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The tale of molecule vi: a benchmark sulfonimide in crystal structure prediction

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Many compounds can crystallize into more than one unique crystal structure, a well documented phenomenon known as polymorphism. [1] There can be significant variations in physical properties between the polymorphs of a compound. [2] Crystal structure prediction (CSP) makes an important contribution to understand polymorphism, to help exploit its opportunities and to help avoid potential problems. To assess the progress in CSP technologies, a series of Blind Tests has been organized by the Cambridge Crystallographic Data Centre.

Molecule VI (see Figure 1) was one of the target compounds in the 2001 Blind Test. [3] No participant predicted the then only known experimental polymorph (form I). Two additional polymorphs, forms II and III, were later discovered. [4], [5] It was concluded that CSP failed because these calculations tend to focus on the thermodynamically most stable structures, whilst the Molecule VI polymorphs may be kinetically favored. [4], [5] It further led to a comment on "structure prediction, which would be most valuable for process chemistry, has still a way to go". [6]

To investigate fully the polymorphism of Molecule VI, a CSP was conducted using the GRACE software, [7] which correctly predicted the structures of all four target compounds in the 2007 Blind Test. [8] In the current study, the rank 1, 2 and 3 predictions were in good geometric agreements with the forms I, III and II experimental structures of Molecule VI respectively. [9] The relative stabilities of these predicted polymorphs were consistent with differential scanning calorimetry results. [5]

In conclusion, it is feasible to predict the crystal structures of small organic molecules by considering crystallization thermodynamics only, provided that the accuracy of the lattice energy calculation method used is sufficient. Yet, it is not possible to predict the outcome of a specific crystallization experiment, because it would be beyond current computational capabilities to consider all relevant kinetic effects on the crystallization process.

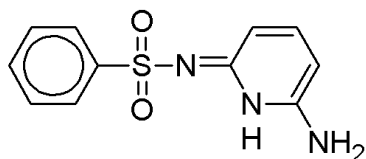


Figure 1 The molecular structure of molecule VI

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Hybrid evolutionary approach for material design: search for superhard materials

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We have developed a method for prediction of the hardest crystal structures in a given chemical system. It is based on the evolutionary algorithm USPEX and involves the concept of *hybrid global optimization*, where global optimization with respect to a desired property (hardness) is conducted in the space of local minima of the (free) energy. To calculate the hardness of a crystal, we employed the electronegativity-based hardness model [1] which we have augmented with bond valence model and multi-color graph theory. These extensions enable correct description of the hardness of layered, molecular and low-symmetry crystal structures.

Applying our method to C and TiO₂, we have (i) obtained a number of low-energy carbon structures with hardness slightly lower than diamond and (ii) proved that TiO₂ in any of its possible polymorphs cannot be the hardest oxide, its hardness being below 17 GPa, thus resolving a long-standing controversy.

The same concept of hybrid global optimization can be used for optimizing other properties of materials.

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Crystal energy landscapes of intrinsically porous molecules

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Nanoporous materials have potential applications in heterogeneous catalysis, gas storage and separation. While this research area has been dominated by nanoporous network materials such as metal-organic frameworks (MOFs), significant recent attention has been given to the preparation of nanoporous solids from synthetically pre-organized molecular pores [1]. These molecular materials offer advantages such as solution processability and controlled modular assembly of chemically distinct pores *via* crystallization. A major obstacle which has limited the rational design of molecular porous materials is the challenge of predicting the assembly of molecular crystals.