

PS11.07.10 HYDROGEN BOND (HB) PATTERNS AROUND THE PICRATE ANION. by Paola Gilli¹, Claudine Pascard² and Luba Tchertanov², Centro di Strutturistica Diffraattometrica, Università di Ferrara (Italy)¹ ICSN-CNRS, 91198 Gif-sur-Yvette (France)²

Within a project on systematic analysis of anion environments we have undertaken a Cambridge Structural Database search of the free picrate anion: 99 structures having $R < 0.10$, $\sigma_{c-c} < 0.010$ Å and located H atoms were retrieved. The H-bonding capability of picrate is mainly due to the negatively charged phenolic oxygen: out of 80 structures of picrates containing one or more potential HB donor groups, 79 form at least one D-H...O bond ($DHO > 90^\circ$, $H...O < 3.0$ Å), one shows strong S...O-interactions, while in the 19 structures with no HB donors the phenolic oxygen interacts only with C-H groups pointing to it. Although each of the three nitro groups may act as HB acceptor, it is worth mentioning the role played by ortho-NO₂: most of the D-H...O interactions are bifurcated, with the H atom bonded both to the phenolic and to the nearest ortho-NO₂ oxygen. Intermolecular associations of picrate may involve one, two, but no more than three D-H...O bonds (D=O,N; all NH are positively charged or belong to a positively charged moiety). When only one HB donor is present, the crystal inevitably consists of ion pairs, held together by rather strong HBs (distances down to 2.52 and 2.62 Å for O...O and N...O, respectively). All OH groups lie close to the picrate phenyl plane, whereas NH groups can approach the anion from all possible directions, OH being more accessible than aminic or amidic NH. With two HB donors we can get pairs again, as well as less common molecular associations, such as H-bonded infinite chains or 4-membered rings. Chains and rings are the more interesting cases: each picrate forms two HBs, one above the phenyl plane, one under. As for the HB distances, we have so far studied their dependence on the number of HBs formed, on the chemical nature of the donors (O or N), and on charge; their dependence on HB donors pK_a , as well as the comparison with related compounds (dichloropicrate, picric acid, phenols) are under investigation.

According to our opinion, the great variety of HB patterns and especially the frequent formation of an ion pair between the positively charged moiety and the picrate anion, strongly tightened by short HBs, can explain the successful use of picrate salts in crystallization processes.

PS11.07.11 HYDROGEN BONDING TO AROMATIC PI SYSTEMS. Katherine N. Robertson, Pradip K. Bakshi, T. Stanley Cameron, and Oswald Knop. Department of Chemistry, Dalhousie University, Halifax NS, Canada B3H 4J3.

The preliminary investigation of the electron-density distribution in the NH... π (phenyl) bond in dabco(BPh₄)₂ (reported at the 1995 ACA meeting in Montreal) has been followed up by a more thorough study (LT data, multipole refinement) intended to demonstrate unambiguously the existence, and describe the geometry, of the H...phenyl bond in this crystal. Details are also reported of our recent determinations of the crystal structures of the tetraphenylborates of the guanidinium (-60°C), biguanidinium, 2,3-bis(2-pyridyl)pyrazinium, 1,2,3,4-tetrahydro-9-acridinammonium (tacrine), [Ni(MeCN)₂(N,N'-Me₂-en)₂]²⁺, and [Ph₃BNH₂(CH₂)₂-NMe₂]⁺ cations, with particular attention to the hydrogen bonding in these crystals.

PS11.07.12 HYDRATES AND HYDROGEN BONDING: CRYSTAL CHEMISTRY OF AND WITH SOME SELECTED ACIDS AND BASES. Dietrich Mootz, Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität, 40225 Düsseldorf, Germany.

Work in this laboratory over the last few years on hydrated and other hydrogen-bonded systems and crystal structures, in part already published, will be surveyed. The emphasis is on some twenty low-melting hydrates of Bronsted-type small-molecule acids and bases, weak and strong, of inorganic and organic chemistry. Their formation has been studied using thermal analysis and temperature-dependent X-ray powder diffraction. Crystals for structure determination have typically been grown *in situ* on a low-temperature diffractometer by miniature zone melting [1].

The bases selected are charged as well as uncharged, like cesium and tetramethylammonium hydroxide [2] on one hand and certain new phosphazenes, aliphatic and aromatic amines [3], and the prototype synthetic macrocyclic polyether 18-crown-6 [4] on the other. The acids are mainly halogenoacetic ones [5].

In contrast to the charged-base hydrates, ionic *a priori*, all hydrates of the uncharged bases, even of the highly basic phosphazenes, are found to be molecular. The acid hydrates are partly also molecular and partly H₅O₂⁺ salts, including the unusual case of either type realized, with a lower and a higher hydrate, by the same acid. Some of the higher hydrates are new representatives of the polyhedral clathrate or semi-clathrate hydrates. Others contain characteristic 2D water layers. These display various patterns of condensed four-, five- and/or six-membered rings and in some cases can clearly be attributed to their low temperature of formation.

Particular features of hydrogen bonding will be discussed also for the anhydrous acids and some interacid adducts. They embrace a new 1D chain conformer for a substituted acetic acid and the reversal of all OH...O bonds in the otherwise unaltered chain of formic acid when this is cocrystallized with hydrogen fluoride.

[1] Brodalla *et al.*: J. Appl. Crystallogr. 18 (1985) 316.

[2] Mootz & Stäben: J. Am. Chem. Soc. 116 (1994) 4141.

[3] Mootz & Born: Z. Naturforsch. 49b (1994) 243;

Born *et al.*: Z. Naturforsch. 50b (1995) 101;

Stäben & Mootz: J. Incl. Phenom. 22 (1995) 145.

[4] Mootz *et al.*: J. Am. Chem. Soc. 116 (1994) 12045.

[5] Schilling *et al.*: J. Fluorine Chem. 73 (1995) 225;

Schilling & Mootz: J. Fluorine Chem. 74 (1995) 255.

PS11.07.13 DIRECTIONALITY OF NON-BONDED INTERACTIONS IN SOLVATED MOLECULAR CRYSTALS H. Oswaldo Aldas-Palacios and Raymond E. Davis. Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712-1167, USA

The correlation between the molecular electrostatic potential (MEP) of solvent molecules and the geometrical preferences of their non-bonded interactions with electrophilic and nucleophilic species in molecular crystals is examined. Pyridine and benzene solvents are chosen due to their similar size and shape, but different electrostatic characteristics.

The crystal structures used in this study were obtained from the Cambridge Structural Database (CSD). Structures with no disorder and with R values less than 15% were selected for the study. The environment of each solvent molecule was studied at distances ranging from 2.0 to 4.2 Å from its non-hydrogen atoms. Non-hydrogen atoms within this contact range were found and characterized as to their chemical identity. Contact atom locations and functional group orientations with respect to the solvent molecule were determined.

Ab initio calculations using the Gaussian 92 computer programs were performed, with the geometry optimization at the 6-