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Structure and Dynamics of Hydrogen-Bonded Systems

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The Evolution of Hydrogen Bonds in Molecular Materials under Changing External Conditions by Neutron Diffraction and Complementary Methods

Chick WILSON

Chemistry Dept., West CHEM Research Sch.
University of Glasgow, Joseph Black Building.
Glasgow G12 8QQ
U.K.

The Evolution of Hydrogen Bonds in Molecular Materials under Changing External Conditions by Neutron Diffraction and Complementary Methods

Chick Wilson
Department of Chemistry and WestCHEM Research School, University of Glasgow

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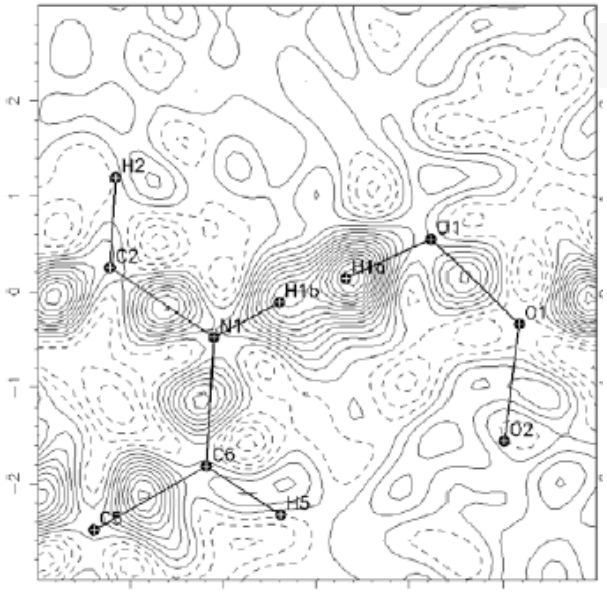
The Problem

- **Even Excellent experiments can lead to ambiguous interpretation**
- We use multi-condition X-ray and neutron diffraction (usually single crystal), including high resolution X-ray
- But we can still have ambiguities



*Schmidtmann et al, CrystEngComm, 2007, **9**, 743*

- We also constrain our systems to be in the solid state
- **Can modern computational chemistry methods help us to understand better our experiments?**

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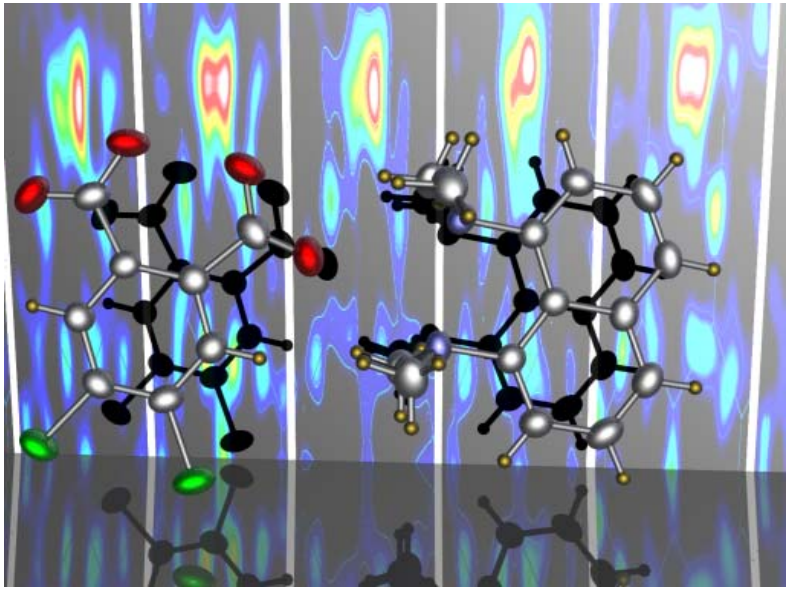
One Concept: Evolving Molecules in the Hall of Mirrors

Structural Evolution

- Materials whose structure or properties change with external variables

Materials

- Molecules or molecular complexes with “tuneable” atoms – often protons



Our “Laboratory”

- We work in the solid-state – periodic crystalline arrays – The Hall of Mirrors

Techniques

- Crystallisation – self-assembly in the solid-state
- Variable condition diffraction – X & n
- Solid-state quantum chemical calculations

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Pushing the Limits of Diffraction Techniques

- **X-ray single crystal diffraction**
  Strong focus on variable temperature for examining evolving structures
- **Neutron Single crystal diffraction**
  Multiple condition, shorter data collection times
- **High throughput X-ray diffraction**
  Powder and single crystal
- **High throughput neutron single crystal**
  Exploiting new instrumentation
- **Neutron powder diffraction**
  Just becoming possible for these materials

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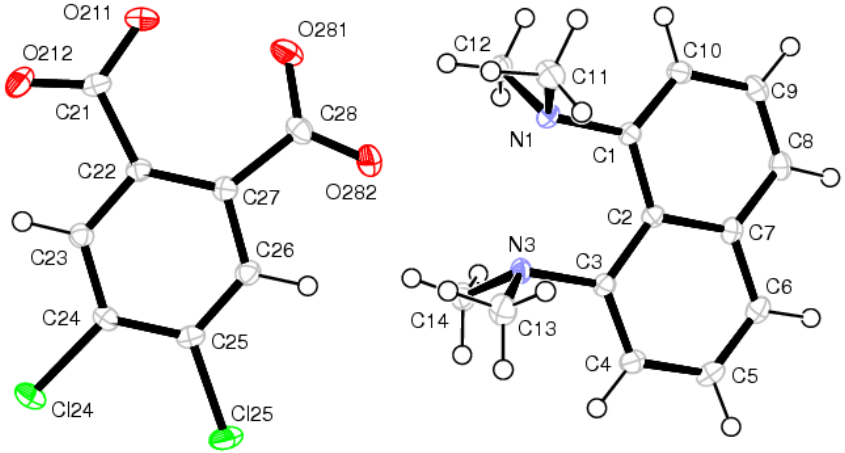
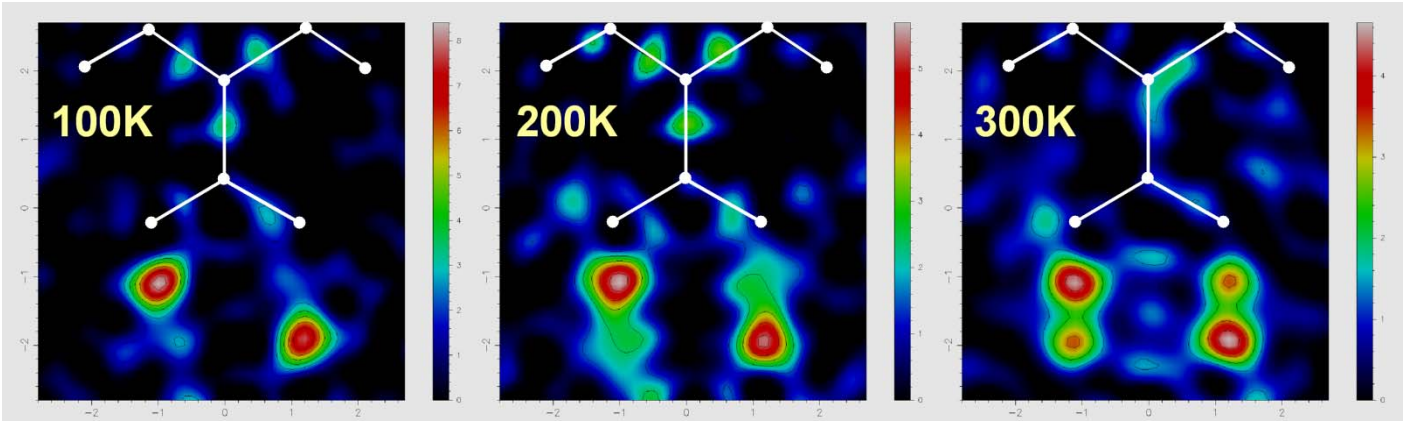
Motifs with Predictable (and tuneable?) HB Properties?

- **Short, strong HB – Transfer, Migration**



- **Proton sponges – Proton Transfer**

- **COOH dimers – Disorder**



- **“bifurcated” motifs**

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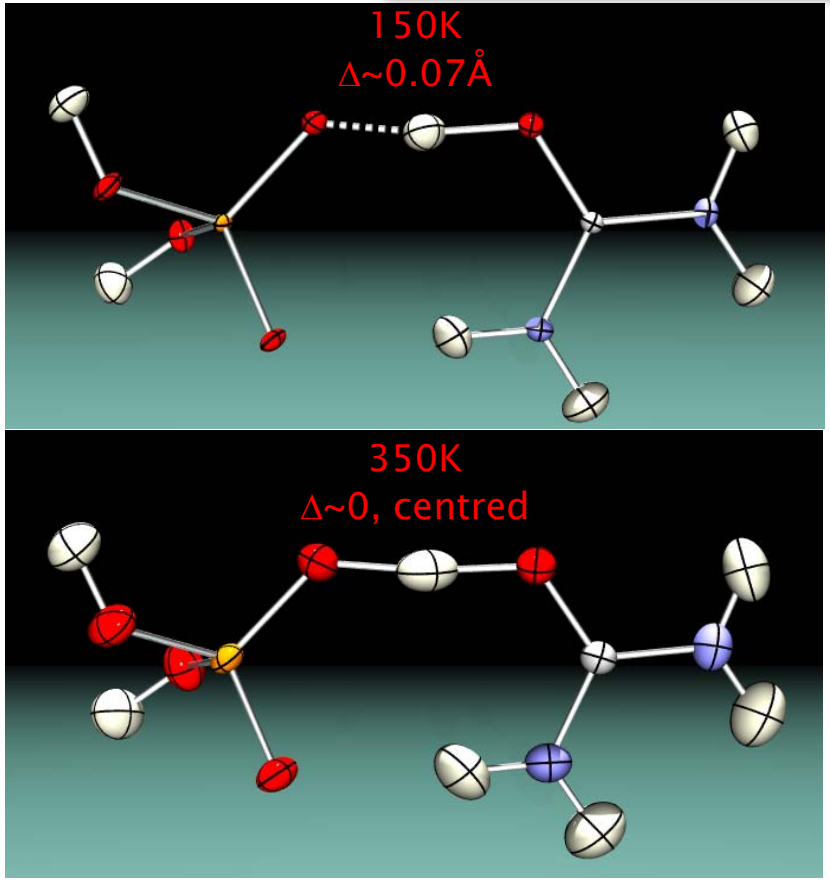
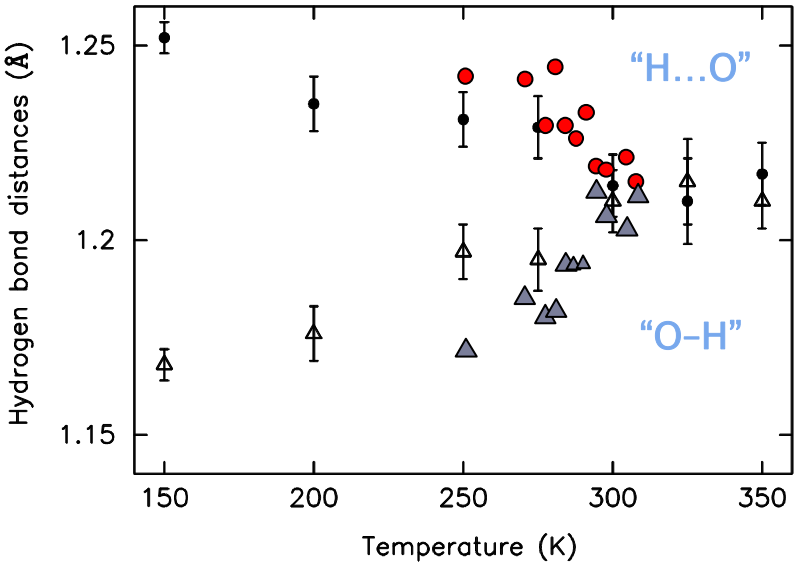
An old favourite* - proton migration in urea-phosphoric acid



* But still not fully understood!

Wilson & Morrison,
*Chem Phys Letters, 2002, **362**, 85*



VT neutron diffraction

Computational Chemistry of the short HB

Neutron, 15K	O-H, 1.158Å	O...O, 2.41Å	H…O, 1.267Å
Isolated molecule	O-H, 1.004Å	O...O, 2.65Å	H…O, 1.604Å
Plane-wave DFT	O-H, 1.105Å	O...O, 2.42Å	H…O, 1.329Å

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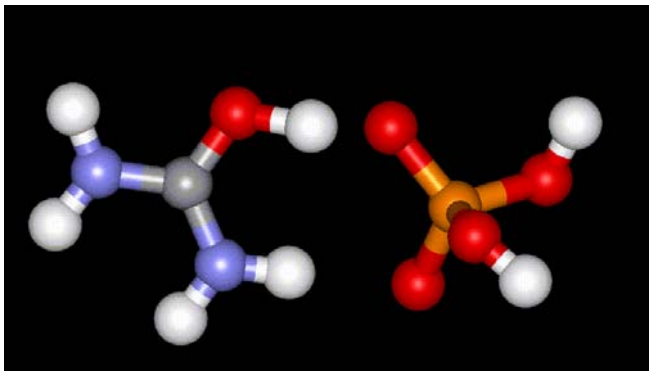
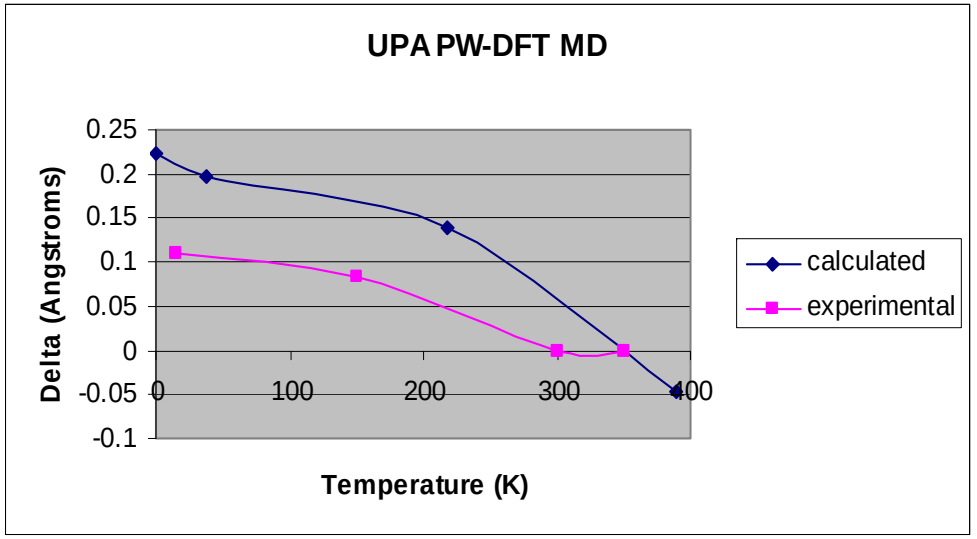
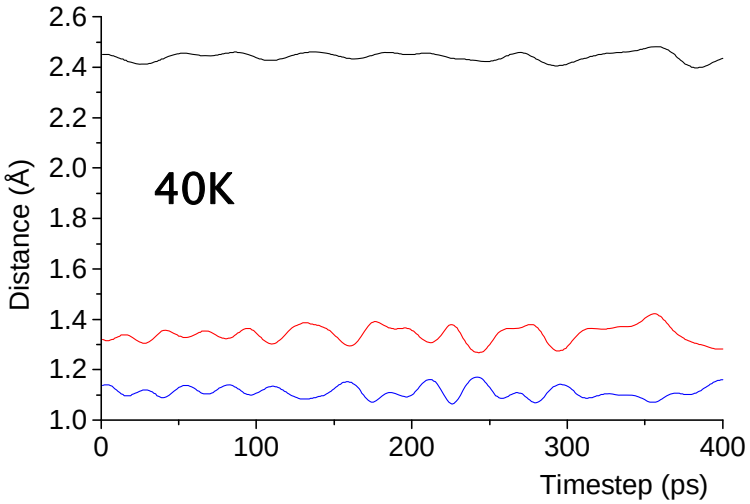
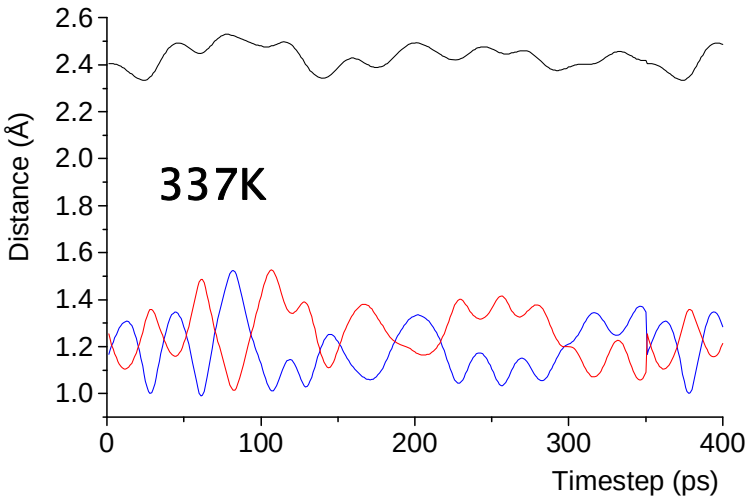
Raise the stakes, raise the Temperature (MD-DFT)



*Morrison et al, JACS, 2005, **127**, 4042*







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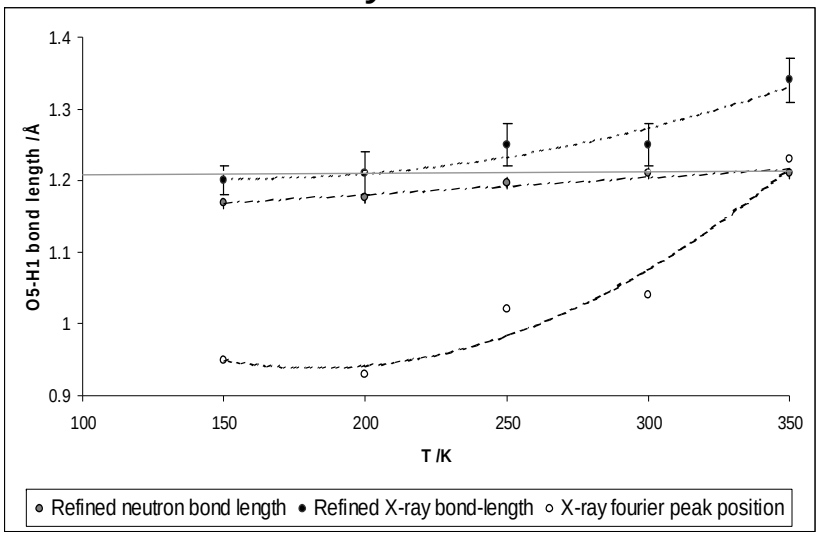
Urea-phosphoric acid / uronium phosphate

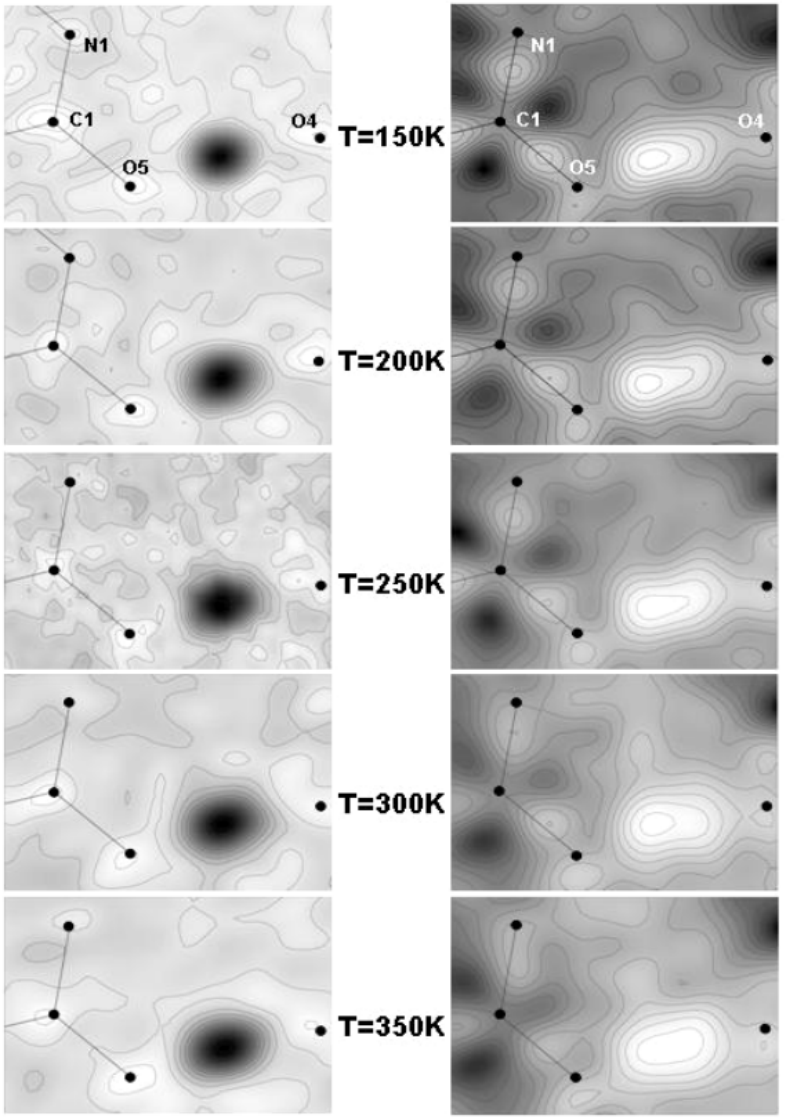
Imaging Hydrogen Bonds in UPA: added value from X/n

Joint X-n Analysis of proton/electron density evolution in hydrogen bonds

Migration can also be followed by XRD - and additional information obtained about the nature of the electron density in the HB



Parkin, Harte, Goeta & Wilson
*New J Chem, 2004, **28**, 718-721*



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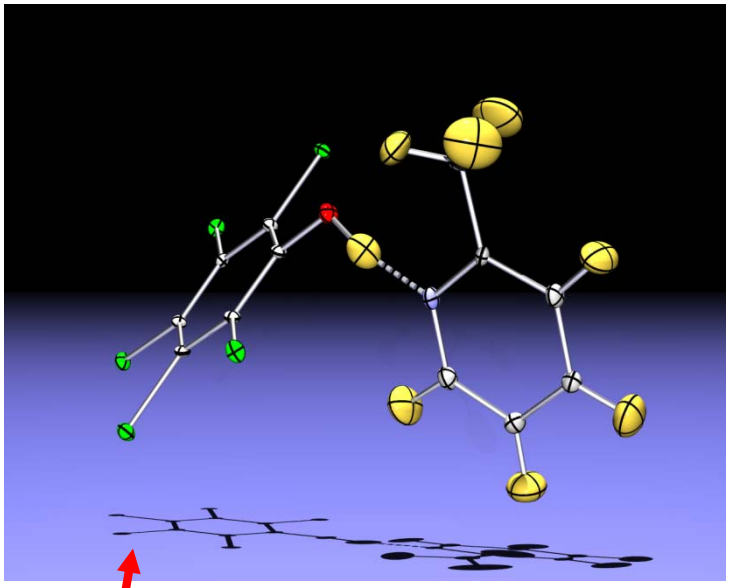
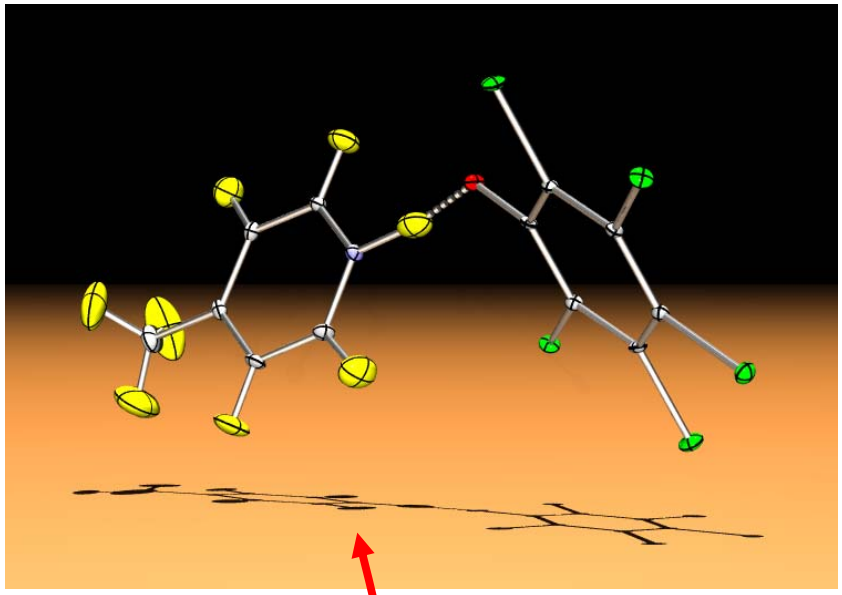
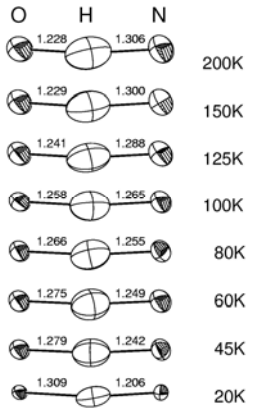
Designing Molecular Complexes for proton migration

Pentachlorophenol: Methylpyridines





Position of proton in the short N-H…O HB tuned by chemistry and by temperature



Steiner, Majerz & Wilson,
Chem Comm, ***2000****, 1231*
Angewandte Chemie, 2001, ***40****, 2651*

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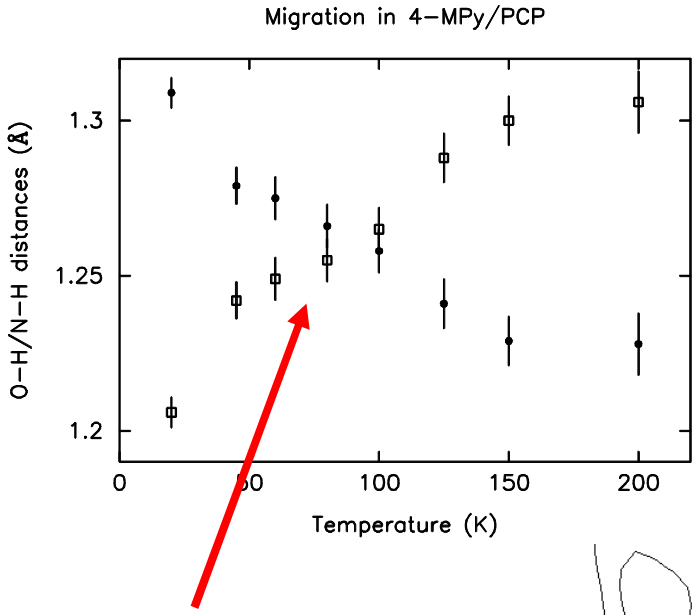
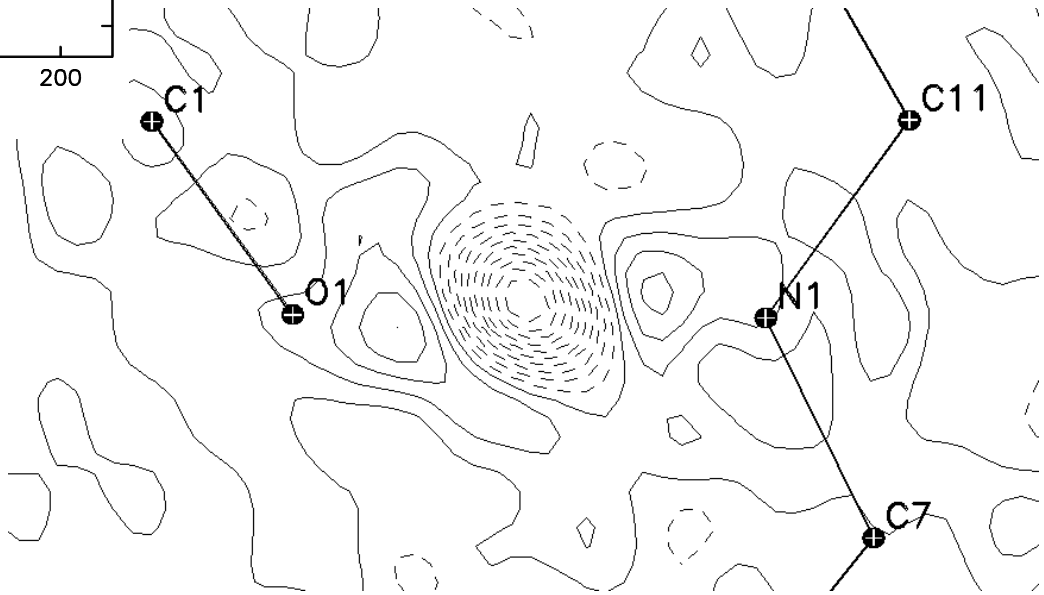
Temperature tuning of proton migration





First observed centred N-H-O HB obtained by thermal tuning at 95K

*Steiner, Majerz & Wilson, Angewandte Chemie, 2001, **40**, 2651*

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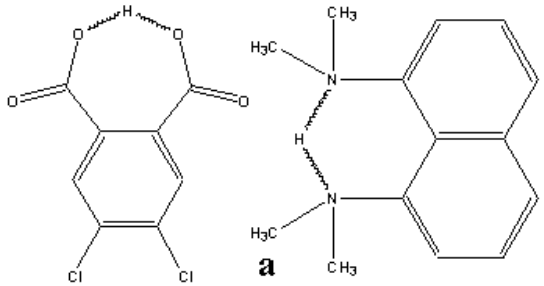
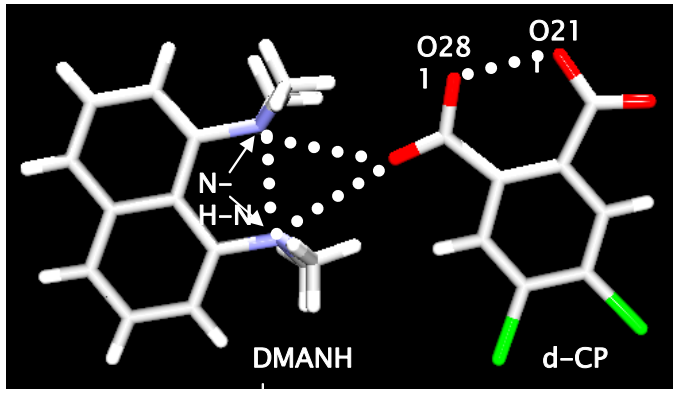
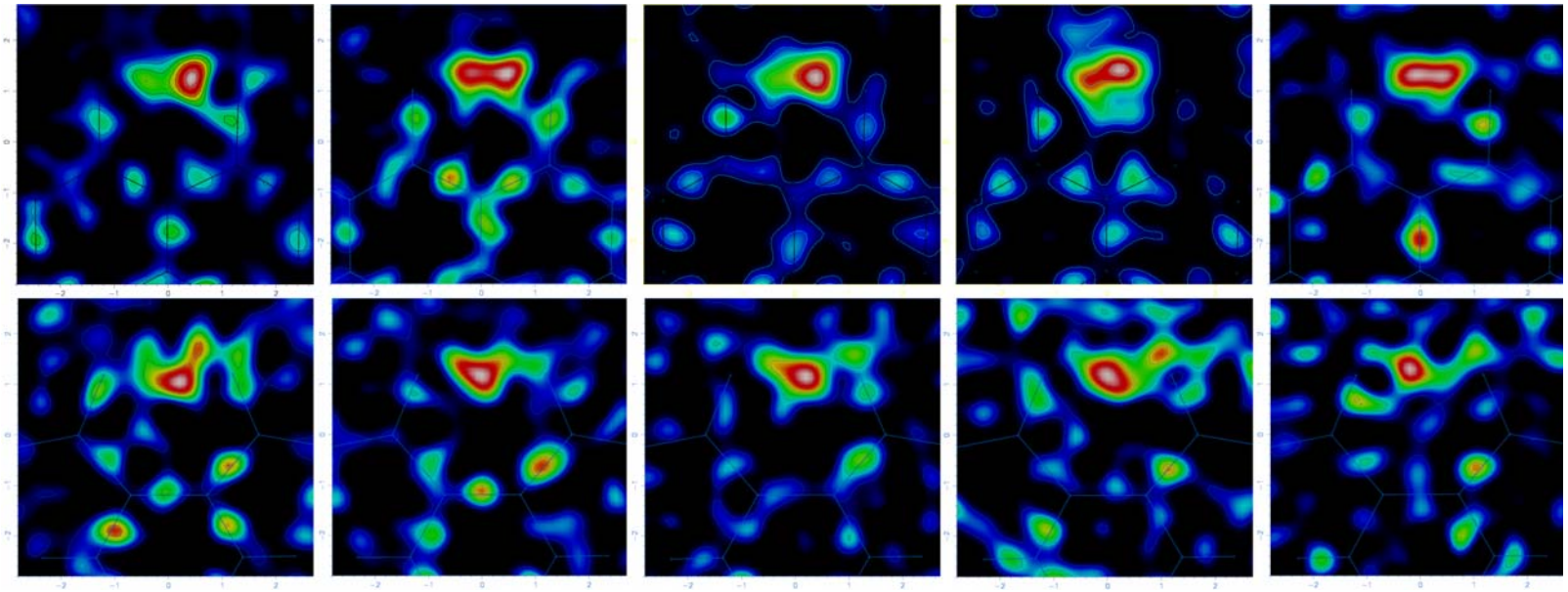
From proton disorder to proton migration?

A continuum in the hydrogen bond of a proton sponge complex



1,8-bis(dimethylamino)naphthalene
and 4,5-dichlorophthalic acid





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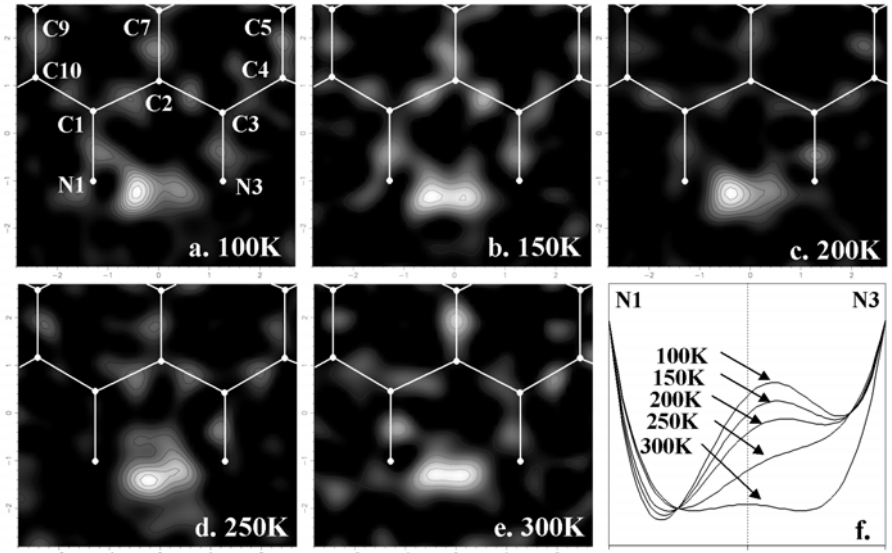
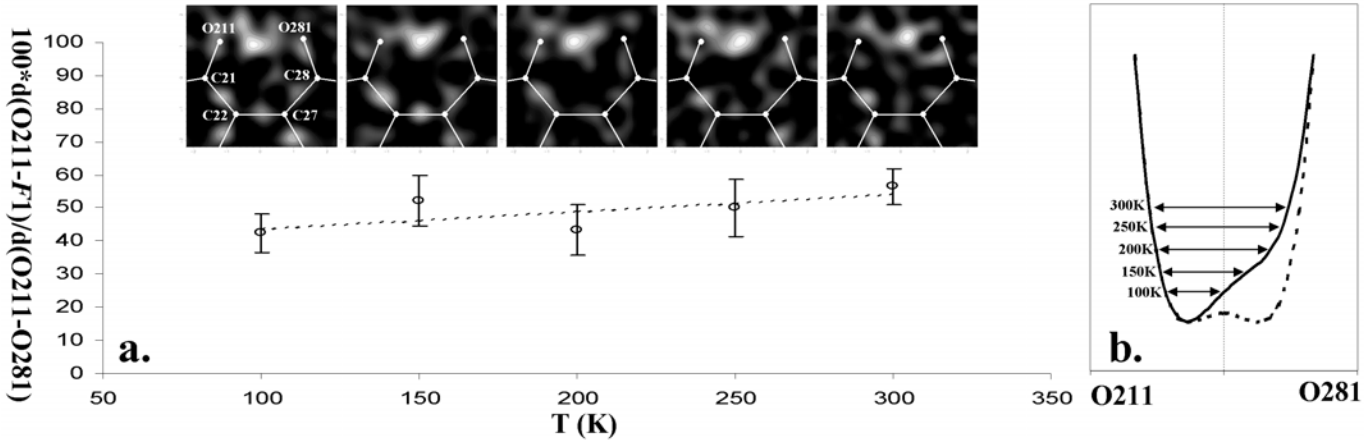
DMAN:DCP – only X-ray data so far – ambiguous!



Disorder/transfer?

Tempting, but unproven and unsubstantiated – VT neutron collected

and "migration"?



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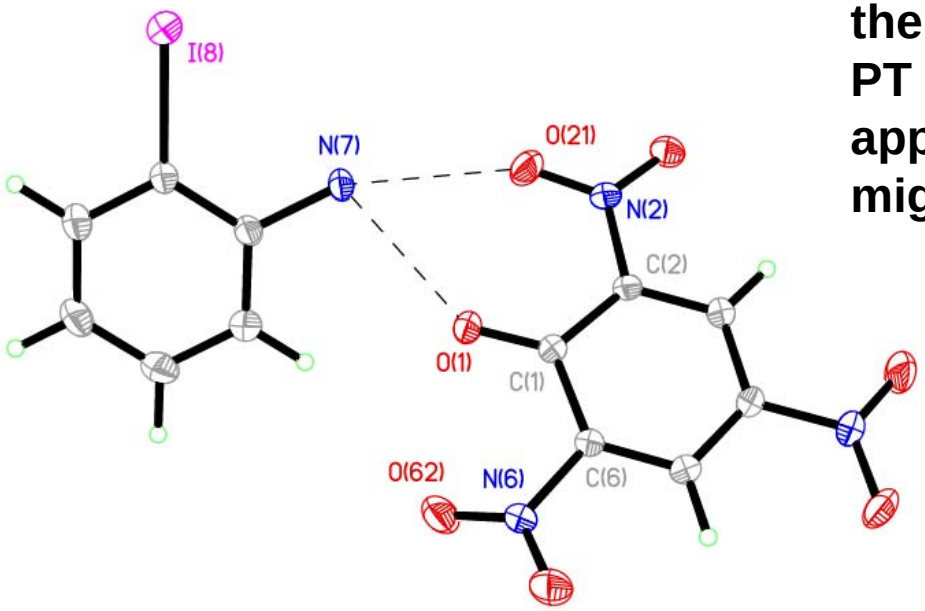
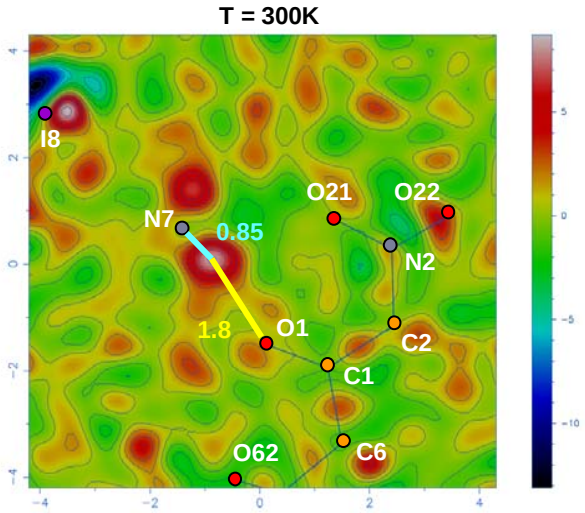
Application to physical changes

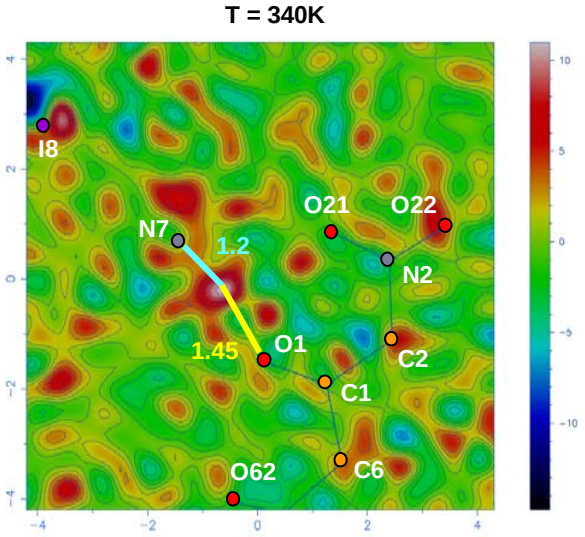
Picric acid forms charge transfer complexes with many organic compounds, some of which also exhibit thermochromism



2-iodoanilinium picrate: colour change at ~320K

Only obvious structural change on thermochromic PT is an apparent H migration..





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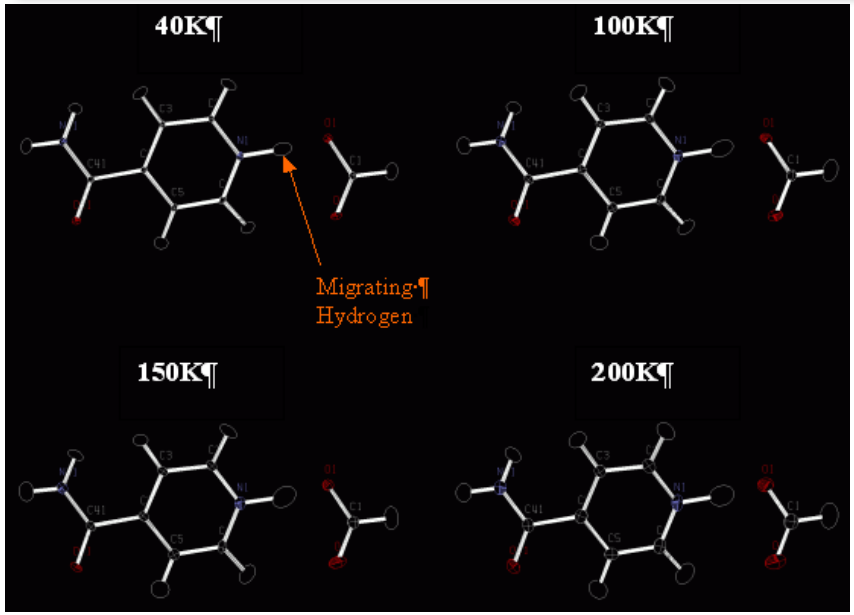
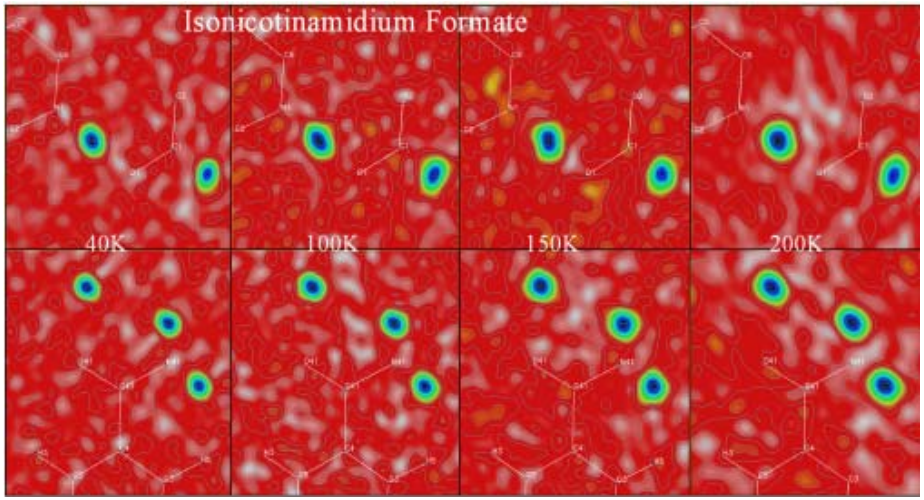
Look for disorder, find migration – isonicotinamidium formate





Temperature	Type	A-H	H...D	A...D	angle
40K	N1-H1...O1	1.213	1.344	2.556	176.35
°	N41-H6...O2	1.011	1.845	2.831	164.08
°	N41-H7...O41	1.032	1.888	2.917	175.51
100K	N1-H1...O1	1.254	1.298	2.551	176.21
°	N41-H6...O2	1.029	1.841	2.842	163.53
°	N41-H7...O41	1.033	1.887	2.919	176.07
150K	N1-H1...O1	1.263	1.296	2.554	173.09
°	N41-H6...O2	1.019	1.858	2.85	163.62
°	N41-H7...O41	1.015	1.904	2.918	176.78
200K	N1-H1...O1	1.274	1.29	2.562	175.42
°	N41-H6...O2	1.015	1.863	2.854	168.41
°	N41-H7...O41	1.037	1.882	2.916	174.73

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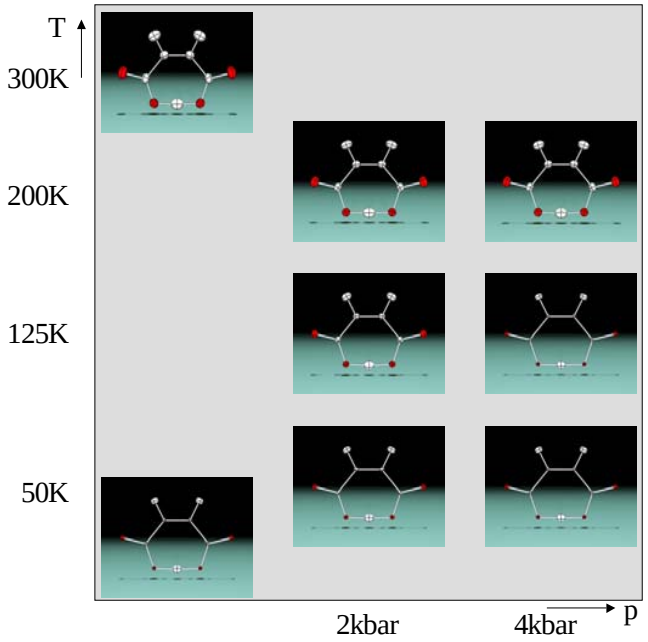
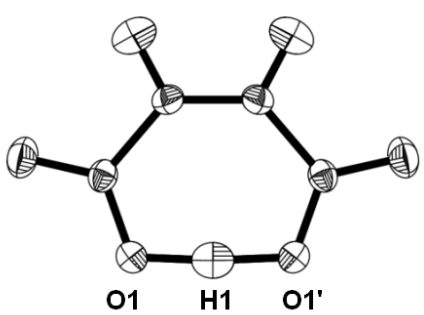
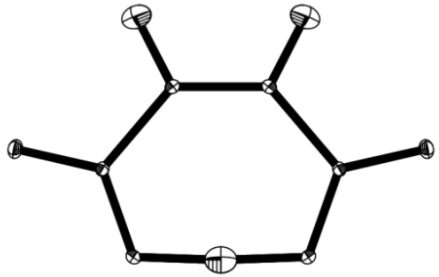
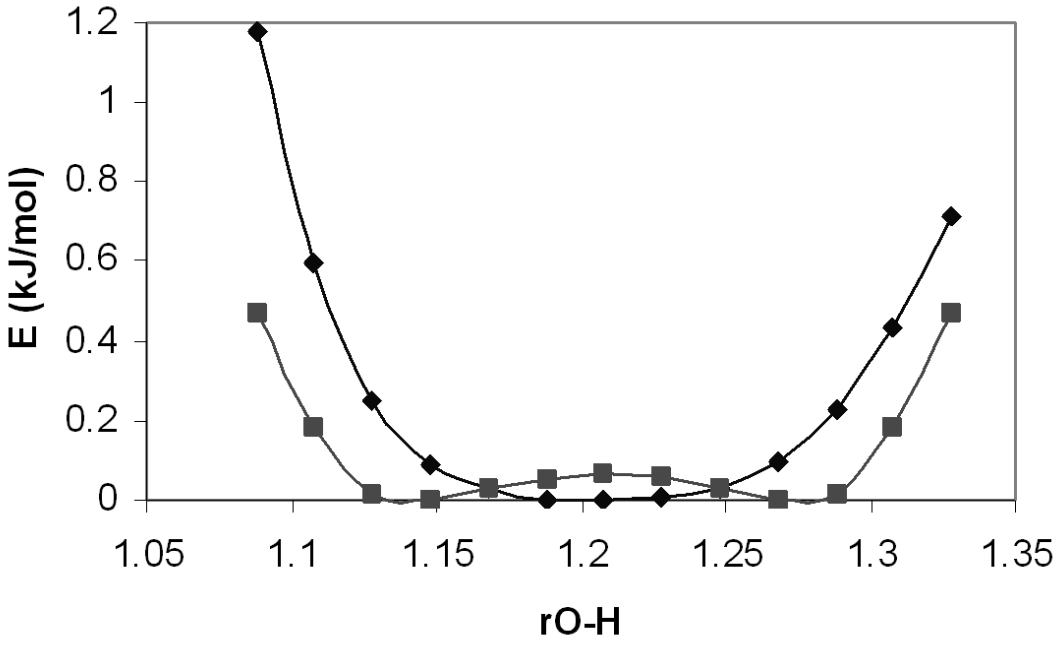
Potassium hydrogen maleate – centred HB









Wilson, Thomas & Morrison,
*Chem Phys Letters, 2003, **381**, 102*

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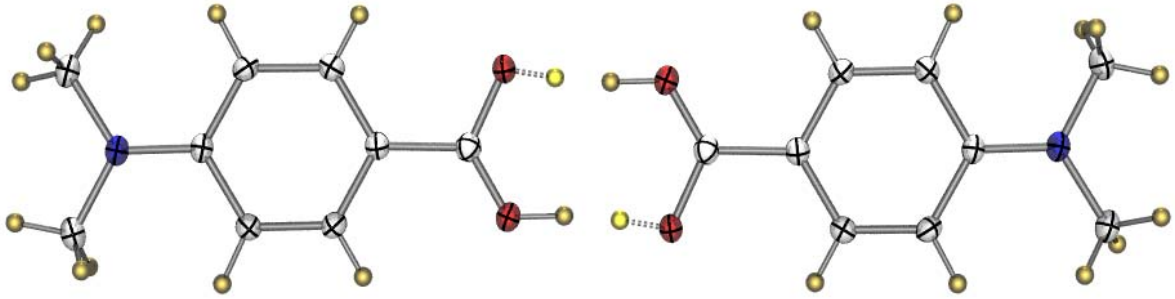
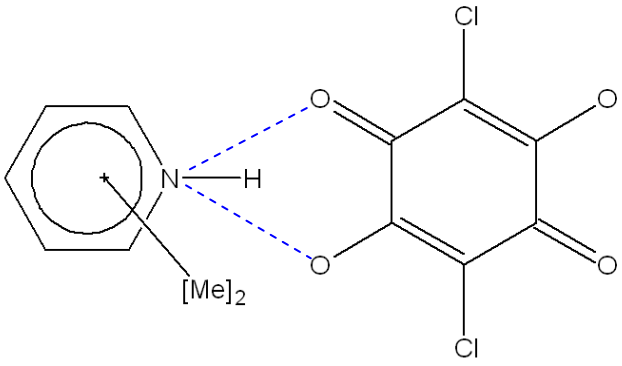
Crystal Engineering – Predictable HB Motifs?

- **COOH dimers; carboxylic acids**





- **Bifurcated HB**
- **HB-matching – Etter, Aakeroy**
- **[Short, strong HB]**
- **Metal-mediated**
- **Supramolecular synthons**

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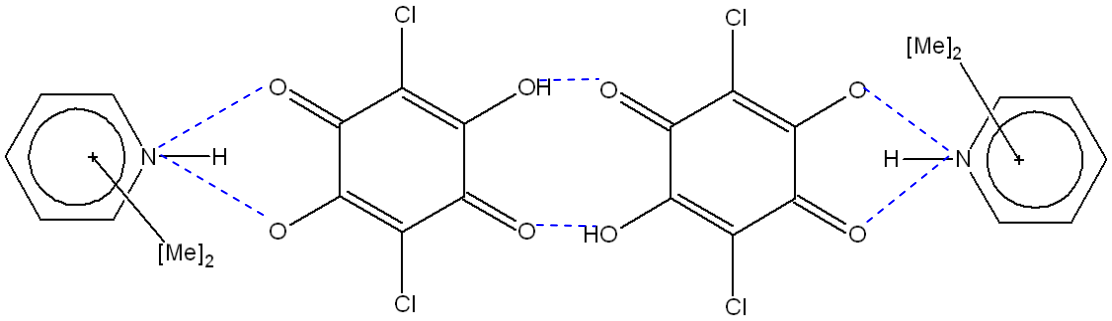
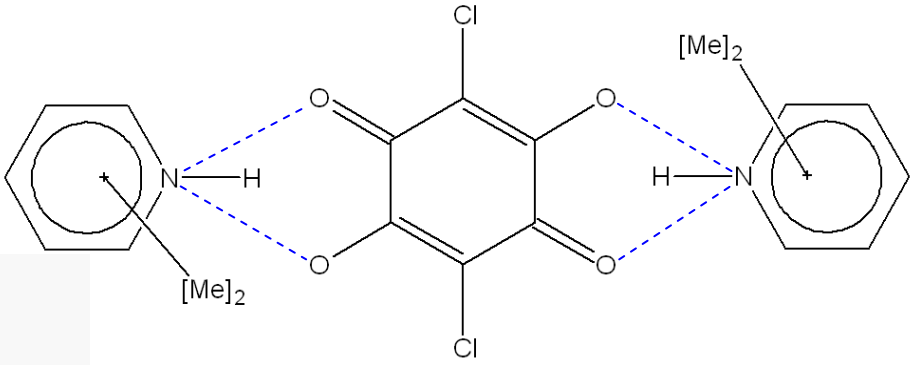
Designing Molecular Complexes for HB proton transfer

Chloranilic acid:Methylpyridines (lutidines, picolines)

- Supramolecular motifs (different in 1:1 & 2:1 complexes)





Adam et al, CrystEngComm, in press

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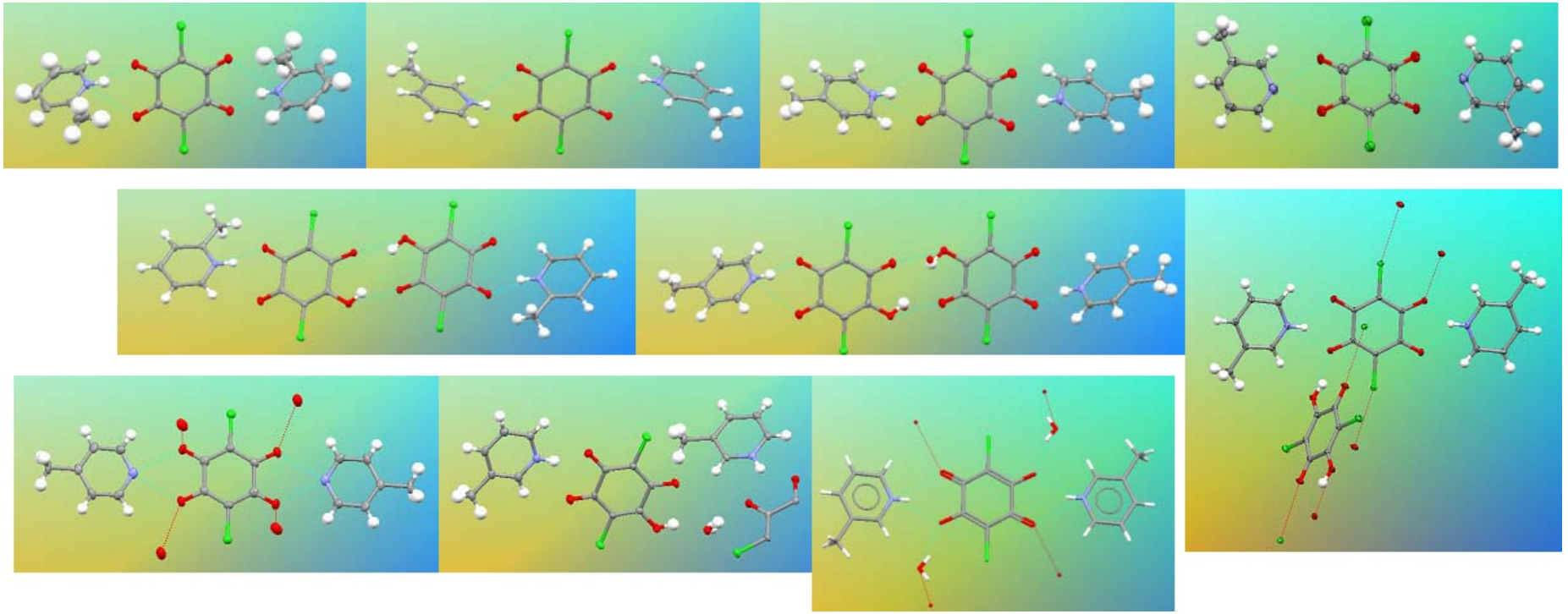
Chloranilic acid:n.Methylpyridine complexes



Hydrogen bonded hydrogen almost always transferred – charge/resonance assisted HB

Adam et al,
CrystEngComm, in press

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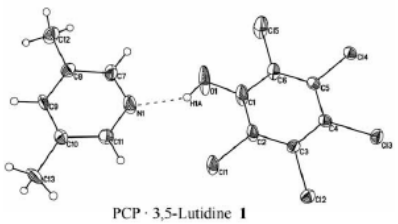
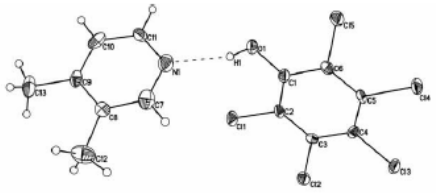
Designing Molecular Complexes: pKa matching?

Pentachlorophenol:Lutidine

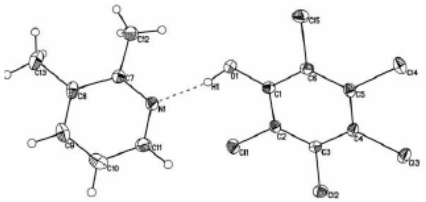
- pKa matching to “predict proton transfer?
- Pattern difficult to discern in solid-state



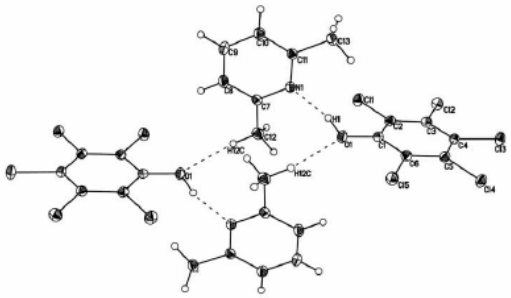
PCP · 3,5-Lutidine **1**



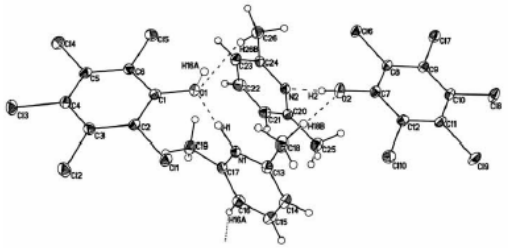
PCP · 3,4-Lutidine **2**



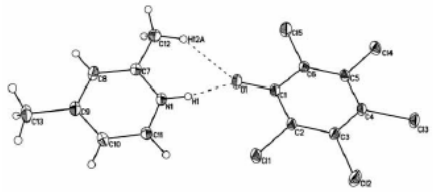
PCP · 2,3-Lutidine **3**



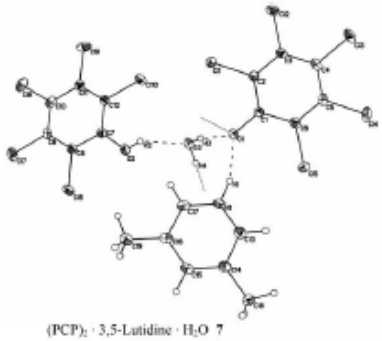
PCP · 2,6-Lutidine Form I **4**



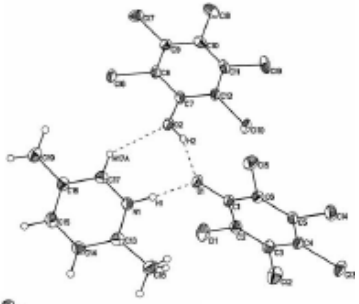
PCP · 2,6-Lutidine Form II **5**



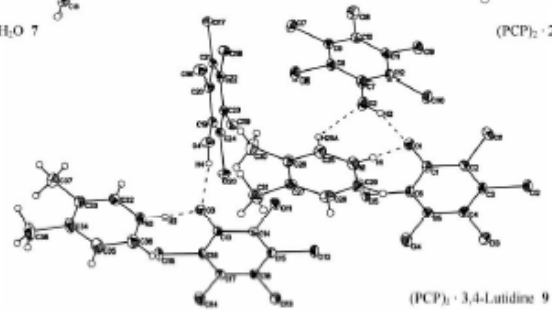
PCP · 2,4-Lutidine **6**



$(PCP)_2 \cdot 3,5\text{-Lutidine} \cdot H_2O$ **7**



$(PCP)_2 \cdot 2,5\text{-Lutidine}$ **8**



$(PCP)_2 \cdot 3,4\text{-Lutidine}$ **9**

Schmidtmann & Wilson
*CrystEngComm, 2008, **10**, 177*

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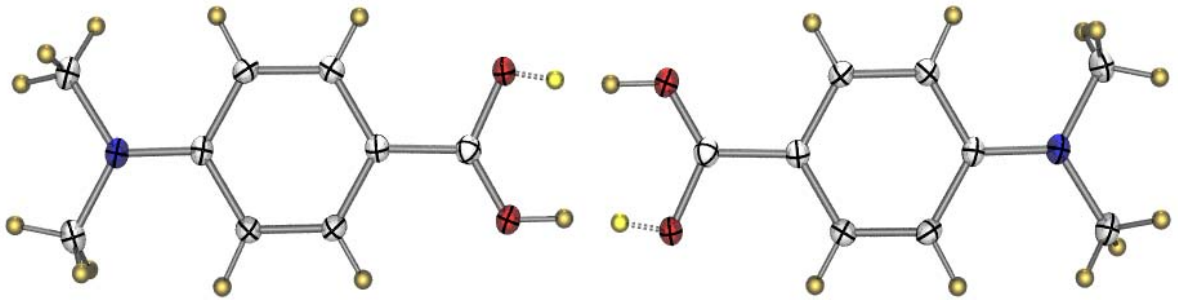
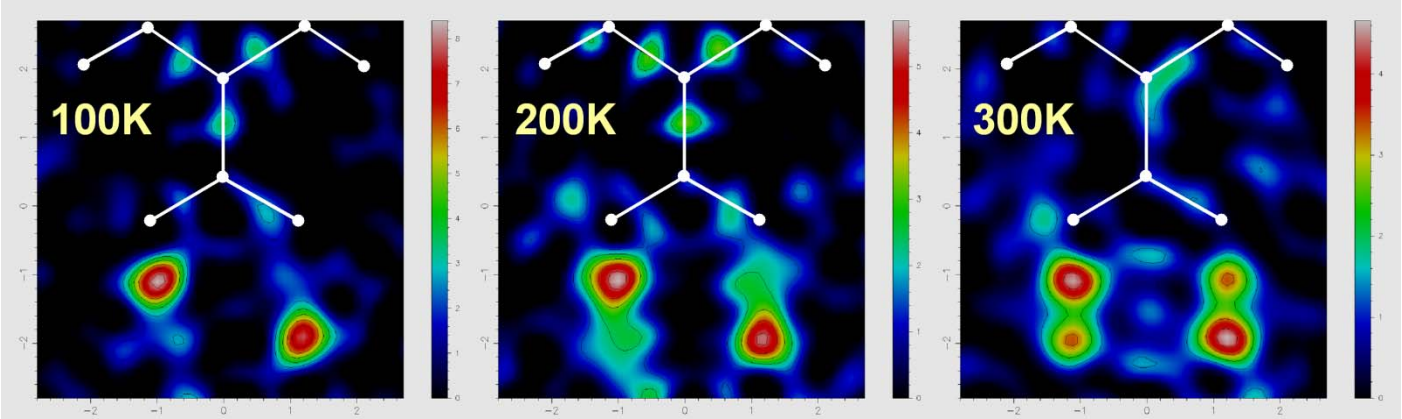
Designing Molecular Complexes for proton disorder in HB

Tuning proton disorder

- 4-dimethylaminobenzoic acid (4DMBA)



- Proton disorder in native structure

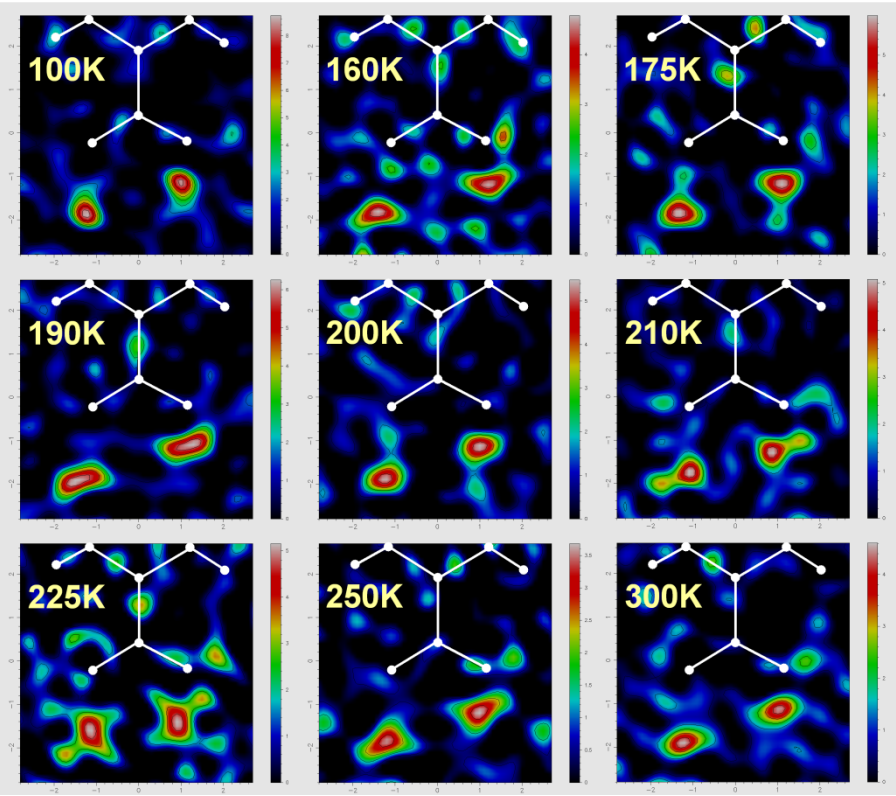


Parkin et al
Cryst Growth Design
*2007, **7**, 531*

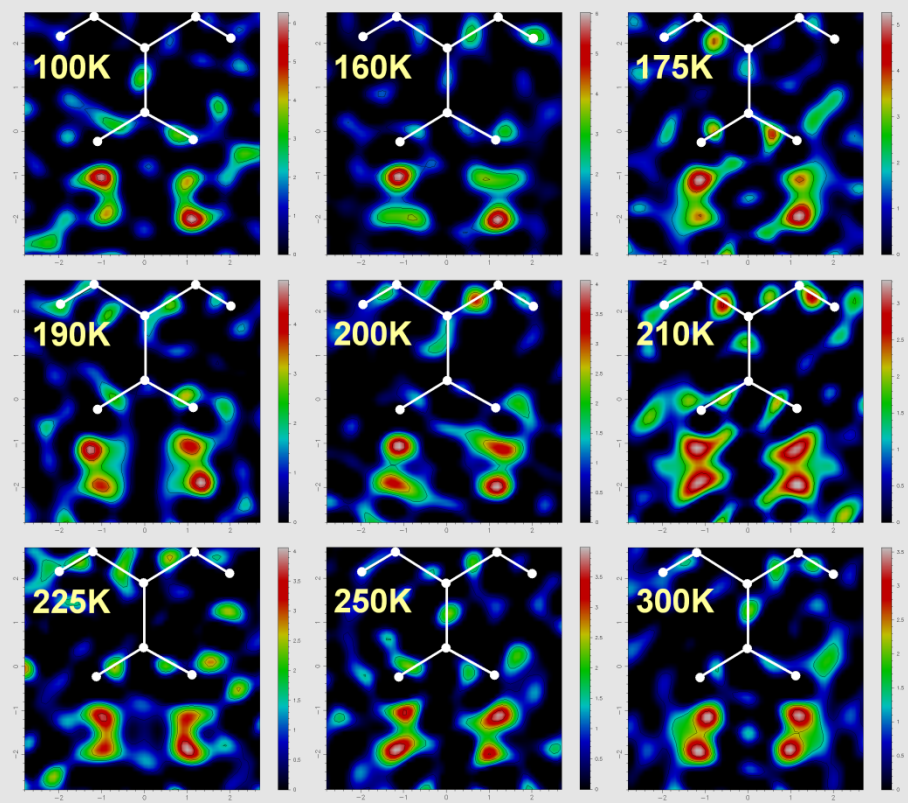
University of Glasgow

4-dimethylaminobenzoic acid (4DMBA)

Different disorder patterns in molecular complexes 4DMBA-4DMBA:35DNB-35DNB



with 3,5-dinitrobenzoic acid 4DMBA NO disorder



BUT the 3,5-dinitrobenzoic acid DOES show disorder

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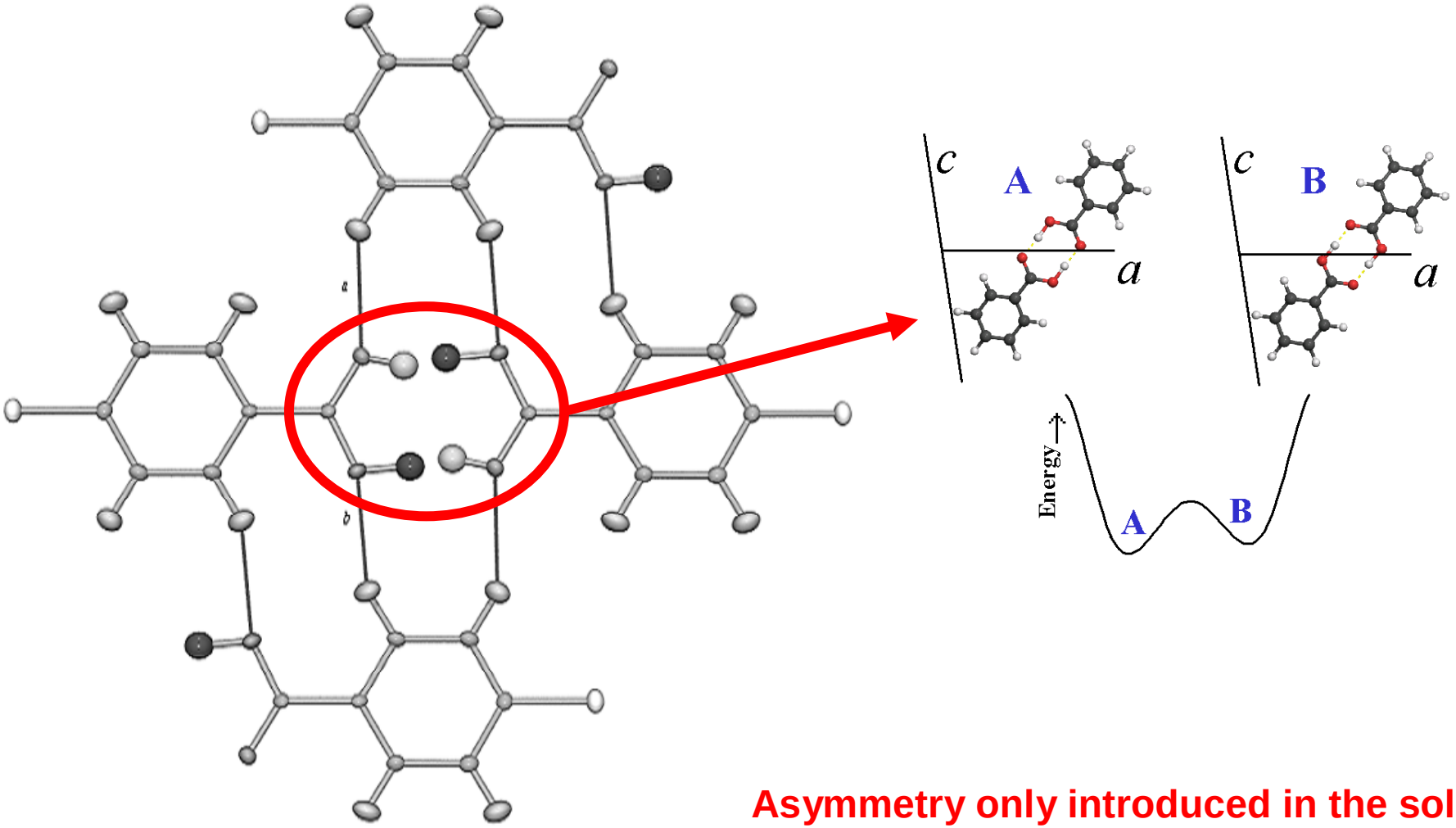
H disorder/transfer in solid-state HB dimers



Asymmetry only introduced in the solid state - in the local crystalline environment

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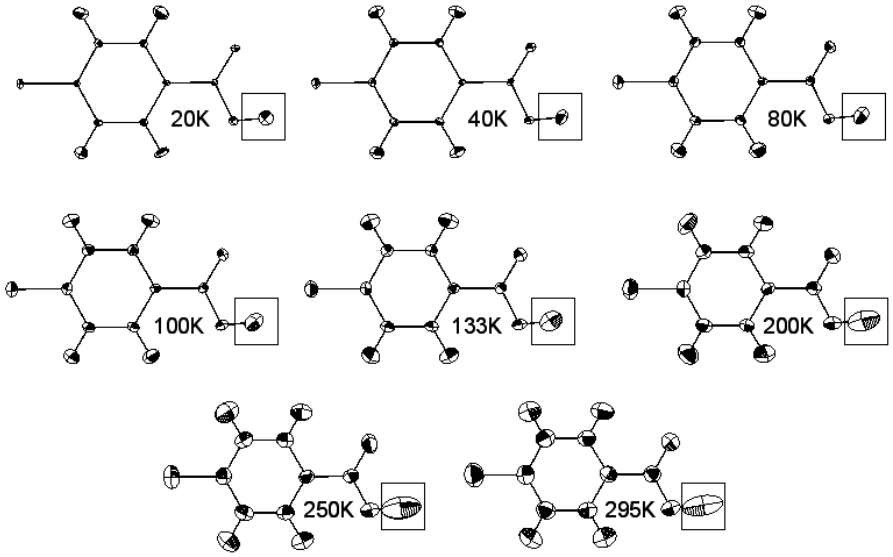
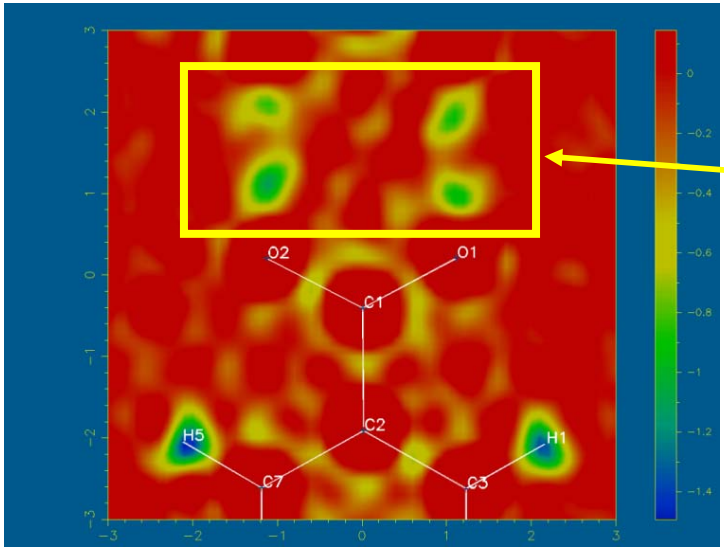
Modelling Disordered Protons: from T dependence to ΔE



Modelling of HB H atom in carboxylic acid dimers clearly breaks down at higher T– second (disordered, tautomeric) site



Clearly a split site

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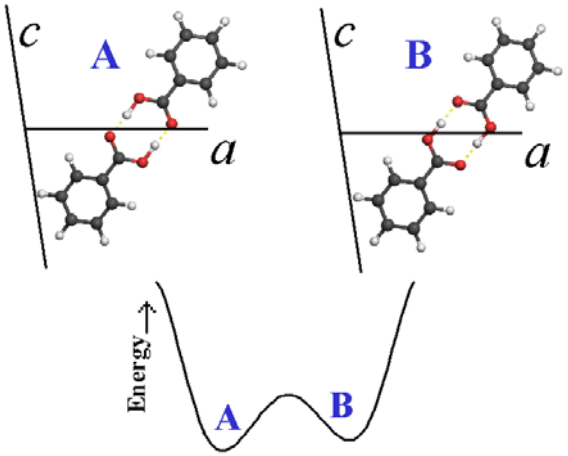
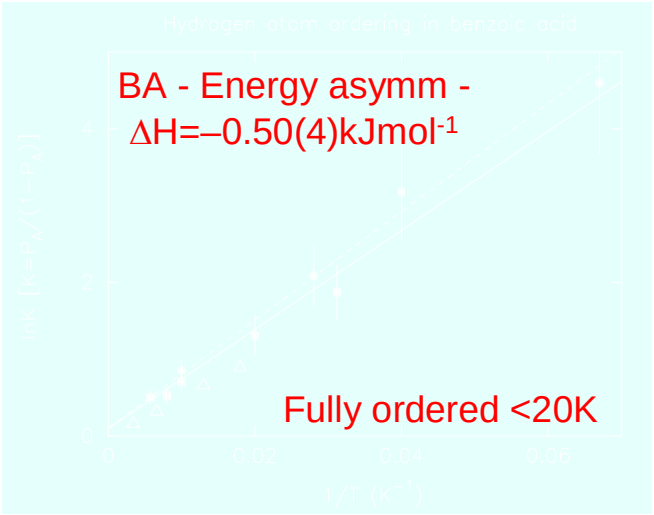
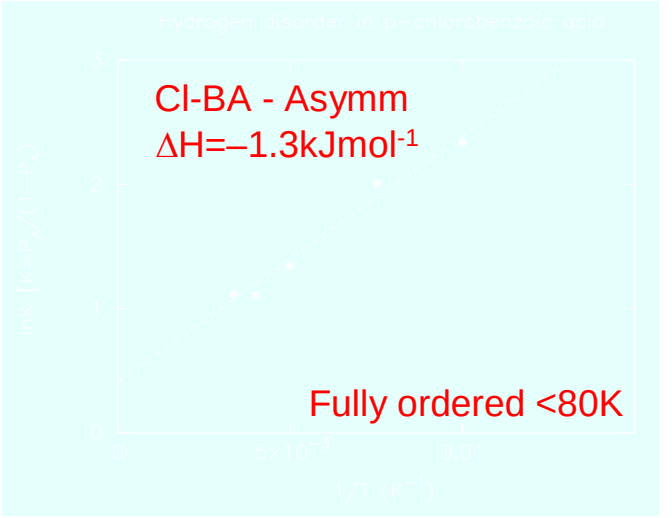
Modelling Disordered Protons: from T dependence to ΔE



Site occupancies can be modelled in simple Van't Hoff model and Energy Asymmetry extracted





This allows us to establish a Tautomerism energy scale in HB carboxylic acid dimers

Experimentally, and...

*Wilson et al, Chem Phys Letts, 1996, **253**, 103*
*& New J Chem, 2006, **30**, 979*

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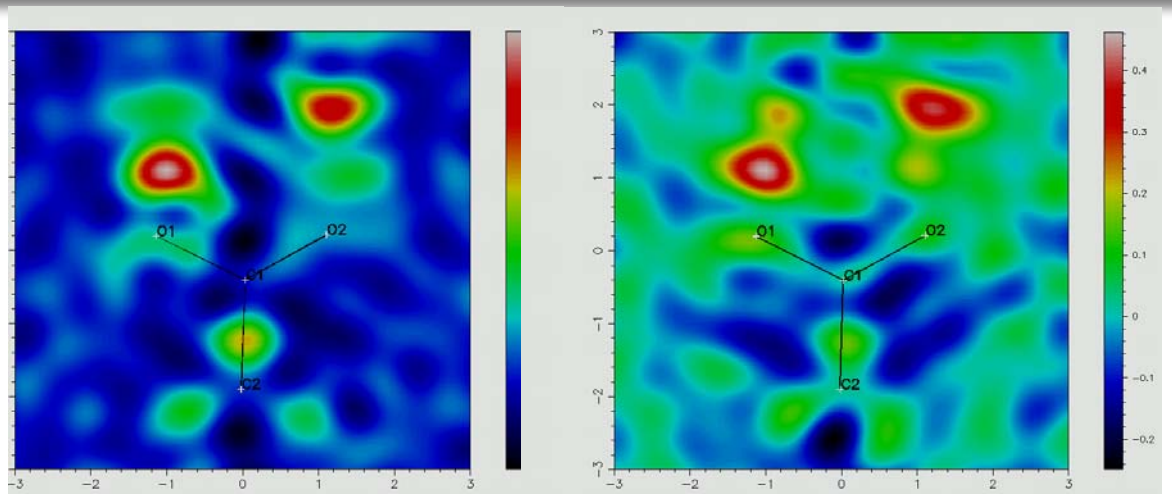
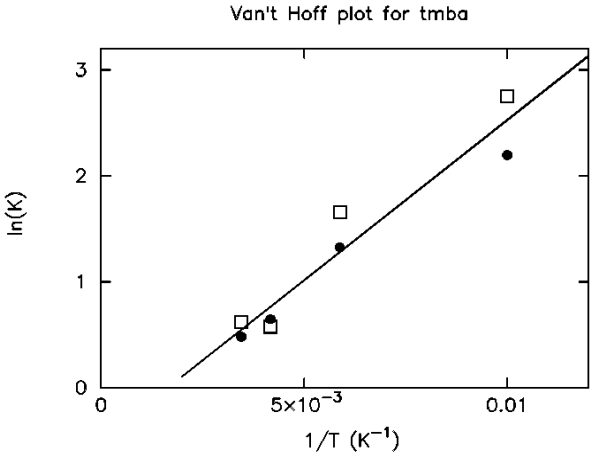
VT XRD: 2,4,6-trimethylbenzoic acid

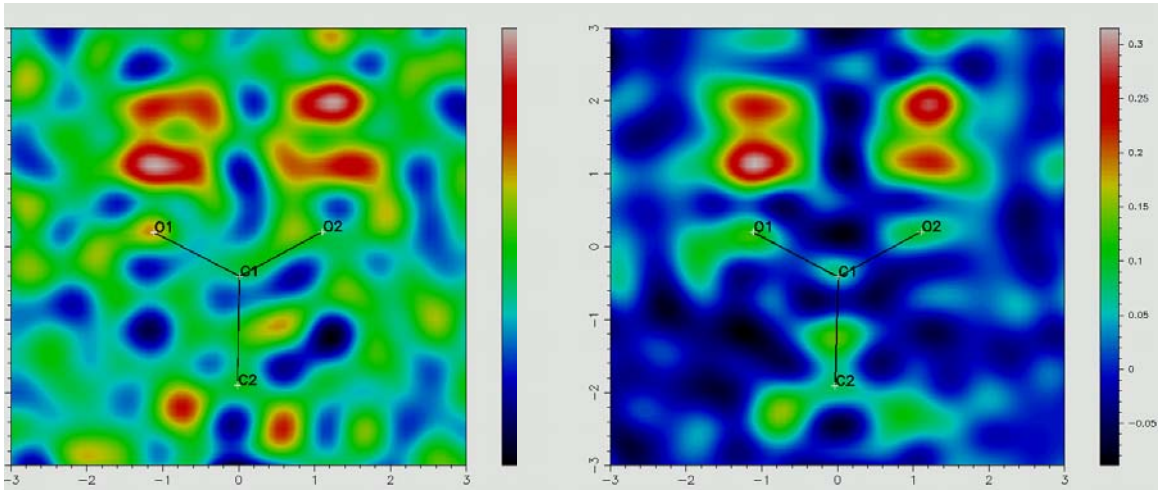
Wilson & Goeta
*Angew Chemie, 2004, **43**, 2095*



100K **170K**



tmba, $\Delta H = -2.5(3)$ kJ.mol^{-1}



240K **295K**

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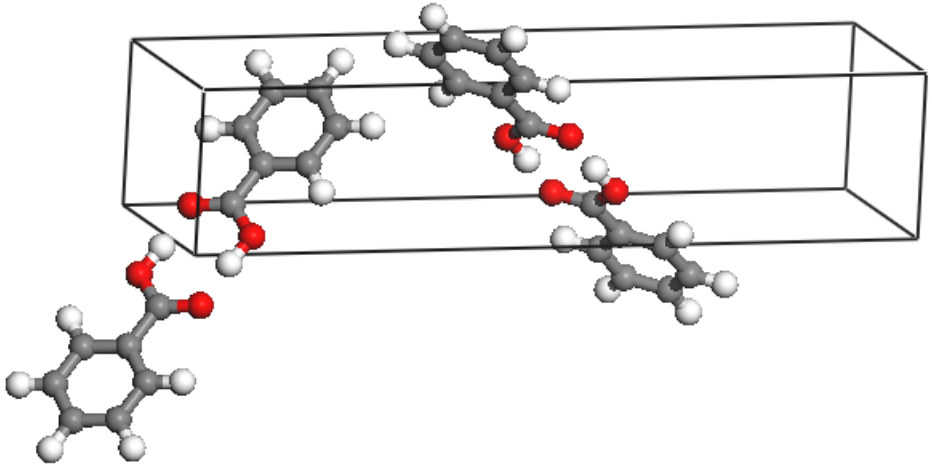
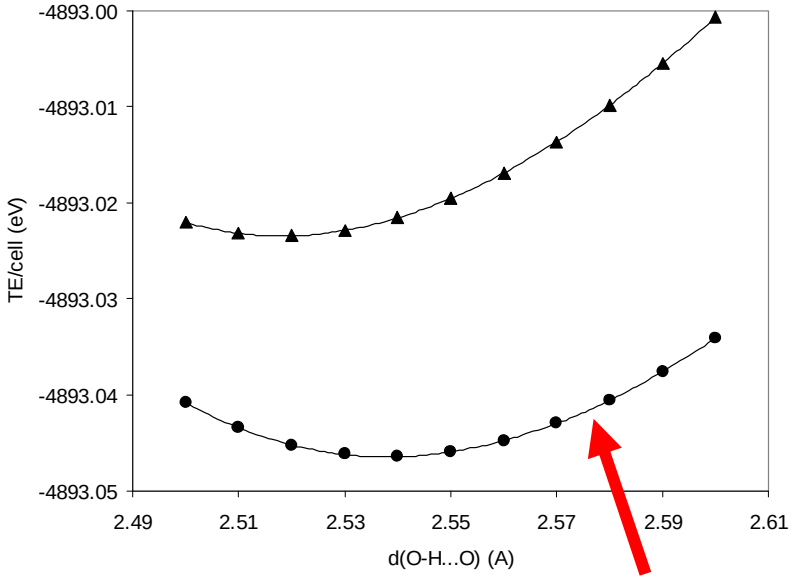
Computing the Asymmetry in H-transfer tautomerisation

Can solid state, periodic computation do the same?





Energies of low and high E tautomers

Benzoic Acid

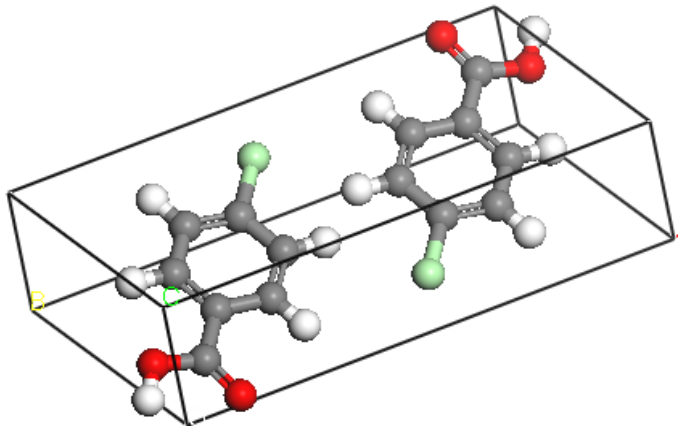
Computed asymmetry = 0.46 kJ.mol^{-1}

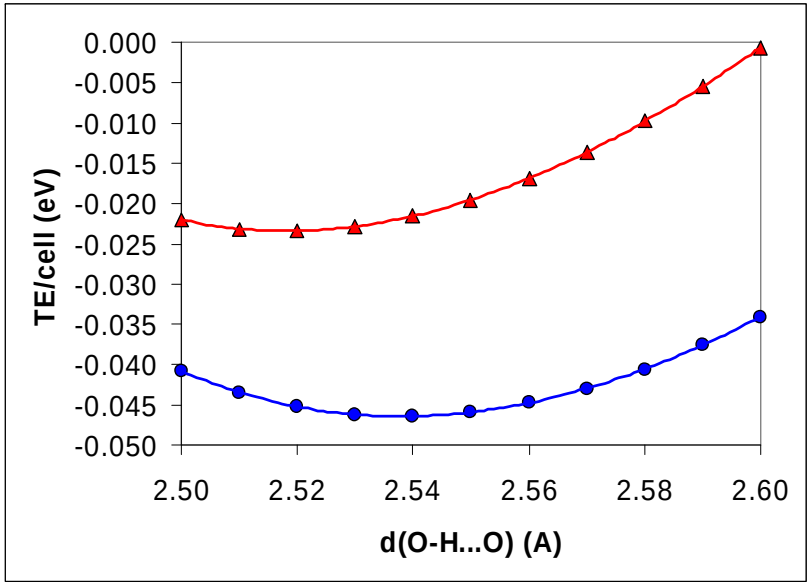
cf NMR 0.4-0.65; neutron diffraction 0.50 kJ.mol^{-1}

*Middlemiss et al, CrystEngComm, 2007, **9**, 777*

University of Glasgow

A second example of promising agreement



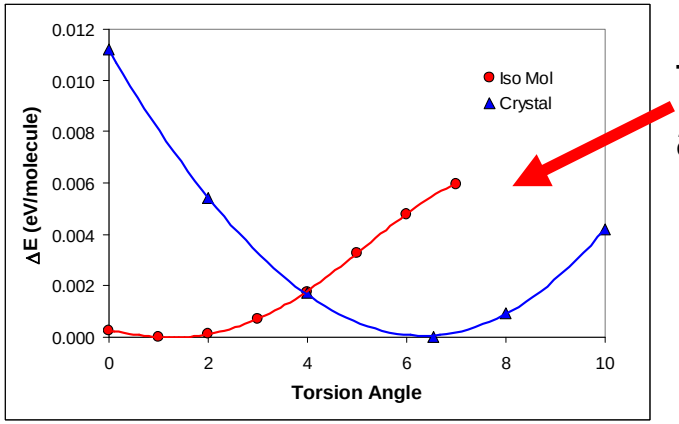


p-chloro-benzoic acid

Computed asymmetry = 1.15 kJ.mol^{-1}

cf NMR 1.5;

neutron diffraction 1.60 kJ.mol^{-1}



Torsion angle also

*Middlemiss et al, CrystEngComm, 2007, **9**, 777*

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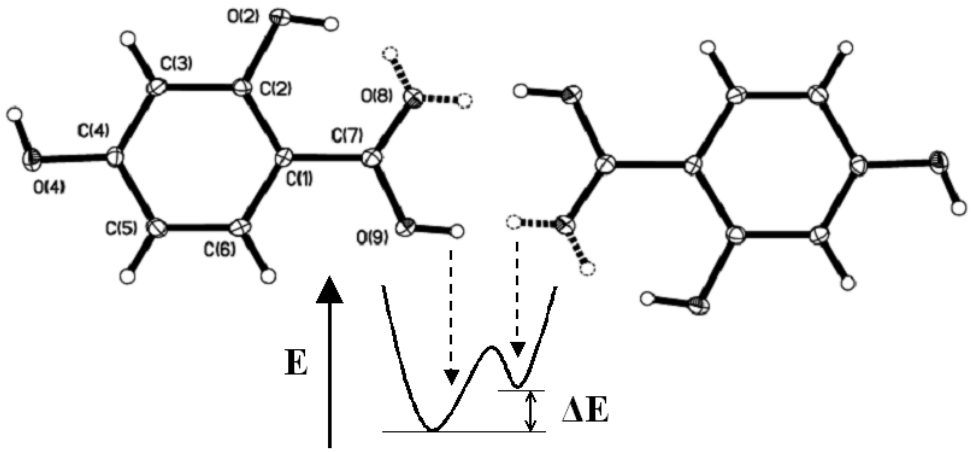
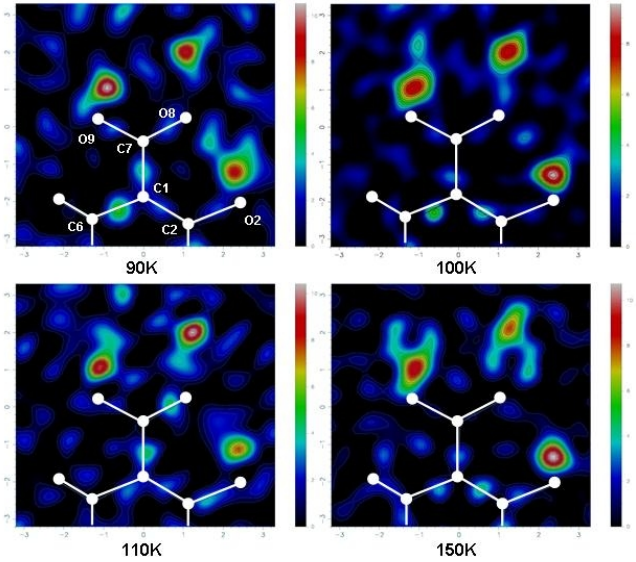
Co-operative hydrogen bonding?



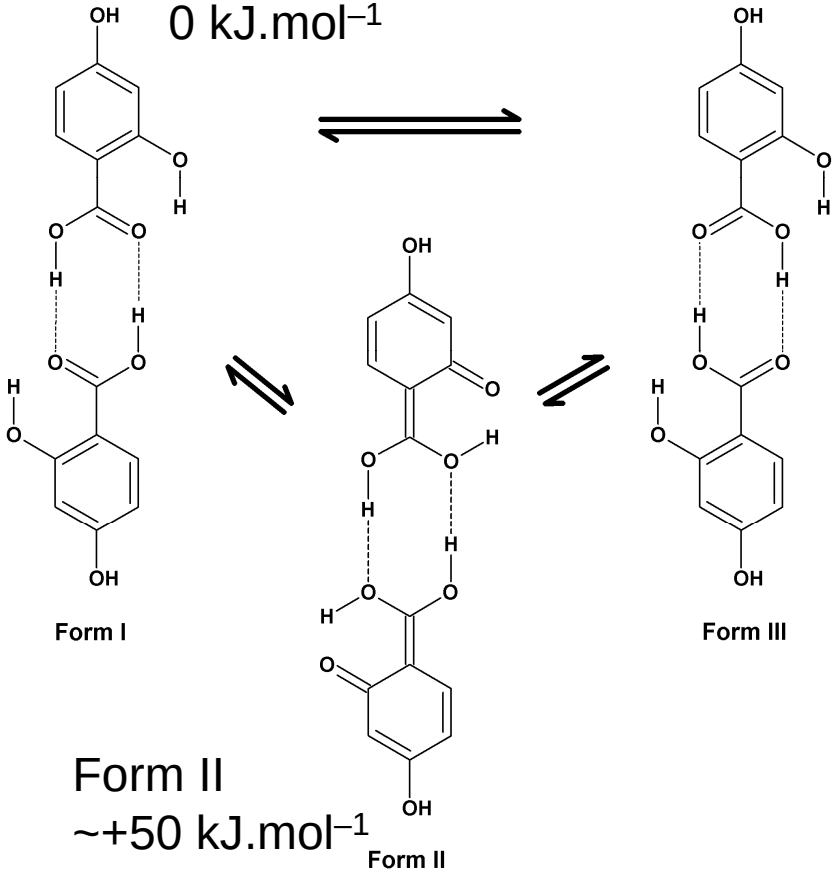


*Parkin et al, Acta Cryst, 2007, B**63**, 303*

Relative Energies of tautomeric forms

Form I
0 kJ.mol^{-1}

Form III
+8.6 kJ.mol^{-1}



Form II
~+50 kJ.mol^{-1}

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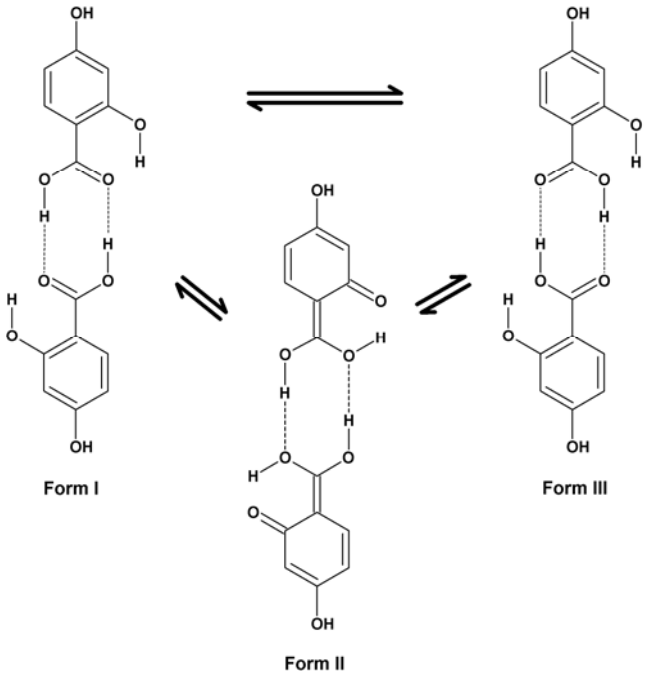
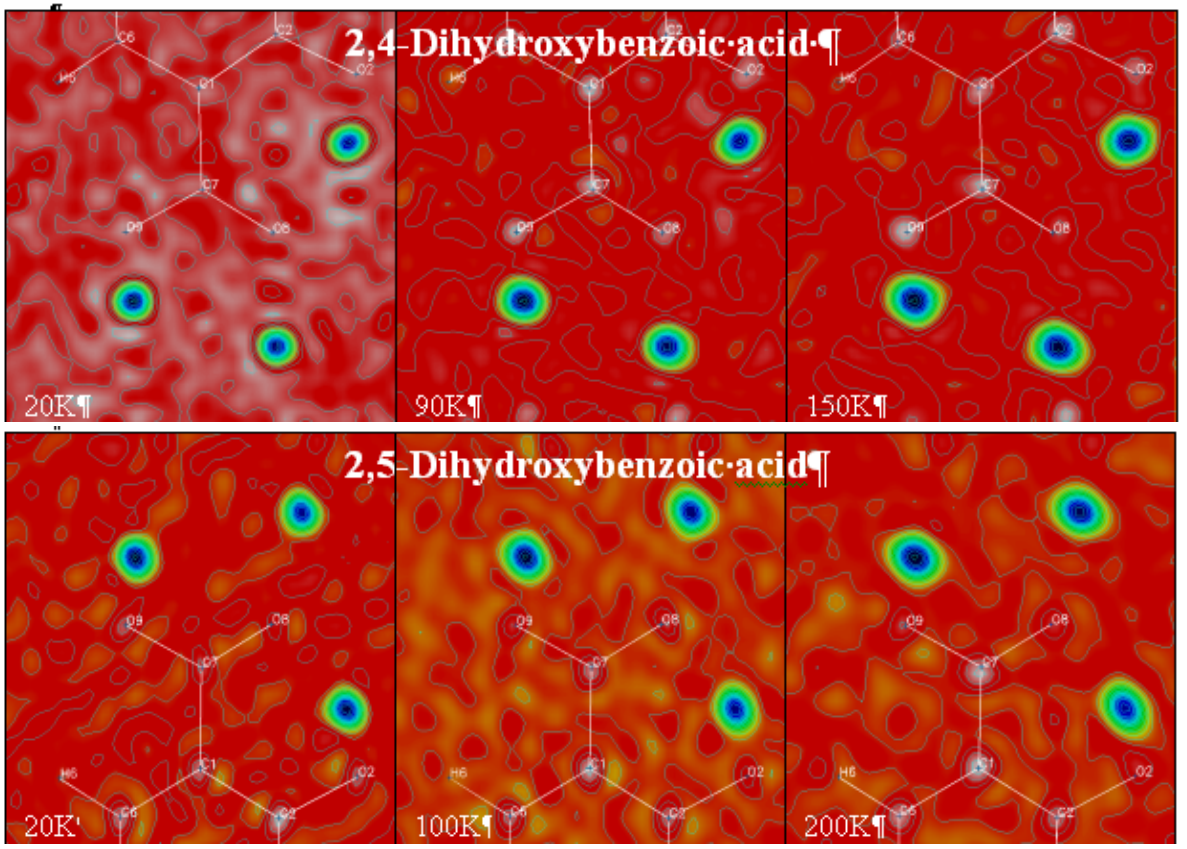
Screening for subtle proton behaviour – VT neutron





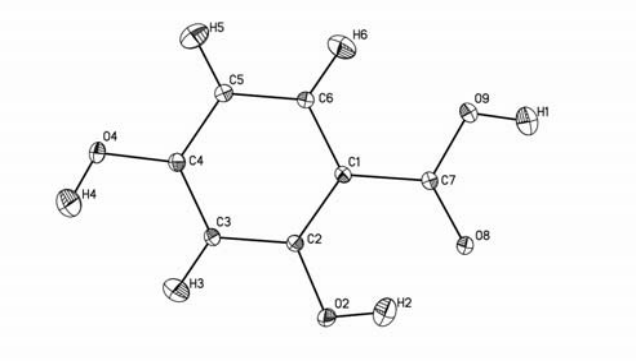
Neutron diffraction supports the computational conclusion that only one tautomer should be expected in these T ranges

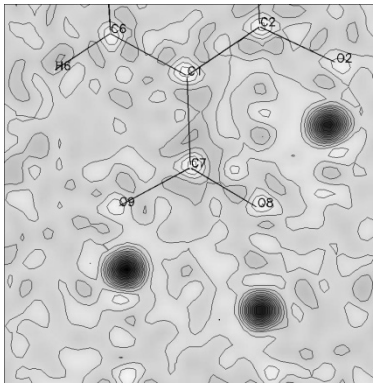
Potential tautomerism / cooperative hydrogen bonding in dihydroxybenzoic acids

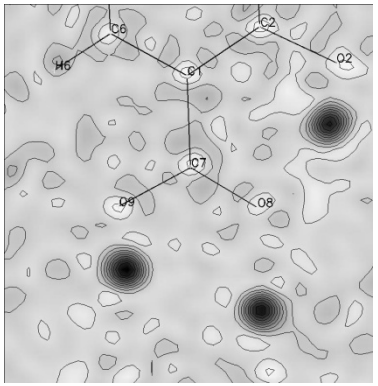
Adam et al, New J Chem, in press

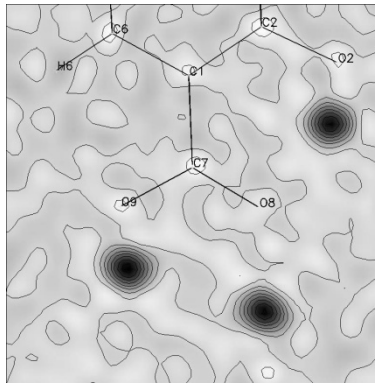
University of Glasgow

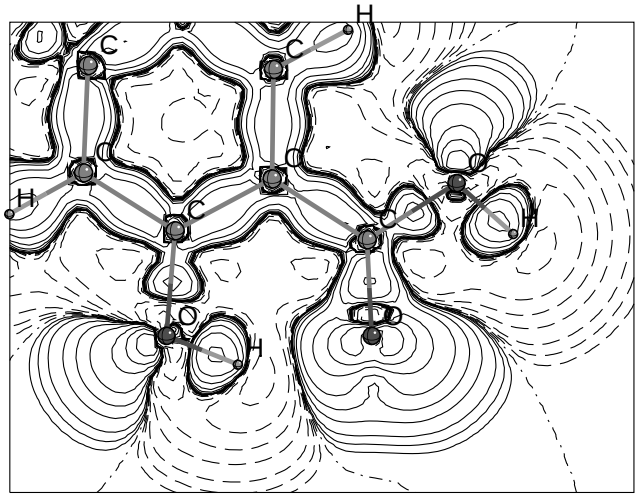
Neutron and Theoretical Deformation









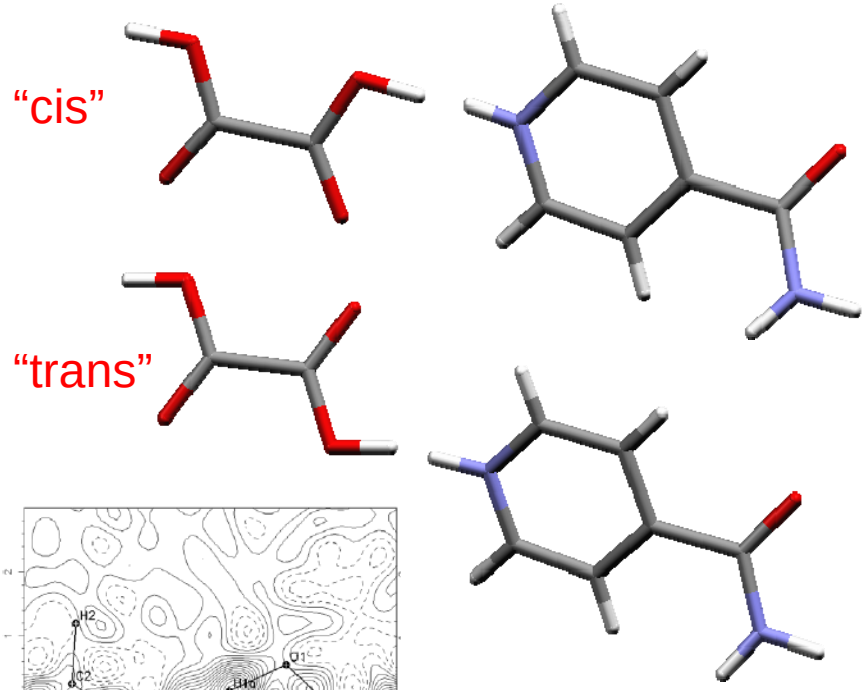


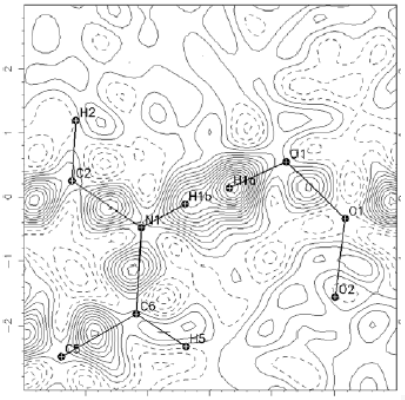
Adam et al, New J Chem, in press

University of Glasgow

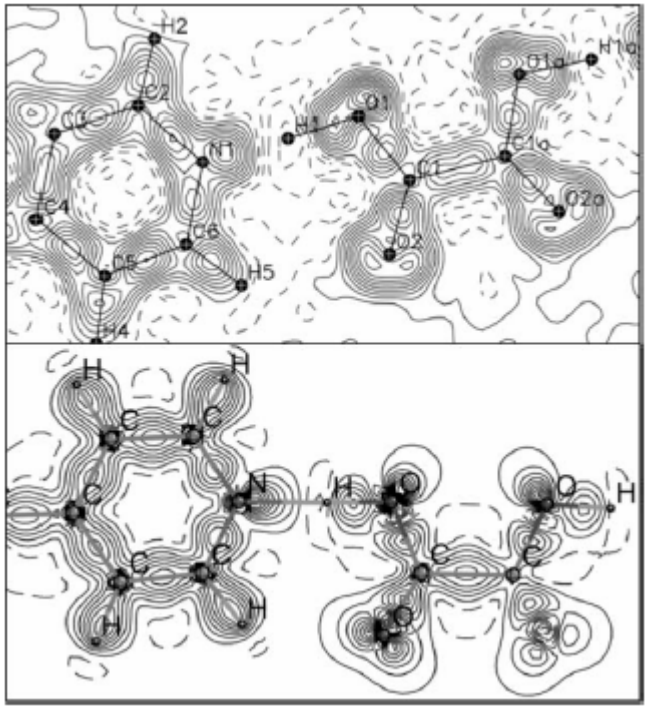
An energy scale for polymorphism

Polymorphism in molecular complexes of isonicotinamide and oxalic acid





Serious ambiguity in “good” SX X-ray



CRYSTAL03
B3PW91, 6-31G**
Energy difference, Form I favoured over form II by **3.41 kJ.mol^{-1}**

*Schmidtmann et al, CrystEngComm, 2007, **9**, 743 & J Phys Chem A, in press*

University of Glasgow

Conclusions – Next Steps

- Modern computational methods can underpin our careful multi-condition X-ray, neutron, etc experiments
- Interrogating both experiment and calculations allows questions not accessible by each alone to be asked

So… it's all solved - No

- Still must benchmark any models through reproducing experimental findings
- Still "semi-empirical" choice of theoretical method, functional, etc
- Some answers still "wrong", some models inconsistent between good theoretical methods
- Eventual aim – towards prediction of property in the molecular solid-state from structure – proton transfer, conduction, optical activity, colour, etc.

University of Glasgow

The Team

The Glasgow Group

Martin Adam, Suzanne Harte, Lorreta Lawton, Alan Martin, Craig Martin, Derek Middlemiss, Andy O'Neill, Andy Parkin, Marc Schmidtmann, Lynne Thomas, Craig Wales and the rest!

Visiting students (school, undergraduate)

Adam Jibson, Jennifer Kennedy, Bobby McTaggart, Caitlin Newlands

And many others

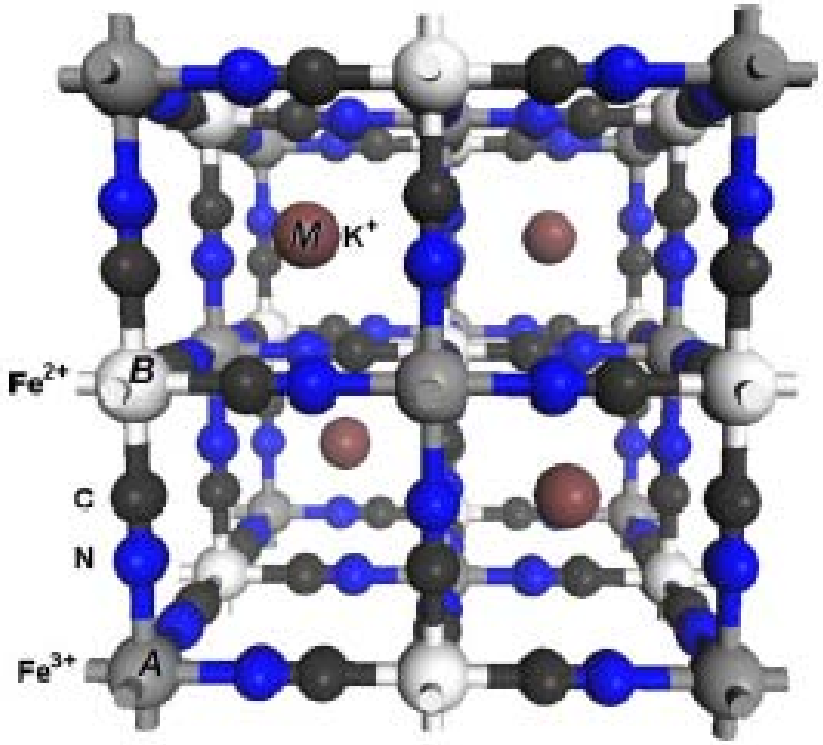
Colleagues in Glasgow, U. Western Australia, Natural History Museum, CCDC, CPOSS, Edinburgh, Bradford, Durham, TU Munich, Wroclaw, Warsaw, etc

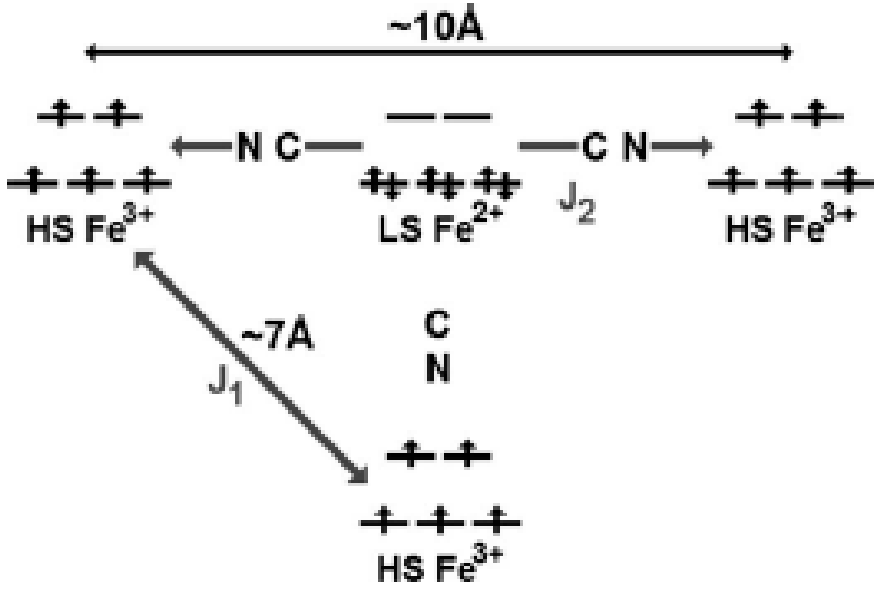
Funding

EPSRC, CCLRC-STFC, CMSD, Nuffield Foundation, Oxford Cryosystems, Rigaku, University of Glasgow

University of Glasgow

Ferromagnetism and spin transitions in Prussian Blue





Previous ferromagnetic coupling model based on J_2, ignores J_1

*Middlemiss & Wilson, Phys Rev B, 2008, **77**, 155129*

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Calculation of spin densities

CRYSTAL03

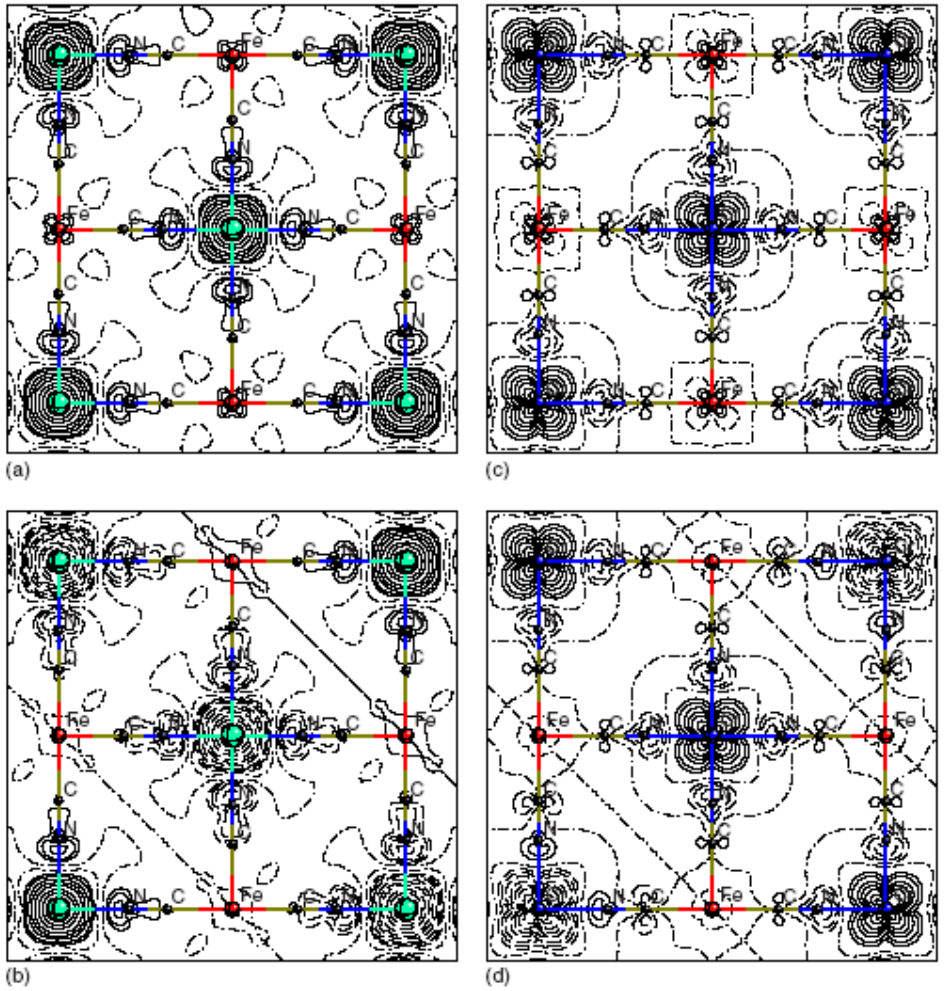
Hybrid functionals

$$f^{xc} = \frac{100 - F_0}{100}(f^x_{\mathrm{LSDA}} + 0.9\Delta f^x_{\mathrm{B88}}) \cdot$$

$$+ \frac{F_0}{100} f^x_{\mathrm{UHF}} + 0.81 f^c_{\mathrm{LYP}}$$

$$+ 0.19 f^c_{\mathrm{VWN}},$$

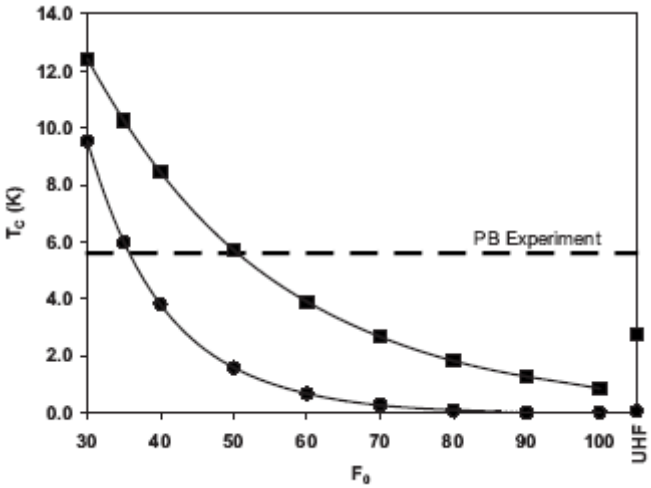
Varying HF content – vary F_0 from 30 to 100%



*Middlemiss & Wilson, Phys Rev B, 2008, **77**, 155129*

University of Glasgow

Critical Temperatures and Coupling Constants



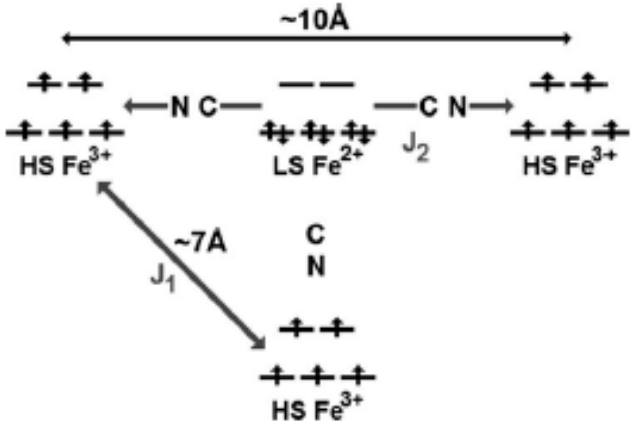


TABLE VII. The variation with lattice constant, a_0 (Å), in the FM band gap, ΔE_g (eV), exchange interaction strengths, J_1 and J_2 (K), ratio $x=J_1/J_2$, and estimated critical temperature, T_C (K), in PB at $F_0=35\%$.

a_0	State	ΔE_g	J_1	J_2	x	T_C
10.35	FM	3.823	0.1980	0.1045	1.89	5.28
10.28	FM	3.870	0.2241	0.1190	1.88	5.98
10.20	FM	3.951	0.2566	0.1342	1.91	6.83
10.13	FM	4.037	0.2853	0.1509	1.89	7.61
10.06	FM	4.158	0.3169	0.1671	1.90	8.45

J_1, more significant contribution to FM coupling than J_2

*Middlemiss & Wilson, Phys Rev B, 2008, **77**, 155129*

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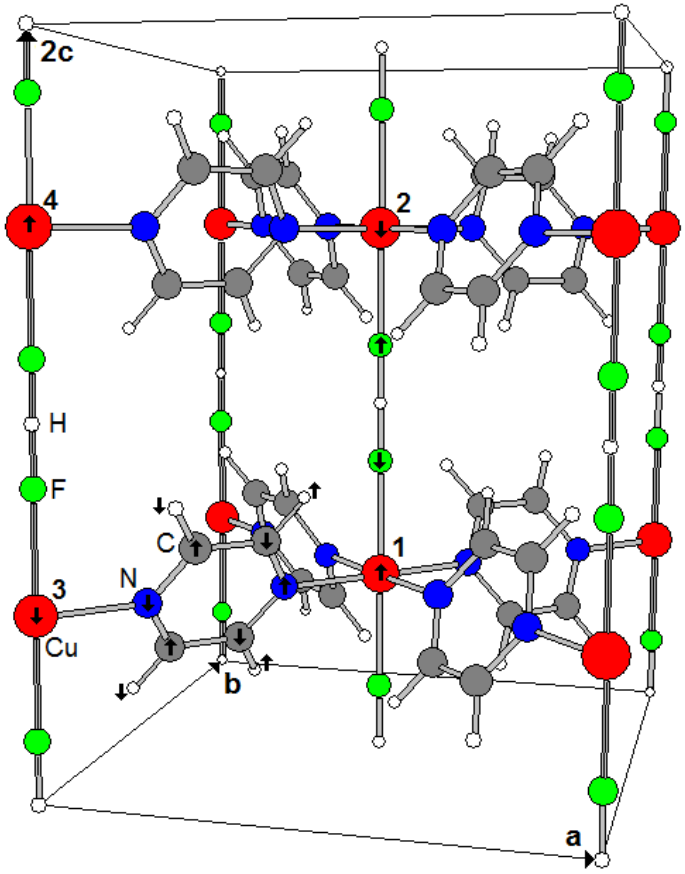
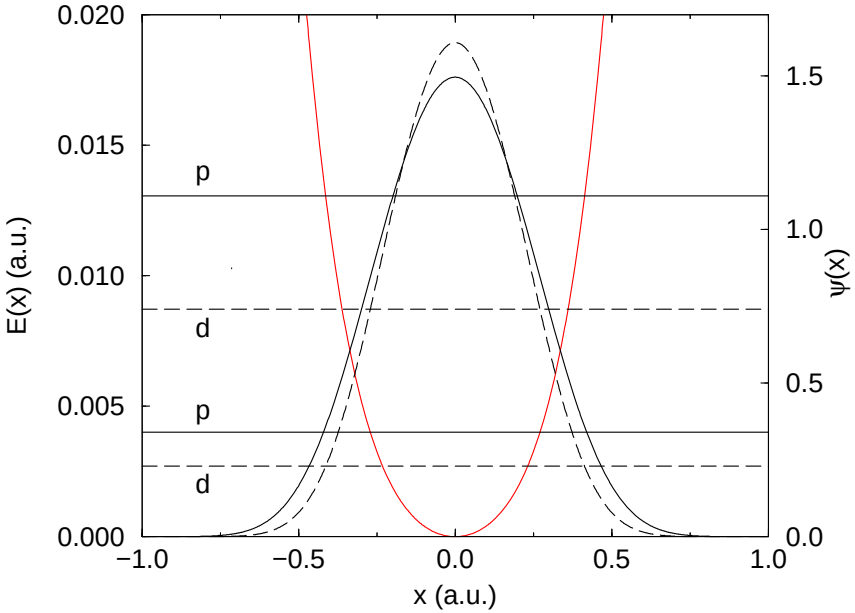
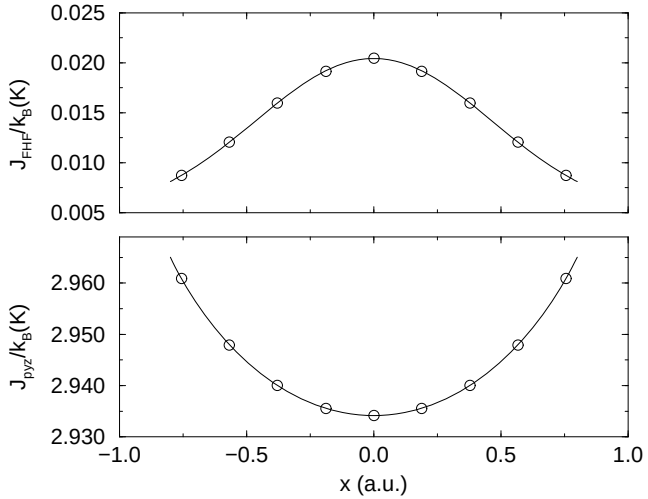
Hydrogen-bonded copper pyrazine coordination polymer

$[Cu^{II}(HF_2)(pyz)_2]BF_4$ (pyz = pyrazine)







*Middlemiss et al, Chem Phys Letters, 2008, **459**, 119*