

A Hybrid Method for the Accurate Energy Ranking of Molecular Crystals

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A major obstacle for the prediction of the crystal structures of organic molecules is the discrepancy between the small size of typical lattice energy differences and the limited accuracy of force fields or pure density functional theory (DFT) calculations. We present a hybrid method for the calculation of accurate lattice energy differences that combines DFT calculations using the VASP program with empirical Van der Waals (VdW) potentials.

The key to success is the careful adjustment of the empirical potentials, in particular in the region of intermediate interatomic distances, where both the DFT component and the VdW component yield a significant contribution to the total interaction energy. We have fitted the empirical parameters for H, B, C, N, O, S, F, Cl and Br to molecular C_6 coefficients and to the unit cells of low temperature crystal structures. The unit cell volumes and the cell lengths are typically reproduced to within 1%.

Energy ranking studies have been conducted for a variety of molecules, including acetylene, ethylene, ethane, methane, acetic acid, urea, paracetamol and several molecules from the first two CCDC blind tests on polymorph prediction. The experimental low temperature crystal structures are generally found as the most stable predicted crystal structures. In several cases, the most stable packing motif is expressed in more than one space group, giving rise to tiny energy differences of less than 1kcal/mol per molecule.

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