

s9.m2.o3 Crystal Structure Predictions, and Their Use for Solving Crystal Structures from Powder Data.

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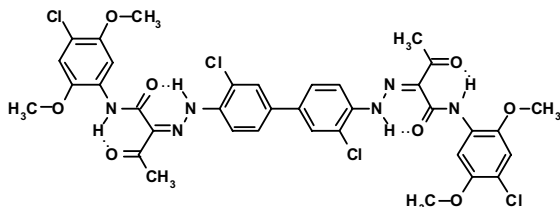
Keywords: prediction of crystal structures, powder diffraction, pigments.

A global optimization of the lattice energy (including the intramolecular energy) is used to predict possible crystal structures of molecular compounds. The main intramolecular degrees of freedom are optimized simultaneously with the crystal packing ¹.

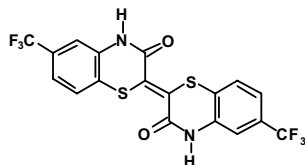
Generally, it is not possible to predict "the" crystal structure, instead a number of possible polymorphic forms is found, including the experimentally known structure(s) ². However, there are compounds, where one of the calculated packings has a considerably more favorable energy than all others; in such cases it was possible to predict the crystal structure successfully, e.g. for (C₅H₅)Fe(C₅(CH₃)₅) ³. The predicted structures are close to the experimental ones.

The prediction of possible crystal structures can be used to solve crystal structures from X-ray powder data ³. If lattice parameters and possible space groups are known from the powder diagram (or from electron diffraction data), they are used as input. For each calculated possible crystal structure, the powder diagram is simulated and compared to the experimental powder diagram in order to select, which of the possible structures corresponds to the experimental one. Finally the crystal structure is refined by Rietveld analyses. This procedure for structure determination can be used even if the molecule is relatively large or if the diagram is of low quality, or if indexing fails.

Examples: (1) Pigment Yellow 83 (C₃₆H₃₂Cl₄N₆O₈):



(2) Thiazine-Indigo pigment:



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s9.m2.o4 A Knowledge-Based Costfunction for Selection from Low-Energy Crystal Structures in Crystal Structure Prediction.

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Keywords: crystal structure prediction, CSD, intermolecular interactions.

Currently, the problem of crystal structure prediction of small organic molecules is usually addressed by the calculation of a lattice energy, assuming that the lowest energy structure coincides with the experimental crystal structure. This is a very difficult problem, especially for small molecules, as there are many ways to form closed-packed crystal structures with low energy. The calculated lowest energy structure is often not experimental one, so the real problem is to select the right low-energy structure from, typically, tens or even hundreds of possible structures which are in a small energy window from the lowest energy [1].

Here we present an alternative way to rank low-energy structures, which helps to decide which of the calculated structures will be the experimental one. The costfunction is based on calculation of a fit of interacting functional groups within the crystal structure using the knowledge base IsoStar [2], which is derived from the Cambridge Structural Database [3].

The IsoStar library implicitly includes information which is not captured in the lattice energy of a crystal structure only, such as vibrational energies and the kinetics of crystal growth. Furthermore, as IsoStar contains information about interacting functional groups rather than atoms, directional effects can be accounted for in a direct manner.

Examples will include crystal structure predictions of carboxylic acids, which can crystallise into dimers or chains structures, as well as conformationally flexible structures with alcohol functional groups.

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