

## 1.4 Crystal Packing Calculations on Nonlinear Optical Molecules

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The optimization of the nonlinear optical properties of organic materials requires the optimization of both the nonlinear optical response of the molecules and arrangement of the molecules in the crystals. The fundamental requirement for the observation of second-order nonlinear optical processes is the noncentrosymmetric crystallisation. Unfortunately however, most organic substances crystallise centrosymmetrically. If we were able to predict the crystal structure, in which a given molecule crystallises, the development of new organic crystals with optimised properties could be made much more efficient.

As a first step towards this prediction we investigated the crystal packing of nonlinear optical molecules, whose crystal structure is already known. The crystal structures were calculated by minimising the intermolecular lattice energies, treating the molecules as rigid bodies. The intermolecular energies were calculated with the empirical *atom-atom potential method* taking into account Van der Waals, electrostatic, and hydrogen bonding interactions. If the crystal periodic potential was defined to correspond to the experimentally observed space group, the correct crystal structure could be obtained. These lattice energy minimisations were subsequently performed for the space groups most populated by organic materials. For each space group the best structure found was compared with the experimentally observed packing. In this way, the observed structure was shown to be the most closely packed structure having the largest intermolecular binding energy. The energy differences between the different local minima, however, is very small, so that a prediction of the crystal packing for a new molecule would still be difficult with this method.