ABC stackings of double-six-ring (d6r) secondary building units and can be crystallized with N,N,N-trimethyl-1-adamantylammonium (TMAda\(^+\)) OSDA. CHA zeolites crystallized solely with TMAda\(^+\) are observed to exhibit no Co\(^{2+}\) uptake capacity and to exchange Cu\(^{2+}\) only in its monovalent, CuOH\(^+\) form, both indicating that the framework contains no six-membered-rings (6MRs) containing two Al\(^{3+}\). In contrast, synthesis with Na\(^+\) as a secondary, inorganic SDA results in an enrichment in these Al–Al pair features in the
6MRs. Vibrational spectroscopy provides independent verification of these differences. Synthesis with the larger K$^+$ cation as the secondary SDA again results in CHA zeolites that lack the 6MR Al−Al pair feature.

Charge compensation thus has a determining effect on Al$^{3+}$ siting in CHA. Density functional theory (DFT) calculations show that the proximity-dependent energy of an Al$^{3+}$ pair depends sensitively on the identities of the charge-compensating ions. Energy is a decreasing function of Al−Al separation in the Brønsted form and exhibits minima at other separations in the presence of mono- (Na$^+$)$^{35}$ or divalent (Cu$^{2+}$)$^{36}$ cations. The oblong TMA$^{+}$ OSDA is found to occupy the CHA cage in alignment with the long axis; further, the energy of an Al$^{3+}$ charge-compensated by TMA$^{+}$ is a strong function of the separation between Al$^{3+}$ and the charged end of the OSDA, reflecting underlying electrostatic interactions. Similar calculations of TMA$^{+}$ and Na$^+$ or K$^+$ co-occlusion within the CHA cage are consistent with the former pair resulting in an enrichment in 6MR Al−Al pairs while the latter promotes Al−Al pairs at greater separation.

These results highlight the potential to explore the relationship between OSDA and Al siting and proximity more generally. While DFT calculations in principle can provide reliable energy predictions, they are in general too expensive to be used to explore over a wide configuration space of Al$^{3+}$ and OSDA locations. Classical forcefields, however, can be evaluated rapidly and are well suited to capturing the non-bonded and electrostatic interactions most important to the relative energies of Al$^{3+}$ distributions in a field of OSDAs. To explore this approach, we focus here on the CHA/TMA$^{+}$ system. As shown in the schematic representation in Figure 1, this system has the advantages of a single, symmetry-distinct T-site and an OSDA that can orient in only one of two equivalent directions within the zeolite cage. We start with the Dreiding force field successfully applied to neutral analogs of OSDAs and augment with charges derived from DFT calculations. We enumerate and explore all possible combinations of OSDA orientation and Al location (attending to Löwenstein’s rule) within a 36 T-site supercell. We find that interaction energies vary over 60 kJ/d6r. Further,
analysis of configurations reveals that energies are sensitive to Al−Al proximity, such that low energies are associated with Al$^{3+}$ pairs in 8-membered rings and higher energies associated with Al$^{3+}$ in smaller 6- and 4-membered rings. Comparisons with Al siting inferred from CHA zeolite crystallized with TMAda$^+$ suggests that these computed interaction energies are useful reporters of Al siting.

![Figure 1](image.png)

Figure 1: Schematic representation of the CHA/TMAda$^+$ system. Nodes represent Si$^{4+}$ T-sites, lines bridging oxygen, and red dots Al$^{3+}$ substitutions. Adamantyl body and quaternary nitrogen centers of TMAda$^+$ represented as black spheres and lines, respectively.

2 Simulation Details

2.1 DFT and Ab Initio Molecular Dynamics Simulations

DFT simulations were performed on 36 T-site supercells of varying Al configurations and TMAda$^+$ orientations using the Vienna Ab initio Simulation Package (VASP), version 5.4.1. Lattice constants were obtained from the Database of Zeolite Structures. Core-valence interactions were treated using the projector augmented wave (PAW), exchange and correlation treated within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA), and the DFT model augmented with the D3 method to describe van
der Waals interactions.\textsuperscript{43} Plane waves were included to a 400 eV cutoff and the first Brillouin zone sampled at the Gamma point only. Energies and forces for structures used to parameterize the charge model were converged to $1 \times 10^{-6}$ eV and 0.03 eV/Å, respectively (CONTCARs included in the Supporting Information). Single-point calculations were performed on the relaxed structures to generate AECCAR0, AECCAR2, and CHGCAR files required for performing subsequent atomic population analysis.\textsuperscript{44}

Ab initio molecular dynamics (AIMD) simulations were performed at 633 K in the canonical (NVT) ensemble, using a Nosé-Hoover thermostat with Nosé mass-parameter (SMASS) of 0.01. A 1 fs time step was used, and hydrogen atoms were replaced by deuterium to accommodate a longer time step. Zeolite framework atoms (Si, Al and O) were fixed at positions used in the classical simulations described below during the AIMD simulations to facilitate comparisons with the classical models. At each step, self-consistent-field (SCF) electronic energies were converged to $1 \times 10^{-5}$ eV. Dynamics simulations were run for 10 ps for each configuration. The first 2.5 ps of the trajectory was discarded and the remaining 7.5 ps was used to calculate the average potential energy.

\subsection*{2.2 Classical Force Field Parameterization}

We used the Dreiding force field,\textsuperscript{38} previously shown to provide good predictions for interactions between OSDAs and siliceous zeolite frameworks,\textsuperscript{4,6} to describe TMAda$^+$ and its van der Waals interactions with the silica-alumina CHA frameworks considered here. We treated TMAda$^+$ as flexible and the CHA framework as rigid. Lattice constants and framework atom positions were fixed at those from the Database of Zeolite Structures.\textsuperscript{45}

We augmented the Dreiding model with fixed partial charges on TMAda$^+$ and framework atoms to capture electrostatic interactions. To derive the partial charges, we choose three arbitrary initial 36 T-site structures and three occluded TMAda$^+$, relaxed the structures, and used the Density Derived Electrostatic and Chemical (DDEC) approach\textsuperscript{46–48} to extract atomic net charges. XYZ files containing raw partial charges obtained from the different
minimizations are provided as a zipped file in Supporting Information. To reduce the number of distinct atom types, and based on analysis of the DDEC-derived charges, we characterized atoms based on distinct chemical environments (Table 1 and Figure 2). We reserved one atom type for Al and two atom types for O, including O_b ions that connect Al and Si and O_z ions that connect two Si. The Si charge is sensitive to the number of neighboring AlO_4^- tetrahedra, leading to four distinct Si atom types. TMAda⁺ C and H atoms are categorized based on their positions relative to the quaternary ammonium group. Atomic charges were derived by averaging over raw charges from the three configurations and imposing overall electroneutrality. The procedure was repeated on ten additional relaxed DFT structures and charges found to vary by less than 5%. The relative energies are also insensitive to the partial charge variations, as two different partial charge sets only lead to 1.0 kJ/mol energy difference across tested configurations.

Table 1: Net atomic charges on zeolite and TMAda⁺ atoms

| Molecule  | Atom type | q(e)  | Molecule  | Atom type | q(e)  |
|-----------|-----------|-------|-----------|-----------|-------|
| CHA zeolite | Al        | 1.79584 | TMAda⁺    | n         | 0.22348 |
|           | O_bᵃ      | -1.05771 |           | cnh       | -0.30327 |
|           | O_zᵇ      | -0.93365 |           | hx        | 0.14625  |
|           | Siᶜ       | 1.84506  |           | cn        | 0.20907  |
|           | Siᵈ       | 1.82378  |           | cb        | -0.27065 |
|           | Siᵉ       | 1.8025   |           | hb        | 0.10192  |
|           | Siᶠ       | 1.78122  |           | cj        | 0.05556  |
|           |           |        |           | hj        | 0.0712   |
|           |           |        |           | ce        | -0.22186 |
|           |           |        |           | he        | 0.0907   |

ᵃ Oxygen bridging Al and Si.
ᵇ Oxygen bridging two Si.
ᶜ Si without first-neighbor Al.
ᵈ Si with one first-neighbor Al.
ᵉ Si with two first-neighbor Al.
ᶠ Si with three first-neighbor Al.
Figure 2: The structure of tetrahedra aluminosilicate unit, TMAda\(^+\) and the definition of each atomic type used in Table 1. Atomic charges are labeled in red beside the atom types.

### 2.3 Classical Molecular Dynamics Simulations

The LAMMPS\(^{49}\) package was used to carry out all classical molecular dynamics (CMD) simulations. The cell parameters and locations of atoms, which were obtained from the Database of Zeolite Structures,\(^{45}\) are the same as used in AIMD simulations. Each simulation was equilibrated for 500 ps followed by a production run of 1500 ps, all using a time step of 0.2 fs. The production runs were divided into three sections, from which three block-averaged potential energies and their standard deviations were calculated to reflect the fluctuation of the energies. The NVT ensemble with the Nosé-Hoover\(^{50,51}\) thermostat at 433 K was applied. A cutoff of 10 Å was used for non-bonded and electrostatic interactions. A standard long-range van der Waals tail correction was added to the energy and pressure, while a particle-particle particle-mesh solver\(^{52}\) was used to describe the long-range electrostatics.
3 Results and Discussion

3.1 Al Configurations and OSDA Orientations

We seek to explore the relationship between Al siting, TMAda$^+$ orientation, and system energy. To that end, we systematically enumerated all combinations of Al location and TMAda$^+$ orientations possible within a 36 T-site supercell containing three unique cages, shown in Figure 3. Three Al were distributed over all possible T-sites, excluding those that contain Al-O-Al linkages that violate Löwenstein’s rule and are not properly described by the classical force field. Three TMAda$^+$ were then introduced to these 4908 configurations either all in the same orientation (“AAA”, ) or with two TMAda$^+$ cations oriented in one direction and the third pointing in the opposite one (“AAB”), as illustrated in Figure 3, resulting in 9816 separate initial configurations that span all possibilities within the 36 T-site supercell.

Molecular dynamics simulations were performed at 433 K on each of these 9816 configurations. Consistent with prior work, TMAda$^+$ maintain their orientation throughout the simulation. Potential energy fluctuations, which were calculated from three block averages, during the MD simulations are less than 5 kJ/mol after initial equilibrations of 500 ps. The
average potential energy $\langle U \rangle_i$ of each configuration $i$ was computed every 1000 timesteps and the relative energy of each configuration $\Delta U_i$ was computed as

$$\Delta U_i = (\langle U \rangle_i - U_{\text{ref}})/N_{\text{d6r}}$$ (1)

where the reference potential energy $U_{\text{ref}}$ is taken as the lowest energy configuration

$$U_{\text{ref}} = \min_i \{\langle U \rangle_i\}$$ (2)

and the energy is normalized by the number of d6r units. The left panels of Figure 4 report $\Delta U_i$, sorted from lowest to highest energy, for the Al configurations in a field of AAA- and AAB-oriented TMAda$^+$, respectively. Several observations are immediately evident. First, energies span nearly 40 and 60 kJ/mol$_{\text{d6r}}$ in the AAA and AAB data sets, respectively, reflecting a substantial sensitivity to Al configuration within a given field of TMAda$^+$ and different sensitivities to different fields. Second, the lowest energy Al configurations in the AAA and AAB sets are of similar energy. And third, a small handful of configurations dominate the low energy (and high energy) regimes.
Figure 4: Mean potential energies ($\Delta U_i$) of AAA configurations, sorted in ascending order (top left and inset); each dot represents the energy for an individual configuration. Histograms of Al–Al proximity features vs potential energy (top right and inset). Histogram bin size is 2.0 kJ/mol$_{d6r}$; consecutive bins are connected by straight lines. Corresponding results for AAB configurations in bottom left and right.
Before analyzing the relationship between configurations and energy, we tested classical model predictions against AIMD results. We chose the ten lowest- and ten highest-energy configurations from the AAA and AAB sets and augmented with a number of intermediate energy configurations to create a basket of 72 configurations. Initial structures were extracted from the last frame of the 2 ns CMD simulations (POSCARs available in the Supporting Information). AIMD simulations were run at 633 K for 10 ps and the last 7.5 ps of trajectory used to calculate the average potential energy. Uncertainties were taken as the standard deviation obtained from three equal length blocks from the trajectory. Figure 5 plots the mean CMD energies against the AIMD energies, color coding according to TMAda$^+$ orientation, and choosing the lowest energy AIMD AAB configuration as reference. The uncertainties in the AIMD and CMD energies span comparable ranges. Mean energies and uncertainties are listed in Table S1 in Supporting Information.

The energy range spanned by the AIMD results are consistent with the CMD-predicted spans and differences between the AAA and AAB subsets. Further, the best fit line through the data has a correlation coefficient of 0.91, consistent with a robust correlation between the two models. Nonetheless, some substantial differences are evident. Within the envelope of low energy structures, the AIMD energy variations are a factor of four greater than the CMD. Similar but smaller variations are evident in the higher energy envelope. Figure S1 of the Supplementary Information shows the correlation between CMD and AIMD energy differences for 20 structures with lowest CMD energies and the average of the reciprocals of Al–Al distances in those structures. The CMD and AIMD energy differences are obtained by $E_{\text{CMD}} - E_{\text{AIMD}}$ using data plotted in Figure 5. Al–Al distances are obtained by calculating the distances among three Al in the supercells considering the minimum-image convention. The CMD-AIMD errors correlate with the Al–Al separation. The correlation shows CMD overpredicts the stability of the structures that contain short Al–Al separations. Structures that contain most 2NN Al–Al pairs have the largest errors. These discrepancies may represent limitations of the number of distinct atom types in the classical model. We conclude
that the CMD model properly captures the larger energy variations in the system.

To explore the relationship between gross structure and energy, and in particular to look for the signatures of an electrostatic contribution to the large energy spans seen in Figure 4, we created parity plots of relative potential energies against ensemble-averaged $1/r_{N-N}$ (Supplementary Figure S2), $1/r_{Al-Al}$ (Supplementary Figure S3), and $1/r_{Al-N}$ (Figure 6) across all AAA and AAB configurations. Averages here are over the three shortest minimum image distances, which would be expected to capture the leading electrostatic contributions of each pair-wise interaction. $\Delta U_i$ is essentially uncorrelated with $1/r_{N-N}$ and $1/r_{Al-Al}$. In contrast, and as seen in Figure 6, energy and $1/r_{Al-N}$ are anti-correlated, so that configurations with lower mean reciprocal Al–N distances are generally lower in energy. The energy span is larger and correlation clearer for the AAB orientation (Figure 6 left) than for the AAA. The results suggest that the ability of cationic quaternary N centers to form close contacts with Al-substituted T-sites is a leading, although not sole, contributor to the potential energy differences, and that those close contacts are more common in the AAA than the AAB orientation of TMAda$^+$. 
Figure 6: Relative potential energies ($\Delta U_i$) vs reciprocal Al to quaternary ammonium N distances ($1/r_{Al-N}$) across Al configurations in a field of AAB (left) and AAA (right) TMAda$^+$. 

3.2 Al Ordering Analysis

We next explored the relationship between energy and Al configuration in the AAA TMAda$^+$ subset. As shown in the top left panel in Figure 4, configurations span relative energies between 0 and 40 kJ/mol$\cdot$d$^6$r, with a large density of configurations in the intermediate energy regime and sharper variations at the two extremes. By construction, the points include symmetry redundant configurations; for example, by inspection, the six lowest energy configurations are symmetry-equivalent realizations of the same structure. The energy spread of less than 2 kJ/mol$\cdot$d$^6$r is within the threshold of energy fluctuation within the block-average sampling method.

To fingerprint each configuration, we identified the three shortest Al–Al contacts and classified each pair either as one of the features shown in Figure 7 or as an “isolated” pair. The right panel of Figure 4 reports histograms of these pair types vs energy in 2.0 kJ/mol$\cdot$d$^6$r wide bins, with histogram points plotted at the low-energy side of the bin. The areas beneath each histogram reflect the relative probabilities of each pair type using the 36 T-site configuration construction algorithm and the assumed 11/1 Si/Al ratio. Isolated pairs are statistically most common, followed by 8MR. Generally, in the low energy region, configurations are rich in 8MR and isolated pairs and poor in 4MR and 6MR pairs. In contrast,
high energy configurations contain a mix of features, with 6MR slightly more prominent at the highest energies. Figure 8 shows five non-degenerate representative low- and five non-degenerate representative high-energy Al configurations from the AAA set. All five low energy Al configurations have Al pairs on an 8MR, while the five high energy Al configurations have Al pairs on the d6r unit, 6MR or 4MR. This placement on the 8MR appears to maximize the close contacts with the quaternary ammonium center of TMAda^+. AIMD results agree with CMD predictions of the large energy difference between the low and high energy Al configurations. AIMD and CMD predictions do not agree on the precise identity of the lowest energy configuration. Among all AIMD-computed configurations, AIMD predicts a configuration that contains only isolated Al as the lowest average potential energy (2.0 kJ/mol_{d6r} lower in energy than the lowest energy configuration in structures 1-5 of Figure 8). AIMD and CMD predict the same highest energy configuration (structure 10 of Figure 8).

To uncover patterns in energy vs features, we separated the configurations into three subsets by fitting the energy vs configuration data to two 3rd order polynomials across the
Figure 8: Lowest-energy (1-5) and highest-energy (6-10) AAA CMD supercells and corresponding Al pair features. Features within the supercell are highlighted in gray and features across cell boundary indicated with blue dashed arrows. Color: blue, Al; yellow, Si; red, O.

First and second halves of the profile and partitioning at the two inflection points. This partitioning resulted in 1499, 3098, and 311 configurations in the low, medium, and high energy bins. We then Boltzmann-weighted the configurations within each bin, arbitrarily choosing 433 K because it is representative of typical zeolite synthesis conditions. $RT$ at 433 K is 3.6 kJ/mol, so that averaging captures significant fractions of each bin. The configurational integral of the system with the AAA TMA$	ext{Ada}^+$ orientation is

$$Z^\text{AAA} = \sum_i e^{-\Delta U_i/kT}$$  \hspace{1cm} (3)
where \( i \) denotes an Al configuration, \( \Delta U_i \) is defined by Equation (1), \( k \) is the Boltzmann constant, \( T \) is the averaging temperature, and only AAA orientations are considered in the summation. The probability of an Al configuration \( i \) with an AAA TMAda\(^+\) orientation is

\[
P_i = \frac{e^{-\Delta U_i/kT}}{Z_{AAA}}
\]

(4)

Finally, the probability \( \Pi_j \) of a particular Al pair feature \( j \) is

\[
\Pi_j = \sum_i \frac{n_{j,i}}{3} P_i
\]

(5)

where the \( n_{j,i} \) stands for the number of Al pair types \( j \) in Al configuration \( i \). The factor of 3 accounts for the fact that there are three Al pairs in each configuration.

Figure 9 compares the probabilities of Al pair types within each energy bin with that expected from a random distribution of Al subject to Löwenstein’s rule, corresponding to the integral of the histograms in Figure 4. Within this random distribution the most probable Al pair types are 8MR and “isolated”, with a relatively small population of 6MR. The low-energy bin is similarly dominated by 8MR and “isolated” features; further, the 6MR and 4MR Al pair features occur at a very low probability. Those 6MR pair features, in contrast, are common in the high energy bin. Results are consistent with the AAA orientation of TMAda\(^+\) biasing against Al close contacts.

The bottom left panel in Figure 4 reports the mean potential energies of the AAB configurations, plotted using the same reference energy as that for the AAA configurations. Lowest energy configurations are of similar energy, but AAB energies span 60 kJ/mol\(_{d6r}\), exceeding the AAA span by more than 20 kJ/mol\(_{d6r}\). The bottom right panel in Figure 4 shows the corresponding Al–Al feature histogram. 6-MR, 4-MR, and d6r Al pairs are represented more prominently at low energy in the AAB orientation than in AAA.

Figure 10 shows snapshots of six lowest and six highest energy AAB configurations, while Figure 11 shows the probabilities of Al pair types for the AAB orientation, calculated
Figure 9: Probability distributions ($\Pi_j$) of the AAA TMAda$^+$ orientations. Left panel (green) represents the random Al distribution with Löwenstein’s rule. “Low” (blue), “middle” (black), and “high” (red) distributions from Boltzmann weightings over configurations subpartitioned by relative energy.

using the same strategy as described above for the AAA orientation (1629, 2920 and 359 Al configurations for low energy, medium energy and high energy region, respectively). Similar to the AAA orientation, all five low energy snapshots have 8-MR Al pair types, and most of these also have isolated Al pairs. But in the AAB orientation, two of the low energy configurations also contain 4-MR pairs. The five high energy configurations all contain 6-MR Al pair types, as observed in the AAA orientation. As with the AAA orientation, AIMD and CMD predictions for AAB agree in terms of gross energy differences but differ in terms of the lowest energy structures. Among all AIMD-computed configurations, AIMD predicts a configuration that contains only isolated Al to have the lowest average potential energy ($2.0 \text{ kJ/mol}_{d6r}$ lower in energy than the lowest energy configuration in structures 1-5 of Figure 10). AIMD and CMD predict the same highest energy configuration (structure 10 of Figure 10).
Figure 10: Lowest-energy (1-5) and highest-energy (6-10) AAB CMD supercells and corresponding Al pair features. Features within the supercell are highlighted in gray and features across cell boundary indicated with blue dashed arrows. Color: blue, Al; yellow, Si; red, O.

Figure 11 shows the Al pair type probabilities computed at 433 K for the AAB orientation. Overall, the probability distribution is similar to the AAA orientation. Frameworks are predicted to be enriched in 8-MR pairs relative to a random distribution and to have a large fraction of isolated pairs. The probability of 6MR and 4MR pairs, however, is comparable to the random distribution and considerably greater than the probability in the AAA orientation. Al pair distributions are thus sensitive to TMAda$^+$ relative ordering, suggesting a strategy for controlling that distribution. CHA zeolites crystallized with TMAda$^+$ as the sole SDA, with no additional Na$^+$, are observed to be poor in 6MR Al pairs, consistent with a large manifold of low energy AAA configurations and the lowest-energy AAB
configurations.

Figure 11: Probability distributions ($\Pi_j$) of the AAB TMAda$^+$ orientations. Left panel (green) represents the random Al distribution with Löwenstein’s rule. “Low” (blue), “middle” (black), and “high” (red) distributions from Boltzmann weightings over configurations subpartitioned by relative energy.

To further explore the sensitivity of potential energy to TMAda$^+$ orientation, we selected the lowest-energy Al configurations from the AAA set, which contains only 8MR pairs, flipped the orientations of each TMAda$^+$ to create eight OSDA orientations, and computed averaged potential energies. Results are shown in Figure 12 top. Flipping OSDAs within the low energy configuration results in a number of degenerate structures due to system symmetry. The energy cost to flip TMAda$^+$ is modest (10 kJ/mo$^6r$) and essentially constant—this 8MR-only structure, which avoids 6MR pairs, is relatively robust to OSDA orientation. We applied the same strategy to an Al configuration that contains a 6MR and d$6r$ pairs. As shown in the bottom of Figure 12, the energy of this configuration is highly sensitive to TMAda$^+$ orientation. While its lowest energy realization is competitive in energy with the 8MR-only structure, most orientations lead to much higher energies. These results suggest that some features, such as the 8-MR pair, may be preferentially biased for because they are agnostic to local OSDA orientation, while others, such as the 6-MR pair, are biased against because they are more sensitive to local OSDA orientation.
Figure 12: Mean potential energies of an 8-MR-pair-only configuration (top) and a configuration containing 6-MR and d6r pairs (bottom), each in the field of all possible TMAda\(^+\) orientations. Al T-sites highlighted in blue and arrows indicate periodic images.

We doubled the supercells shown in Figure 12 along the \(c\) direction and repeated the TMAda\(^+\) flipping procedure, creating 64 OSDA orientational combinations per supercell. Supercells and mean potential energies are shown in Figure 13. Results mirror those of Figure 12: the 8-MR-only Al configuration is minimized in energy when all TMAda\(^+\) are aligned in the same orientation (“AAAAAAA”) but energy costs to “flip” OSDA are relatively small and constant. In contrast, the 6-MR Al configuration is higher in energy across all configurations save number 50; further, energies are much more sensitive to TMAda\(^+\) orientations.
4 Conclusions

While the ability to guide zeolite structure through OSDA selection, and approaches to simulate this influence, are well established, the relationship between OSDA choice and the distribution of Al on a zeolite framework is less clear. CHA is an ideal template for exploring these effects, as it has only one symmetry-distinct T-site; all T-sites thus see identical void environments within the framework, and non-random Al distributions must reflect either kinetic or thermodynamic factors at play during crystallization. Here we explore the thermodynamics of Al distributions in the field of TMAda$^+$ structure directing agents, using a combination of \textit{ab initio} and classical dynamics models of TMAda$^+$ occluded within the three cages of a CHA unit cell. System energies are observed to be sensitive both to Al proximity and to the field of TMAda$^+$, and energy variations are consistent with a substantial contribu-
tion from OSDA-Al electrostatics, related to the ability of quaternary nitrogen to approach Al T-sites. Configurations the place Al pairs in 8MRs maximize favorable electrostatic contacts with TMAda$^+$ and are low in energy. Further, the energies of those configurations are less sensitive to TMAda$^+$ orientation than are Al pairs in smaller rings. This robustness to OSDA order (or disorder) may thus be a relevant factor determining Al distributions. Al configurations that place two Al within the same 6MR are high in energy, consistent with experimental observations that these features are rare on CHA zeolite prepared with TMAda$^+$ as the sole structure-directing agent.$^{31,32}$ This correspondence suggests that lattice energies are, at least in this system, a useful predictor of Al siting preferences, as has been observed in similar simulations exploring the influence of Na$^+$ and TMAda$^+$ co-occlusion on Al siting.$^{33}$

The results highlight the potential to apply similar strategies to other OSDAs and frameworks. The CHA-TMAda$^+$ system is simplified by the fact that TMAda$^+$ can adopt only one of two primary orientations within the cha cage, and models here are limited to Al as the sole charge-carrying site on the framework. Further extensions will benefit from improvements in forcefield parameterization, in configurational sampling, and in model generalizations to framework compositions away from 1:1 OSDA to Al.

**Acknowledgement**

The authors gratefully acknowledge financial support from the National Science Foundation CBET-DMREF program under award number 1922154. The computing resources for this work were provided by the Notre Dame Center for Research Computing.

**Supporting Information Available**

A PDF file is provided that contains:
• CMD, AIMD energies and uncertainties plotted in Figure 5.

• Analysis of data scattering in Figure 5.

• Analysis of the correlations of the Al-Al distance and N-N distance with the relative potential energy ($\Delta U_i$).

A ZIP file (link: https://doi.org/10.5281/zenodo.6422186) is provided that contains:

• VASP input files for geometry optimization, charge generation, and AIMD simulations.

• LAMMPS input file for CMD simulations.

• CONTCARs of DFT optimized structures used for charge analysis and corresponding XYZ files that contain raw partial charges.

• POSCARs of 72 structures that are used for the analysis of CMD and AIMD correlations.

• TXT files containing raw data that is used to plot figures.

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Supporting Information: Modeled Influence of a Structure Directing Agent on Al Siting Energetics: N,N,N-trimethyl-1-adamantyl ammonium (TMAda\textsuperscript{+}) in Chabazite

Xiaoyu Wang,\textsuperscript{†} Yujia Wang,\textsuperscript{‡} Ahmad Moini,\textsuperscript{¶} Rajamani Gounder,\textsuperscript{§} Edward Maginn,\textsuperscript{†} and William F. Schneider\textsuperscript{*\textdagger\textdoubleprime}

\textsuperscript{†}Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA
\textsuperscript{‡}Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA
\textsuperscript{¶}BASF Corporation, Iselin, New Jersey 08830, USA
\textsuperscript{§}Charles D. Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
\textsuperscript{∥}Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556 USA

E-mail: wschneider@nd.edu
Table S1: CMD and AIMD relative average potential energies and standard deviations (errors) plotted in figure 3. The first column contains the label of each structure. Corresponding structures have been provided in the zipped file in both xyz and POSCAR format.

| AAB orientation | CMD (kJ/mol_{d6r}) | error | AIMD (kJ/mol_{d6r}) | error |
|-----------------|--------------------|-------|---------------------|-------|
| 1               | 0.00               | 1.28  | 0.00                | 0.90  |
| 2               | 11.21              | 0.30  | 9.16                | 0.78  |
| 3               | 10.86              | 1.04  | 8.11                | 0.88  |
| 4               | 18.82              | 0.73  | 14.59               | 1.10  |
| 5               | 14.65              | 0.43  | 10.03               | 2.25  |
| 6               | 14.49              | 0.17  | 7.80                | 3.17  |
| 7               | 7.72               | 0.89  | 2.75                | 0.84  |
| 8               | 6.84               | 0.59  | 7.68                | 0.75  |
| 9               | 27.74              | 1.21  | 23.74               | 0.75  |
| 10              | 7.82               | 0.95  | 5.75                | 4.25  |
| 11              | 18.98              | 0.94  | 10.11               | 1.45  |
| 12              | 18.27              | 0.35  | 10.85               | 0.90  |
| 13              | 12.51              | 0.86  | 10.60               | 0.24  |
| 14              | 10.51              | 0.82  | 8.52                | 0.81  |
| 15              | 12.77              | 1.44  | 8.31                | 0.93  |
| 16              | 7.71               | 1.51  | 4.59                | 2.27  |
| 17              | 9.40               | 0.79  | 7.19                | 0.96  |
| 18              | 7.55               | 0.91  | 3.69                | 2.01  |
| 19              | 1.31               | 0.42  | 5.81                | 1.56  |
| 20              | 20.43              | 0.15  | 13.81               | 2.40  |
| 21              | 27.78              | 0.38  | 22.59               | 1.66  |
| 22              | 26.26              | 0.75  | 23.69               | 1.49  |
| 23              | 9.75               | 0.24  | 3.21                | 3.42  |
| AAA orientation | CMD (kJ/mol$_{\text{d6r}}$) | error | AIMD (kJ/mol$_{\text{d6r}}$) | error |
|-----------------|----------------------------|-------|-----------------------------|-------|
| 1               | 11.54                      | 0.32  | 11.37                       | 1.60  |
| 2               | 7.16                       | 0.96  | 2.54                        | 1.47  |
| 3               | 11.59                      | 0.82  | 11.91                       | 1.63  |
| 4               | 6.41                       | 0.60  | 6.14                        | 1.48  |
| 5               | 11.74                      | 0.94  | 12.70                       | 0.59  |
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| 6 | 1.52  | 1.35  | -5.09 | 1.43  |
| 7 | 16.80 | 0.48  | 16.17 | 1.58  |
| 8 | 4.80  | 0.41  | 3.56  | 3.86  |
| 9 | -8.06 | 1.10  | 11.44 | 1.08  |
| 10| -4.72 | 0.74  | -2.94 | 1.00  |
| 11| -4.64 | 1.28  | 4.70  | 0.20  |
| 12| -4.60 | 1.38  | 4.45  | 0.27  |
| 13| -4.29 | 0.37  | 4.65  | 0.87  |
| 14| -4.13 | 0.54  | -1.38 | 0.61  |
| 15| -3.98 | 0.46  | 0.40  | 2.34  |
| 16| -3.44 | 1.19  | 5.66  | 1.26  |
| 17| -3.23 | 0.95  | -0.25 | 1.68  |
| 18| -2.62 | 0.67  | 1.29  | 0.75  |
| 19| 26.33 | 0.72  | 44.08 | 0.35  |
| 20| 22.92 | 0.59  | 29.53 | 1.02  |
| 21| 21.66 | 0.65  | 30.46 | 0.74  |
| 22| 21.48 | 0.39  | 27.99 | 1.46  |
| 23| 21.40 | 0.50  | 28.80 | 0.22  |
| 24| 20.94 | 0.23  | 28.55 | 1.42  |
| 25| 20.85 | 1.38  | 33.13 | 1.26  |
| 26| 20.52 | 0.14  | 29.90 | 0.83  |
| 27| 20.66 | 0.78  | 29.83 | 0.37  |
| 28| 20.67 | 1.32  | 30.82 | 2.22  |
Figure S1: The correlation between CMD and AIMD energy differences for 20 structures with lowest CMD energies and the average of the reciprocals of Al–Al distances in those structures. The CMD and AIMD energy differences are obtained by $E_{\text{CMD}} - E_{\text{AIMD}}$ using data from table S1. Al–Al distances are obtained by calculating the distances among three Al in the supercells considering the minimum-image convention.
Figure S2: Averaged reciprocal Al to Al distances (1/r_{Al-Al}) versus relative potential energies ($\Delta U_i$). Left: “AAB” orientation in red. Right: “AAA” orientation in blue.

Figure S3: Averaged reciprocal quaternary ammonium N to quaternary ammonium N distances (1/r_{N,N}) versus relative potential energies ($\Delta U_i$). Left: “AAB” orientation in red. Right: “AAA” orientation in blue.