

Chlorothalonil: Unexpected and Unpredictable Polymorphic Structures

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Chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) is a general-use pesticide that is used as a broad-spectrum fungicide, and as a biocide in paints and wood preservatives. Although the commercially available form (form 1) had been fully structurally characterised [1], the patent indicated the possibility of another polymorphic form that shows reduced biological activity and undergoes irreversible hardening in production. However, there was no reliable crystallographic information regarding this second form, and hence a simultaneous theoretical prediction and experimental search for new polymorphs was carried out. This was done independently, so that it would be a test of crystal structure prediction methods if all the polymorphs could be characterised independently from powder or single-crystal diffraction data. The result is a prediction study and subsequent Rietveld refinement of three polymorphs of chlorothalonil, with two polymorphs uncharacterised before prediction [2]. In the event, the unexpected complexity of the both the new polymorphic crystal structures of this simple molecule rendered them unpredictable, although related approximations to these structures were located within the constraints of prediction techniques. Form 2 is disordered and is therefore of a type that cannot be predicted by current theoretical methods. The determination of this structure from powder diffraction data also turned out to be more problematical than expected, both at the indexing stage and in structure solution, despite being a seemingly trivial structure in terms of global optimisation direct-space techniques. Refinements based on the hypothetical 'ordered' structures predicted in the theoretical search facilitated an interpretation of this disorder. The presence of multiple molecules in the asymmetric unit of form 3 determined from single-crystal data presents another structure that cannot be predicted by current theoretical methods. However, the theoretical search did locate two hypothetical structures that show significant similarities to the form 3 structure. Rietveld refinement of these predicted structures, which are clearly only approximations to the true structure, warns against over-interpretation of powder diffraction data in such cases.

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[2] M.Tremayne, L.Grice, J.C.Pyatt, C.C.Seaton, B.M.Kariuki, H.H.Y.Tsui, S.L.Price, J.Cherryman, *J. Am. Chem. Soc.* (2004) in press