We have applied crystal structure prediction methods based on global lattice energy minimization using anisotropic atom-atom models to investigate the predictability of the packing of a series of chiral imine-linked cage molecules, synthesized by the [4 + 6] condensation of 1,3,5-triformylbenzene with different vicinal diamines. The resulting tetrahedral molecules (see figure for example molecular structures) have four arene faces and four open windows whose dimensions are large enough to allow gases or small organic molecules to pass through. Therefore, the porosity of the resulting crystal structures is dictated by the alignment of the faces and windows on neighboring molecules.

We find that the nature of the vertices on the cage molecules has a strong influence on the crystal energy landscapes of these materials, including the energy spacing between structures and the alignment of the molecular windows. The results also demonstrate that the crystal packing of these molecules are predictable, starting from the molecular structure alone: for most systems studies, the known crystal structures are located as the global minimum in lattice energy. We also show that the structures of cocrystals of these molecules are predictable using the same methods, including the molecules' preferences for homochiral or heterochiral packing [2]. These results suggest that computed crystal energy landscapes will be able to provide valuable guidance in a computationally-led strategy for the design of new porous molecular materials.
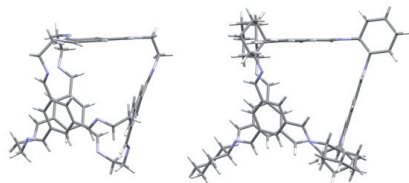
[1] A.I. Cooper, *Angewandte Chemie Int. Ed.* **2011**, *50*, 996-998. [2] J.T.A. Jones *et al*, *Nature*, **2011**, accepted for publication.

Keywords: structure prediction, porosity, modelling

MS06.P04

The lowest energy calculated structure of acridine was found

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At current count, eight crystal forms of acridine have been identified, including the latest, designated form IX, solved from XRPD. The crystal energy landscape of this amazingly rich system was surveyed computationally for $Z'=1$ structures in the most common space groups. The optimized conformation of acridine was used in CrystalPredictor to generate the energetically accessible structures for the rigid molecule. The structures were lattice energy minimized with intermolecular potentials comprising a distributed multipole model of the MP2 6-31G(d,p) charge distribution and an empirical repulsion-dispersion potential using DMACRYS. There are a large number of structures within the lattice energy range of the known polymorphs, most of which are $Z'>1$. The crystal structure of form IX found recently corresponds to that of the global minimum structure with an overlay of the coordination sphere $RMSD_{15}$ of 0.126 Å. Another experimentally unknown structure is calculated at the same energy, just slightly (0.2 kJ/mol) below the known $Z'=1$ polymorph form III. The crystal energy landscape is compared with the relative stability of the different forms

determined experimentally, and the prospects for a full understanding of the complex solid state of this simple molecule discussed.

Keywords: polymorphism, energy landscape

MS06.P05

Unexpected Crystals: Kryptoracemates and Co-Crystals of Isomers

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Lists of unexpected organic co-crystals (*i.e.*, co-crystals formed from molecules in which the heteromolecular *A…B* interactions have no clear advantage over the homomolecular *A…A* and *B…B* interactions) have been compiled from structures in the Cambridge Structural Database (the CSD). These lists include:

1. Co-crystals of molecules that are isomers (*i.e.*, either diastereomers or skeletal isomers but not tautomers) (160 examples)
2. Quasiracemates, *i.e.*, co-crystals of molecules that would be enantiomers but for small substitutions [*e.g.*, (R)-2-bromobutane and (S)-2-chlorobutane] (114 examples)
3. Co-crystals of molecules that are almost isomers (but not almost enantiomers) and of molecules that are almost the same (70 examples)
4. Kryptoracemates, *i.e.*, racemic compounds that happen to crystallize in space groups without any improper symmetry elements (*e.g.*, $P1$, $C2$, $P2_12_12_1$) so that the two resolvable enantiomers are crystallographically independent. (181 examples)

Compiling the lists of co-crystals of isomers and of kryptoracemates was made semi-automatic by comparing InChI™ strings created for each molecular unit in a large subset of the structures in the CSD. Compiling the other two lists was more labor intensive. All structures were evaluated carefully. The kryptoracemates were vetted using *PLATON* [1] to make sure that no improper symmetry relating the two enantiomers had been overlooked.

Examination of the structures in the final lists led to the following conclusions:

1. The existence of so many co-crystals of closely related molecules (and some that are less closely related) demonstrates just how unpredictable crystallization can be.
2. The large number of quasiracemates is strong evidence for inversion symmetry being very favorable for crystal packing.
3. If two diastereomers would be enantiomers but for the exchange of an H atom and a methyl, hydroxyl, or amino substituent, or but for the inversion of a [2.2.1] or [2.2.2] cage, then co-crystal formation is so likely that it should be considered predictable.
4. The conformations of the enantiomers in kryptoracemates are usually very similar, but the deviations from improper symmetry in the crystal are usually easy to identify.
5. Kryptoracemates were found to account for only 0.1% of all organic structures containing either a racemic compound, a meso molecule, or some other achiral molecule.
6. The probability of spontaneous resolution of racemic material is about 6%.

This work has been published recently [2], [3].

[1] A.L. Spek, *Acta Crystallogr.* **2009**, *D65*, 148-155. [2] S.P. Kelley, L. Fábián, C.P. Brock,. *Acta Crystallogr.* **2011**, *B67*, 79-93. [3] L. Fábián, C.P. Brock, *Acta Crystallogr.* **2010**, *B66*, 94-103.

Keywords: co-crystals, quasiracemates, kryptoracemates