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Searching Organic Structure Directing Agents for the Synthesis of Specific Zeolitic Structures: An Experimentally Tested Computational Study

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Molecular mechanics techniques and the use of atomic force fields have been used to calculate the energy of the system zeolite + structure directing agent (SDA), as well as the different energetic terms with their respective weights in deciding the final zeolite synthesis product. A new SDA has been found that discriminates energetically between two closely related zeolitic structures, ISV and BEC, that strongly compete during the crystallization process. The subsequent synthesis experiments with this new SDA led to the selective formation of ISV, thus supporting the predictions made by the computational chemistry calculations.

1. Introduction

A large number of zeolites have been synthesized using organic molecules as structure directing agents (SDA). The role of these organics can be summarized by saying that some of them act as a pore filling agent, and when this occurs the structure directing effect of the organic is limited. In other syntheses an important interaction between the SDA and the framework occurs and in those cases the selectivity of the organic toward the formation of a given structure is higher than in the previous case. Finally, there are very few structures in which a full match between the organic and the inorganic counterpart exists and the SDA can be considered as a template for that particular structure.[1−4] It was shown[5] that the zeolite structure specificity (selectivity) for SDAs increases when increasing their rigidity. Rigid molecules span a narrower conformational range and the strain required to adapt to other zeolites with different pore structure will be too high, thus precluding their nucleation, and leading to formation of few structures or even a single one in some cases.[6]

The discrimination between different structures only on the basis of the organic SDA will be even more difficult in the case of related structures with similar topology. This is the case of ITQ-7[7] and polymorph C of β,[8,9] hereby called β-C, or in the case of SSZ-33, SSZ-26,[10] and ITQ-24.[11] Phase specificity in zeolite formation can be changed through the use of F^- instead of OH^-[7] or through the isomorphic substitution of Ge by Si in the framework,[12−18] while the use and design of organic SDAs specific for zeolites with similar structures remains a scientific challenge. Computer simulations may play a significant role and they can be used to rationalize the nature and magnitude of the zeolite−SDA interactions as well as any other thermodynamic parameters that come into play in a zeolite synthesis.[19−21]

ITQ-7, with IZA code ISV[22] is a zeolite with a tridirectional system of large pore channels whose structure is closely related with that of polymorph C of Beta zeolite whose IZA code is BEC.[22] ITQ-7 has been synthesized using 1,3,3-trimethyl-6-azonium-tricyclo [3.2.1.4^{6,6}] dodecane hydroxide as structure directing agent[7] that appears to be quite

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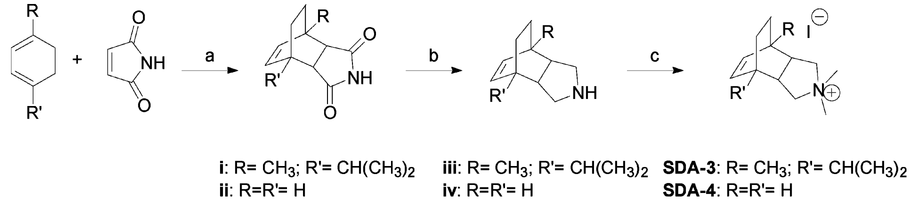

Figure 1. Synthetic organic route to the structure directing agents: (a) maleimide, toluene, 100%; (b) $LiAlH_4$, diethyl ether, 80−90%; (c) $KHCO_3$, CH_3I, MeOH, 80−85%.

specific for the synthesis of this zeolite. Unfortunately, the commercial amine employed as precursor (1,3,3-trimethyl-6-azabicyclo octane) is not longer commercially available, and this has also encouraged the search for a new SDA that can selectively yield the ISV structure.

Recently, it has been reported that Ge stabilizes the structure of ITQ-7 zeolite and reduces the crystallization time by selectively occupying positions at the T sites in the double four rings units,[23] so Ge incorporation to the synthesis mixture can facilitate a new synthesis procedure for this material. Nevertheless, both ISV and BEC structures possess double four rings and both are stabilized by germanium incorporation, so there is a strong competition between them also in the presence of Ge. Since Ge containing β-C (ITQ-17) can be obtained with a great variety of structure directing agents,[9] but none of them direct to ITQ-7 zeolite, computational studies were performed to design a new and adequate SDA for the synthesis of ITQ-7.

On the basis of the specific template of ITQ-7 we have tried other SDAs with slight differences in the substituents aimed to minimize the energetic interactions within the ITQ-7 micropores hoping that this will produce an additional specificity and will bring β and β-C out of the synthesis competition. Following this, we have calculated the interaction energies between the zeolite and the new SDAs as well as their components to rationalize our search and to expand this knowledge to future applications. Apart from some SDAs that will favor the synthesis of β-C, we have found one that favors ITQ-7. The synthesis of these SDAs and their use in zeolite synthesis shows a good correlation with the computational predictions.

2. Experimental Section

All chemicals were obtained from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively, in $CDCl_3$ solvent; chemical shifts are reported in δ (ppm) values, using TMS as internal standard. The assignment of ^{13}C spectra is supported by DEPT experiments.

The SDAs used in this work were obtained through a general synthetic route (Figure 1) which initially involves a Diels−Alder reaction between maleimide and the corresponding 1,3-diene (α-terpinene or 1,3-cyclohexadiene); reduction of the resulting imides with $LiAlH_4$ provided the required amines in a straightforward manner. Finally, methylation of the N gave the desired ammonium salts SDA-3 and SDA-4 (Figure 1).

General Description of the Procedure to Prepare Diels−Alder Adducts. A toluene solution (350 mL) of the respective 1,3-diene (103 mmol) and maleimide (103 mmol) was refluxed for 4 days. After cooling, the resulting precipitate was filtered and washed with hexane to give the Diels−Alder product in quantitative form.

3a,4,7,7a-Tetrahydro-4-methyl-7-(1-methylethyl)-4,7-ethano-1H-isoindole-1,3(2H)-dione (i). ^1H NMR δ_H 7.9 (br s, 1H, NH), 6.0 (dd, $J = 25$, 8 Hz, 2H, H-5 + H-6), 3.0 (d, $J = 8$ Hz, 1H, H-7a), 2.5 [m, 2H, H-3a + CH(CH_3)], 1.5 (s, 3H, CH_3), 1.4−1.1 (m + m, 4H, CH_2−CH_2), 1.0 and 0.9 [d + d, $J = 7$ Hz, 6H, CH(CH_3)$_2$]. ^{13}C NMR: δ_C 178.7, 178.3 (C_1, C_3), 128.8, 128.0 (C_5, C_6), 51.3 (C_{3a}), 47.5(C_7), 43.3 (C_{7a}), 36.5 ($C$$H_2$−$CH_2$), 34.0 [$C$H($CH_3$)$_2$], 29.2 ($CH_2$−$C$$H_2$), 22.4 ($CH_3$), 18.2 and 16.7 [CH($C$$H_3$)$_2$].

3a,4,7,7a-Tetrahydro-4,7-ethano-1H-isoindole-1,3(2H)-dione (ii). ^1H NMR δ_H 6.1 (m, 2H, H-5 + H-6), 3.1 (m, 2H, H-3a + H-7a), 2.9 (m, 2H, H-4 + H-7), 1.6 and 1.4 (m + m, 4H, CH_2−CH_2). ^{13}C NMR: δ_C 179.0 (C_1, C_3), 132.4 (C_5, C_6), 45.6 (C_{3a}, C_{7a}), 31.5 (C_4, C_7), and 23.5 ($C$$H_2$−$C$$H_2$).

General Description of the Procedure to Reduce Imides. A 1.0 M solution of $LiAlH_4$ in anhydrous diethyl ether (128 mmol) was added dropwise under N_2 to a stirred suspension of the Diels−Alder adduct (40 mmol) in anhydrous diethyl ether (70 mL) at 0 °C. When the addition was finished the mixture was refluxed for 5 h and stirred at room-temperature overnight. Then, the reaction was quenched by addition of H_2O (10 mL), 15% aqueous solution of NaOH (10 mL), and distilled H_2O (10 mL). After being stirred 30 min at room temperature the solution was filtered and then extracted with diethyl ether. The combined organic extracts were washed with brine, dried, and concentrated to dryness providing the corresponding reduced product.

2,3,3a,4,7,7a-Hexahydro-2,2,4-trimethyl-7-(1-methylethyl)-4,7ethano-1H-isoindole (iii). 90% yield. ^1H NMR δ_H 5.9 (dd, $J =$ 25, 8 Hz, 2H, H-5 + H-6), 3.0 (m, 2H, H-3a + H-7a), 2.3 and 2.0 (m, 4H, H-1 + H-3), 1.7 (m, 1H, CH(CH_3)$_2$), 1.4 and 1.1 (m + m, 4H, CH_2−CH_2), 1.1 (s, 3H, CH_3), 1.0 and 0.9 [d + d, $J = 7$ Hz, 6H, CH(CH_3)$_2$]. ^{13}C NMR: δ_C 135.8, 134.7 (C_5, C_6), 50.0 (C_{7a}), 49.1, 48.3 (C_1, C_3), 46.3 (C_{3a}), 40.1 (C_4), 34.2 ($C$$H_2$−$CH_2$), 32.4 [$C$H($CH_3$)$_2$], 29.1 ($C_7$), 22.2 ($CH_2$−$C$$H_2$), 21.2 ($CH_3$), 16.4 and 14.9 [CH($C$$H_3$)$_2$].

2,3,3a,4,7,7a-Hexahydro-4,7-Ethano-1H-isoindole (iv). 83% yield; ^1H NMR δ_H 6.2 (m, 2H, H-5+H-6), 2.9 (m, 2H, H-3a+H-7a), 2.5 (m, 4H, H-1+H-3), 2.2 (m, 2H, H-4+H-7), 1.4 and 1.2 (m+m, 4H, CH_2−CH_2); ^{13}C NMR: δ_C 134.2 (C_5, C_6), 53.3 (C_1, C_3), 45.6 (C_{3a}, C_{7a}), 33.7 (C_4, C_7) and 24.9 ($C$$H_2$−$C$$H_2$).

General Description of the Procedure to Methylate Secondary Amines. To a solution of the secondary amine (83.5 mmol) in MeOH (135 mL) was added $KHCO_3$ (1.2 mol) and CH_3I (4.2 mol). The mixture was stirred 7 days at room temperature. Then it was filtered while washing with CH_2Cl_2. The resulting solid after evaporation was recrystallized with hexane−CH_2Cl_2 providing the desired quaternary salt.

2,3,3a,4,7,7a-Hexahydro-2,2-dimethyl-4-methyl-7-(1-methylethyl)-4,7ethano-1H-isoindolium, iodide (SDA-3). 85% yield. ^1H NMR δ_H 6.0 (dd, $J = 25$, 8 Hz, 2H, H-5 + H-6), 4.0 (m, 2H, H-3a + H-7a), 3.5 and 3.4 (s + s, 6H, 2×NCH_3), 2.9−2.5 (m, 4H, H-1 + H-3), 1.7 [m, 1H, CH(CH_3)$_2$], 1.4 and 1.2 (m + m, 4H, CH_2−CH_2), 1.1 (s, 3H, CH_3), 1.0 and 0.9 [d + d, $J = 7$ Hz, 6H, CH(CH_3)$_2$]. ^{13}C NMR: δ_C 137.9, 136.6 (C_5,C_6), 69.7, 69.3 (C_1,

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Table 1. Synthesis Conditions and Detected Phases at 150 °C

SDA	Si/Ge	time (days)	phase
(SDA 3)	5	2	ITQ-7
		20	ITQ-7
	10	2	ITQ-7
		18	ITQ-7
	20	4	ITQ-7 + amorphous
		19	ITQ-7
	50	14	ITQ-7 + amorphous
		30	ITQ-7 + amorphous
	∞	15	amorphous
		35	amorphous
(SDA 4)	5	2	ITQ-17
		21	ITQ-17
	10	2	ITQ-17
		17	ITQ-17
	20	3	ITQ-17
		18	ITQ-17
	50	5	ITQ-17 + β
		16	ITQ-17 + β
	∞	7	β
		17	β

C_3), 53.9, 52.4 (2xN*C*H_3), 48.2 (C_{7a}), 43.2 (C_{3a}), 36.2 (C_4), 33.4 [*C*H(CH_3)$_2$], 31.1 (*C*H_2−CH_2), 28.8 (C_7), 23.7 (CH_2−*C*H_2), 22.8 (CH_3), 18.3 and 17.1 [CH(*C*H_3)$_2$].

2,3,3a,4,7,7a-Hexahydro-2,2-dimethyl-4,7-ethano-1H-isoindolium, iodide (SDA-4). 83% yield. ^{1}H NMR δ_H 6.2 (m, 2H, H-5 + H-6), 4.1 (m, 2H, H-3a + H-7a), 3.4 (s + s, 6H, 2×NC*H*$_3$) 2.8, 2.7 (m + m, 6H, H-1 + H-3 + H-4 + H-7), 1.6 and 1.4 (m + m, 4H, C*H*$_2$−C*H*$_2$). ^{13}C NMR: δ_C 133.9 (C_5, C_6), 70.2 (C_1, C_3),64.3, 60.7 (2×N*C*H_3), 41.7 (C_{3a}, C_{7a}), 31.5 (C_4, C_7) and 23.9 (*C*H_2−*C*H_2).

All the organic cations prepared were transformed into the corresponding hydroxides with an anion-exchange resin (Amberlite IRN-78). The exchange yield was always higher than 90% and the solutions obtained were used as SDA and OH source for the synthesis mixture.

A typical synthesis was carried out by dissolving the germanium oxide (if present) in the SDA solution. Then, the tetraethyl orthosilicate (TEOS) was mixed with the solution formed and was left under stirring until all the TEOS had been hydrolyzed. The ethanol formed was evaporated at room temperature. The water content was adjusted to the final composition required and, finally, a HF solution (48 wt %) was added to the synthesis gel. The final composition was x:(1 − x):0.50:0.50:4 GeO_2/SiO_2/SDAOH/HF/H_2O where x was varied to obtain the ratios shown in Table 1.

The crystallization was carried out at 150 °C under autogenous pressure in static conditions in Teflon-lined stainless steel autoclaves. The solids were filtered, washed with deionized water and dried at 100 °C overnight. Several crystallization times were essayed until crystalline materials were obtained. The synthesis conditions are collected in Table 1. The XRD patterns of representative ITQ-7 and ITQ-17 samples obtained with SDAs 3 and 4, respectively, are shown in Figure 2.

3. Computational Methods

The calculations have been performed using lattice energy minimization techniques[24,25] and the GULP code,[26] employing the Ewald method for summation of the long-range Coulombic interactions, and direct summation of the short-range interactions with a cut off distance of 12 Å. The RFO technique was used as the cell minimization scheme with a convergence criterion of a gradient norm below 0.001 eV/Å. The empirical shell model force field for Si/Al/Ge/F zeolites[27,28] has been used throughout. A (Si+Al)/Ge ratio of 15 has been selected for the simulations and this corresponds to 4 Ge in a unit cell of 64 T atoms which contains four D4Rs. Two Ge atoms have been located in the opposite corners of two D4R. For the calculations including the effect of the SDA in the Al incorporation, the force fields by Kiselev et al.[29] and by Oie et al.[30] have been used for the SDA−zeolite and SDA−SDA interactions, respectively. For the organic SDA, the Mulliken charge distribution has been obtained by means of the quantum chemistry Hartree−Fock method by using a 6-31G**[31] basis set and the calculations have been performed by means of the NWCHEM package.[32] The SDAs used in the simulations are shown in Figure 3. Each SDA monopositive molecule is compensated by an Al atom (which substitutes a Si) which is introduced in the framework. More details of the methodology and the force field used can be found in previous studies.[33] Additional calculations were performed to study the effect of fluoride anions in the final stability, and for that purpose F$^-$ anions rather than Al are used to compensate

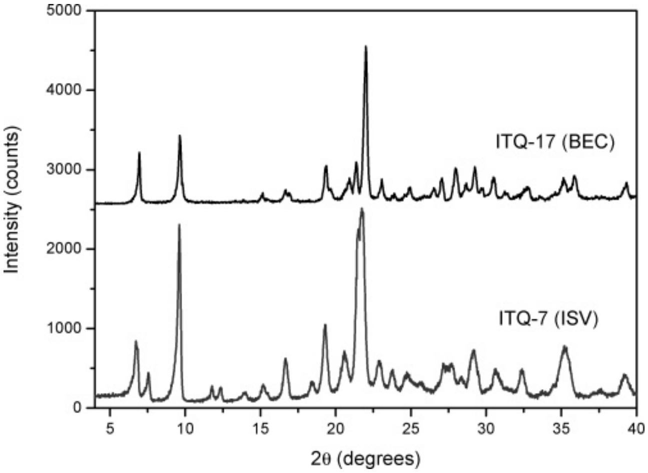

Figure 2. XRD patterns of ITQ-7 and ITQ-17 samples synthesized with SDA 3 and SDA 4 (see Figure 3), respectively.

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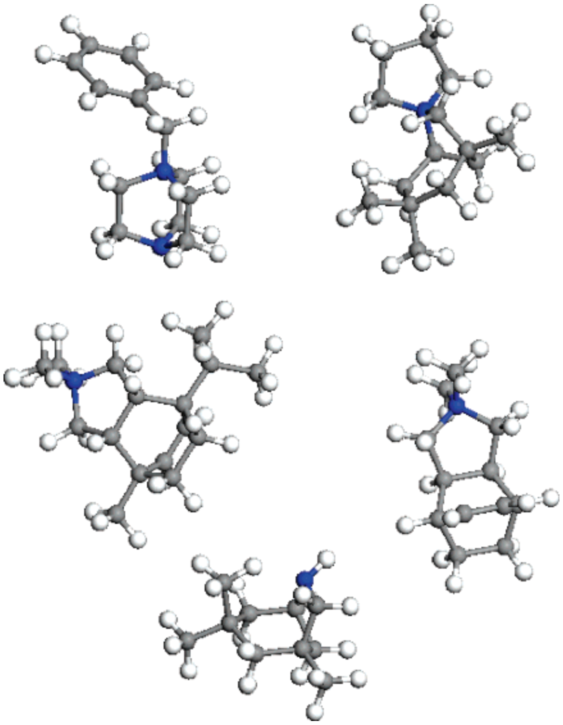

Figure 3. SDAs tested in the synthesis of ITQ-7 zeolite. Top, left: SDA 1, Benzyl DABCO ($C_{13}H_{19}N_2OH$). Top, right: SDA 2, 1,3,3-trimethyl-6-azonium-tricyclo[3.2.1.4^{6,6}] dodecane hydroxyde ($C_{14}H_{26}NOH$). Middle, left: SDA 3, 1-isopropyl-4,4,7-trimethyl-4-azonia-tricyclo[5.2.2.0] undecane-8-ene iodide ($C_{16}H_{28}N$). Middle, right: SDA 4, 4,4-dimethyl-4-azonia-tricyclo[5.2.2.0] undecane-8-ene iodide ($C_{12}H_{20}NOH$). Bottom: SDA 5, 1,3,3-trimethyl-azabicyclo[3.2.1] octane ($C_{10}H_{19}N$).

the SDA charge. Therefore, calculations including F^- were performed on pure silica frameworks.

4. Theoretical Aspects

A preliminary study taking into account the thermodynamic aspects of the synthesis of zeolites as well as a rough estimation of some aspects related to the kinetics has been presented.[21] Starting from that approach, an essential aspect of the synthesis of zeolites is that the whole microporous voids are filled by the structure directing agent. In syntheses where alumino-silicate oligomers are present in the gel, the template charge will neutralize the amount of Al incorporated by the zeolite structure and this will be done by charged template (SDA^+) as follows:

$$\mathrm{Gel}(\mathrm{m_1Si}, \mathrm{n_1Al}) + \mathrm{n_1SDA^+} \rightarrow \mathrm{Zeo{-}SDA} \qquad (1)$$

Here Zeo−SDA refers to the final system of template incorporated in the crystallized zeolite. Instead of Al, fluoride anions may also act to compensate the charge and give an electroneutral system. In the present study, all the template molecules will be considered with their corresponding monopositive charge except for the case of SDA-5 (see Figure 3) which is a neutral SDA, and in that case, pure silica frameworks were considered.

Following with the energetic considerations above, the energies of the initial and final states represented in eq 1 will be

$$E_{initial} = E_{gel} + \frac{n}{N}E_{sda_0} \qquad (2)$$

$$E_{final} = E_{zeo'} + \frac{1}{N}\sum_{i}^{n}E_{sda'_i} + \frac{1}{N}\sum_{i}^{n}E_{zeo'-sda'_i} + \frac{1}{2N}\sum_{i,j}^{n}E_{sda'_i-sda'_j} \qquad (3)$$

In these two equations, the notations *zeo′* and *sda′* refer to the geometry of the final system where both the zeolite and the template are more or less far from the optimized ground state conformations. Obviously if the synthesis is viable this will be reflected in the fact that the energetic penalty will be low due to the matching between zeolite and template, which precisely justifies the use of templates in the synthesis of zeolites. The energies are per TO_2 unit and the number of them in the unit cell of the choice for the calculations is called N, thus we divide by N where appropriate, whereas the energy of the zeolite and the gel are always defined per TO_2 unit. On the other hand, n is the number of templates fitted in the corresponding unit cell selected for the calculations and this applies to the summations over the number of templates considered. Now, taking the approximation that the template−template interactions can be neglected with respect to the more important terms of eq 3, and taking into account that the gel is taken as the zero energy, we find the following expression which indicates the energetic factors that control the synthesis of zeolites:

$$\Delta E = E_{final} - E_{initial} = E_{zeo'} + \frac{1}{N}\sum_{i}^{n}(E_{sda'_i} - E_{sda_0}) + \frac{1}{N}\sum_{i}^{n}E_{zeo'-sda'_i} \qquad (4)$$

This energy refers to systems with SiO_2-GeO_2 composition (neutral frameworks) and neutral templates, and it can also be applied to systems with non-neutral frameworks containing Al as well as Si/Ge provided the energy of the framework is calculated by taking into account the uniform background neutralizing charge scheme[34] that corrects the infinite terms in the Ewald summation of charged periodic systems and which we have applied, as implemented in GULP, for the cells containing aluminum. The energy expression above contains the three more important energetic factors controlling the synthesis of zeolites from the thermodynamic viewpoint: (i) Stable zeolite structures will be favored as indicated by $E_{zeo'}$ and also the final zeolite conformation will be favored when the template does not lead to sensible strain in the zeolite framework. (ii) Templates have to be close to the ground energy when optimized inside the microporous space, thus fulfilling what they are aimed to. (iii) Intermolecular interactions between the zeolite and the template will tend to produce the maximum possible stabilization by a close matching between the sizes and shapes of the template molecular surface and the zeolite microporous voids. Apart from the short-range contributions, the electrostatic is also taken into account and included in each of the terms of interaction between zeolite and template.

In our energetic analysis we will focus not only on the final energetic value (ΔE), but also on the template strain

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Table 2. Calculated Energy Necessary to Form the System Zeolite−Template from the Components as Defined in Equations 1−4[a]

SDA	ΔE_{SDA}[b] (eV/mol)	$E_{zeo'-SDA}$[c] (eV)	ΔE[d] (eV/TO_2)	E_{Fluor}[e] (eV/TO_2)	template concn[f] (molecules/unit cell)
1 ($C_{13}H_{19}N_2$)					
Ge−ITQ-7	0.014	−4.201	−125.87	−0.30	4
Ge−β-C	0.028	−4.001	−125.88	−0.31	4
2 ($C_{14}H_{26}N$)					
Ge−ITQ-7	0.029	−4.449	−125.89	−0.27	4
Ge−β-C	0.050	−4.305	−125.88	−0.26	4
3 ($C_{16}H_{28}N$)					
Ge−ITQ-7	0.016	−5.334	−125.89	−0.28	4
Ge−β-C	0.487	−4.189	−125.85	−0.21	4
4 ($C_{12}H_{20}N$)					
Ge−ITQ-7	0.016	−5.601	−124.65	−0.25	6
Ge−β-C	0.032	−6.001	−124.68	−0.25	6
5 ($C_{10}H_{19}N$)					
Ge−ITQ-7	0.031	−4.708	−124.63		6
Ge−β-C	0.030	−5.088	−124.66		6

[a] The different templates are shown in Figure 3 and optimized systems for ITQ-7 with SDAs 2 and 3 are shown in Figures 4 and 5. A (Si+Al)/Ge ratio of 15 has been used in Ge−ITQ-7 and Ge−β-C and two Ge atoms have been located in opposite corners of two D4R units. [b] This is the total energy deformation of the SDA molecules in the unit cell with respect to the ground state and divided by the number of SDA molecules, thus giving an average of the energy strain per SDA molecule due to the optimization inside a microporous space. [c] Energy of the interactions between all the SDA molecules in the unit cell and the zeolite structure. This number, when introduced in eq 4, has to be divided by the number of TO_2 units of the cell. [d] Total energy as defined in eq 4. [e] This is the electrostatic energy of a different system in which the SDA is positive charged and Fluorine anions have been kept fixed in the center of double four rings, giving a neutral cell. Calculations have not been performed with the neutral SDA 5 ($C_{10}H_{19}N$). The electrostatic contribution is a summation over the following terms: zeo−SDA^+, zeo−F^-, SDA^+−SDA^+, F^-−F^-, and SDA^+−F^-. [f] Loadings refer to number of organic molecules in the unit cell used for the calculations, whose stoichiometry is $Si_{60-x}Al_xGe_4O_{128}$, where x is the number of charged SDA^+ in the unit cell.

(ΔE_{sda} in Table 2), and the intermolecular interaction zeolite-template ($E_{zeo'-sda}$ in Table 2).

Finally, the role of F^- ions will be studied and the final structures will be considered with the charged templates and the neutralizing F^-. The additional electrostatic stabilization will be computed as the summation over the terms involving zeolite−SDA^+, zeolite−F^-, SDA^+−SDA^+, SDA^+−F^-, and F^- −F^-. This electrostatic contribution will be called E_{Fluor} in Table 2. Further stabilization is expected by the effect of fluorine because the SDA^+ cations tend to locate close to the F^- and then the attracting terms are expected to have more weight in the electrostatic summation than the repulsive terms (SDA^+−SDA^+ and F^- −F^-) due to the comparatively longer distances between ions of the same charge than with respect to ions of opposite charge. For this, the fluorine anions will be located in the middle of the double four rings present in ITQ-7 and β-C as this is their position reported experimentally.

5. Results and Discussion

The following SDAs were used in our study: SDA 1 ($C_{13}H_{19}N_2^+$), SDA 2 ($C_{14}H_{26}N^+$), SDA 3 ($C_{16}H_{28}N^+$), SDA 4 ($C_{12}H_{20}N^+$), and SDA 5($C_{10}H_{19}N$) (see Figure 3). The SDAs were introduced in cells of 64 TO_2 ($Si_{60-x}Al_xGe_4O_{128}$, where x is the number of charged SDA^+ in the unit cell) frameworks of ITQ-7 and β-C, and then the structure and the SDA were fully minimized without symmetry constraints. Where necessary, several SDA conformations were tested to find those that minimize the final energy and maximize the stabilization between the zeolite and the SDA with a minimum strain in the SDA conformation. This was done by using a quench-dynamics methodology as implemented in the Cerius^2 software.[35] The NVE ensemble (constant number of atoms, volume, energy) was selected and the temperature for the quenching was incremented from 800 to 950 K until the stable conformations were found. The number of dynamic steps varied from 2000 to 20 000 depending on the cycles necessary to reach the minimum energy conformations.

Zeolite ITQ-7 was synthesized first[7] from a gel with the composition $SiO_2/C_{14}H_{26}NOH/HF/H_2O$ in a molar ratio of 1:3:3:7, where $C_{14}H_{26}NOH$ (SDA 2 in Figure 3) is 1,3,3-trimethyl-6-azonium-tricyclo[3.2.1.4^{6,6}] dodecane hydroxyde. According to the experimental results, four organic SDAs fit into the microporous void space of the ITQ-7 unit cell. Thus we have first minimized the energy of the four molecules of $C_{14}H_{26}NOH$ (SDA 2) in the ITQ-7 unit cell (Figure 4). This has been done by taking into account that the SDA fits tightly in the microporous space of the ITQ-7 and therefore the van der Waals interactions can give us a first estimation of the SDA minimum energy positions. In this optimization all the atoms of the zeolite and the SDA have been relaxed. Three SDA orientations into the void space were tested in a previous study[36] and the final results gave the orientation indicated in Figure 4 as the most stable configuration. The same procedure was followed with the other template molecules tested for ITQ-7 and β-C.

The energetic contributions corresponding to the template strain (ΔE_{sda}) and to the zeolite-template interactions ($E_{zeo'-sda}$), as well as the final energy stabilization (ΔE) with the different templates of ITQ-7 and β-C are shown in Table 2. The energetic differences between different structures are small and this is due to two factors: (i) the fact that differences are referred to per TO_2 unit and these values become larger when taking into account unit cells; and (ii) energetic differences between zeolites are small, within the order of what the results in Table 2 show, as can be seen from previous studies.[37,38]

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(35) *Cerius^2 Software, Version 4.6*; Accelrys Inc: San Diego, CA.

(36) Sastre, G.; Fornes, V.; Corma, A. *J. Phys. Chem. B* **2002**, *106*, 701.

(37) Petrovic, I.; Navrotsky, A.; Davis, M. E.; Zones, S. I. *Chem. Mater.* **1993**, *5*, 1805.

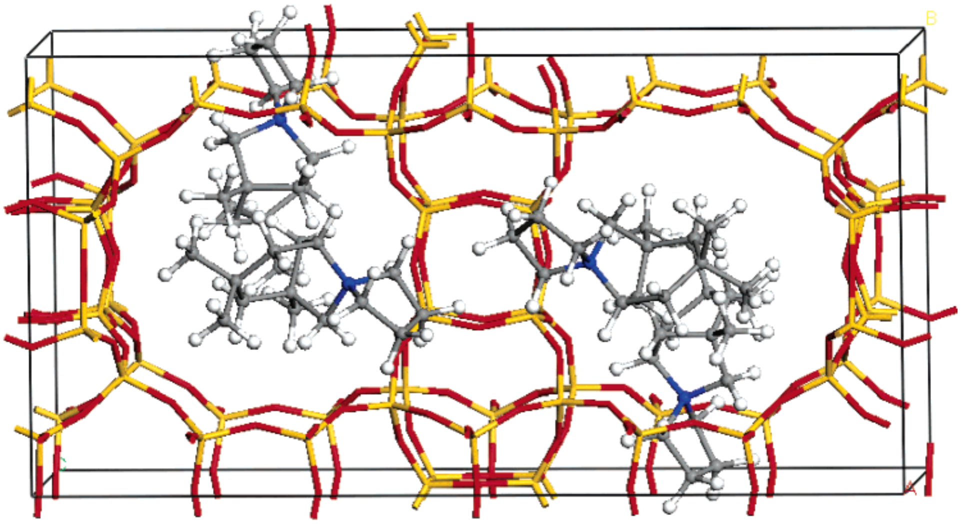

Figure 4. Optimized structure of ITQ-7 with 1,3,3-trimethyl-6-azonium-tricyclo[3.2.1.4^{6,6}] dodecane hydroxyde ($C_{14}H_{26}NOH$) used as a structure directing agent. Two organic molecules are located in the channel parallel to [100] and two molecules are located in the channel parallel to [010]. The dimensions of both channels are 6.3 × 6.1 Å.

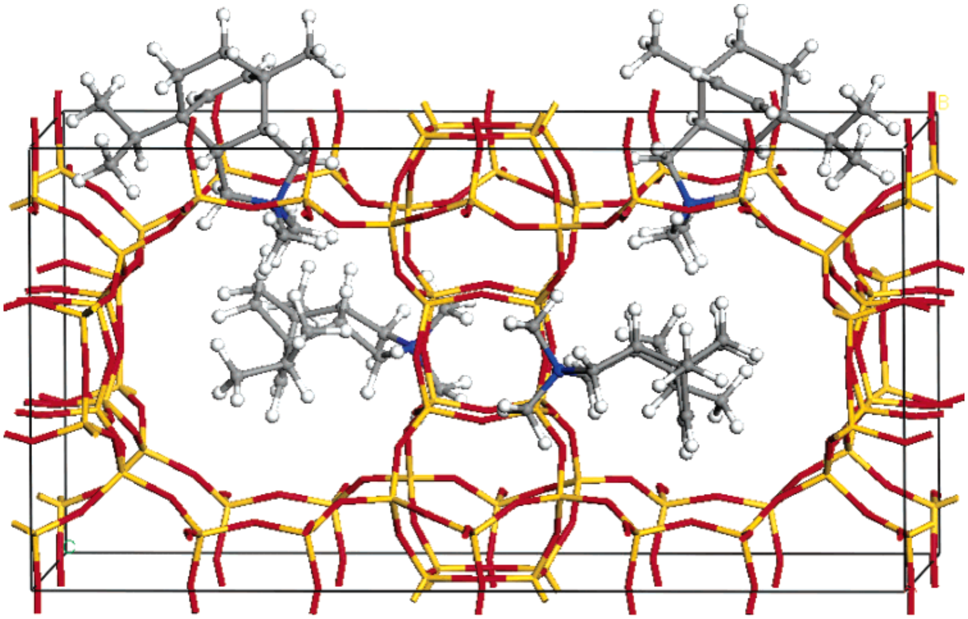

Figure 5. Optimized structure of ITQ-7 with 1-isopropyl-4,4,7-trimethyl-4-azonia-tricyclo[5.2.2.0] undecane-8-ene iodide ($C_{16}H_{28}NI$) used as a structure directing agent.

SDA 1 is the one experimentally used for the synthesis of β-C and it can be seen that the final energy is slightly more favorable for β-C than for ITQ-7 (−125.88 and −125.87 eV/TO_2 for β-C and ITQ-7, respectively); with the template strain being negligible inside both zeolite structures. SDA 2 is the only SDA reported for the synthesis of ITQ-7, and the final energy is lower for ITQ-7 than for β-C (−125.89 and −125.88 eV/TO_2, respectively). With SDA 3 the calculations show final energies of −125.89 and −125.85 eV/TO_2 for ITQ-7 and β-C, respectively, indicating that this SDA molecule should preferentially direct to the synthesis of ITQ-7. The optimized system with four SDA 3 molecules in the ITQ-7 structure is shown in Figure 5. With SDA 3, the strain in β-C is considerable (0.487 eV per SDA molecule as shown in Table 2) which also points to the preferential synthesis of ITQ-7. SDA 4 gives final energies of −124.65 and −124.68 eV/TO_2 for ITQ-7 and β-C, respectively, which indicates that the synthesis of β-C is favored. Finally, we tested the neutral SDA 5 and the calculations gave energies of −124.63 and −124.66 eV/TO_2 for ITQ-7 and β-C, respectively, indicating that β-C would be the preferred synthesis according to our energetic considerations. It is important to note that in all cases but one the template can be optimized inside the microporous space with practically no energetic strain. The similarity of the structures from the point of view of the sizes of the channels makes almost no difference in this regard and this points to the difficulty of finding templates that direct the synthesis toward the formation of the ISV structure. SDA 3 should be one of these cases in which one of the structures (β-C) is discriminated due to excessive template strain and this points to a larger selectivity of SDA 3 for the synthesis of ITQ-7. Taking this

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(38) Piccione, P. M.; Laberty, C.; Yang, S.; Camblor, M. A.; Navrotsky, A.; Davis, M. E. *J. Phys. Chem. B* **2000**, *104*, 10001.

into account, SDA 3 (1-isopropyl-4,4,7-trimethyl-4-azonia-tricyclo[5.2.2.0] undecane-8-ene iodide, $C_{16}H_{28}NI$) is therefore seen as a good choice for the selective synthesis of ITQ-7. However, it should be recognized that the synthesss of ITQ-7 and β-C are carried out in the presence of F^-, which compensates the positive charge of the SDA, and therefore, the corresponding Coulombic interactions should also be considered in the overall energetics of the system. Thus, an estimation on how the electrostatics influences the synthesis has been done here by taking into account a different system, formed by the same structure and organic, but including fluoride anions fixed at the center of the double four rings present in the structures of ITQ-7 and β-C. The same geometries for the zeolite and the organic as in the previous cases have been taken into account, and the electrostatic contribution corresponds to a summation over the following terms: zeo$-$SDA$^+$, zeo$-$F$^-$, SDA$^+-$SDA$^+$, F$^--$F$^-$, and SDA$^+-$F$^-$. This resembles the synthesis conditions more closely and the electrostatic contribution should be viewed as an additional term, apart from the total energy, that further contributes to the stabilization of the system. In this way, we want to see whether electrostatic factors point toward the same synthesis products as before. The results of E_{Fluor} in Table 2 indicate that the electrostatic factors point in the same direction as the previously studied factors. For example, with SDA 1, the values -0.30 and -0.31 eV/TO_2 are found for the electrostatic contribution (Table 2) for ITQ-7 and β-C, favoring again the formation of β-C. A slight difference, more favorable for ITQ-7, is found with SDA 2; whereas a larger electrostatic stabilization for SDA 3 is found with ITQ-7 (-0.28 eV/TO_2) with respect to β-C (-0.21 eV/TO_2), thus further supporting our previous conclusion that ITQ-7 should be the preferred material synthesized when using SDA 2 and SDA 3. The same electrostatic stabilization values are found for SDA 4 in ITQ-7 and β-C structures. In this case, four fluoride anions and six charged templates imply that two aluminum atoms are introduced in the framework to give a neutral cell. SDA 5, not having quaternary nitrogen and therefore being neutral, has not been calculated.

The inspection of Table 2 may give the impression that all the energies for a given template are very similar in the case of ITQ-7 and β-C, and in fact the differences are only within ± 0.03 eV/TO_2. Bear in mind that we are comparing closely related structures, at least from the point of view of the synthesis, and it is clear that the energy differences would be larger if two more different structures were compared. Finally, zeolites in general are shown to have very similar enthalpies of formation.[37,38]

In conclusion, from a theoretical point of view, SDA 3 directs toward the synthesis of ITQ-7, whereas SDA 4 preferentially directs to β-C zeolite. When the experimental zeolite synthesis work was carried out with the above SDAs, we observed[9] that, in agreement with the computational results, SDA 1 yields pure β-C zeolite in a wide range of Si/Ge ratios. The SDA 2 (1,3,3-trimethyl-6-azonium-tricyclo [3.2.1.4^{6,6}]dodecane hydroxide) gives zeolite ITQ-7 in a wide range of compositions, from the pure silica material[7] to a Si/Ge ratio of 1.[23] The other two structure directing agents, SDA 3 and SDA 4, have been studied here in a wide range of synthesis conditions and the results are given in Table 1. It can be seen, in agreement with the computational predictions, that pure ITQ-7 is indeed obtained with SDA 3, whereas pure β-C, and β-C + β, are synthesized with SDA 4.

It has to be pointed out that the rate of crystallization with SDA 3 is slower than with the original SDA (SDA 2), and even after 35 days of crystallization, the pure silica polymorph of ITQ-7 was not obtained.

The excellent agreement between the predictions made by the computational calculations and the experimental results obtained indicate that the methodology shown in this work could help in finding adequate SDAs for new hypothetical zeolite structures.

6. Conclusions

There are many factors playing a significant role in orienting the synthesis of zeolites toward a particular structure. The use of computational techniques has shown to be a good aid in unveiling all the energetic factors that may be of interest in this regard. The understanding and quantification of zeolite$-$SDA interactions is crucial when related structures compete and small differences in this interaction, due to small differences in the SDA structure, may shift the synthesis toward one or the other structure. This is the case for ITQ-7 and β-C materials, with closely related structures, and where several SDAs were reported to synthesize β-C and only one for ITQ-7. Finding alternative routes to synthesize zeolites, especially in those with potential commercial application, is always important because this provides a suplementary library of SDAs which can be used when the others are not possible or become too expensive. A set of five organic azocompounds have been used for the calculations in ITQ-7 and β-C structures. The original SDAs reported in the literature were first used and it was found that the computational results are in agreement with the experimental findings, this being a first check showing that the methodology works well. Among the other three SDAs, one of them, 1-isopropyl-4,4,7-trimethyl-4-azonia-tricyclo-[5.2.2.0] undecane-8-ene iodide ($C_{16}H_{28}N^+$, SDA 3) has been found to minimize considerably all the energetic factors for zeolite ITQ-7, and, at the same time, some conformational restraint appears in β-C. When the syntheses were carried out, the experimental results confirmed the theoretical predictions. Additional rationalization of the energetic contributions was performed and the effect of loading, unloaded zeolite stability, and SDA strain are shown to be the key factors that, when taken together, may contribute to quantify which SDA are more suitable for obtaining a specific zeolite. Further calculations with more SDAs and more zeolite structures are underway to further check this methodology. The finding of a new SDA for the synthesis of ITQ-7 zeolite opens a new route to obtain this material, since the usual ammonium cation used as SDA is no longer commercially available.

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