

Organic Crystal Engineering - Mark Mascall

In-depth analysis of the arrangement of molecules in the solid state is central to the science of organic crystal engineering, a burgeoning technology which is producing novel, functional materials. In our work, we have made extensive use of the Cambridge Structural Database's (CSD) structure search program QUEST3D, the statistical package VISTA, the graphics package PLUTO and most recently the powerful visualisation software IsoStar/IsoGen in studies of various aspects of solid state structure. This suite of programs were accessed through the EPSRC's Chemical Database Service in Daresbury, where expert assistance was always readily at hand when required. Aspects of our research which have been sustained by the use of the Chemical Database Service are described below:

(i) Despite their ubiquity in nature, an area which had previously received little attention was the role of halogen anions as hydrogen bond acceptors. This is indeed a phenomenon which is difficult to search in the literature by traditional means, since many instances of halide \cdots HA (A = OR, NR₂, N⁺R₃) contact in crystal structures go unreported. We thus investigated these interactions using the CSD¹, and published a detailed statistical study which shed light on both the prevalence and nature of this type of hydrogen bonding which, we believe, will be of assistance in the design of future halide receptors and ion channels.

(ii) It was to the surprise of many of the community of hydrogen bond researchers when a paper by a senior and well-respected academic appeared which called into question the existence of the C-H \cdots N hydrogen bond.² Again calling on the CSD, we were able to produce a statistical account of the occurrences of short C-H \cdots N contact in the solid state which overwhelmingly supported the description of such contacts as bonds.³

(iii) Our most recent work has focused on the nature of longer-range π -arene bonding. Again, the CSD proves invaluable in the study of such interactions, since their occurrence is not always commented on in papers, which primarily describe more dominant modes of complexation. Our interest in this area stemmed from our own experimental work on receptors designed to exploit longer range π -metal bonds in combination with heteroatom-metal bridges. It was through preliminary CSD analysis of preferred metal-arene distances that the design of the 'S-cylindrophane' receptor was shown to be ideal for this mode of bonding, and eventually led to the description of the first bis η^6 arene-Ag(I) and Cu(I) sandwich complexes.⁴ The database study also predicted that certain other metals, such as trivalent lanthanides, might also be accommodated in the S-cylindrophane macrocycle,⁵ providing us with important leads for future experimental work.

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