

Analysis of polymorphic systems shows that extended patterns are conserved between polymorphic forms for 75% of cases studied.

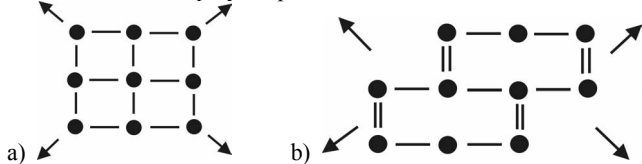


Figure 1. a) An 'R4 sheet' motif. b) An R2R6 sheet motif. Dots represent molecules, lines represent inter-molecular hydrogen bonds. The arrows indicate that these patterns are infinitely repeating in 2D.

[1] Chisholm J. A., Motherwell S., *J. Appl. Cryst.*, 2004, **37**, 311.

**Keywords:** hydrogen bond patterns, hydrogen bonds in organic crystals, database search

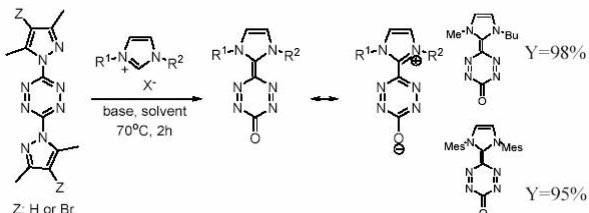
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##### New Class of Compounds: Quinoidal Tetrazines

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Tetrazine compounds are frequently used in pesticides, pharmaceutical products, explosives etc. Using Arduengo-type carbenes [1] we have prepared and characterized a series of air stable quinoidal tetrazines which represent a new class of compounds.



The surprisingly high torsion angle between the pyrazolyl and tetrazine rings (37-43°) as well as C-C, N-N, and C-O bond distances indicate the quinoidal nature of these compounds without conjugation of the rings. The supramolecular motif of quinoidal tetrazines include stack-like ordering of the molecules. Packing, van der Waals interactions as well as chirality of the compounds when R<sup>1</sup> or R<sup>2</sup> are chiral will be discussed.

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[1] Arduengo A., *J. Am. Chem. Soc.*, 1991, **113**, 361.

**Keywords:** crystal packing, chirality, supramolecular chemistry

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##### Rings, Restraints and Resolving the Superbowl in Crystals

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Determination of the structure of the Superbowl<sup>1</sup> (a fused polycyclic penta-cavitand molecule C<sub>268</sub>H<sub>316</sub>Br<sub>4</sub>O<sub>52</sub>·4EtOH·5CHCl<sub>3</sub>, *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<sup>2</sup>. The model was extended by mapping on a known mono-cavitand structure using the CRYSTALS<sup>3</sup> Regularise/Augment routine to complete the rigid part of the superbowl. 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<sup>3</sup> 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<sub>w</sub>* = 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.

**Keywords:** supramolecular assemblies, model building, refinement disorder

#### P.06.06.17

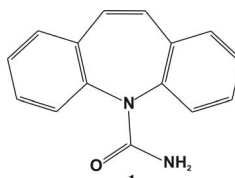
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##### Familial Relationships in Molecular Crystal Structures

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*XPac* is a computer program for the identification of similar "supramolecular constructs" (sub-components of complete crystal structures) of 0-, 1- or 2-dimensionality in different crystal structures of specific molecules (polymorphs) or crystal structures of similar molecules (families) and of 3-dimensionality in isostructural assemblies.

The *XPac* approach is demonstrated using a family of 20 crystal structures of the carbamazepine molecule (**1**) from the CSD, which includes four polymorphic forms, 13 solvates and salt structures. The structural relationships are visualised in a structure family diagram



**Keywords:** software for crystallography, polymorphs, isostructurality

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##### Supramolecular Synthesis of Caffeine Solvates and Cocrystals

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Caffeine is a biologically active compound, widely used in food and drug industry. Besides a 0.8 hydrate, two anhydrous forms are known<sup>1</sup> which still defy a complete structural determination because of disorder phenomena.<sup>2</sup> We recently carried out a large number of solvent crystallizations where we obtained three new solvates. The solvates are formed with formic acid, acetic acid and methanesulfonic acid. Acetic acid and formic acid solvates lose their solvent readily. The crystal structure analysis of these solvates lead us to design two new, hitherto unknown, caffeine cocrystals in addition to the recently reported ones.<sup>3</sup> This report describes the discovery and structural aspects of these new caffeine solvates and cocrystals. The methanesulfonic acid solvate (monoclinic, *C2/c*) has the highest calculated density (1.594 g cm<sup>-3</sup>) of all the solved cocrystal structures so far. The driving force for the formation of the solvates and cocrystals is presumably an additional hydrogen-bond stabilization by the introduction of an acid group as a hydrogen bond donor for the basic imidazole nitrogen of caffeine by the formation of O-H...N interactions.

[1] Griesser U.J., Szelagiewicz M., Hofmeier U.C., Pitt U., Cianferani S., *J. Therm. Anal. Calorim.*, 1999, **57**, 45, and references therein. [2] Carlucci L., Gavezzotti A., *Chem. Eur. J.*, 2005, **11**, 271, and references therein. [3] Trask A.V., Motherwell W.D.S., Jones W., *J. Cryst. Growth Des.*, 2005, in press.

**Keywords:** caffeine, solvent structure, cocrystals