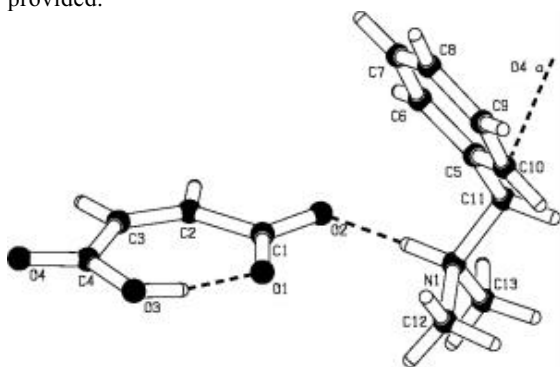


[s9.m3.p19] Structures of solid state supramolecular chemistry: some more models. M. Czugler, *Institute of Chemistry, Chemical Res. Center, Hungarian Academy of Sciences, 1525 Budapest P.O.B. 17, Hungary*

Keywords: H-bonds, supramolecular stereoisomerism

This contribution describes conventional and non-trivial H-bonds with the aim of describing weak interactions and the use of steric repulsion in the growth of crystals.

In the N,N-dimethyl-benzylammonium maleate salt (**1**, $C_9H_{14}N^+C_4H_3O_4$ 1:1, $P2_12_12_1$) crystal space produced environment is such that prochiral $-CH_2$ and $-CH_3$ groups become different. This is caused by the prime H-bonding helix built on the salt H-bond and another $C-H \cdots O$ to one of the $-CH_2$ hydrogens. The logic of *supramolecular synthon* \rightarrow *reaction path* \rightarrow *supramolecular diastereoisomerism* seems to evolve in the spontaneous resolution in this crystal (**1**)¹. Comparison with other cases where achiral tools (acids) produce resolutions will be provided.



Structure of (**1**) with some H-bonds shown

The 1,2,4,5-tetrabromomethylene-benzene (**2**, $C_{10}H_{10}Br_4$, $P2_1/c$) molecule gives another example of a supramolecular mimicry. Here the parent compound easily forms a 1:1 molecular adduct with 1,4-dioxane (**3**, $C_{10}H_{10}Br_4 \cdot C_4H_8O_2$, P 1). The resulting structure (**3**) may be understood as a *supramolecular substitution reaction product*. Accordingly crystal (**3**) results from crystal (**2**) by replacing certain (**2**) molecules in its crystal by the dioxane guest. This occurs precisely at the four $-CH_2$ side arms, where in pure (**2**) the $C-H \cdots Br$ contacts took place². Automated graph set and packing analyses³ shed further light on these phenomena.

[1] Czugler, M., *J.C.S. Chem. Commun.*, 2000, submitted.

[2] Czugler, M., MacNicol, D.D., *J. Supramol. Chem.*, 2000, submitted

[3] Motherwell, W.D.S., Shields G.P., Allen, F.H., 1999, *Acta Cryst.*, **B55**, 1044-1056.

[s9.m3.p20] Supramolecular assembly of diiodoperfluoro-arenes and -alkanes through halogen bonding. T. Pilati, *CNR-CSRSC, Via Golgi 19, I-20133, Milano, Italy*; P. Metrangolo and G. Resnati, *Dip. Chimica, Politecnico di Milano, Via Mancinelli 7, I-20131 Milano, Italy*.

Keywords: molecular interactions, supramolecular assemblies.

Perfluoro-derivatives are compounds of high technological relevance. These compounds show weak residual forces that are responsible for their anti-adhesive and lubricating properties, and for their low melting and boiling points, if compared with hydrocarbons having about the same molecular weights. Seldom these weak intermolecular forces permit the crystallisation or co-crystallisation of such compounds and when it happens, disorder is the rule. A way to incorporate perfluoro-residues into a crystal structure is to bind them to single atoms or groups giving stronger intermolecular interactions.

Here we present some of the last results in studying the ability of halo-derivatives of perfluoroalkanes and arenes, behaving as electron-acceptor modules, to give rise to supramolecular assembly through halogen bond (that is known to be stronger than the equivalent hydrogen bond) to neutral or charged electron-donors. The strength of the halogen bond is there enforced by the presence of the fluorine atoms, so that it is quite easy to produce linear assembly of dimers AB, trimers BAB, or non-covalent polymers $\cdots ABAB \cdots$, where A is a mono- or dihaloperfluoro-alkane/arene, acting as acid, and B is such a base as I-, Br-, the nitrogen atoms of amines and pyridines or the oxygen atom of pyridine-N-oxides. Dimers, trimers or polymers are obviously formed according to the numbers of interacting sites in A and B. In the case of perfluoro-arenes, the benzene ring is particularly poor in electron-density, so this offers the possibility of π - π interactions with electron rich arenes, as we found in the co-crystal obtained starting from a bis(2-pyridyl-methoxy)-calix[4]arene and 1,4-diiodoper-fluorobenzene. Here one-dimensional infinite chains of π - π bonded electron rich / electron poor benzene rings are formed. These chains are also linked together by $I \cdots N(\text{pyridyl})$ halogen bonds, forming a strong two-dimensional framework.

[1] Lommerse, J. P. M.; Stone, A. J.; Taylor, R. and Allen F. H. in "The Nature and Geometry of Intermolecular Interactions between Halogens and Oxygen or Nitrogen", *J. Am. Chem. Soc.*, **1996**, *118*, 3108-3116.