[1] a) S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pramana* **1977**, *7*, 471; b) S. Chandrasekhar in *Handbook of Liquid Crystals*, *Vol. 2B* (Eds.: D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**, p. 749.
[2] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485.
[3] O. Y. Mindyuk, M. R. Stetzer, P. A. Heiney, J. C. Nelson, J. S. Moore, *Adv. Mater.* **1998**, *10*, 1363.
[4] a) J. M. Lehn, J. Malthête, A. M. Levelut, *J. Chem. Soc. Chem. Commun.* **1985**, 1794; b) G. Lattermann, *Mol. Cryst. Liq. Cryst.* **1990**, *182B*, 299.
[5] A. Liebmann, C. Mertesdorf, T. Plesnivy, H. Ringsdorf, J. H. Wendorff, *Angew. Chem.* **1991**, *103*, 1358; *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 1375.
[6] a) S. Höger, A.-D. Meckenstock, S. Müller, *Chem. Eur. J.* **1998**, *4*, 2421; b) S. Höger, *J. Polym. Sci. Part A* **1999**, *37*, 2685.
[7] One of the basic conditions for the formation of columnar liquid crystalline phases is an optimal coverage of the periphery of the central core by lateral chains (B. Kohnke, K. Praefke, *Chem. Z.* **1985**, *109*, 121). Owing to the size of our rigid structure and the attachment of only four octadecyloxy groups, the appearance of such a mesophase is improbable.
[8] When **2** is heated for a longer period above 220 °C, a temperature well above the clearing point of **4**, we cannot eliminate the possibility of partial decomposition.
[9] The exact type of the nematic phase (e.g., nematic discotic, nematic-columnar, etc.) could not be determined yet.
[10] Crystals of **4** were grown from a CH_2Cl_2 solution by slow evaporation. Crystal structure data for **4**: $C_{174}H_{220}O_8$, triclinic, space group $P\bar{1}$, $a = 9.729(4)$ $b = 16.124(4)$ $c = 24.746(7)$ Å, $\alpha = 106.248(21)$, $\beta = 98.083(29)$, $\gamma = 89.741(20)$ °, $V = 3687.6$ Å^3, $\rho_{calcd} = 1.069$ g cm^{-3}, $\mu = 4.633$ cm^{-1}, $T = 165$ K. Nonius CAD4 diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, $\theta/2\theta$ scans, 5958 independent reflections, of which 3028 were observed ($I > 3\sigma(I)$), empirical absorption correction. The structure was solved by direct methods (Shelxs) and refined by full-matrix least-squares analyses on F with anisotropic temperature factors for C an O. The hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode. The refinement converged at $R = 0.0569$ and $R_w = 0.0571$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139443. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[11] Nematic and smectic phases can be also observed for some other alkylated shape-persistent macrocycles, for example, a) C. C. Ling, R. Darcy, W. Risse, *J. Chem. Soc. Chem. Commun.* **1993**, 438; b) N. Usol'tseva, K. Praefcke, D. Singer, B. Gündogan, *Liq. Cryst.* **1994**, *16*, 601. However, in all those cases, the interior of the rings is much smaller, such that a complete intraannular arrangement of the side chains can be excluded.
[12] V. Enkelmann in *Electronic Materials: The Oligomeric Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, p. 295.
[13] B. Wunderlich, *Macromolecular Physics*, *Vol. 1*, Academic Press, New York, **1973**, p. 91.
[14] a) S. Höger, V. Enkelmann, *Angew. Chem.* **1995**, *107*, 2917; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2713; b) D. L. Morrison, S. Höger, *Chem. Commun.* **1996**, 2313.
[15] The investigation of the conformation of **4** in the melt as well as the extension of this concept to macrocycles with a fixed intraannular arrangement of the flexible side groups is part of our current studies.

De Novo Prediction of Inorganic Structures Developed through Automated Assembly of Secondary Building Units (AASBU Method)**

Caroline Mellot Draznieks,* John M. Newsam, Alan M. Gorman, Clive M. Freeman, and Gérard Férey*

Simulations of the crystal structures and of the properties of solids are topical and were recognized early in materials science as a challenging task. Several computational approaches to predicting crystal structures have been described, such as:

1) Local optimization of approximate, preconstructed models by potential or first principles methods.[1, 2]
2) Monte Carlo or genetic algorithm based sampling of packing arrangements of molecular crystals.[3]
3) Assembly of atoms or ions assuming unit cell and symmetry by, for example, simulated annealing[4–9] or a genetic algorithm.[10]
4) Operations for combining two-dimensional periodic sheets.[11]
5) Enumeration of framework structures[12–14] given defined symmetry and connectivity constraints.[15]

The motivation for these efforts is to aid the often difficult process of crystal structure determination, to help rationalize different but related structure types, or to help limit the domain of structures that are possible to a given system.[5] In certain cases, combination with other desired structural attributes, for example microporosity, can allow these structure prediction methods to be applied in a genuine design sense.

In general, we lack an ability to develop viable synthesis routes based solely on a knowledge of the crystal structure. Inspired by molecular chemistry, for which rational synthesis routes are almost invariably developed, it is interesting to consider how rational approaches might be developed for the synthesis of inorganic structures, for example, zeolites[16, 17] or larger pore materials.[18–21] The desire to develop virtual libraries that might be accessible by rational synthesis is made more pressing by the recent emergence of combinatorial and high-throughput experimentation approaches to inorganic chemistry (see [22, 23] and references therein).

The prediction of periodic inorganic structures is a difficult task involving many degrees of freedom, which are related to the chemical and structural diversity of inorganic structures.

[*] Dr. C. Mellot Draznieks, Prof. G. Férey
Institut Lavoisier - UMR CNRS 8637
Université de Versailles St. Quentin
45 Avenue des Etats-Unis, 78035 Versailles Cedex (France)
Fax: (+33) 1-3925-4358
E-mail: mellot@chimie.uvsq.fr, ferey@chimie.uvsq.fr
Prof. J. M. Newsam, Dr. A. M. Gorman, Dr. C. M. Freeman
Molecular Simulations, Inc.
9685 Scranton Road, San Diego, CA 92121-3752 (USA)

[**] This work was supported by Centre National de la Recherche Scientifique. We thank F. J. J. Leusen, G. Engel, and A. K. Cheetham for useful assistance and discussions.

  1433-7851/00/3913-2270 $ 17.50+.50/0

Any means to reduce the number of degrees of freedom is potentially valuable. Assuming, where appropriate, the occurrence of specific secondary building units (SBUs) is one such means. Many periodic inorganic structures can be regarded as elementary units, and, more generally, as SBUs assembled in one, two, or three dimensions. Related structures may be differentiated by the mode of interconnection between the SBUs. However, while SBUs have been used widely for descriptive and characterization purposes,[12, 16, 24] the exploitation of SBUs in a computational means of constructing models has not been developed until now.

Here, we describe a general computational methodology (automated assembly of secondary building blocks, AASBU) for producing virtual libraries of viable inorganic structures based on secondary building units (SBUs), implemented according to the following design criteria: 1) no explicit constraints on the nature or size of the SBUs involved, 2) no explicit constraints on unit cell dimensions but, optionally, on space group symmetry, 3) an ability to accommodate one or more types of SBUs, with the possible inclusion also of occludates, such as template molecules, 4) accommodation of differing modes of inter-SBU connection, allowing, for example, corner-, edge-, and face-sharing modes, and 5) broad flexibility in the definition of the linkage points. This use of SBUs reduces dramatically the number of possible structure types, relative to a 'free atom'[6–10] or even 'free tetrahedron' approach;[5] the huge number of generated structures has been a major hindrance to the broader application of previous structure prediction methods.[5] Perhaps more importantly, however, we consider that the virtual libraries of inorganic structures developed by this method will, at least for certain structural families, prove more amenable to rational synthesis. The building unit comprising two octahedra and two tetrahedra in a corner-shared configuration (see Figure 1), for example, is known to form under synthesis conditions[25] that can be adjusted to yield two different periodic assemblages, the three-dimensional structure AlPO-CJ2[26] and its layered form isotype with the minyulite structure.[27]

Apart from the SBU itself, the two assumptions in a given simulation are the number of SBUs per unit cell and the space group symmetry. For the most general case a search can be performed in the space group *P*1. A final determination of the symmetry of the generated structures is systematically performed with a "Find_Symmetry" analysis. The simulations provide a list of candidate structures, sorted by cost, with their final space group, cell parameters, and atomic positions that can then be compared with existing structures by using any of a portfolio of crystallographic tools.

The preliminary step in the AASBU method consists of elaborating a suitable library of SBUs, for example in the subsequent discussion, M_xL_y (M: central metal atom; L: coordinating or 'ligand' atoms). Figure 1 shows illustrative examples of SBUs extracted from known families of inorganic structures. The next step consists of defining the rules that control the possible assembly of the SBUs during the subsequent simulation stages. These rules are encapsulated in a forcefield that includes 'sticky-atom' pairs. The SBUs are treated as rigid bodies, with the inter-SBU interactions parameterized on an atom–atom basis by a simple Lennard-Jones expression for the energy of interaction between pairs of atoms *i* and *j*, as defined in Equation (1). The 'sticky

$$E_{ij} = \varepsilon_{ij}[(r_{ij}^{*}\, r_{ij}^{-1})^{12} - 2(r_{ij}^{*}\, r_{ij}^{-1})^{6}] \quad (1)$$

atom' pairs are those that, when combined, form the inter-SBU linkages; these are parameterized as a highly attractive potential well with a minimum at a very short $L_i \cdots L_j$ separation. This potential function has no direct physical meaning. It serves simply to 'glue' together the SBUs at the linkage points during subsequent simulation steps.

A repulsive potential between $M_i \cdots M_j$ pairs prevents SBUs from overlapping with each other, and this repulsive potential is also tuned in order to favor either corner-, edge-, or face-sharing during the assembly process. This tuning provides a bias in favor of the target mode of linkage, but does not exclude other connection modes, which can then occur also as local minima in the sampled configurational space. A repulsive potential between $M_i \cdots M_j$ pairs discourages undesirable local minima corresponding to proximate, but unconnected SBUs. For example, typical values of the various atom–atom potential parameters in the Lennard-Jones expression for a corner-shared target configuration in the case of octahedra-based and tetrahedra-based building units is given in Table 1. The total cost or "energy" of a given

Table 1. Typical Lennard-Jones potential parameters used in developing the cumulative cost function[a] favoring corner-shared configurations.

	Octahedra-based building units		Tetrahedra-based building units	
	ε_{ij} [kcal mol^{-1}]	r_{ij}^{*} [Å]	ε_{ij} [kcal mol^{-1}]	r_{ij}^{*} [Å]
$L_i \cdots L_j$	400	0.20	400	0.2
$M_i \cdots M_j$	1.00	4.40[b]	1.00	3.9
$M_i \cdots L_j$	1.00	2.24	1.00	1.9

[a] Charge terms are not included in this implementation of the AASBU methodology. [b] A reduction of the r_{ij}^{*} parameter for the $M_i \cdots M_j$ pairs (3.5 Å, for example) favors edge-sharing configurations of octahedra-based building units.

configuration of SBUs in a unit cell, E_{total}, is then computed as the sum over the set of unique SBUs of the Lennard-Jones terms involving dissimilar $L \cdots L$, $M \cdots L$, and $M \cdots M$ pairs, as defined in Equation (2). The magnitude of this cost function

$$E_{\text{total}} = \sum_{\text{SBUs}} (E_{L\cdots L} + E_{M\cdots L} + E_{M\cdots M}) \quad (2)$$

provides an estimate of the degree of connectivity of a given arrangement of SBUs. Since a given SBU is defined by its geometry and its set of potential connection points, specific connection modes are easily favored or discouraged by assigning each ligand atom L with attractive or repulsive parameters. The simulations will then typically yield structures with different degrees of connectivity, their final ranking by cost being dependent on the initial parameter choices. Differing modes of interconnection, such as corner-, edge-, face-sharing, can be promoted, not only through the tuning of the $M_i \cdots M_j$ repulsive potential, but also by direct inclusion of corner-, edge-, face-sharing polyhedra within the SBUs themselves (Figure 1).

  1433-7851/00/3913-2271 $ 17.50+.50/0

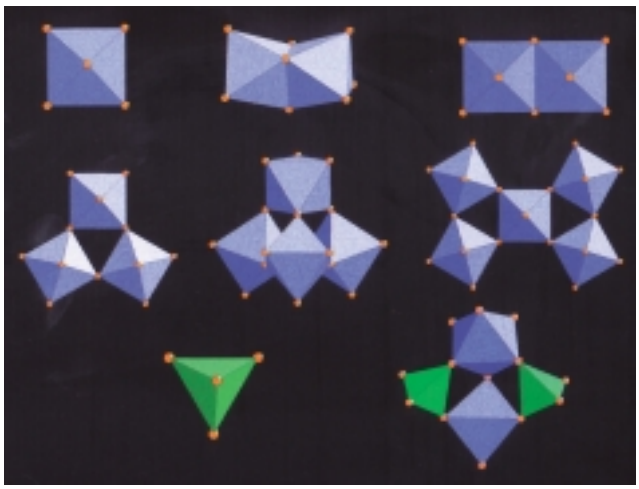

Figure 1. Examples of building units used in the AASBU method (green: tetrahedra, blue: octahedra). Simple polyhedra, including specimens with corner-, edge-, and face-sharing polyhedra, are shown together with a more complex SBU made of both octahedra and tetrahedra.

With the set of SBUs and potentials defined, the candidate periodic structures are generated by using a cascade of simulations[28] that entails five major steps:

1) Periodic SBUs trial arrangements are randomly generated by a simulated annealing procedure.[3] The angular degrees of freedom of each unique SBU are sampled by a Metropolis Monte Carlo algorithm.[29] At each such step, both the cell size and the distances between SBUs are adjusted to relieve close interatomic contacts, leading to successive phases of cell contractions and expansions. As the simulated annealing proceeds configurations of lower cost are stored;[3, 5] a typical simulation run within a 10000–300 K 'temperature' range, yields a final set of some 10^4 trial periodic configurations of SBUs.
2) The trial arrangements are reduced to a set of unique arrangements, corresponding to unique local minima; redundancies are removed through the comparison of radial distribution functions and simulated diffraction patterns.[3]
3) The resulting set, which contains typically some 10^3 unique arrangements, is minimized with respect to the cost (energy).
4) After the structure optimization, the redundant arrangements are removed. At this stage, the simulation yields typically a few hundred possible SBUs configurations, which are ranked by cost or degree of connectivity.
5) For each such configuration, the sets of 'sticky atoms' at short separations (typically pairs) are reduced to single atoms, and the space group symmetry of the arrangement determined automatically by the Find_Symmetry algorithm.[30, 31]

The result is a list of predicted structures sorted according to space group and cost, with cell parameters and atomic positions suitable for direct comparison with other libraries of inorganic crystal structures, or based on corresponding crystallographic data. The computing time depends on the number of atoms in the SBU, the stipulated number of SBUs per unit cell, and the details of the simulated annealing schedule. A typical run for an SBU composed of a trimer of octahedra (Figure 1) requires some three hours CPU time on an Octane SGI R12000 workstation operating at 300 MHz.

To demonstrate the viability of the AASBU method in structure prediction, we use simple building units extracted from known families of inorganic structures. First, to explore structure types based on corner-sharing octahedra, such as the perovskite, bronze, and pyrochlore families, SBUs composed of a discrete octahedron, ML_6, and of the trimer M_3L_{15}, the tetramer M_4L_{18}, and the pentamer M_5L_{24} were built according to the known geometry of TiO_6 in rutile (M–L = 2 Å) (Figure 1). Using a corner-sharing oriented forcefield (Table 1), we generated candidate structures with one SBU per asymmetric unit, either in *P*1 or using various space group symmetry constraints.

The known three-dimensional structure types based on corner-sharing octahedra were sucessfully generated (Table 2). For example, a simulation with ML_6 as the SBU in the space group *C*2/*c*, yields the cubic perovskite-type structure (space group $Pm3-m$). The other well-known tilted perovskite arrangements were also obtained in other space groups.[32] The pyrochlore structure type ($Fd\bar{3}m$) was generated in *P*1 using the tetrameric SBU, M_4L_{18}, appearing ranked as the lowest cost structure among a list of 50 candidates. The AASBU simulations generated all known three-dimensional structure types based on corner-sharing arrangements of the pentameric SBU, M_5L_{24}, namely the $Ba_4CoTa_{10}O_{30}$ type structure, the intergrowth tungsten bronze and the tetragonal tungsten bronze (Figure 2A), demonstrating the ability of the AASBU method to highlight topological affiliations within related materials.

Table 2. Examples of existing structures based on octahedra as predicted by the AASBU method, using various SBUs and space groups.

SBU	Space group used	Predicted structure	Symmetry analysis of the predicted structure
three-dimensional structures based on corner-sharing octahedra			
ML_6	*C*2/*c* (15)	cubic perovskite	$Pm\bar{3}m$ (221)
ML_6	$P2_12_12_1$ (19)	tilted perovskite	$P2_12_12_1$ (19)
M_3L_{15}	*P*1 (1)	hexagonal tungsten bronze	*P*6/*mmm* (191)
M_4L_{18}	*P*1 (1)	pyrochlore	$Fd\bar{3}m$ (230)
M_5L_{24}	*P*1 (1)	$Ba_4CoTa_{10}O_{30}$	*Cmmm* (65)
M_5L_{24}	*C*2 (5)	intergrowth tungsten bronze	*Fmm*2 (42)
M_5L_{24}	*P*4/*m* (83)	tetragonal tungsten bronze	*P*4/*m* (83)
other structures			
ML_6	*C*2/*c* (15)	NaCl	*Cmca* (64)
ML_6	*C*2/*c* (15)	V_2O_5	*C*2/*c* (15)
ML_6	$P2_12_12_1$ (19)	rutile (TiO_2)	$P\bar{4}2_1m$ (113)
ML_6	$P2_12_12_1$ (19)	ramsdellite (γ-MnO_2)	*Pnma* (62)

Using an elementary octahedron as SBU with a corner-sharing oriented forcefield (Table 1), generates a series of known structure types containing both edge- and corner-sharing octahedra in addition to rutile (TiO_2), such as ramsdelite (γ MnO_2), V_2O_5, and NaCl (see Table 2). Combining the use of an edge-shared dimer, M_2O_{10}, as SBU with a corner-sharing oriented forcefield (Table 1) leads to a series of structure types, including both known types such as $CaTa_2O_6$

  1433-7851/00/3913-2272 $ 17.50+.50/0

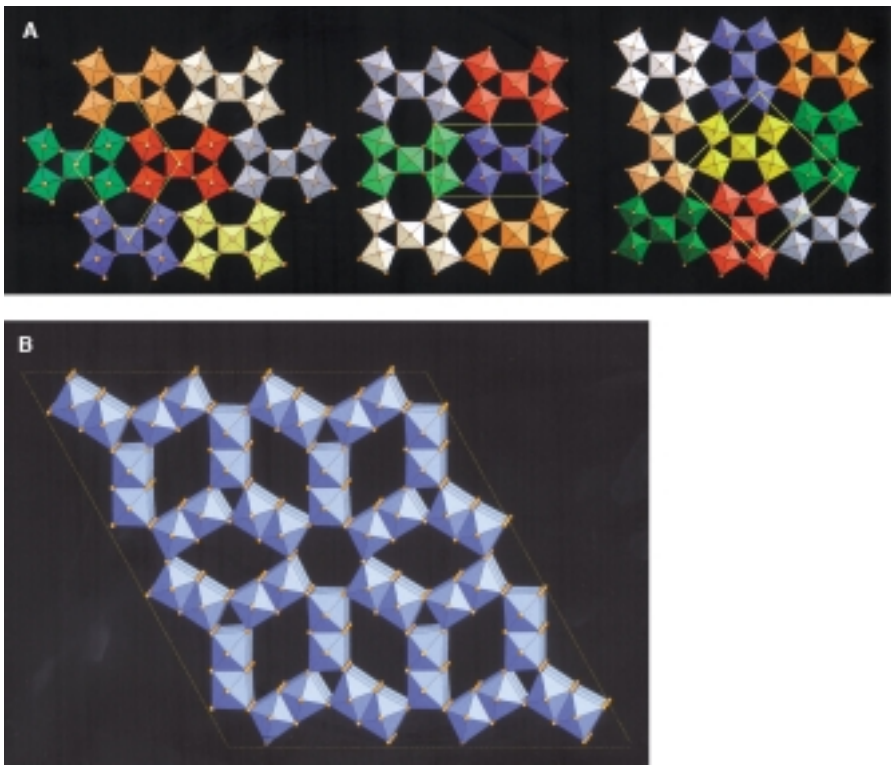

Figure 2. A) Topologic filiation between existing inorganic structures based on the pentameric SBU, M_5L_{24}, as predicted by the AASBU method. Left: $Ba_4CoTa_{10}O_{30}$, center: intergrowth tungsten bronze ($TlCa_2Ta_5O_{15}$), right: tetragonal tungsten bronze. B) New framework topology of a porous oxide (MO_3) as predicted by the AASBU method, using an edge-shared dimer, M_2O_{10}.

and $PbSb_2O_6$, as well as apparently novel microporous frameworks (Figure 2B). New metal oxides with structures based on interlinked octahedral units are topical; for example, several manganese oxide structures show interesting ion-exchange, adsorptive, magnetic, and electrochemical properties.[33] The present simulation results demonstrate the feasibility of the AASBU approach, and suggest possibilities for the a posteriori synthesis of multifunctional microporous oxides.

Continued progress in the synthesis and characterization of zeolites and related crystalline microporous solids has led to an expanding family of more than 100 observed framework structure types;[16] libraries containing many thousands of hypothetical framework structures have already been developed by several authors. Given this history of differing approaches to framework structure prediction, we have applied the AASBU method using a corner-sharing oriented forcefield to the case of an elementary tetrahedron, ML_4 (M–L = 1.65 Å), as SBU (Table 1). The number of structural possibilities is known to be large,[5, 15] so we restricted the simulations to the illustrative cases of one or two SBUs per asymmetric unit, and a selected set of space groups. In each case the anticipated, known structure types were predicted, for example the GME-, FAU-, RHO-, and LTL-frameworks.[16] New frameworks were also produced (Figure 3). Of the two structures ((a) and (b) in Figure 3) that were identified for space group P6/*mmm*, and related to the LTL-framework, the first structure (Figure 3A) is composed of a 3D arrangement of gmelinite cages[12] interconnected through their 6-rings, in contrast to the cancrinite cages[12] in the LTL-framework, but has a similar 12-ring channel system. The second structure (Figure 3B, Table 3) also contains gmelinite cages and has channels that run in the (001) direction circumscribed by 24 tetrahedra, with free aperture dimensions of 17.2×19.4 Å. Each 24-ring channel connects with its six neighbors through gmelinite cages and through six double 8-rings. The pore volume of this hypothetical structure is large; grand canonical Monte Carlo simulations of N_2 adsorption at 1 bar and 298 K, indicate an adsorption capacity of 0.25 mmol g^{-1}. Lattice energy calculations of the LTL-framework and of these two hypothetical frameworks, both with pure silicate compositions, were performed by using the GULP software and default potentials.[34] Relatively small internal energy differences (with -77.10 eV per formula unit, SiO_2, for the LTL-framework, -77.09 eV for structure (a) and -77.05 eV for structure (b)) suggest similar framework stabilities. These results underscore the vast known scope of structural possibilities for microporous framework structures composed of corner-shared tetrahedra, and highlight one advantage of the AASBU method, compared to other approaches, in its being able to accommodate SBUs substantially larger than individual tetrahedra.

In a simple, yet illustrative application of the AASBU method to structures with more than one type of SBU, a series of simulations was performed by using a 1:1 combination of an octahedron and a tetrahedron per asymmetric unit. Figure 4 illustrates a selection of the corresponding structures thus generated.

To conclude, the AASBU method offers a useful means of developing virtual libraries of viable, periodic structures for inorganic solids than can be constructed from predefined secondary building units. The use of a simple cost function developed from atom–atom Lennard-Jones potentials supports both conventional nonbonded interactions and 'sticky atom' pairs parameterized to form the SBU interlinkages during the simulated annealing and minimization procedures. Tailoring of the atom–atom potential parameters allows differing modes of interconnection to be promoted or disfavored. The AASBU method accommodates SBUs of varying complexity and size and its general applicability is demonstrated through generation of both known and apparently novel structures in various families of materials, including bronzes and zeolites. The AASBU approach provides a new de novo methodology for developing virtual libraries of viable structures, a means of rationalizing existing structures in terms of topologic affiliations, and a potential aid

  1433-7851/00/3913-2273 $ 17.50+.50/0

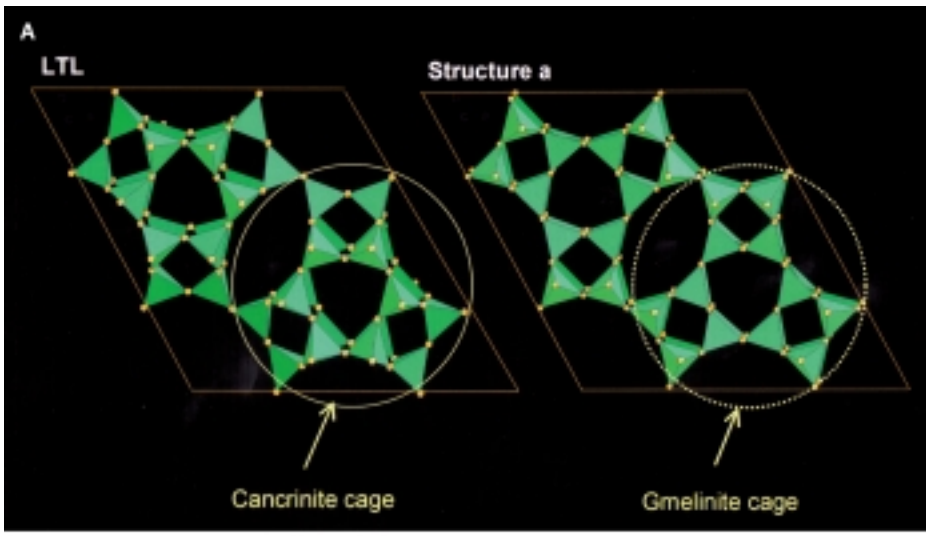

Figure 3. A) Comparison between the LTL-framework and a hypothetical 12-ring channel zeotype-structure (a) as predicted by the AASBU method. B) A second zeotype structure (b) was predicted. The simulated X-ray pattern is shown for its $Si_{48}O_{96}$ form. The associated atomic coordinates as obtained from the simulations are listed in Table 3 (cell volume: 5604.15 Å^3; channels: $24 \times 8 \times 8$; simulated N_2 adsorption capacity at 1 bar and 298 K: 0.25 mmol g^{-1}; framework density: 8.56 tetrahedra (T) per 1000 Å^3).

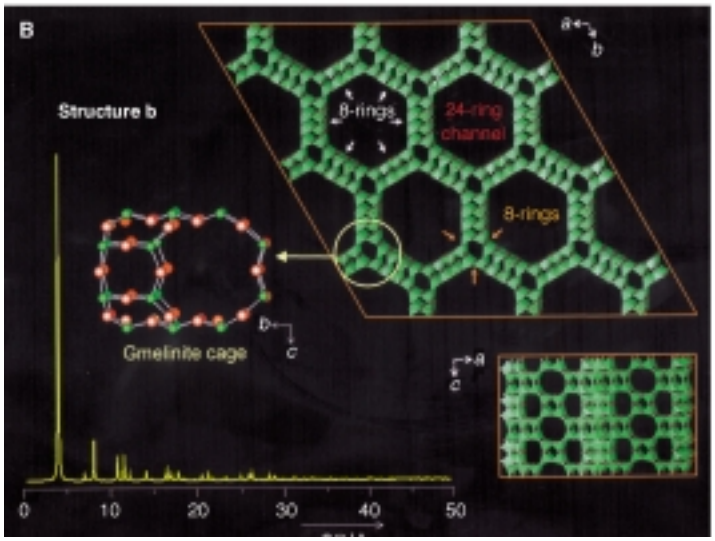

Table 3. Atomic coordinates of the hypothetical zeotype structure given in Figure 3B for the pure silicate form, which was generated by the AASBU method (P6/*mmm* symmetry, $a = b = 24.73$, $c = 10.58$ Å); two elementary tetrahedra served as building units.

Atom	*x*	*y*	*z*
Si(1)	0.530	0.333	0.336
Si(2)	0.466	0.393	0.153
O(1)	0.604	0.396	0.297
O(2)	0.476	0.341	0.264
O(3)	0.526	0.263	0.293
O(4)	0.521	0.333	0.500
O(5)	0.403	0.403	0.192
O(6)	0.455	0.363	0.000
O(7)	0.535	0.465	0.157

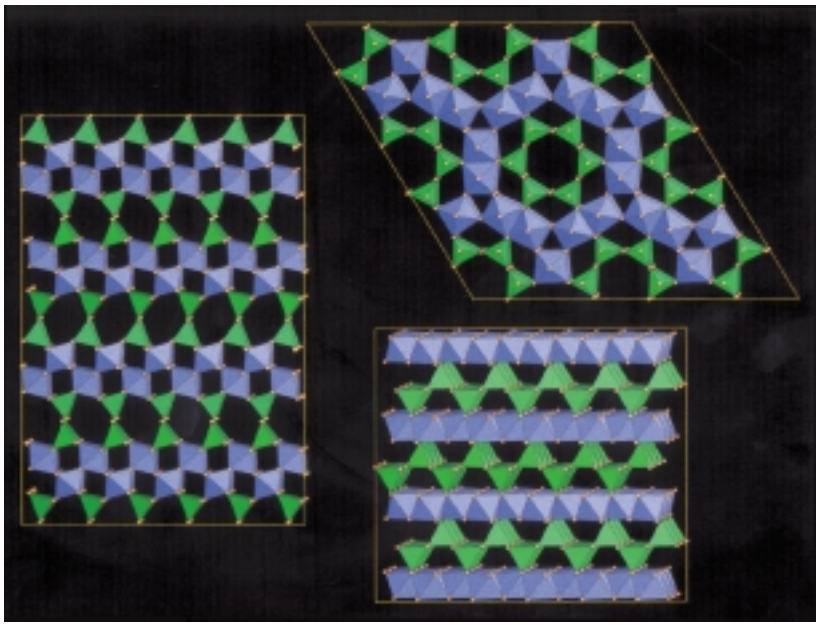

Figure 4. Examples of structures made of two independent SBUs (tetrahedra and octahedra) as predicted by the AASBU method.

in the solution of crystal structures that cannot be solved with conventional methods and for which some insight into the nature of SBUs is available. While not yet proved in practice, it is also considered likely that this SBU-based approach will yield virtual libraries whose members prove more amenable to directed synthesis: this approach opens the field to the a posteriori synthesis of inorganic structures, that is the search for a chemical match between a new predicted topology and adequate framework elements. In addition to more exhaustive studies of tetrahedral, octahedral, and mixed tetrahedral-octahedral frameworks, it will be interesting now to apply the AASBU method to other areas such as the prediction of combined framework plus template structures,[17] the 'design' step in the design-make-test-model high-throughput experimentation cycle, and to the aggregation of larger motifs as SBUs, such as polyhedra, cages, or local structures described in noncrystalline solids.

Received: July 26, 1999 [Z13781]
Revised: March 17, 2000

  1433-7851/00/3913-2274 $ 17.50+.50/0

[1] J. Maddox, *Nature* **1988**, *335*, 201; M. L. Cohen, *Nature* **1989**, *338*, 291; F. C. Hawthorne, *Nature* **1990**, *345*, 297; C. R. A. Catlow, G. D. Price, *Nature* **1990**, *347*, 243.
[2] *New Methods for Modelling Processes within Solids and at Their Surfaces* (Ed.: C. R. A. Catlow), Oxford University Press, London, **1993**; *Journal of Computer-Aided Materials Design*, *Vol. 3* (Eds.: A. K. Cheetham, U. W. Suter, E. Wimmer, S. Yip), ESCOM, Leiden, Netherlands, **1996**.
[3] P. Verwer, F. J. J. Leusen in *Reviews in Computational Chemistry*, *Vol. 12* (Eds.: K. B. Lipkowitz, D. B. Boyd), Wiley, New York, **1998**, p. 327.
[4] S. Kirkpatrick, C. D. Gelatt, M. P. Vecchi, *Science* **1983**, *220*, 671.
[5] M. W. Deem, J. Newsam, *Nature* **1989**, *342*, 260; M. W. Deem, J. Newsam, *J. Am. Chem. Soc.* **1992**, *114*, 7189; M. Falcioni, M. W. Deem, *J. Chem. Phys.* **1999**, *110*, 1754.
[6] J. Pannetier, J. Bassas-Alsina, J. Rodriguez-Carvajal, V. Caignaert, *Nature* **1990**, *346*, 343.
[7] C. M. Freeman, J. M. Newsam, S. M. Levine, C. R. A. Catlow, *J. Mater. Chem.* **1993**, *3*, 531.
[8] J. C. Schön, M. Jansen, *Angew. Chem.* **1996**, *108*, 1358; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1286; H. Putz, J. C. Schön, M. Jansen, *Comput. Mater. Science* **1998**, *11*, 309.
[9] M. B. Boisen, G. V. Gibbs, M. S. T. Bukowinski, *Phys. Chem. Miner.* **1994**, *21*, 269; D. M. Teter, G. V. Gibbs, M. B. Boisen, D. C. Allan, M. P. Teter, *Phys. Rev. B* **1995**, *52*, 11; M. B. Boisen, G. V. Gibbs, M. O'Keeffe, K. L. Bartelmehs, *Micropor. Mesopor. Mater.* **1999**, *29*, 219.
[10] S. M. Woodley, P. D. Battle, J. D. Gale, C. R. A. Catlow, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2535.
[11] D. E. Akporiaye, G. D. Price, *Zeolites* **1989**, *9*, 23.
[12] J. V. Smith, *Chem. Rev.* **1988**, *88*, 149, and references therein.
[13] M. O'Keeffe, B. G. Hyde, *Philos. Trans. R. Soc. London A* **1980**, *295*, 38; M. O'Keeffe, N. E. Brese, *Acta Crystallogr. Sect. A* **1992**, *48*, 663.
[14] J. Klinowski, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 79, and references therein; O. D. Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowski, *Nature* **1999**, *400*, 644.
[15] M. M. J. Treacy, K. H. Randall, S. Rao, J. A. Perry, D. J. Chadi, *Z. Kristallogr.* **1997**, *212*, 768.
[16] *Atlas of Zeolite Structure Types* (Eds.: W. M. Meier, D. H. Olson, C. Bärlocher), Elsevier, London, **1996**; update on: http://www.iza-sc.ethz.ch/IZA-SC.
[17] D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas, G. J. Hutchings, *Nature* **1996**, *382*, 604; F. Cora, D. W. Lewis, C. R. A. Catlow, *Chem. Commun.* **1998**, 1934.
[18] J. V. Smith, W. J. Dytrych, *Nature* **1984**, *309*, 607.
[19] M. E. Davis, C. Saldarriga, C. Montes, J. Garces, C. Crowder, *Nature* **1988**, *331*, 698.
[20] D. E. Akporiaye, *Angew. Chem.* **1998**, *110*, 2594; *Angew. Chem. Int. Ed.* **1998**, *37*, 2456.
[21] G. Férey, A. K. Cheetham, *Science* **1999**, *283*, 1125.
[22] J. M. Newsam, F. Schüth, *Biotechnol. Bioeng.* **1999**, *61*, 203.
[23] B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 2648; *Angew. Chem. Int. Ed.* **1999**, *38*, 2494.
[24] G. Férey, *C. R. Acad. Sci. Ser. II c* **1999**, *1*, 1.
[25] F. Taulelle, M. Pruski, J. P. Amoureux, D. Lang, A. Bailly, C. Huguenard, M. Haouas, C. Gérardin, T. Loiseau, G. Férey, *J. Am. Chem. Soc.* **1999**, *121*, 12148.
[26] F. Taulelle, M. Haouas, C. Gérardin, C. Estournes, T. Loiseau, G. Férey, *Colloids Surf. A* **1999**, *158*, 299; S. Dick, G. Grossmann, G. Ohms, M. Müller, *Z. Naturforsch. B* **1997**, *52*, 1447.
[27] S. Dick, G. Grossmann, G. Ohms, T. Zeiske, *Z. Naturforsch. B* **1997**, *52*, 1439.
[28] Cerius2 Software Suite, Version 3.9, Molecular Simulations Inc., USA.
[29] N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, E. Teller, *J. Chem. Phys.* **1953**, *21*, 1087.
[30] *Biosym Catalysis 2.0 Software Manuals 1993*, Molecular Simulations Inc., USA. The MSI Catalysis and Sorption Project is supported by a consortium of member companies.
[31] *Accuracy in Powder Diffraction II (NIST Special Publication No. 846)* (Eds.: J. M. Newsam, M. W. Deem, C. M. Freeman, E. Prince, J. K. Stalick), National Institute of Standards and Technology, Bethesda, MD, USA, **1992**, p. 80.
[32] A. M. Glazer, *Acta Crystallogr. Sect. B* **1972**, *28*, 3384.
[33] F. Cora, D. W. Lewis, C. R. A. Catlow, *Chem. Commun.* **1998**, 1943; Q. Feng, H. Kanoh, K. Ooi, *J. Mater. Chem.* **1999**, *9*, 319.
[34] J. Gale, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 629.

Template-Induced, Stereoselective Cyclizations in the Cyclopolymerization of TADDOL-Dimethacrylate**

Günter Wulff,* Anja Matussek, Christian Hanf, Stefan Gladow, Christian Lehmann, and Richard Goddard

In the context of the synthesis of main-chain chiral copolymers, Kakuchi et al.[1] cyclo-copolymerized[2] 2,3-*O*-isopropylidine-D-threitol-1,4-(dimethacrylate), derived from D-tartaric acid, with styrene. After removal of the 2,3-*O*-isopropylidine-D-threitol template, the resulting copolymers containing methylmethacrylate and styrene units showed relatively small optical rotations, in contrast to copolymers prepared from D-mannitol derivatives previously obtained by us.[2] In order to obtain increased asymmetric induction, we used (*R*,*R*)-TADDOL, introduced by Seebach et al.,[3] instead of the threitol derivative, and prepared for the first time the dimethacrylate **M** (see Scheme 1).[4, 5] Surprisingly, copolymerization with styrene followed by removal of the template resulted in a copolymer with a significantly smaller optical activity. This can only be explained if the methacrylate units are arranged as *meso* diads to one another. Homopolymerization should lead to an isotactic arrangement in the chain, and this was indeed the case. After anionic polymerization, removal of the template, and esterification, the polymethacrylate obtained was completely isotactic, but it exhibited a small but distinct optical rotation, which decreased with increasing molecular weight.

Independent of our work, Sogah, Okamoto, and co-workers[6, 7] also prepared the monomer **M** and homopolymerized it by radical, anionic, and group-transfer polymerization. They obtained a homopolymer with a large optical rotation, from which they assumed that it exists as an atropisomeric single-handed helix, as found for tritylmethacrylate. After removal

[*] Prof. Dr. G. Wulff, Dr. A. Matussek, Dr. C. Hanf, Dr. S. Gladow
Institut für Organische Chemie und Makromolekulare Chemie
Heinrich-Heine-Universität Düsseldorf
Universitätsstrasse 1, 40225 Düsseldorf (Germany)
Fax: (+49) 211-8114788
E-mail: wulffg@uni-duesseldorf.de
Dr. C. Lehmann, Dr. R. Goddard
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr (Germany)

[**] This work was supported by the Fonds der Chemischen Industrie.

  1433-7851/00/3913-2275 $ 17.50+.50/0