

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.

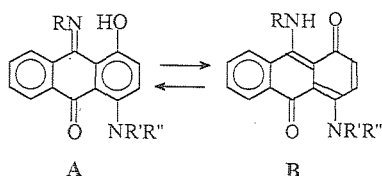
Ab initio calculations using the Gaussian 92 computer programs were performed, with the geometry optimization at the 6-

31 level, and the MEP calculation, corresponding to the location of each non-bonded atomic contact, at the 6-311** level. The MEP was stored incrementally on a grid with its origin at the centroid of the solvent molecule. Computer programs were then used to analyze geometrical preferences and the correlation of the MEP with the directionality of the intermolecular interactions.

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PS11.07.14 STRUCTURES OF SOME ANTHRAQUINONE DYES. E.S.Alekseyeva, A.V.Yatsenko, V.A.Tafeenko and L.A.Aslanov, Chemistry Dept., Moscow State University, 119899 Moscow, Russia.

The impact of crystal packing and specific intermolecular interactions on molecular structure has been illustrated by the example of five anthraquinone derivatives. Compounds **1** and **2** show analogous behaviour in solutions: in non-polar solvents the form **A** is a predominant one, whereas polar solvents displace the equilibrium towards ketoenamine form **B**.



1: R = H, R' = Ac, R'' = *p*-tolyl; 2: R = mesityl, R' = Ph, R'' = H

The crystal structure of **1** is built up from centrosymmetric dimers (interplanar distance 3.43 Å), where two molecules are H-bonded in addition. As a result only form **B** takes place in crystal. No signs of H-bonding or other specific interactions are observed in the crystal structure of **2**, hence the crystal surrounding displaces here the equilibrium towards form **A** like low-polar solvent.

Visible spectra of anthraquinone dyes are also related to the motif of crystal packing. The crystal structures of 1,4-bis(mesitylamino)anthraquinone (**3**), 1,4-bis(phenylamino)anthraquinone (**4**) and 1-hydroxy-4-(*p*-tolylamino)anthraquinone (**5**) are built up from separated molecules, dimers and stacks with interplanar distance 3.35 and 3.50 Å respectively. As a result the maximum in reflection spectrum of **3** is blue shifted by 1000 cm⁻¹ relative to the absorption spectrum in solutions, whereas **4** shows red shift by 700 cm⁻¹ accompanied by the direct manifestation of vibrational structure.

PS11.07.15 ATTRACTIVE EDGE-TO-FACE AROMATIC INTERACTIONS IN A RANGE OF SIMPLE NITRONES, OXAZIRIDINES AND IMINES. By J.F. Malonea, D.R. Boyda, T.A. Evans and A. Smitha, W.B. Jenningsb and W. O'Sullivanb, School of Chemistrya, The Queen's University of Belfast, Belfast, N. Ireland and Department of Chemistryb, University College, Cork, Republic of Ireland.

Attractive intramolecular edge-to-face type interactions between aromatic moieties have been identified by X-Ray studies and NMR in a range of simple nitrones, oxaziridines and imines. Intramolecular hydrogen to mid-aromatic ring distances of 2.60Å, 2.66Å, 2.70Å, 2.73Å and 2.78Å are observed. The Hunter-Sanders rules (C.A. Hunter and J.K. Sanders, *J. Am. Chem. Soc.*, 1990, 112, 5525) are applied to the interactions and are found to be in agreement with the observations. Analysis of the crystal lattices have shown similar intermolecular interactions affecting the crystal packing, in some cases quite significantly. One case showed evidence in the NMR for an intramolecular edge-to-face type interaction which was not observed in the solid state where several intermolecular aromatic-aromatic interactions seemed to be controlling the geometry. The σ polarization of the atoms in the rings is proposed as being of importance in determining the type of interaction observed and hence the geometry.

PS11.07.16 ORIENTATIONAL DISORDER OF SOME ORGANIC MOLECULAR CRYSTALS STUDIED BY ATOM-ATOM POTENTIALS. Chitra Samanta, Dept. of Physics, Jadavpur University, Calcutta, India

Systematic analysis of molecular geometry and conformation were studied by atom-atom potential method.

The vander waal's inter molecular attraction concept leads to the pairwise nonbonded interaction potentials. Concerning the arrangements of atoms in a regular distribution the potential of Buckingham's type $-AA/r^6 + B e^{-\alpha r}$ were applied to the study of organic molecular crystals.

The universal potential parameters, AA, B, α are used from those of Giglio, E².

The evaluation of lattice energies (Kcal/mol) with rotation of the molecules about an axis passing through the centre of gravity and normal to the molecular plan yields the interesting results regarding the confirmation of the molecular disorder.

The following crystals were studied:-

Crystals	Molecular Formula	Cell Parameters
1. 1,2 Dichloroethane	C ₂ H ₄ Cl ₂	A ₀ =4.66° A
2. P- nitrobenzoic acid	NO ₂ C ₆ H ₄ COOH	AO=12.97° A BO=5.07° A CO=21.43° A AO=6.083° A
3. Pentaerythritol	C(CH ₂ OH) ₄	AO=8.726° A

Ref:

- Acta Cryst., Roychowdhury and Basak, B31, 1969.
- Acta Cryst., Govezzotti, A and Simonetta, M, 17.559 1964.

PS11.07.17 C-H... π INTERACTION OBSERVED IN COMPLEXES OF SURFACTANT MOLECULES WITH AROMATIC COMPOUNDS. Keiju Sawada[‡], Yuji Ohashi[‡], Nahoko Iimura[‡] and Hirotaka Hirata[‡], [‡]Department of Chemistry, Tokyo Institute of Technology, Japan and [‡]Niigata College of Pharmacy, Japan

A C-H... π interaction has been found between surfactant molecules and aromatic compounds. Various complexes were obtained from an aqueous solution with cationic surfactants, such as cetyl-(C₁₆H₃₃N(CH₃)₃, CTAB), myristil-(C₁₄, MTAB), lauril(C₁₂, LTAB) and decyl(C₁₀, DTAB) trimethylammoniumbromide, and aromatic compounds. The grinding of the two compounds in a mortar gave the same complexes as obtain in the solution.

In order to examine the interaction between surfactant molecules and aromatic compounds, we tried to form the complexes of CTAB, MTAB, LTAB, DTAB with biphenyl (C₁₀H₈) which has no functional groups. After many trials, all the complex crystals were successfully obtained. Moreover, the same complexes were formed by grinding in a mortar. The analyzed structures of the complexes clearly suggest a special interaction, C-H... π , between the alkyl group and phenyl rings. This interaction should be a driving force of these formation.

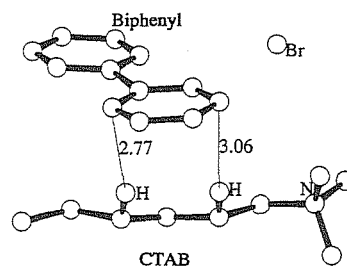


Fig.1 The Proposed C-H... π Interaction