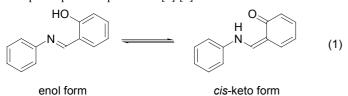
## STRUCTURE/PROPERTY RELATIONSHIP

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Proton tautomerism is a general phenomenon in organic molecules and plays a vital role in many fields of chemistry and biochemistry. The tautomerism of salicylideneanilines [eq(1)] has attracted a considerable attention because it is closely related to thermo- and photochromism. Salicylideneanilines greatly favor the enol form over the *cis*-keto form in the gas phase. We demonstrate here that the instability of the *cis*-keto form is substantially reduced by intermolecular hydrogen bonding and also by self-association, on the basis of our variable temperature X-ray crystallographic and UV-vis absorption spectroscopic studies.[1]-[3].



 Ogawa K., Kasahara Y., Ohtani Y., Harada J., J. Am. Chem. Soc., 1998, 120, 7107. [2] Ogawa K., Harada J., Fujiwara T., Yoshida S., J. Phys. Chem. A, 2001, 105, 3425. [3] Fujiwara T., Harada J., Ogawa K., J. Phys. Chem. B, 2004, 108, 4035.

Keywords:	proton	tautomerism,	self-association,
salicylidenean	ilines		

#### P.08.08.12

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### The First Observation of All Six Elastic Constants in Tetragonal Hen Egg-white Lysozyme Crystals

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It is interesting to investigate the elastic property of protein crystals. Previously, we have reported the longitudinal sound velocity of tetragonal hen egg-white (HEW) lysozyme crystals which are one of typical protein crystals using an ultrasonic pulse-echo method [1]. However, there is no measurement of all components of elastic constants, C<sub>ii</sub> in tetragonal HEW lysozyme crystals since the measurements of transverse ultrasonic wave have not been carried out yet. In case of pulse-echo method, in order to generate a transverse ultrasonic wave in the crystals, a transducer must be in close contact with the crystal. However, hydrated protein crystals are fragile, and consequently, it was difficult to glue a transducer to a protein crystal. Recently, we found that the sound velocity increases with exposure to open air and approaches a constant value [2]. This suggested that the protein crystals became harder due to dehydration. Therefore, we have succeeded in the contact between a crystal and a transducer using dehydrated crystals. This led us generating a transverse ultrasonic wave through the dehydrated HEW lysozyme crystals at 42% relative humidity (RH). As a result, all components of elastic constants in dehydrated crystals were determined.

[1] a) Tachibana M., Kojima K., Ikuyama R., Kobayashi Y., Ataka M., *Chem. Phys. Lett.*, 2000, 332, 259; b) Tachibana M., Kojima K., Ikuyama R., Kobayashi Y., Ataka M., *Chem. Phys. Lett.*, 2002, 354, 360. [2] Tachibana M., Koizumi H., Kojima K., *Physical Review E*, 2004, 69, 051921.

### Keywords: ultrasonics, elastic properties, protein crystals

#### P.08.08.13

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# 5,5'-Disubstituted-3,3'-Methanediyl-*bis*-Indoles as Potential Antitumorals

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Certain compounds found in the diet are a potential source of new

classes of chemotherapeutic and chemopreventive agents. Indole-3carbinol, a major indole metabolite from cruciferous vegetables, and its natural condensation product 3,3'-diindolylmethane, have been found to inhibit the development of tumors in breast, uterus and liver [1-3]. However, both compounds may exhibit adverse tumor promoting activity in other organs. In search for new *anti* cancer agents we have decided to investigate 3,3'-diindolylmethane derivatives which may reduce the growth of human tumor cell lines by the inhibition of the binding of some transcription factors to the adequate sequences in DNA.

To determine structural parameters important for the biochemical activity we have performed the <sup>1</sup>H and <sup>13</sup>C NMR data and single crystal X-ray analysis of 5,5'-disubstituted-3,3'-methanediyl-*bis*-indoles. The results of these studies indicate insignificantly different molecular structures of the investigated compounds but significantly different networks of intermolecular interactions in crystals. Interesting NH···· $\pi$  hydrogen bonds are observed which may have a functional role in biological features.

 Grubbs C.J., et al., Anticancer Res., 1995, 15, 709. [2] Cover C.M., et al., J. Biol. Chem., 1998, 273, 3838. [3] Hong C., et al., Bioch. Pharmacol., 2002, 63, 1085.

Keywords: anticancer compounds, 5,5'-disubstituted-3,3'methanediyl-*bis*-indoles, X-ray single- crystal diffraction

#### P.08.08.14

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Intermolecular Interactions in 1,1'-Binaphthyl, Polymorphs and Symmetry Breaking

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A theoretical-experimental work is presented related with the chiral symmetry breaking of melting crystallization of 1,1'-binaphthyl derivatives and polymorphism. We confirm that the chiral symmetry breaking can be observed in crystallization from a melt of 1,1'binaphthyl by a constant stirring during the crystallization. Crystallographic studies by Powder X-ray diffraction (PXRD) reveal two crystallographic forms of 1,1'-binaphthyl: one chiral form (P42<sub>1</sub>2<sub>1</sub>) with either R or S enantiomers of the trans-1,1'-binaphthyl conformer and another racemic crystal (C2/c) with both enantiomers of the cis-1,1'-binaphthyl conformer. Quantum mechanical calculations of the crystal lattice for 1,1'-binaphthyl and 2,2'dihydroxy-1,1'-binaphthyl polymorphs were performed by Density Functional Theory approximation. Our calculations reproduce the crystal lattice parameters and PXRD pattern finding the P42<sub>1</sub>2<sub>1</sub> form with lower energy than the C2/c form for 1,1'-binaphthyl. The main intermolecular interactions in 1,1'-binaphthyl crystals are weak aromatic CH/ $\!\pi$  hydrogen bonds, which are responsible for enantiomeric discrimination in the molecular recognition during crystallization. The C2/c form achieves a more efficient packing than the chiral one, but intermolecular interactions in  $P42_12_1$  form are stronger than in C2/c form. In 2,2'-dihydroxy-1,1'-binaphthyl the intermolecular interactions are stronger with hydrogen bonds between the hydroxyl groups and polymorphs can be predicted by Monte Carlo simulated annealing.

Keywords: 1,1'-binaphthyl, intermolecular interactions, chiral recognition

#### P.08.08.15

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# Experimental and Theoretical Study of Weak Interactions in Simple Molecular Solids

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The aim of this work is the study of weak intermolecular interactions in molecular crystals, by both diffraction methods and ab initio calculations using the new version of the CRYSTAL [1] program, which is designed to treat infinite periodic systems. Two molecular systems were chosen: i) formamide [2]: each molecule is linked to three other molecules by two types of hydrogen bonds; ii) boric acid [3]: each molecule forms six almost equivalent hydrogen bonds with three neighbouring molecules. The CRYSTAL03 calculations were carried out employing the HF and DFT (B3LYP) methods with the 6-31G(d,p) basis set, also using the new geometry optimisation options. The electron density, the electrostatic potential, the binding energies and the structure factors were derived. In formamide the cooperative effects of packing on the hydrogen bond interactions leading to the formation of linear chains and on those connecting the chains were analyzed. Hydrogen bonded molecules of boric acid form layers held together by weak B---O interactions, which may play a role in dictating the inter-layer packing. The comparison of the experimental and theoretical results and the most recent results obtained using the geometry optimisation facilities in CRYSTAL03 will be presented.

[1] Saunders V.R., et al., *CRYSTAL03*, www.crystal.unito.it [2] Stevens E.D., *Acta Cryst.*, 1978, B**34**, 544. [3] Gajhede M., Larsen S., Rettrup S., *Acta Cryst.*, B**42**, 545, 1986.

Keywords: hydrogen bond, weak interactions, *ab-initio* calculations

#### P.08.08.16

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# Orientations of Axially Coordinated Ligands in Model Systems of Cytochromes

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Many properties of cytochromes and model systems depend on orientations of axial ligands. In this work we elucidated role of substituents of porphyrin on orientation of axial ligands in model systems of cytochromes. The orientations of axially coordinated imidozoles and pyridines in crystal structures of model systems of cytochromes were analyzed and data were compared with previous quantum-chemical calculations.

The results show that eight ethyl groups on porphyrin ring strongly favor parallel orientation, hence, in all these complexes axial ligands, pyridines or imidazoles, are mutually parallel. Four phenyl or mesityl groups at *meso*-carbons also favor parallel orientation but less strong. Hence, in most of the bis-imidazole complexes orientation is parallel, while in bis-pyridine complexes orientation of pyridines depends on oxidation state of Fe.

In Fe(II) complexes orientation is parallel, in Fe(III) it is orthogonal. In Fe(III) complexes influence of the interaction of pyridine with porphyrin ring, dominates over influence of phenyl or mesityl groups on porphyrin ring, and the orientation is parallel. Namely, by previous quantum chemical calculations it was shown that in bis-pyridine Fe(III) porphyrinato complexes without substituents orthogonal orientation is favored by 16 kcal/mol.

Keywords: ligands, porphyrins, cytochromes

#### P.08.08.17

### Acta Cryst. (2005). A61, C332

# $CH/\pi$ Interactions between Chelate and Phenyl Rings in Acetylacetonato Complexes

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By coordinating to metal atom with acetylacetonato ligand makes planar chelate ring, with delocalized bonds. Hence, coordinated acetylacetonato ligand could be involved in CH/ $\pi$  interactions with

phenyl ring in two ways, as hydrogen atom donor, or as hydrogen atom aceptor. In first case hydrogen atoms of acetylacetonato ligand could make MLAC $\pi$  interactions with phenyl ring. Acetylacetonato ligand has negative charge, but by coordinating to metal cation partial positive charge is transferred from the metal cation to the ligand. If enough positive charge is transferred hydrogen atoms of acetylacetonato ligand will get enough positive charge to be involved in MLAC $\pi$  interactions. In second type of interactions phenyl ring and chelate ring change roles; phenyl ring is hydrogen atom donor whereas chelate ring with delocalised  $\pi$ -system is hydrogen atom acceptor.

Here we report on CH/ $\pi$  interactions between acetylacetonato chelate rings and phenyl rings in acetylacetonato complexes. The results were obtained by searching and analyzing crystal structures in Cambridge Structural Database (CSD) and by quantum chemical calculations. Dependence of CH/ $\pi$  interactions on delocalization in chelate rings that is connected with type of metal in the ring was studied. To the best of our knowledge this is the first time that influence of metal in a chelate ring on CH/ $\pi$  interactions in metal complexes was studied.

Keywords: CH/ $\pi$  interactions, DFT, chelates

#### P.08.09.1

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Structural Characterisation of *p*-semiquinone Radical in a Crystal: X-ray Structure and EPR Evidence

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In membrane-located proteins, quinone system plays a significant role in electron-transfer reactions. The described work illustrates that semiquinone radical is stabilized in the solid state.

Thin dark-red plate-like crystals of *p*-semiquinone radical were grown by evaporation of mildly alkaline, saturated water solution of hydroquinone. Although stable in air, larger single crystals decay after ca. 20 h exposure to X-rays or UV radiation producing amorphous yellow substance identified as a mixture of quinone and quinhydrone.

Solid-state electronic paramagnetic resonance spectra of crystalline *p*-semiquinone detected its paramagnetic propetries revealing four symmetrically equivalent protons.

Crystal strucure was determined at 100 and 150 K (monoclinic, space group P 21/c, a = 3.78 Å, b = 5.98 Å, c = 10.79 Å,  $\beta = 90.66^{\circ}$ ). In both of them, *p*-semiquinone molecule is centrosymmetric (four protons are, therefore, equivalent), with C-O bond length of 1.295 Å, corresponding to bond order of 1.5. Molecules are hydrogen bonded into infinite chains (O-H···O distance of 2.70 Å with the proton disordered between two oxygen atoms. This packing is very similar to that of quinhydrone; the unit cell can be transformed into a half of the unit cell of quinhydrone.

### Keywords: radical, p-semiquinone, EPR

#### P.08.09.2

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## Crystal Structure and Synthesis of New Trinuclear 3d-metal Trifluoroacetates

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Anhydrous acid trinuclear trifluoroacetates of divalent metals  $[M_3(CF_3COO)_6(CF_3COOH)_6]CF_3COOH$  where M = Ni (I) and Co partially and hvdrated nickel trifluoroacetate (II), [Ni<sub>3</sub>(CF<sub>3</sub>COO)<sub>4</sub>(CF<sub>3</sub>COOH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>](CF<sub>3</sub>COOH)<sub>2</sub> (III) were synthesized and studied by X-ray diffraction. Compounds I and II were obtained by crystallization from solutions of Ni(CF<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (I), Co(CF<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (II) in trifluoroacetic anhydride in the presence of phosphoric anhydride as the drying agent. Compound I crystallizes in trigonal system, space group. R  $\overline{3}$ , Z=27, a = 13.307(2), c= 53.13(1) Å, V=8148(2) Å<sup>3</sup>,  $R_1 = 0.1112$ . The structure is molecular; trinuclear linear unit is formed by three metal