

**MS11.07.02 DYNAMIC INTERACTION OBSERVED IN HUMIDITY- INDUCED PHASE TRANSITIONS OF NUCLEOSIDES AND NUCLEOTIDES.** Yoko Sugawara, School of Science, Kitasato University, Kitasato, Sagami-hara, Kanagawa 228, Japan

We carried out dynamic analysis of humidity-induced phase transitions in nucleoside and nucleotide crystals, e.g. guanosine and disodium adenosine 5'triphosphate( $\text{Na}_2\text{ATP}$ ), by the X-ray diffraction method and low-frequency Raman spectra.<sup>1-3</sup> There exist flexible or switchable interactions which would be called as dynamic interactions.

In the crystal exhibiting the phase transition, base moieties of nucleosides and nucleotides are stacked to form a columnar structure. There is a water region between the molecular columns. The number of crystal water molecules in this region is a function of humidity, and the reversible crystal transition proceeds.

Intermolecular interactions are classified into two types. The first type is a dynamic interaction. Intercolumnar hydrogen-bonding networks vary together with increase or decrease of water molecules. It is noteworthy that ribose puckering modes contribute to the reconstruction of hydrogen-bonding networks. The second type is, of course, a static or rigid interaction which plays a role in holding the crystal lattice.

It is well-known that transformation of hydrogen-bonding networks induces structural changes of nucleic acids and proteins. Intermolecular interactions of biomolecules should be characterized by coexistence of both types of interactions.

1. Y. Sugawara et al. *J. Am. Chem. Soc.* **113** 5440(1991).
2. Y. Sugawara et al. *J. Biomol. Struct. Dyn.* **11**, 721(1994).
3. H. Urabe et al. *Phys. Rev. B* **51**, 5666(1995).

**MS11.07.03 CHEMICAL CONTROL OF INTERMOLECULAR INTERACTIONS IN PORPHYRIN-BASED HOST MATERIALS.** Charles E. Strouse and Marianne K. Byrn, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90095-1569, USA

The remarkable versatility of metallotetraarylporphyrins as clathrate hosts is the result of several molecular characteristics which are subject to chemical modification. Unlike host materials that possess a complementarity with favored guests, or a self-complementarity that dictates crystal packing, tetraarylporphyrin molecules, for the most part, interact in a non-specific way with both guest molecules and each other. As a result, the crystal packing in these materials is strongly influenced by entropic factors. The driving force for guest incorporation in these materials is the fact that these large, rigid, highly symmetric molecules cannot pack efficiently in three dimensions. Incorporation of guest molecules provides the additional degrees of freedom required for efficient packing. This talk will explore various modifications of the host molecules, and their influence on clathrate thermodynamics. The phase equilibria of these systems, and the importance of these equilibria in technological applications, will also be discussed.

**MS11.07.04 THE N-H...PHENYL(PLANE) INTERACTION HAS ALL THE PERSISTENCE OF A FIVE-YEAR-OLD IN A CANDY STORE.** Stan Cameron, Pradip K. Bakshi, Kathy N. Robertson & O. Knop; Department of Chemistry, Dalhousie University, Halifax N.S. Canada B3H 4J3.

When an aqueous solution of an acidified organic amine is added to an aqueous solution of sodium tetraphenylborate, an immediate thick (often white) precipitate is formed. It does not seem to matter what amine is used or whether the concentration is 0.1 M or 70 ppm, the result is the same. While the anion  $(\text{RnH}_{4-n})^+$  /  $(\text{BPh}_4)^-$  cation interaction is probably the main energy term in the lattice energy which produces these intensely water-insoluble

materials, at the heart of every structure is a 'hydrogen bond' where the N-H bond (or bonds) of the ammonium ion form an attractive interaction to the plane (or planes) of a phenyl ring of the tetraphenylborate cation. This system is remarkably robust and some aliphatic iminium ions with solution lifetimes of fractions of a second have been stabilised for years as crystalline tetraphenylborate salts.

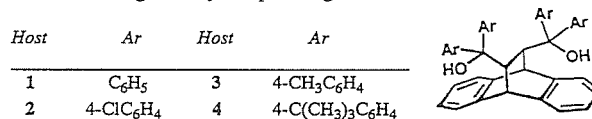
The hydrogen bonds are formed with a number of strategies, but in all the many samples we have studied so far<sup>[1]</sup>, where there is at least one N-H bond in the organo-ammonium ion, a hydrogen to ring-plane bond is always formed. The overwhelming preference of the tetraphenylborate ion is for a 1:1 ratio with the cation even when the amine is di- or multi-functional.

The general overview of the strategies used by this system to form the N-H...phenyl(plane) will be given. Our attempts to persuade the tetraphenylborate ion to take on di-charged (and multi-charged) organodiammonium ions will be described together with the response of the tetraphenylborate ion which invariably decisively outmanoeuvres us. Only a few of the crystal samples survive cooling, but the high-angle, low-temperature diffraction studies of the N-H...Phenyl interaction in the few samples that do survive low temperatures will be outlined.

- 1 Knop, O., Cameron, T.S. and others, *Cand. J. Chem.* (1980), **58**, 1355; (1993), **71**, 1495; (1994), **72**, 1273

**MS11.07.05 PACKING RELATIONS IN SOLID INCLUSIONS OF NOVEL ROOF-SHAPED HYDROXY HOSTS.** Ingeborg Csöreg, Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden; Edwin Weber, Institut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg/Sachsen, Germany.

Intermolecular interactions play a crucial role in molecular recognition and in packing relations of organic crystal structures. The success of crystal engineering seems to lie in understanding the crystal packing forces.



Systematic X-ray analyses of cocrystals of synthetic host molecules, such as hosts 1-4, provide excellent opportunities for investigation of noncovalent interactions between different groups in various environments.

Host	•Guest	Stoichiometry	Space group	Host	•Guest	Stoichiometry	Space group
2•2-pentanol	1:1	<i>Fddd</i>		3•methanol	2:1	<i>P-1</i>	
2•1,4-dioxane	2:5	<i>P2<sub>1</sub>/n</i>		3•toluene	1:1	<i>Fddd</i>	
2•o-xylene	1:2	<i>Pc2<sub>1</sub>n</i>		4•pyridine	2:3	<i>P-1</i>	

The compounds listed above exhibit various sizes and polarities of the hosts and/or different H bonding abilities and polarities of the guests, resulting in different crystalline architectures with a variety of symmetries and host-guest stoichiometries. However, remarkable features repeatedly appearing in different compounds were also observed. Noteworthy is the isostructurality of two, in many respect different compounds, namely 2•2-pentanol (1:1) and 3•toluene (1:1). Structural details with emphasis on the balance of intermolecular interactions will be discussed.