MS.06.3

Disorder in organic crystals: modelling and prediction

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While the prediction of ordered molecular crystal structures is an increasingly mature discipline, the prediction of disordered molecular crystals has received little attention. A useful approach has emerged through the examination of crystal energy landscapes for ordered structures. Groups of similar structures with closely-spaced energies indicate the possibility of a disordered crystal structure incorporating elements found within the group. However, 'predictions' made in this way are qualitative and rely to a high degree on human intuition. A quantitative approach to predicting disordered crystals must address the usual challenges of crystal structure prediction: the generation of candidate structures, and the calculation and comparison of accurate energies for those candidates. A method has been devised for calculating energies (and other properties) for organic crystals with binary disorder, using the recently introduced idea of 'symmetry-adapted ensembles' and implemented using a modified version of the program SOD [1]. Symmetry-adapted ensembles allow for the calculation of average lattice energies and configurational entropies by summing over many copies of a supercell of the disordered crystal, each representing a different distribution of the disorder elements (e.g. different molecular orientations). Only symmetry-unique distributions are explicitly considered, saving an order of magnitude in computer time. Calculations have been carried out on three systems which were not previously open to modelling. The solid solution of dichloro- and dibromo-benzene[2] has been shown to possess a random distribution of the two species, and the observed miscibility gap has been accounted for by calculation of free energy as a function of composition. β-caffeine is a more complicated case, with two independent molecules displaying orientational disorder. Modelling of this system has confirmed the stability, largely founded on entropy, of the disordered structure proposed by Enright et al. [3] Finally, it has been shown that crystals of 5-ethynyl uracil (eniluracil[4]) display stable disorder, but only in two crystallographic directions. Hydrogen bonded ribbons enforce order in the third direction.

These examples point to near-symmetries in molecular interactions as a key factor in the appearance of disorder, quantifiable through very similar lattice energies of many different symmetry-unique configurations. Disorder may occur in all three dimensions, or deviations from near-symmetry may restrict it to a smaller subset. For example, the near-symmetry of the eniluracil molecule is broken by a carbonyl group paired with a hydrogen atom. The consequence of this is ordering in one direction. A combination of the assessment of near-symmetry, and the existing tools of crystal structure prediction – crystal energy landscape generation for ordered structures, and crystal structure matching – seems to allow for the generation of candidate disordered structures, the stabilities of which can now be calculated.

In conclusion, disordered organic crystal structures can now be modelled, and there is a clear route to techniques for predicting their appearance on a similar footing to ordered structures.

[1] R. Grau-Crespo, S. Hamad, C.R.A. Catlow, N.H. de Leeuw, *J.Phys.: Condens. Matter* **2007**, *19*, Art.No.256201. [2] A.P. Bussandri, M.J. Zuriaga, C.A.Martin, *J. Phys. Chem. Solids* **1998**, *59*, 201-209. [3] G.D. Enright, V.V. Terskikh, D.H. Brouwer and J.A. Ripmeester, *Crystal Growth and Design* **2007,** *7*, 1406-1410. [4] R.C.B. Copley *et al, Crystal Growth and Design* **2008**, *8*, 3474-3481.

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Validating Multiple DFT-D methods for crystal-structure prediction

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The thus far most successful method for evaluating lattice energies for crystal-structure prediction (CSP) is the dispersion-corrected Density Functional Theory (DFT-D) method as published by Neumann & Perrin in 2005 [1]. Their DFT-D calculations used the PW91 GGA density functional with plane waves in combination with a newly-parameterised dispersion correction. The lattice energies calculated with this method were good enough to predict all four crystal structures of the four small, neutral molecules of the 2007 CSP Blind Test correctly [2].

In the 2010 CSP Blind Test, however, three new categories of chemical compounds were added, for which the results with the 2005 DFT-D method were no longer satisfactory. Especially the relative lattice energies of crystal structures of a hydrate and a molecular salt were poorly reproduced [3].

Since 2005, progress has been made in several areas. First, a new dispersion correction has recently been published by Grimme *et al.* [4]. Both dispersion corrections involve density functional dependent parameters that need to be fitted to reference data. Second, more density functionals have become available, including hybrid functionals for plane-wave codes. Third, our in-house software for fitting dispersion-correction parameters has been rewritten to exploit the much faster hardware that has become available since 2005. And fourth, an improved set of reference data, consisting of very low temperature crystal structures (< 30 K), has been collated for fitting and validation purposes.

The two dispersion corrections were fitted in combination with various density functionals, with the aim of determining the best combination for CSP. The fitting procedure and the results will be discussed. For the most promising DFT-D method, updated energy rankings for the molecular salt and for the hydrate of the 2010 CSP Blind Test will be presented.

[1] M.A. Neumann, M.-A. Perrin, *J. Phys. Chem. B* **2005**, *109*, 15531-15541. [2] G.M. Day *et al.*, *Acta Cryst. B* **2009**, *65*, 107-125. [3] D.A. Bardwell *et al.*, in preparation. [4] S. Grimme, J. Antony, S. Ehrlich, H. Krieger, *J. Chem. Phys.* **2010**, *132*, 154104.

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IsoQuestCSP: analyzing sets of predicted crystal structures and selecting the true structure

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Crystal structure prediction (CSP) has become a powerful and important tool in the study of polymorphism. At the same time CSP is nowadays an alternative route for structure determination when single-crystal or powder diffraction methods fail or are not accessible. The success of this route is strongly dependent on the quality of the CSP method but also on the ability to recognize the true structure.