

## Computational Study of the Structure-Directing Effect of Benzylpyrrolidine and Its Fluorinated Derivatives in the Synthesis of the Aluminophosphate AIPO-5

Luis Gómez-Hortigüela,<sup>\*,†,‡</sup> Furio Corà,<sup>†</sup> C. Richard A. Catlow,<sup>†</sup> and Joaquín Pérez-Pariente<sup>‡</sup>

Contribution from the Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, United Kingdom, and Instituto de Catálisis y Petroleoquímica, C/Marie Curie, 28049 Cantoblanco, Madrid, Spain

Received April 2, 2004; E-mail: jperez@icp.csic.es

**Abstract:** Using a combination of computer modeling techniques, we have investigated the ability of benzylpyrrolidine and its fluorinated derivatives in ortho, meta, and para positions of the phenyl ring to direct the synthesis of the aluminophosphate AIPO-5. The *o*- and *p*-fluoro derivatives are not good templates because of the poor packing of the template molecules inside the AIPO-5 pores, due to a repulsion provoked by the fluorine atoms. However, benzylpyrrolidine and the *m*-fluoro derivative do direct the synthesis of AIPO-5, the latter being a better template due to higher electrostatic interactions with the framework. We demonstrate that, at least when the synthesis is performed with an excess of template molecules, the ability of organic templating molecules to direct the synthesis of microporous materials depends not on the host-guest interaction energy per unit of template molecules, as usually calculated, but on the *density* of interaction energy, i.e., the energy per formula unit of the microporous network. The packing density of molecules inside the channel system must be taken properly into account. From the calculated location of the benzylpyrrolidine molecules and their *m*-fluoro derivative inside the inorganic network, we would expect the formation of stable dimers.

### Introduction

Since their discovery, microporous materials have found industrial application in processes such as catalysis, molecular sieving, gas separation, and ion exchange.<sup>1,2</sup> These materials can be synthesized in different compositions: microporous aluminophosphates (AIPOs) were first reported by Wilson et al.,<sup>3</sup> and since then they have been widely studied. Hydrothermal methods are employed in the synthesis of microporous materials, and the use of organic molecules to direct the formation of structures with novel channel systems has been extensively investigated.<sup>4–6</sup> The organic molecules are encapsulated inside the microporous framework as it crystallizes and are removed, usually via calcination, before the product is put to use. The addition of organic templates, such as amines and quaternary ammonium cations, to zeolite synthesis can affect the rate at which a particular material is formed and may lead to new structures or frameworks with different chemical compositions

(or different crystal lattice substitutions). However, the relationship between the organic agents and the zeolite product they form, usually known as templating effect, is still not fully understood.<sup>7</sup> Templating is thought to occur during either the gelation or nucleation process and involves the organic molecules organizing the inorganic tetrahedral units into a particular topology around themselves and thus providing the initial building block for further crystallization of a particular structure type. Although a true templating effect has been demonstrated in a few cases, such as the synthesis of ZSM-18,<sup>5,8</sup> this structure-directing effect is not as specific as expected. Experimental evidence clearly shows that the gel chemistry and kinetic factors can also have a critical bearing on the nature of the microporous product formed. Particularly for aluminophosphates, a large variety of quite different molecules can direct the synthesis of the same structure, as well as one molecule often being able to synthesize different structures.<sup>4</sup>

Since there are only nonbonding interactions between the template and the microporous frameworks, the ability of a molecule to direct the crystallization of a certain zeolite depends on the nature of these interactions. To date, the most widely used template molecules have been amines and quaternary ammonium cations, where most, if not all, of the hydrogen atoms are bonded to organic carbon atoms. These hydrogen atoms

<sup>†</sup> Davy Faraday Research Laboratory, The Royal Institution of Great Britain.

<sup>‡</sup> Instituto de Catálisis y Petroleoquímica.

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provide the major component of the host–template interaction. Therefore, the wide diversity of template molecules that has been used in zeolite synthesis relates only to the shape of the molecules but not to the chemical character of the interactions between template and framework; these occur only through hydrogen bonded to carbon atoms. With this factor in mind, our aim has been to change the type of nonbonded interactions between the template molecule and framework by substituting some of the hydrogen atoms with fluorine atoms in the template molecules. By doing so, new interactions are introduced in the overall template–framework interactions due to the introduction of C–F bonds in the template molecules. Fluorinated molecules have rarely been used as templates for the synthesis of microporous materials.<sup>9</sup> However, several differences in the crystallization of microporous materials have already been found when this new class of fluorinated templates is used instead of their hydrocarbon equivalents.<sup>9,10</sup>

Experimental studies of the location and conformation adopted by the template molecules inside the zeolite hosts are difficult, due to the nature of the crystals obtained in the synthesis, although some systems have been studied with success.<sup>11–13</sup> A complementary tool for increasing our understanding of these problems is provided by computer modeling techniques, whose rapid growth in recent years has made increasingly feasible the accurate calculation of molecular structures, energetics, dynamics, and reactivities. Several approaches have been developed to study the location and orientation adopted by organic molecules within a zeolite host, as well as their interaction energy.<sup>14–25</sup> Manual and Monte Carlo docking procedures, energy minimization, and simulated annealing techniques have been employed with success to predict the location and the templating ability of several molecules in zeolite synthesis. These calculations are usually performed with molecular mechanics techniques, because of the large computational cost associated with ab initio quantum mechanical (QM)

approaches, and the inability of standard methods based on density functional theory (DFT) to describe van der Waals forces.

Previous experimental work<sup>26</sup> showed that benzylpyrrolidine directed the synthesis of AIPO-5 (AFI), which is a microporous structure composed of straight one-dimensional channels along the *c* crystallographic direction. The channels comprise 12-membered rings of tetrahedra, with a channel diameter of 7.3 Å. When one H atom of the aromatic ring in a meta position is substituted by a F atom, the templating ability of this molecule increases (this feature being measured in terms of the crystallinity of the solid formed), but when H is substituted by F in an ortho or para position, the templating ability decreases. In the following, we shall refer to the templates as bp (benzylpyrrolidine), oF (*o*-fluorobenzylpyrrolidine), mF (*m*-fluorobenzylpyrrolidine), and pF (*p*-fluorobenzylpyrrolidine). In this paper, we investigate with a computational approach the different abilities of benzylpyrrolidine and its fluorinated derivatives to direct the synthesis of AIPO-5. Our aim is to calculate the template location within the AFI structure and the interaction energies between the different molecules and the framework. Different computational models of the template–framework interaction are compared. The model will capture the essential chemistry of the templating effect only when the relative interaction energies, which are the calculated measure of the templating ability, agree with results of the experimental work.<sup>26</sup> This order of templating ability is mF > bp > oF > pF, and the same trend should be expected for the interaction energies.

## Methodology

To calculate the interaction energies between the template molecules and the inorganic network and the location of the templates inside the channel systems, we have used a combination of molecular mechanics simulation techniques including Monte Carlo docking, energy minimization, and molecular dynamics.

We used the CVFF force field<sup>27</sup> to model the host–template interactions, all of which included electrostatic terms. The van der Waals and electrostatic terms were calculated by use of the Ewald summation, excluding the bonded (1–2 and 1–3) interactions. The atomic charges for the template molecules were calculated by the charge-equilibration method,<sup>28</sup> while the net charges for the framework O, Al, and P atoms were fixed to –1.2, 1.4, and 3.4, respectively. Periodic boundary conditions (PBC) were applied in order to ensure effective treatment of template–template interactions, except for specified cases employing a cluster model representation of the solid. The geometry of the AFI structure without any organic molecule inside was previously optimized by use of the GULP<sup>29</sup> code with the interatomic potential parameters developed by Gale and Henson,<sup>30</sup> and it remained fixed for all the subsequent calculations. The fixed-framework approximation is commonly adopted in statistical procedures, where several million configurations of the molecule inside the host channels are evaluated. This approach also enables us to use an accurate force field<sup>30</sup> to describe the AIPO-5 framework, instead of the CVFF in which the AIPO geometry is reproduced less accurately.

The interaction energies were calculated by subtracting the energy of the isolated molecules optimized in vacuo from the total energy of the system.

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**Table 1.** Calculated Interaction Energies for the Different Models<sup>a</sup>

molecule	1temp	2temp-opposite	2temp-facing	4temp-sa
bp	-45.49	-46.12	-45.99	-68.0
mF1(1-1)	-48.15	-47.58	-46.94	-71.4
mF2(1-2)	-44.25		-49.50	-73.0
oF1	-45.22	-48.05	-46.53	unstable
oF2	-53.23		-46.04	unstable
pF	-48.89	-42.05	-46.79	unstable

<sup>a</sup> All energies are given in kilocalories per mole. Energies in 1temp, 2temp-opposite, and 2-temp-facing are per template molecule; energies in 4temp-sa are per unit cell of the AFI framework (density of interaction energy).

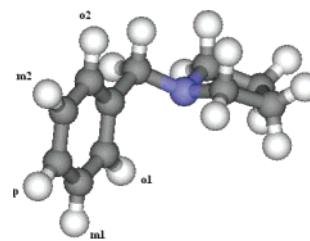
Our first model includes just one template molecule and the periodic framework (1temp model). The initial geometries of the organic molecules were obtained by a QM study in vacuo by use of density functional theory (DFT). Full details will be given in a forthcoming paper.<sup>31</sup> To find the most stable location, rigid template molecules were inserted randomly in the AFI structure, one molecule in a supercell composed of  $2 \times 2 \times 3$  unit cells of AIPO-5, by using a Monte Carlo (MC) docking procedure.<sup>32</sup> The molecule was then energy-minimized inside the host, by use of the CVFF force field.

The next step was to study the packing between the molecules. Starting from the optimized geometry of the 1temp model, we manually inserted a second molecule in the required position. Then, 10 ps of molecular dynamics (MD) at 300 K were simulated to relax the organic molecules. These MD simulations<sup>33</sup> were carried out without PBC but by construction of a large cluster model of the framework, composed of the wall atoms of the 12-ring channel and of length 5 or 8 unit cells in the *c* direction. We studied the packing of 2 and 6 molecules (2temp and 6temp models, respectively) by relaxing the position of the organic molecules in a rigid framework. The conditions of the dynamic simulation were constant NVT and 1.0 fs time step. After the MD runs, the systems were energy-minimized under PBC. The choice of the cluster model for the MD simulations rather than a model of the solid based on PBC has two consequences. First, it makes the calculations faster, enabling us to perform a better sampling of the potential energy surface. Second, it removes completely any constraint in the packing density of the template molecules along the AFI channel, which would be dictated by a periodic solution along the *c* direction. Any computationally feasible PBC model would in fact enforce an integer ratio between the number of template molecules and the number of unit cells of the channel.

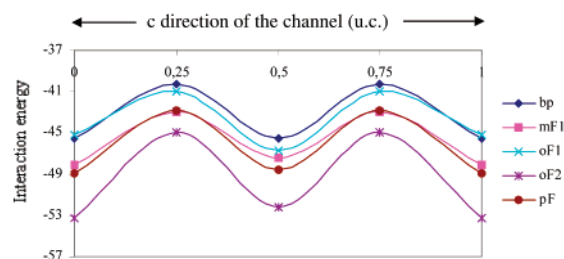
The packing of bp and mF molecules in the 6temp model was found to be very close to 4/3. To find the definitive interaction energy and location of these two template molecules in the AFI network, we used a simulated annealing protocol for a system with four template molecules in three unit cells using PBC. We refer to this choice as 4temp-sa model. The system started at 300 K, was heated with temperature increments of 10 K until 700 K, and then cooled again in the same way. Three hundred steps of 1.0 fs (0.3 ps) were run in every heating step. This protocol was repeated five times, and the most stable configuration was taken as representative of the stable adsorption structure.

## Results and Discussion

The calculated interaction energies per template molecule, for the different models of the solid described above, are reported in Table 1. In the case of mF and oF template molecules, two possible conformers were studied, indicated as mF1 and mF2 and oF1 and oF2. They are characterized by



**Figure 1.** Benzylpyrrolidine (without fluorine atoms) and its fluorinated derivatives: two conformers for *o*-fluoro (fluorine in o1 or o2 position), two for *m*-fluoro (fluorine in m1 or m2 position), and one for *p*-fluoro (p position). The N atom is marked in blue.



**Figure 2.** Energy diagram corresponding to the translation of the different molecules along one unit cell in the *c* direction. The interaction energy (*y* axis) is expressed in kilocalories per mole.

different relative orientations of the F substituent with respect to the pyrrolidine ring (see Figure 1).

First of all, we studied the interaction between one template molecule and the framework, excluding packing effects (1temp model). All the molecules, except the oF1 case, are located with the benzyl moiety parallel to the direction of the channel. In contrast, the oF1 template is stable with the benzyl moiety bent with respect to the direction of the channel. This feature is caused by the larger effective size of the oF1 molecule, generated by the repulsion between the lone pairs of the fluorine and nitrogen atoms, which prevents the pyrrolidine ring from being perpendicular to both the aromatic ring and the direction of the framework channel. This feature, obtained with the CVFF force field, is confirmed by DFT calculations of the template molecules in vacuo.

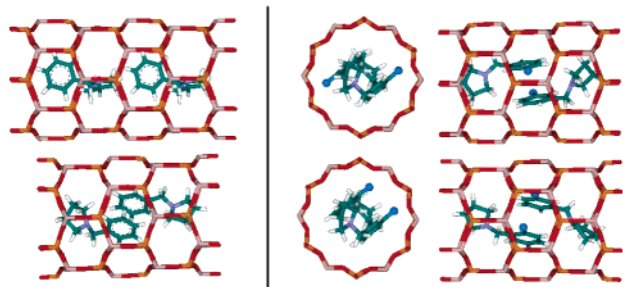
The calculated interaction energies for the 1temp model are shown in Table 1 for the four templates. The van der Waals terms, which are the main contribution to the interaction energy, are very similar for each template, except oF1 because of its different location. Otherwise, the main differences arise from the electrostatic term. By analyzing the results of our calculations, we notice that the fluorine substituent stabilizes the system when it is closer to the walls of the channel, with the C–F bond perpendicular to the channel direction and pointing toward the center of a six-membered ring of tetrahedra in the channel. This configuration develops a stabilizing electrostatic interaction with the channel atoms.

An additional set of calculations was carried out to investigate whether there is an optimal location of the molecules along the *c* direction of the channel. The molecules were minimized at different positions along the AFI channel, in which the *z* coordinate of the N atom was constrained to be 0, 0.25, 0.5, and 0.75 in fractional coordinates. The modification of the interaction energy along the *c* direction is shown in Figure 2. The results show that effectively there is an optimal position along the *c* direction of the channel when the center of the benzyl

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(32) Sorption module, version 4.6, Accelrys Inc., San Diego, CA, 2001.

(33) Dynamics simulation, version 4.6, Accelrys Inc., San Diego, CA, 2001.



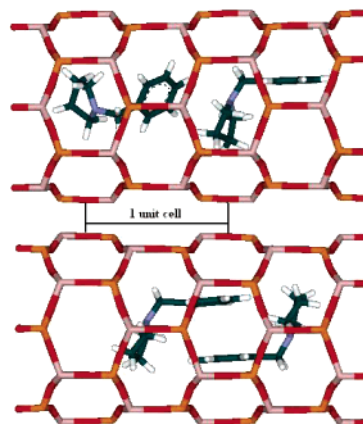
**Figure 3.** (Left) Two possible orientations for the two bp molecules: with benzyl moieties opposite each other (top, 2temp-opposite model) or facing (bottom, 2temp-facing model). (Right) Two possible orientations of fluorine atoms, with fluorine on opposite sides [top, mF(1-2) model] or on the same side [bottom, mF(1-1) model].

ring coincides with the center of the 6-rings of the channel; these are centered at fractional coordinates  $z = 0.0$  and  $z = 0.5$  (see Figure 2).

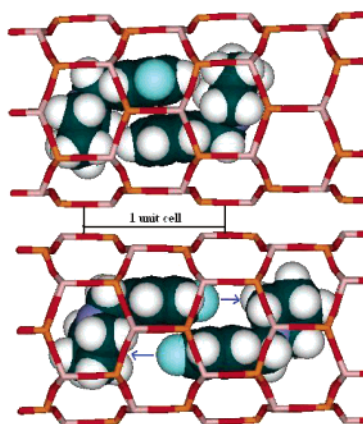
The relative templating ability of the molecules, known from experimental work, does not correspond to the order of calculated interaction energies obtained from the 1temp model (see Table 1). This disagreement is probably due to the neglect of packing effects (template–template interactions) in this model. The consequence of introducing packing effects over the interaction energy has been previously studied,<sup>14</sup> improving the correspondence between calculated and experimental results, compared to simpler models that neglect the template–template interaction.

In our work, template–template interactions have been investigated initially with the 2temp model. There are two possible ways of approaching two bp molecules: with benzyl rings opposite or facing each other (Figure 3, left), which we define as opposite and facing, respectively. Both possibilities have been investigated with the MD and minimization procedure described earlier, by not only calculating the interaction energy but also examining the packing density inside the channels. We recall that, in the 2temp model, the packing density (i.e., the number of molecules per unit cell) is not constrained by the choice of PBC; the molecules are therefore able to relax and locate at the optimal intermolecular distance. The energy results are reported in Table 1 (2temp-opposite and 2temp-facing models). Two possible orientations in the facing configuration of mF molecules have been investigated, with fluorine atoms of the two molecules on the same side [mF(1-1)] or on opposite sides [mF(1-2)] with respect to the molecular axis (Figure 3, right).

The interaction energies per template molecule of facing and opposite configurations are similar, but the density of packing is not. Let us start by examining results for the unsubstituted bp templates. In the 2temp-opposite configuration, the packing is not effective (the framework can accommodate less than one molecule per unit cell) since the adjacent molecules do not fit well (Figure 4, top). In the 2temp-facing configuration, instead, the packing is of more than one molecule per unit cell, because the fitting between the benzyl moieties is very effective (Figure 4, bottom). This change of arrangement does not imply a large change of the interaction energy per template molecule with the framework (see Table 1), but it modifies substantially the number of template molecules per unit cell, and hence also the total interaction energy per unit cell of the AIPO framework. We refer to this quantity as *density* of interaction energy. Figure



**Figure 4.** Location of the bp molecules inside the 12-ring AFI channel after the MD simulation and minimization with the 2temp model for the opposite (top) and facing (bottom) configurations.

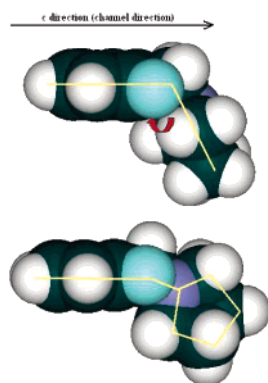


**Figure 5.** Location of the mF (top) and pF (bottom) template molecules in the 2temp model, after the MD simulation and minimization in the facing configuration. The less effective packing and void filling of the pF template molecule is shown.

4 shows the arrangement adopted by two bp molecules after the MD simulation and minimization. In the “facing” configuration, the molecules pack almost perfectly, shaping a rectangle and enabling the packing of ca. 2 molecules per 1.5 unit cells (1.33 mol/unit cell). The same arrangement is adopted by the mF molecules (Figure 5, top) with the templates being more stable when the fluorine atoms of the two molecules are on opposite sides, as this arrangement minimizes the repulsion between the F atoms in the dimer. In light of this result, we propose that the arrangement of the bp and mF templates inside the channels occurs via the formation of dimers, with the benzyl rings in the facing configuration.

This increased packing density does not occur in the case of the pF derivative. A strong repulsion is established between the two molecules, which forces them to move away from each other, as shown in Figure 5 (bottom). This repulsion generates some vacant space between the molecules, decreasing the density of packing and hence the density of the interaction energy in the system.

The packing of the oF derivatives is not effective either. This time, however, the less effective interaction is not due to an electrostatic repulsion between the two fluorine atoms as in the pF case. The problem here is related to the orientation of the pyrrolidine ring, which cannot be perpendicular to the direction of the channel, as already discussed for the 1temp model. In



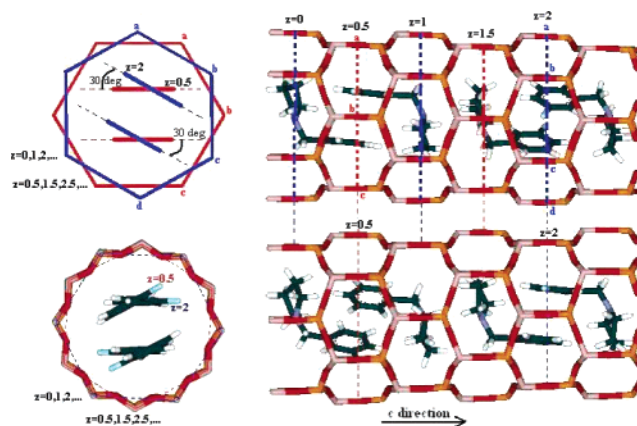
**Figure 6.** Conformation of the oF molecules: top, in the stable geometry of bp and mF (with the pyrrolidine ring perpendicular to the benzyl moiety and to the channel direction), and bottom, in its stable conformation. The arrow indicates the region of short-range repulsion between fluorine and the pyrrolidine ring.

the stable configuration required for the formation of stable dimers with effective packing properties (like those of bp and mF), the benzene ring is parallel to the channel direction and the pyrrolidine ring is perpendicular to both the aromatic ring and the direction of the channel. This configuration, however, cannot be achieved by the oF template because of a repulsion between the fluorine and hydrogen or nitrogen atoms of the pyrrolidine ring (Figure 6).

When we consider the calculated interaction energy per template molecule, in either facing or opposite configurations, the relative order of the interaction energies for the four templates calculated with the 2temp model is still unable to rationalize the experimental results. We have shown, however, that mF and bp molecules pack in a more efficient way than oF and pF. The latter result, we consider, must be taken into account to explain the different templating ability of these four organic molecules. In other words, the problem relates not only to the interaction energy between molecules and framework but also to the packing density. Experimentally, the synthesis of microporous materials is often performed in excess of template, suggesting that indeed the calculated interaction energies should be referred to the amount of oxide and not of template.

To calculate the packing density of the dimers, our computational model of the solid must be able to estimate the equilibrium distance between subsequent dimers, without imposing computational constraints (for instance, by use of PBC). To this aim we have constructed the 6temp model, described in the computational details, in which a cluster of the AFI channel 8 unit cells long contains three adjacent dimers. A MD simulation was carried out to study the interaction between the pyrrolidine rings of neighboring dimers; the real packing density was then calculated by measuring the distance of the central nitrogen to the next equivalent ones, which is then normalized to the  $c$  lattice parameter. The values of the N–N distances are 12.76 and 12.83 Å for the bp dimers and 12.91 and 12.92 Å for the mF dimers, compared with a  $c$  lattice parameter of 8.60 Å. Thus, the theoretical packing was found to be 1.344 in the bp and 1.332 in the mF (mF(1-1) and mF(1-2)) case, corresponding to approximately four molecules (two dimers) per three unit cells. This value is comparable to that found experimentally, of  $\sim 1.2$  molecules per unit cell.<sup>26</sup>

Once renormalized for the packing density, the values of the density of interaction energy reproduce the relative templating

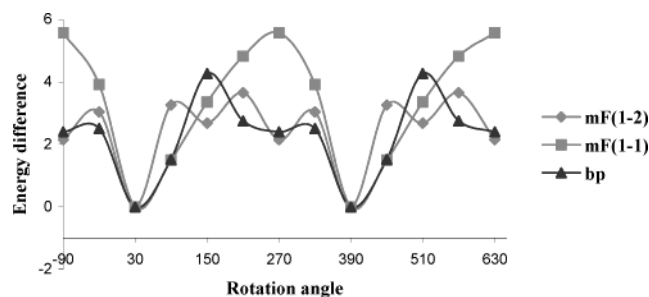


**Figure 7.** Final location of the template molecules [mF(1-2) case, mF molecules with fluorine on opposite sides] in the 4temp-sa model. (Right) Two views of the mF-AFI system, rotated by 30°, to highlight how the benzyl moieties point always to the center of the 6-rings of the channel. (Left) Schematic view of the AFI channel and its relation to the position of the benzyl moieties of the templates (top) and projection of the real system (bottom) perpendicular to the  $c$  axis.

ability of the four organic molecules, known from the experimental work. This feature increases our confidence that the results of the computational model capture the fundamental features of the templating effect.

Having identified the effective packing of the molecules, the last step was to calculate accurately the interaction energy for a fully periodic system (by use of PBC) containing the stable bp and mF dimers, so as to include all the interactions. These calculations were performed with the simulated annealing procedure as described above. Since the unconstrained packing density of bp and mF dimers from the 6temp model corresponds closely to 4/3, we have restored the PBC treatment of the solid, with four template molecules (two dimers) in three unit cells along  $c$ ; we refer to this choice as the 4temp-sa model. The final results of the interaction energies are shown in Table 1 (4temp-sa model), and the location of the template molecules is shown in Figure 7 (the location of the bp molecules in this model is exactly the same as the mF ones). The van der Waals energies are again similar, and the difference is due to the electrostatic term: fluorine in meta position generates an additional stabilization due to the electrostatic interactions with the framework, which is a maximum when the fluorine atoms are on opposite sides, as discussed earlier. This factor therefore explains why mF molecules are better templates for the synthesis of the microporous AFI structure than bp molecules. The relative contributions of template–framework and template–template interactions are calculated as  $-59.0$  and  $-9.0$  kcal/mol for bp and  $-61.9$  and  $-11.1$  kcal/mol for mF(1-2). Both values are higher for mF than for bp, suggesting that the better templating ability of the former is due to a combination of both template–template and template–framework interactions.

Figure 7 contains two views of the optimized structure, one turned with respect to the other. Subsequent dimers are rotated by  $\sim 30^\circ$  with respect to each other; this relative orientation is required to preserve the stable configuration for each template molecule, with the benzyl moieties placed with atoms in a meta position pointing to the center of the 6-rings of the channel. Consecutive 12-rings of the AFI channels (separated by half unit cell along the  $c$  direction) are rotated by  $30^\circ$ , as shown in Figure 7 (top left); since there are two dimers for each three



**Figure 8.** Energy difference diagram (kilocalories per mole) for the rotation angles between subsequent dimers that satisfy the condition of  $(30^\circ + n60^\circ)$ . Zero energy corresponds to the stable rotation angle of  $30^\circ$ .

unit cells, they have to rotate by  $30^\circ$  to preserve the most stable orientation of the molecules with benzyl moieties pointing to the center of the 6-rings of the channel. Although relative orientations of  $30^\circ + n60^\circ$ , i.e.,  $30, 90, 150, \dots$ , satisfy the condition for the stable orientation, that with the angle of  $30^\circ$  has been found computationally to be the most stable, due to a stronger interaction between the pyrrolidine rings of consecutive dimers, since the orientation of the templates relative to the framework is equivalent in all possible rotations. Only relative orientations of the template dimers that satisfy the condition of a rotation angle of  $\sim(30^\circ + n60^\circ)$  are minima in the potential energy surface. Different values of the rotation angle are unstable and revert into one of the  $(30^\circ + n60^\circ)$  structures upon geometry optimization. The calculated relative energies of the different  $(30^\circ + n60^\circ)$  relative orientations of the dimers for the bp, mF(1-1) and mF(1-2) systems are shown in Figure 8. The energy difference between these configurations ranges between 1.5 and 6.0 kcal/mol. The lower end of this range is comparable to the thermal energy under the hydrothermal synthetic conditions ( $kT$  at  $150^\circ\text{C}$  is  $\sim 0.85$  kcal/mol), which indicates that thermal disorder may prevent a perfect long-range ordered arrangement of the template dimers inside the channels. In principle, if the relative orientation of subsequent templates could be controlled with long-range order, the template dimers would provide a helical (and hence chiral) chain inside the channel that could eventually transfer the chirality to the solid. This is not achieved with the bp-related templates currently employed, but both experimental and computational work is under way at present to design novel template modifications that can stabilize the chiral long-range ordered arrangement.

## Conclusions

We have explained the different ability of bp molecules and their fluorinated derivatives to direct AFI synthesis. Depending on the position of fluorine in the aromatic ring, it can reduce

the templating ability because of poorer packing, as in the case of pF and oF, or improve it by the development of stabilizing electrostatic interactions with the framework atoms, as in the mF case. Thus, even a small chemical modification in the template molecule, such as the replacement of a hydrogen atom with a fluorine, can drastically alter its structure-directing properties and may lead to new structures.

We have also demonstrated that, at least when the synthesis is performed in excess of template molecules, the template ability of organic molecules to direct the synthesis of microporous materials depends not on the host–guest interaction energy per unit of template, as usually calculated, but on the *density* of interaction energy, i.e., the energy per formula unit of the microporous network. The packing density of molecules inside the channel system must be taken properly into account, although this feature requires the removal of computational constraints and can make the computational work very demanding.

The calculated location of the bp and mF molecules inside the inorganic AFI network predicts a close geometric match, and the formation of facing dimers, which maximizes the space filling. The same dimerization process cannot occur for the oF and pF derivatives, thus rationalizing the relative templating ability of the four molecules known from experimental work.

The relative orientation of consecutive 12-rings of the AFI channels forces the molecular dimers to orient in the same pattern. In a polar solvent, such as the aqueous solution employed in the hydrothermal synthesis of zeolites, the formation of facing bp dimers, in which the aromatic (hydrophobic) part of two bp molecules is paired, is likely to be a stable arrangement, able to minimize the hydrophobic surface of the templates exposed to the polar solvent. In our view, the present case of bp derivatives and AFI is therefore another example of a true templating effect, rather than the void-filling effect that has been often suggested, because of the close relation between the shape and position of the templates and the inorganic network. This effect is explained in terms of short-range order between subsequent bp dimers; more experiments and calculations are in progress to investigate whether long-range order can be induced by appropriate chemical modifications of the bp template.

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