Crystal Packing: Molecular Shape and Intermolecular Interactions

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The Box Model of crystal packing describes unit cells and their contents in terms of "packing patterns".[1] The packing patterns were derived from a consideration of the ways in which boxes of unequal dimensions can be stacked with faces touching and edges aligned. The resulting arrays of boxes have the same total volume but different surface areas. An examination of thousands of experimental structures contained within the Cambridge Structural Database[2] has shown that these packing patterns are a viable description of crystal structures and that molecular dimensions are related to unit cell dimensions in a systematic way. The packing patterns are not populated equally by experimental structures; packing patterns characterised by low surface area and most equal dimensions are preferred. Thus molecular shape appears to be of primary importance in crystal packing.

However, high surface area packing patterns do exist and a possible explanation is that these structures contain strong, "structure-determining" hydrogen bond interactions. Subsets of structures containing strong motifs have been examined within the context of the Box Model. Changes in populations of packing patterns are observed and these changes can be rationalised in terms of the symmetry requirements of the motif. However, the presence of hydrogen bond motifs does not appear to greatly perturb the principal of the Box Model - that minimum surface area is preferred.

[1] Pidcock E., Motherwell W.D.S., *Crystal Growth Des.*, 2004, **4**, 611. [2] Allen F.H. , *Acta Cryst*., 2002, **B58**, 380.

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