

PS06.05.11 C-Cl... π (Ar) INTERACTIONS. Anne Irving, Department of Chemistry, University of Cape Town Rondebosch 7700, South Africa.

Geometry consistent with a C-Cl... π (Ar) interaction has been shown to exist in a wide variety of compounds(1), (from information retrieved from the CambridgeStructural Database(2)). An example(3) showing the geometry of a C(sp³)-Cl... π (Ar) interaction is given below.

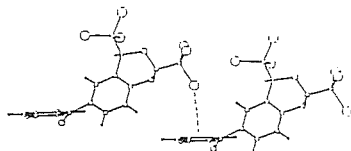
The angle [C-Cl... π (Ar)] between the C-Cl bond and the normal to the aromatic ring varies widely, from about 90° to a more nearly linear arrangement.

There is some tendency for the distance of the chlorine atom from the plane of the aromatic ring to be shorter as the angle [C-Cl... π (Ar)] becomes closer to 180°.

In most compounds the C-Cl... π (Ar) geometry is of the 'edge' rather than the 'centroid' type ie the chlorine atom is closer to one (or two) carbon atom(s) in the aromatic ring rather than to the ring centroid.

References

1. Irving A, unpublished results.
2. Allen, F.H., Bellards, S., Brice, M.D., Cartwright, B.A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B.G., Kennard, O., Motherwell, J.R., Rodgers, J.R., and Watson, D.G. (1976) *Acta Crystallogr.* **B35**, 2331.
3. Irving, A., and Irving, H.M.N.H. (1993) *J. Cryst. Spec. Res.* **23**, 725.



PS06.05.12 SUBSTITUENT EFFECTS ON THE HYDROGEN BONDS IN ALCOHOL•AMINE COCRYSTALS. James H. Loehlin, Department of Chemistry, Wellesley College, Wellesley, MA 02181, USA

Alcohol•amine cocrystals provide a unique system in which to study hydrogen bonding, since each N and O atom participates in three independent hydrogen bonds. Each oxygen atom acts as a donor in one hydrogen bond and as acceptor in two others to separate nitrogen atoms. The amines form the complementary two donor and one acceptor hydrogen bonds to neighboring oxygen atoms. We have grown a series of cocrystals between 1,4-phenylene diamine and various phenols and a complementary series between hydroquinone and anilines.

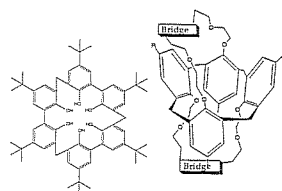
Our present study involves structures in which the H atom at the para position on the phenol or aniline in the parent compound [Loehlin, Etter, Gendreau & Cervasio (1994), *Chem. Mater.*, **6**, 1218-1221 and K.J.Franz, *Senior Honors Thesis*, Wellesley College, 1995] is replaced by -CH₃, -Cl, and -phenyl. Data from our structures will be correlated with that from the published structures by Ermer and Eling [*J. Chem. Soc. Perkin Trans. 2*, **1994**, 925] with -OH, -NH₂, -phenol and -aniline substituents in the para position on the phenol or aniline. Most of the structures have parallel networks of hydrogen bonds in a hexagonal grid with the difunctional moieties bridging between the networks. The para substituents are located between the molecular layers where they interact with similar or complementary groups on the adjacent hydrogen-bonded sheet. The steric interactions affecting the hydrogen-bond networks are almost identical, allowing correlation with models predicting substituent-induced electronic effects through

the aromatic ring. In our structures, the layers are held to one another by weak van der Waals' forces.

The hydrogen bonds are oriented in a nearly ideal tetrahedral arrangement, with almost linear N•••H-O or O•••H-N geometry. A detailed comparison of the hydrogen bond lengths and angles will be presented for all the structures studied to date.

PS06.05.13 MACROCYCLES FOR RADIONUCLIDE CAPTURE. Alexander Sobolev,^A Zouhair Asfari,^B Volker Böhmer,^C Jack Harrowfield^A and Jacques Vicens^B ^AUniversity of Western Australia, ^BUniversité Louis Pasteur de Strasbourg, ^CUniversität Mainz

Many derivatives of the macrocyclic oligophenols known as the "calixarenes" have attracted considerable interest for their metal ion binding ability, and it is well established that they may both selectively and strongly bind to heavy metals such as caesium, the lanthanides and the actinides. Some of these ligands are therefore under consideration as reagents for use in the treatment of nuclear waste. As part of the analysis of coordination selectivity and ultimately the optimisation of ligand design, it is essential to know the structures and conformations of the "free" ligands, and in the conduct of such a programme of research we have recently determined the structures of the ligands 1, 2, 3 and 4.



- (2) R = H, Bridge = OCH₂CH₂O
- (3) R = (CH₃)₃C, Bridge = OCH₂CH₂O
- (4) R = H, Bridge = 1,3 -C₆H₄O₂

PS06.05.14 SUPRAMOLECULAR DESIGN AND SYNTHESIS. THE CONTROL OF SYMMETRY AND INTERMOLECULAR SPACING. Joseph W. Lauher, Frank W. Fowler, Brian Dinkelmeyer, John Kane, Ruey-Fen Liao, Eric Matwey, Tam Nguyen, Caroline Schauer, and Leticia Toledo. Department of Chemistry, State University of New York, Stony Brook, NY 11794.

A library of molecular functionalities has been developed that allows us to systematically prepare molecular crystals with designed supramolecular structures with control of symmetry and intermolecular spacing. Each functionality leads to a hydrogen bonded network with a characteristic intermolecular spacing: ureas (4.6 ≈), oxalamides (5.0 ≈) and vinylogous ureas (6.7 ≈). With a proper selection and combination of additional substituents specific supramolecular structures can be constructed in one dimension (α -networks), two dimensions (β -networks) or three dimensions (γ -networks).

Consider, for example, symmetrical ureas and oxalamides synthesized from the 3- and 4-amino-methylpyridines. Employing co-crystallization methodology we can use these molecules as hosts to build supramolecular structures with a wide variety of carboxylic acid and alcohol guests. Conversely we can reverse the substituents and use ureas or oxalamides with carboxylic acid or phenol substituents as the hosts to align and space various pyridyl guests.

This host-guest/co-crystallization technique is now being applied to various real problems in supramolecular chemistry. Significantly we have designed and synthesized layered supramolecular structures containing various diacetylenes that exhibit structural parameters in accordance with those needed for a topochemical polymerization reaction. Similarly some of the same host molecules have been used to space various transition metals at designated positions within a crystal. Extensions of the methodology to new functionalities and new problems are underway.