

Template–Framework Interactions in Tetraethylammonium-Directed Zeolite Synthesis

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Abstract: Zeolites, having widespread applications in chemical industries, are often synthesized using organic templates. These can be cost-prohibitive, motivating investigations into their role in promoting crystallization. Herein, the relationship between framework structure, chemical composition, synthesis conditions and the conformation of the occluded, economical template tetraethylammonium (TEA^+) has been systematically examined by experimental and computational means. The results show two distinct regimes of occluded conformer tendencies: 1) In frameworks with a large stabilization energy difference, only a single conformer was found (BEA, LTA and MFI). 2) In the frameworks with small stabilization energy differences (AEI, AFI, CHA and MOR), less than the interconversion of TEA^+ in solution, a heteroatom-dependent (Al, B, Co, Mn, Ti, Zn) distribution of conformers was observed. These findings demonstrate that host–guest chemistry principles, including electrostatic interactions and coordination chemistry, are as important as ideal pore-filling.

Microporous materials (MMs) are crystalline solids that contain pores of less than 2 nm, and find applications ranging from separations and ion exchange to catalysis (zeolites are aluminosilicate MMs).^[1,2] Although over 230 frameworks are known, economic considerations, of which the cost of the organic templates, referred to as organic structure-directing agents (OSDAs), dominate, mean only a handful are commercial, even though others could offer superior performance in a given application.^[3–5] This has inspired investigations into the complex processes governing the crystallization of MMs, with the goal of supplanting the use of expensive organics.^[6–8] The role of OSDAs in MM synthesis falls into three broad categories of templation, structure direction and pore-filling, depending on the geometric match between the framework and organic, with templation exhibiting a strong geometric

match, and pore-filling showing none.^[9] These categories are generally reflected in the complexity, and thus cost, of OSDAs, driving investigations to replace costly but selective OSDAs with cheaper alternatives through a combination of serendipity and computational guidance.^[10–16] Research endeavors to this end are non-trivial, as space-filling, electrostatics and coordination chemistry all must be considered to unravel the factors influencing the relationship between OSDA and crystalline product.^[1,2,9,17–20]

Tetraethylammonium (TEA^+), a common OSDA, is among the simplest quaternary ammonium molecules, and its pore-filling role is evident from the number of frameworks it is known to form: AEI,^[21] AFI,^[22] BEA,^[21,23] CHA,^[22,24] LTA,^[25] MFI,^[24] MOR,^[26] and UFI.^[25] TEA^+ is known to exist in two distinct conformations, designated as *tt* and *tg*, which can be easily distinguished using Raman spectroscopy, highlighted in Figure 1.^[27] Crystalline TEA^+ salts exist as single conformers, but in solution display a temperature, pressure and concentration dependent conformer equilibrium.^[27,28] When occluded in MMs, TEA^+ has been shown to exist predominantly as a single conformer in AFI (*tt* primarily),^[22] BEA (*tt* exclusively),^[23] and CHA (*tg* primarily).^[22,29] Complex framework–OSDA interactions have been previously reported as in an aluminophosphate system $\text{AlPO}_4\text{-5}$ (AFI topology) was formed, but the addition of Zn led to ZnAPO-34 (CHA topology), containing a different occluded conformer distribution.^[22] In aluminosilicate BEA only the *tt* conformer was observed, and it was posited that this is because it allows a closer electrostatic interaction between positively charged TEA^+ and negatively charged framework elements than the *tg* conformer.^[23]

TEA^+ can be easily and economically sourced, motivating us to investigate its role in MM synthesis. Eight different frameworks containing occluded TEA^+ were prepared, with further variations in chemical composition, for a total of 20 distinct materials, so that space-filling, electrostatic and coordination chemistry interactions could be examined. The samples are listed in Tables 1 and S1, and the Supporting Information contains complete synthesis procedures (section S1), Powder X-ray diffraction patterns (PXRD, section S2, Figures S1 to S3), Raman spectra (Figures 1 and S4, with a discussion of the deconvolution procedure in section S3, Figure S5, and results in Tables 1 and S1), as well as OSDA occupancy determination (section S4, Table S2). The role of space-filling was assessed using molecular modelling (section S5) to calculate the stabilization energy of each conformer occluded in the ideal MM frameworks, with results in Tables 1 and S3, and the reliability of the method used herein has been well established.^[11,14–16]

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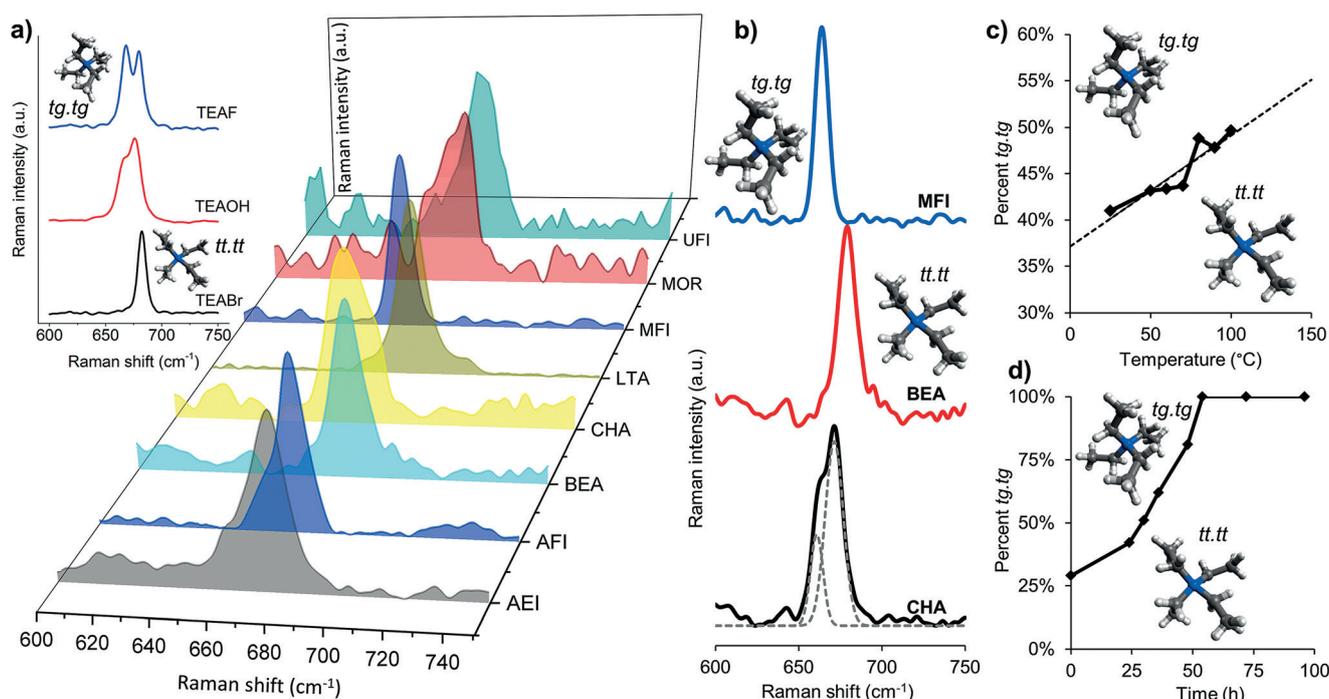


Figure 1. a) Representative Raman spectra of each framework showing the region of interest from 600 to 750 cm^{-1} , complete results are in Figure S4. The inset graph shows the Raman spectra of the TEA^+ salts: TEABr (crystalline salt), TEOH (35% in water) and TEAF (dihydrate), with the peaks corresponding to the *tg.tg* and *tt.tt* conformers indicated. b) A representative deconvolution of the Raman spectra for CHA (SAPO-34) at room temperature, containing both conformers, as well as Raman spectra for BEA and MFI, which contain only a single conformer. For CHA, the collected data is in black and the Gaussian fits are in gray. The results for all materials are given in Tables 1 and S1, with a complete explanation of the deconvolution procedure in the Supporting Information, section S3. c) The temperature-dependent conformer distribution of TEOH in water (35%). d) Ocluded conformer distribution in MFI as a function of synthesis time, corresponding PXRD patterns are in Figure S3.

Table 1: Description of the 20 distinct materials prepared including framework, composition, calculated stabilization energy difference between the occluded conformers and the experimentally determined conformer distribution in each material.

Framework	Material	$\Delta E_{\text{tg.tg-}tt.tt}$ [kJ (mol TEA^+) $^{-1}$] ^[a]	% <i>tg.tg</i> conformer ^[b]
AEI	AlPO ₄ -18	3.2	20
AFI	AlPO ₄ -5	0.0	17
	SAPO-5		12
BEA	AlSi ^[c] (OH ⁻)	8.7	0
	AlSi(OH ⁻)		0
	Borosilicate(OH ⁻)		0
	Pure-silica(F ⁻)		0
	Ti-AlSi(OH ⁻)		0
	Titanosilicate(F ⁻)		0
	Zincosilicate(OH ⁻)		0
CHA	AlSi(OH ⁻)	3.4	23
	CoAPO-34		22
	MnAPO-34		29
	SAPO-34		25
	SAPO-34		16
LTA	UZM-9(AlSi)	17.3	0
	ZSM-5(AlSi)	-9.8	100
MOR	MOR(AlSi)	2.1	12
UFI	UZM-5(AlSi)	1.9	0

[a] Complete results are in Table S1. [b] From Raman spectroscopy, complete spectra and explanation of deconvolution are in S3.

[c] AlSi = aluminosilicate composition.

Raman spectra of the TEA^+ salts are shown in Figure 1 a, and the crystalline TEABr shows only the *tt.tt* conformer,^[27] while crystalline TEAF dihydrate and TEOH solution both contain a distribution of conformers. The temperature-dependent conformer distribution of TEOH in solution is shown in Figure 1 c, the *tt.tt* conformer dominates at lower temperatures, and the conformer distribution becomes nearly equal as temperature increases, with an overall variation in the conformer ratio of ca. 10%. The interconversion energy difference in solution between the two conformers is $\Delta E_{\text{tg.tg-}tt.tt} = 4.1 \text{ kJ (molTEA}^+)^{-1}$, and higher concentrations are known to lead to a greater proportion of the *tg.tg* conformer due to its lower volume.^[27,28]

In the large 12-membered ring, 3D pore system of BEA, TEA^+ exists in clusters of six molecules per unit cell. It was previously reported that only the *tt.tt* conformer is occluded as it minimizes the distance between the positively charged nitrogen atom in TEA^+ and negatively charged oxygens bonded to aluminum framework atoms.^[23] We have explored this idea by preparing seven distinct compositions of BEA, including an electrically neutral pure-silica framework, and containing isoelectronic (Ti^{4+}) and charged (Al^{3+} , B^{3+} , Zn^{2+}) heteroatoms, with both hydroxide and fluoride media utilized, to study the influence of electrostatics versus space-filling optimization and determine if electrostatic interactions are the underlying cause influencing the formation of BEA by favoring the *tt.tt* conformer. The *tt.tt* conformation is favored

by $8.7 \text{ kJ (molTEA}^+)^{-1}$, a value that is significantly higher than the interconversion energy difference of $4.1 \text{ kJ (molTEA}^+)^{-1}$ for the molecule in solution. The initial conformer ratio of the pure-silica sample in fluoride media (sample 7) prior to crystallization is 41 % *tg.tg*, similar to the reported distribution in the hydroxide synthesis of BEA.^[23] Only the *tt.tt* conformer is found in all crystalline samples, despite the wide range of compositions and possible electrostatic interactions, meaning that the conformational rearrangement happened during crystallization and was due only to space-filling considerations. The correct prediction in BEA underscores the capability of the molecular model in this work as it is able to accurately simulate the interaction of a large number of OSDAs in a complex framework. It also demonstrates that when space-filling considerations are energetically significant that electrostatic interactions cannot overcome them, as no interactions should be present in the neutral materials prepared in fluoride media.

MFI, one of the most commercially significant zeolites, is normally synthesized using selective tetrapropylammonium (TPA^+), though it can also be prepared using less expensive TEA^+ . We found that when MFI was synthesized using TEA^+ , only the *tg.tg* conformer was occluded (Figure 1 b), making MFI the second known framework synthesized with TEA^+ containing a single occluded conformer.^[23] The occluded conformer distribution in MFI during the synthesis process was monitored, and is shown in Figure 1 d, with the corresponding PXRD patterns in Figure S3. In the synthesis gel there is initially a distribution of conformers, with a high proportion of *tt.tt*, as would be expected to minimize interaction distance, additionally, this can be expected to represent the conformer distribution at the concentration and pH value typical for hydroxide mediated zeolite synthesis with inorganic cations.^[23] Then, at 24 h, a slight change in the conformer ratio occurs with the appearance of weak diffraction peaks. Between 24 and 48 h there is a drastic change in the occluded conformer distribution, even though the PXRD has not changed significantly, likely caused by the formation of X-ray amorphous domains containing occluded TEA^+ . Once MFI is fully crystalline, all the TEA^+ is in only the *tg.tg* conformation. The *tg.tg* conformer is more stable by $9.8 \text{ kJ (molTEA}^+)^{-1}$, and is occluded at the channel intersections (Figure 2 f), similar to TPA^+ .^[30] This large stabilization energy difference is the likely reason behind finding a single conformer in this framework, even though the *tt.tt* conformer should be favored by the charged framework (see above) as evidenced by its prevalence in the synthesis gel.

Both the LTA (UZM-9) and UFI (UZM-5) frameworks have large *lta*-cages that can accommodate two molecules of TEA^+ .^[31] Experimentally, both materials were found to have only a single occluded conformer, *tt.tt*, which was calculated to be more stable in LTA by $17.3 \text{ kJ (molTEA}^+)^{-1}$, and in UFI by $1.9 \text{ kJ (molTEA}^+)^{-1}$, with the positions shown in Figure 2. The LTA framework is more appropriate to compare the results of molecular modelling with experiment, as the UZM-5 is synthesized using a second OSDA, known to stabilize the *wbc*-cage, but was not included in the energy calculation, leading to an overall lower framework stabilization, as reflected in the lower energy values calculated per mol of Si

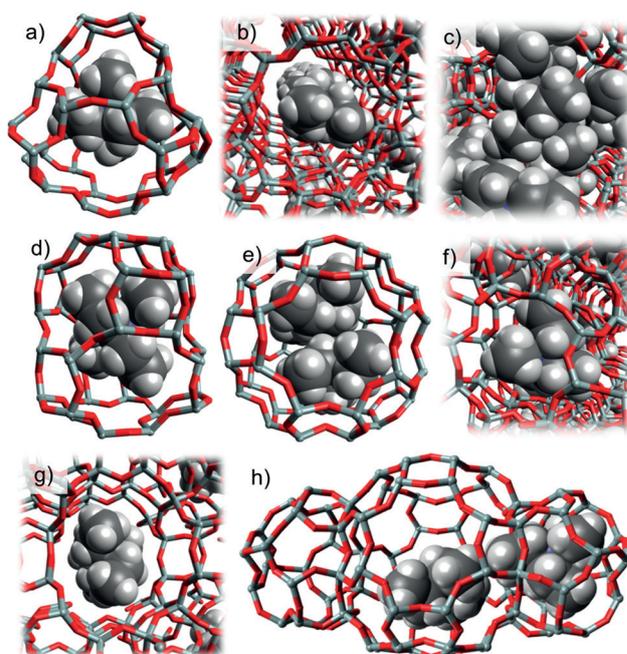


Figure 2. The location of TEA^+ molecules occluded in the 8 microporous material frameworks in this study, with TEA^+ shown to be in the conformer experimentally determined to be preferentially occluded, given in parentheses, and the position determined using molecular modelling. For AEI, CHA, LTA and UFI only the cage is shown for clarity. a) AEI (*tt.tt*), b) AFI (*tt.tt*), c) BEA (*tt.tt*), d) CHA (*tt.tt*), e) LTA (*tt.tt*), f) MFI (*tg.tg*), g) MOR (*tt.tt*) and h) UFI (*tt.tt*).

(Table S3). The crystallization of UZM-5 commences with the formation of *lta*-cages around TEA^+ , before any other building units, meaning the low Si/Al ratio of the synthesis gel will lead to significant charged species in the gel, favoring the *tt.tt* conformer (see above), which then nicely stabilizes the *lta*-cages, shown to be formed before complete crystallization. Thus, the importance of electrostatics in favoring the ideal space-filling conformer for this system is evident, and further illustrates the complex relationship between space-filling and electrostatics.^[32]

The AEI and CHA frameworks contain cages that are large enough for a single TEA^+ molecule, and the position of TEA^+ in each framework, as determined by molecular modelling, is shown in Figure 2. Six different compositions of CHA were prepared (Table 1), so that the influence of heteroatoms, framework composition and electrostatics could be assessed. In the aluminophosphate materials, the conformer distributions are in line with previous reports, with both conformers present.^[22] In the AEI framework ($\text{AlPO}_4\text{-18}$) a similar distribution was also observed. There are two underlying explanations for the observed conformer distributions: 1) The molecular modeling calculated the *tt.tt* conformer to be favored by $3.4 \text{ kJ (molTEA}^+)^{-1}$ in CHA and $3.2 \text{ kJ (molTEA}^+)^{-1}$ in AEI, both smaller energy differences than that of the interconversion of conformers in solution. As both conformers are observed in solution, it should be expected to find both occluded in the materials, as the cages do not restrict the TEA^+ . 2) The heteroatoms influence the conformer distributions observed in the CHA

materials. Differences in the position and conformation of the OSDA in aluminophosphate CHA synthesized with Mg, Mn, Si or Zn have been previously reported, and were attributed to varying template-framework interactions due to the different heteroatoms.^[33] The present results are consistent with previous observations that the differences in occluded conformer ratios within the CHA framework are likely the result of varying template-framework interactions caused by differences in acid site strength as well as different d-electron counts between the metals substituted into the CHA framework.^[33] This study reinforces the proposal that the charged framework plays a role in determining the conformer ratio, with a demonstrated dependency on the acid site strength and d-electron count, showing the importance of electrostatic and coordination chemistry interactions.^[22] Furthermore, the CHA framework highlights that when a low interconversion energy is calculated from space-filling considerations that electrostatics become relevant, even though they are not accounted for by the computational model.

AFI and MOR contain 1D systems of 12-membered rings, so a TEA⁺ molecule can only interact with neighbors on either side, and views of the two frameworks with the occluded TEA⁺ position determined by molecular modelling are shown in Figure 2. In the AFI framework, 12% of the TEA⁺ was occluded as the *tg.tg* conformer for the SAPO material and 20% for the AlPO₄ composition, and the molecular modelling showed no energy difference between the TEA⁺ conformers. The presence of electrostatic interactions should favor the *tt.tt* conformer, which is precisely what is observed in the charged SAPO composition compared to the neutral AlPO₄, reinforcing the influence of electrostatic interactions when a low energy difference is calculated. In the MOR framework, it was found that most of the TEA⁺ was occluded as the *tt.tt* conformer (88%), and the *tt.tt* conformer was preferred by 2.1 kJ mol⁻¹ TEA⁺. The high tendency towards *tt.tt* is again attributable to electrostatic interactions favoring this conformation as the energy difference is low.

The occluded conformation of TEA⁺ has been investigated in a wide range of MM frameworks and compositions. It has been found, by experimental and theoretical means, that the conformation of the TEA⁺ molecule depends on the framework geometry as well as material composition. Two regimes of occluded conformer tendency have been experimentally determined that are separated by the interconversion energy of TEA⁺ in solution: 1) In frameworks with a high energy difference only one conformer was observed (i.e., for BEA, LTA and MFI), regardless of their composition. 2) In frameworks with a low energy difference both conformers were observed (i.e., for AEI, AFI, CHA and MOR), with the conformer distribution found to depend on framework heteroatoms. These results highlight the complex role that TEA⁺ plays in MM synthesis as it is influenced by optimal space-filling considerations as well as electrostatic and coordination chemistry interactions.

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