Rings, Restraints and Resolving the Superbowl in Crystals

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Determination of the structure of the Superbowl[1] (a fused polycyclic penta-cavitand molecule $C_{268}H_{316}Br_4O_{52}$.4EtOH.5CHCl$_3$, ***MWt*** ≈ **5000**) presented numerous challenges. Crystals diffracting to 1.25 Å resolution were obtained which, in addition to 35% by volume disordered solvent, were found to be built up from supramolecular assemblies comprising the superbowl molecule holding one chloroform and four ethanol molecules in its interior and four more chloroform molecules lying in smaller non-rigid external cavities. Seventy percent of the non-hydrogen atoms of the superbowl were found by Direct Methods[2]. The model was extended by mapping on a known mono-cavitand structure using the CRYSTALS[3] Regularise/Augment routine to complete the rigid part of the super-bowl. Refinement of a mostly isotropic model required application of restraints, first holding geometries to values seen in comparator structures, and later setting chemically equivalent bond lengths to their mean values in the structure. Of special utility in the refinement were the Special Shapes available in CRYSTALS[3] which facilitated modelling the internal chloroform as a combination of fully occupied sites, fractionally occupied sites, and a ring of electron density accounting for 60% of two disordered chlorine atoms. Only 15 non-H Superbowl atoms are unresolved in the final model *R =0.10, R_w =0.07*

[1] Barrett E.S., Irwin J.L., Edwards A.J., Sherburn M.S., *J.A.C.S.,* 2004, 16747-16749. [2] Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R., SIR 97, *J. Appl. Crystallogr.,* 1999, 115-119 [3] Watkin D.J., Prout C.K., Carruthers J.R., Betteridge P.W., Cooper R.I., *CRYSTALS Issue 11 Chemical Crystallography Laboratory*, Oxford.