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Designing templates for the synthesis of microporous solids using de novo molecular design methods

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Abstract

De novo design techniques are used to grow (computationally) candidate template molecules for specific microporous materials. Detailed studies are reported for both EU-1 and chabazite where our simulations are able to rationalise known templates and suggest new templating molecules for the synthesis of such structures.

Keywords: Microporous solids; Template molecules; Zeolites

1. Introduction

Microporous solids are industrially important materials used for catalysis, ion exchange and gas separation. These applications exploit both their chemical properties, particularly their strong solid Brønsted acidity, and their structural properties especially their cage and channel structures. Synthesis of such materials usually involves crystallisation from a gel medium under hydrothermal conditions. These gels are multicomponent systems, with the final framework being formed from the aluminosilicate or aluminophosphate species present. One crucial component of the gel is a base, which regulates the pH. However, by utilising organic bases it has been found that new materials can be formed [1], and that the organic base gives additional synthesis control through structure-directing or *templating* effects. This templating effect has been central to much of the recent research into forming new materials [2]. However, at present, the route to new structural types depends either on trial and error modification of existing templates or on exhaustive searches for templates with particular motifs thought to be conducive for a desired end structure. Whilst there is a growing confidence in being able to target a particular type of microporous product [2] — good examples being DAF-1 [3], SSZ-26 [4], MeAPO-18 [5], CIT-1 [6], DAF-4 [7] and ZSM-18 [8] — there is, as yet, no a priori way of determining if the selected template will indeed be successful in nucleating a particular framework. In this paper we show how computer modelling techniques may be used to design templates for specific hosts.

We have previously demonstrated [9] such

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techniques may be used to understand, in an interpretative sense, the templating of microporous materials. Thus we can rationalise the qualities (or molecular features) of successful templates in terms of their interactions with the framework and indeed, determine the efficacy of a molecule at directing synthesis toward a particular framework; moreover, we can use this information to modify the properties of the material. Other workers have also shown how such methods can provide insights into the kinetics of the synthesis [10] and the subsequent processes of crystal growth. Along side this work, quantitative descriptions of template shape using moments of inertia have been shown to be useful in determining whether a given molecule is likely to form a particular framework [11]. These studies represent the progress made to date in quantifying the empirical evidence that for a template to be successful there must be a 'good fit' between the molecule and the framework formed [12,13].

Despite these successes, no one has yet achieved the goal of a priori design of a microporous solid. We have recently demonstrated the successful application of de novo ligand design methods as a new approach to the design of templates molecules for the synthesis of such materials [14]. In this paper we will discuss further the methodology and provide new examples of the method's utility.

De novo ligand design has been applied, for some time, in the search for biologically active materials, see Refs. [15–21] for further details and applications. In such systems, the techniques allow a molecule to 'grow' so as to fit accurately into a targeted active site. Growth is permitted until there is favourable interaction between the substrate and the surrounding cavity. Often the target site is ill defined and is therefore described using property mapping (such as CoMFA maps [22]) or grid based representations [17], rather than explicit atomic coordinates. Usually, the growth of the molecule is restricted to growing linking units between functional groups positioned in favourable geometries in the active sites [17–19]. Molecules can also be grown to fit the available volume and then subsequently refined by changing the atoms in the initial molecule to improve its binding [21]. These methods have met with some success in designing new pharmacological inhibitors including those for HIV-1 protease [16]. Template molecules suited for microporous inorganic solids are usually simpler and smaller than their biologically active counterparts. Likewise, the regular crystalline nature of microporous materials imposes more rigorous constraints viz. the rigidity and symmetry of the framework, which are reflected in the molecules which can act as templates.

There is, therefore, a strong incentive for the development of de novo design techniques for template selection in these systems. Here, we will describe two recent application of the methods to design new templates for the zeolites EU-1 and chabazite.

2. Methodology

We employ the new code ZEBEDDE [14] (zeolites by evolutionary de novo design) which has been written for the application of de novo techniques to microporous materials. We will now outline the technique of de novo ligand design and its implementation in our code.

From previous work [9,11,12] it has been shown that for a molecule to be effective as a templating agent, it must effectively fill the void space of the cavity of the host framework. We therefore propose that a cost function based on overlap of van der Waals spheres will provide a suitable measure of the efficacy of a particular molecule for the synthesis of a target framework. Hence, we control the development of new templates via the cost function

$$f_c = \sum_t C(tz)/n, \tag{1}$$

where $C(tz)$ signifies the closest contact between a template atom t and any host atom z

and n is the number of atoms in the template. In order to ensure that the molecule is effectively positioned within the available void space, the value of f_c must be a maximum at any given time. Similarly, different template molecules can be compared by their ability to minimise f_c. That is, to facilitate growth of a molecule, it must be positioned as far as possible from the framework. Once grown, we should arrive at a position where further growth is no longer possible and now f_c provides a measure of 'tightness of fit'.

New potential templates are grown within the target framework by a series of randomly selected actions. The actions available are:

(1) *Build*: where new atoms are added to the existing template. These atoms are supplied as a library of fragments by the user. A randomly selected fragment is joined to the template by forming a bond between a template atom and a fragment atom such that the bond formed is aligned with a heavy atom–hydrogen bond in each moiety. The hydrogens involved must then be deleted from the resulting molecule. At each stage of this process, the atoms are randomly selected with the option of user weightings being applied. Addition of a new fragment is controlled by a van der Waals function, which determines if any atom of the template overlaps with others, either in the same template or in its symmetry and periodically related images. If the addition of the new fragment violates this overlap criterion, additional actions, as listed below, are performed to reduce the conflict. If the clash is not removed, the new fragment is rejected. To allow better opportunities for growth, van der Waals radii are scaled to allow a degree of overlap, the scaling factor being specified by the user.

(2) *Rotate*: where the last fragment added is rotated about the new bond formed.

(3) *Shake*: where the template is displaced along a random vector with respect to the host.

(4) *Rock*: where the template is randomly rotated as a rigid body with respect to the host.

(5) *Bond twist*: where a randomly selected bond joining fragments in the template is rotated.

(6) *Ring formation*: where atoms which are nth order neighbours and are within a cutoff distance are joined, forming a ring (with consequent elimination of hydrogen). The order n of the neighbours can be specified to form different sized rings; $n = 5$ forms 6-membered rings.

(7) *Template energy minimisation*: the energy of the template is minimised either as an isolated molecule or in the environment of the host. Currently the code utilises either Discover [23] from MSI, using the cff91 parameter set, [24,25] or MOPAC [26] as external minimisers.

After each action the template may, or may not, be assessed according to a user defined probability. If an assessment is required the cost function (Eq. (1)) is evaluated and the template checked for internal clashes or conflicts with its symmetry related images. The new template is accepted only if the cost function has decreased from the last value and there are no van der Waals clashes. Although it may be expected that evaluating the template after every modification may be more beneficial, this would not encourage growth in such confined voids. Typically the growth process is initiated from a supplied seed molecule and continues until the cost function has been reduced to a pre-defined value.

During actions (2)–(6), movements of the template are made as a series of small steps, the action only continues if f_c has increased. We have found that this procedure allows the template to locate rapidly the largest available space in the host and there to achieve its optimum molecular conformation, in terms of complementing the shape of the void.

3. Application to the design of templates for microporous materials

Previously, we have demonstrated the effectiveness of the method by successfully growing known templates for ZSM-5 and NU-3 [14].

Furthermore, we have been successful in predicting a new template for the formation of a Levyne structure, which was independently used to synthesis a CoAlPO analogue (known as DAF-4) of this structure [7]. Here, we will demonstrate further the capability of our method to generate potential templates for both EU-1 and chabazite.

4. A template for EU-1

The zeolite EU-1 (Space group Cmma, framework type EUO [27]) has a uni-dimensional 10 T-ring (5.8 × 4.1 Å) channel structure in the [100] direction with two channels per unit cell. However, the materials also possesses large, 12 T-ring (6.8 × 5.8 Å), side pockets which lead off the main channel in the [001] direction and are arranged alternately on either side of the [001] channel such that they are related by a 2-fold screw axis in the channel direction. The dimensions of the channels and side pockets make this zeolite a useful catalyst for shape selective reactions such as isopropylation of benzene [28] and *m*-xylene isomerisation [29].

Experimentally reported templates for this structure include pentamethonium [30], hexamethonium [31] and dibenzyl-dimethylammonium [32]. There is also a report of the use of an organic cation (dimethylbenzylamine) and anion (benzyl chloride) combination [32]. This template pair occupies a similar molecular volume to dibenzyl-dimethylammonium and so may be expected to direct the zeolite formation in a similar way to that charged template. We have studied the EU-1 structure using ZEBEDDE to test again the methodology and in particular the ability of the method to grow templates into the side pockets.

Our initial runs were performed without taking into account the crystal symmetry of the unit cell but including the cell periodicity. Since our approach does not currently take into account electrostatic interactions between the framework and template, the distinction between nitrogen and carbon species is not very great. However, restrictions were imposed so that a maximum number of two nitrogens were allowed in any template produced and the construction of N–N bonds was not permitted, so that the molecules generated were more likely to be stable. A library of nine fragments was used; methane, ethane, benzene, ammonia, ammonium, propane, pyrrole, adamantane, cyclohexane. Methane was chosen as the seeding molecule and was positioned at a starting position in the centre of mass of the unit cell. As can be seen in Fig. 1, this region is part of the dense wall between the channels and so the cost function will have a very low value. The move-

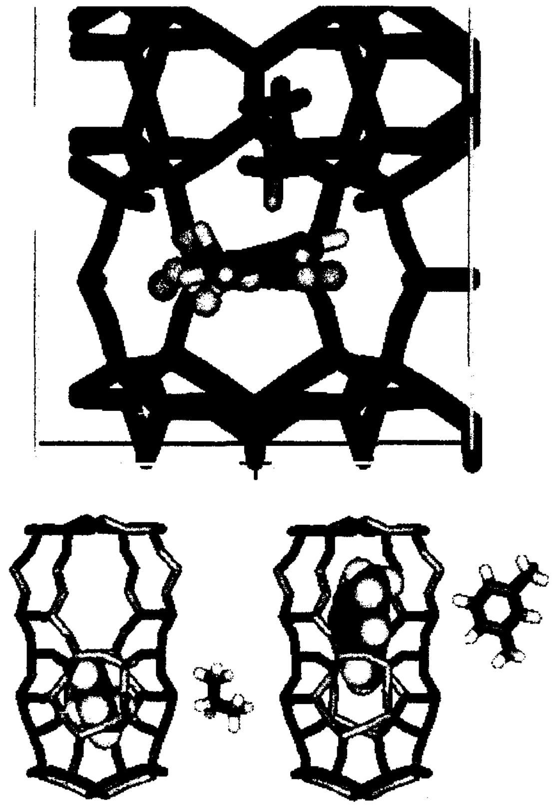


Fig. 1. Initial template constructions for EU-1 with no crystal symmetry imposed. Top: The growth procedure, the template seed is initially placed at the centre of mass of the unit cell, as growth proceeds the maximisation of the cost function forces the molecule to move into the void space of the channel system. After short runs the molecular fragments are found to occupy the side pockets (bottom left) or the intersections of a side pocket and the channel (bottom right).

ment of the molecule is controlled by attempting to maximise the cost function and so the template molecule is quickly moved into one of the channels. After further iterations most of the small molecules grown were found to be located in a side pocket or at the junction of the channel and side pocket, as shown in Fig. 1.

Growth without crystal symmetry, then, suggests one template per side pocket may be an expected arrangement of template molecules in the EUO structure. This result agrees with earlier work on the simulation of the location of both the bis-quaternary amines [9] and dibenzyl-dimethylammonium [33]. The positions of the side pockets may be related by a closed subset of the space group operators and the imposition of the same symmetry on the growing template in our simulation allows us to take account of template–template packing interactions. We chose operators corresponding to the positions x, y, z, $-x$, $-y$, $-z$, which relate the two channels in the unit cell and $x+1/2$, $-y+1/2$, $-z$ and $-x+1/2$, $y+1/2$, z, which give a screw axis relating the side pockets within a channel. This set is closed since a second application of any operator returns to another of the chosen positions. e.g. starting at $-x+1/2$, $y+1/2$, z and applying the inversion operator gives $x-1/2$, $-y-1/2$, $-z$ from whence the unit translation 1, 1, 0 returns to position 3 in the above list.

With this crystal symmetry imposed longer runs (3000 attempted actions) were undertaken using the same library and bonding restrictions as before. The use of hydrogen weighting, to allow preferential substitution at various parts of the template was also investigated using three different weighting schemes; (1) all template hydrogens equally weighted; (2) the hydrogens of new fragments were weighted more favourably than those previously incorporated, a scheme expected to encourage the growth of linear chains of fragments since it is always most likely that addition will occur to the last fragment added; and (3) the hydrogens of new fragments were weighted lower than those previously incorporated, a scheme which was expected to have the reverse effect of (2) i.e. produce templates with many substituents on the initial seed.

Fig. 2 shows a representative set of templates produced by each scheme with the remaining atoms of the methane seed highlighted in each case. With no hydrogen weighting we find a tendency for the program to produce branched aminoalkanes (such as 1.1, 1.4 and 1.5). Weighting scheme 2 again produces long molecules but now the number of additions in the chain direction combined with the pore structure leads to a much higher tendency to form ring structures. For example, in Fig. 2, 2.1, 2.2 and 2.4 all contain rings formed by closure of a chain rather than as a direct consequence of adding a fragment which is itself a ring. Forcing growth to be more centralised by using weight-

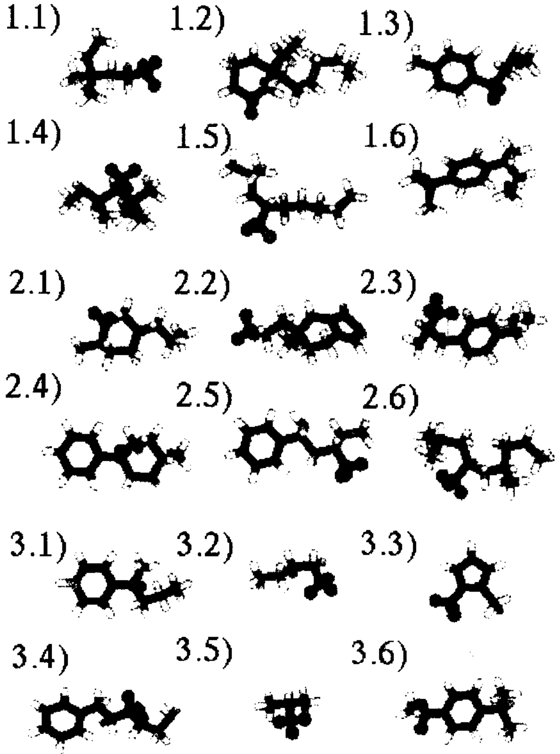


Fig. 2. A typical selection of templates grown for EU-1 with crystal symmetry imposed. These were grown using the weighting schemes discussed in the text and are labeled according to (weighting scheme)·(structure number).

ing scheme 3 leads to much smaller molecules than in the other two cases.

As was noted in our earlier work on the zeolite structure LEV [14] the confined space of the zeolite imposes its shape on the molecules produced by the de novo procedure. Thus, some of the templates produced consist of alkanes with uncharacteristic conformations, for example, 1.2 and 2.6. The use of a ring construction action allows us to impose rigidity on these structures by closing sections into 6-rings. However, currently this ring closure is limited to producing saturated ring structures and so these are more common than we would expect for experimental templates which tend to contain substituted saturated rings (for example dibenzyldimethylammonium in the current case). With this in mind we note that several of the structures we produce are of similar size and shape to the experimental template dibenzyldimethylammonium with 2.4 and 2.6 being particularly close to this structure. The packing of the template in the zeolite is shown in Fig. 3. The code has also produced long chain aminoalkanes of similar dimensions to the known hexamethonium and pentamethonium templates, these too are found to pack at a density of one per side pocket (Fig. 3).

In the case of EU-1 we have found that the large size of the side pockets appears to favour templating by molecules at the level of one per side pocket. Molecules of similar structural form to the known templates have been generated with this level of packing. It is interesting to note that, from experimental reports, there appears to be some control on the level of Al included in the framework by the correct choice of template. Using the hexamethonium ion Si/Al ratios from 20–70 have been reported [28,34] the dibenzyl-dimethylammonium template produces Si/Al ratios in the range 140–300 whilst higher ratios are possible (115–530) using the binary dimethylbenzylamine/benzyl chloride [29] template. This observation ties in with the idea that Al is included in the framework as an anion to the templating cation since the hexamethonium has a formal charge of $+2e$, dibenzyl-dimethylammonium $+e$ and the binary template combination is neutral. Correspondingly this suggests that each template is present in the same concentration, as predicted from our simulations.

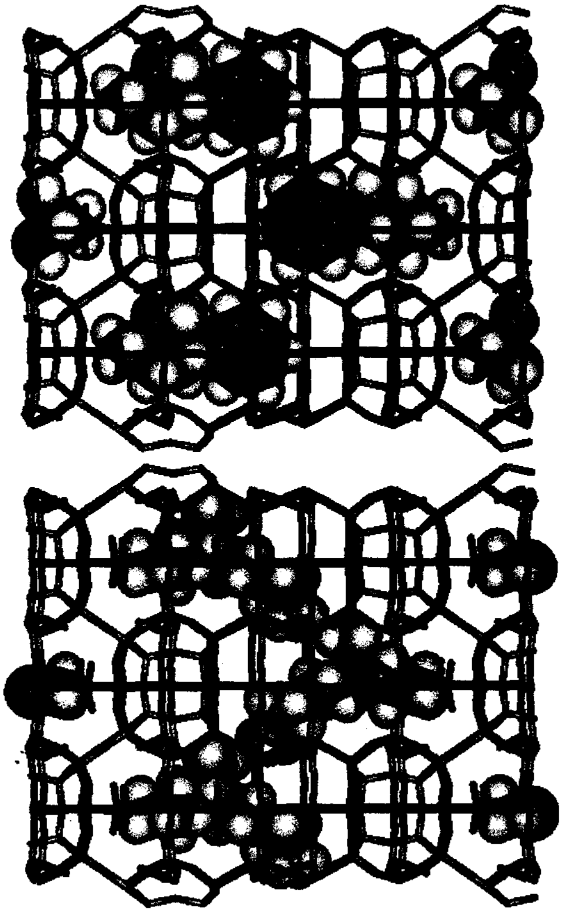
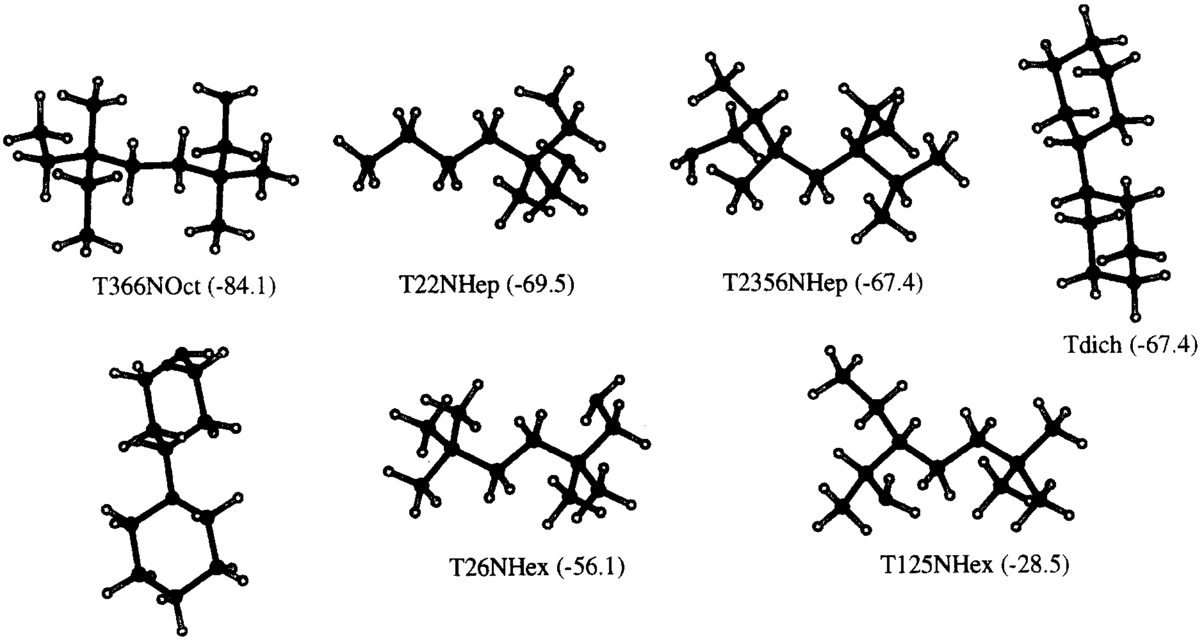


Fig. 3. The packing of template molecules using the symmetry operators imposed during growth. Examples shown are the templates 2.4 (left) and 1.5 (right) from Fig. 2. The structures are viewed down (010) with the channel direction from left to right (one channel is present across the centre of each structure) and the side pockets aligned top to bottom.

5. Optimising a template to form chabazite with low template and metal concentrations

The microporous chabazite structure (IZA code CHA) can be prepared both as an aluminosilicate [35] and an aluminophosphate [36] material with a wide range of substitutents in the framework. The CHA structure consists of cages interconnected via 4, 6 and 8-ring windows. It is particularly interesting to note that neither a pure silica or aluminophosphate analogue has been prepared with this structure and indeed, a common feature of the compositional variants so far prepared is that they all have a relatively high concentration of aliovalient metal in the framework. This metal content, making the framework anionic, compensates for the cationic charge on the template used in the synthesis. Subsequently, the framework metal leads to the generation of Brønsted acid centres and ion exchange capacity. We have recently studied the templating of a CoAPO phase with the chabazite structure which forms with triethylamine as a template [37]. We found that the chabazite phase only becomes stabilised when the structure has a template concentration equivalent to 2 triethylamine molecules per cage and consequently requires two cations with a charge of 2 + to substitute for Al in the framework to maintain charge neutrality. The need for this strict template sub-lattice leads to the possibility of impurity phases and concentration gradients [38]. We consider that these are general features of the synthesis of chabazitic structures. Although essential for catalytic activity, excessive metal concentrations can have deleterious effect, producing for example weaker acid sites. It would therefore be useful to be able to prepare chabazitic materials with lower metal concentrations. Furthermore, it would be of particular interest if, by careful choice of template, the siting of the metal in the framework could be controlled to a degree. One approach to this is to utilise a template which has a lower, yet localised, charge density than triethylammonium and which will form the structure at lower relative concentrations. We have therefore applied ZEBEDDE to design leads for such a template.

A series of runs were performed with the code, using methane, ethane, propane and bu-



T366NOct (-84.1)

T22NHep (-69.5)

T2356NHep (-67.4)

Tdich (-67.4)

T26NHex (-56.1)

T125NHex (-28.5)

Tdipi (-59.2)

Fig. 4. Sample of candidate templates grown in the chabazite structure with their binding energy (kJ mol^{-1}). Nitrogen atoms are shown in the darker colour. Tdipi was generated from Tdich and reoptimised in the unit cell.

tane as seed molecules, a random orientation of the seed being used in each case. The selection of fragments from the library (as used above) was biased towards methyl and ethyl fragments. Further runs were performed with the formation of cyclic structures being strongly encouraged by using a hydrogen weighting scheme [14]. The symmetry of the template was specified to provide one template molecule per unit cell. A total of 25 new templates was generated of which 6 (Fig. 4) satisfied the supplied criteria that the average template-framework distance was less than 3.0 Å. Each of these templates was subsequently minimised in a rigid unit cell of siliceous CHA and also in vacuo. We calculated the binding energy (E_{inter}) as the difference between the energy in the zeolite and in vacuo, which provides a measure of the potential efficacy of the molecule as a template for the structure [9].

In addition to the new templates generated, the method was successful in generating existing experimental templates, or close analogues of these. Cyclohexylamine and both alkyl analogues and positional isomers of tetraethylammonium and diethylethanolamine, were generated, all of which are known to form chabazitic materials [36]. In a separate simulation, we specified an inversion centre in the unit cell so as to generate two templates in a single cage, as we have found the case for triethyamine [37]. In this simulation, we find that of 10 templates, triethylamine and two close analogues, $(CH_3CH_2)_2CH_2NH_2$ and $(NH_2CH_2)_2CC_2H_5$ are generated.

We now focus on the new templates generated shown in Fig. 4. A number of these candidate structures are derivatives of templates found to form chabazitic structures (T22Nhep is similar to diethanethanolamine) or have similar features to homologous series found to be successful templates, in particular the bis-quaternary amines [39] (for example T366NOct, T26NHex). A common feature of many of the acyclic candidate templates is the presence of a $-CH_2CH_2-$ group which bridges the two halves of the chabazite cage. We then find alkyl and amino groups which fill the remaining cage volume. The length of these branches is typically 2 heavy atoms, similar to the ethyl groups found in the experimental template triethylamine. The strongest bound candidate is 3,3,6-trimethyl, 6-ethyl aminooctane (T336NOct) with a binding energy of 84 kJ mol^{-1}. For triethylamine we find a binding energy of 72 kJ mol^{-1} per molecule, although there are two such molecules per cage [37]. Indeed, T336NOct is closely analogous to triethylamine, if two triethylamine molecules are joined by an ethyl bridge. Fig. 5 shows the generated candidate template in a chabazite cage and the calculated position of 2 triethylamine templates [37]. T336NOct appears to possess a very similar void filling volume as the triethylamine molecules. Furthermore, it satisfies our criteria that the charge density is lower. Therefore, if a chabazite material can be prepared with this template, then we would expect the formation of phases with lower metal

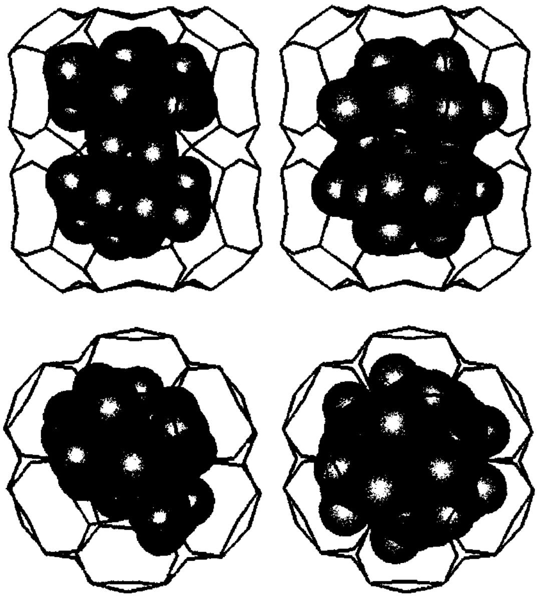

T366NOct 2 triethylamines

Fig. 5. Comparison of the void filling of the most strongly bound generated template T366NOct and the calculated position [37] of the experimental template triethylamine.

concentrations than can be prepared with triethylamine.

A difficulty with the candidate compounds generated so far is their availability for synthetic studies. We have calculated that a number of branched amines are reasonable candidates as templates for chabazite. However, these compound are not readily available from major chemical suppliers and would require specialist synthesis, limiting their applicability as a commercial route for large scale production. Thus, we have modified one such candidate, dicyclohexane, forming 4-piperidinopiperidine (Tdipi) as shown in Fig. 4. Not only is this compound readily available, it will also be more amenable to incorporation in an aqueous gel. However, we should also note that if dicyclohexane could be incorporated into a non-polar synthesis gel, and is indeed suitable shape for the formation of CHA, then such a gel would be conducive for forming the hitherto elusive siliceous or aluminophosphate end-members of this structure type. We note that gallophosphate (analogues of AlPOs) have been recently formed from such non-polar gels [40]. We calculate that the binding energy of 4-piperidinopiperidine is lower than that of dicyclohexane, a consequence of it being slightly longer than its alkyl counterpart. Furthermore, both of these molecules are flatter than the other templates and may therefore favour the formation of layered phases. However, a possible advantage 4-piperidinopiperidine as a template is that the amino groups in this molecule, even when rotational conformations are considered, are more localised than in the acyclic templates, which may result in a localisation of the metal substituents in the framework. Therefore, we consider that 4-piperidinopiperidine may favour the formation of the chabazite cage, and we believe that this molecule has potential as a templating agent and are now conducting a synthetic study using this compound.

In this study we have attempted to demonstrate further the potential of de novo methodologies to generate potential templates for microporous materials. We have specifically attempted to generate candidate compounds which may allow access to new framework compositions by controlling the concentration of the template and its charge and also by attempting to direct the siting of the framework metal. We have generated a number of promising candidates which will now undergo synthetic evaluation.

6. Conclusions

We have shown how de novo molecular design can be used to identify new molecules which have potential as templates in the synthesis of microporous materials. The method clearly has great scope for generating *new* templates for existing materials. Furthermore, an infinite number of periodic structures formed from corner-sharing SiO_4 tetrahedra is possible and it has been shown that there are only small thermodynamic limitations for the formation of these structures [41]. We therefore envisage applications for the formation of new, hitherto regarded hypothetical structures and also for designing templates which allow access to those materials which to date are only known as natural minerals and for the formation of end members of structures which are found as mixed polymorphs.

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