GIPAW: Applications to Organic Materials

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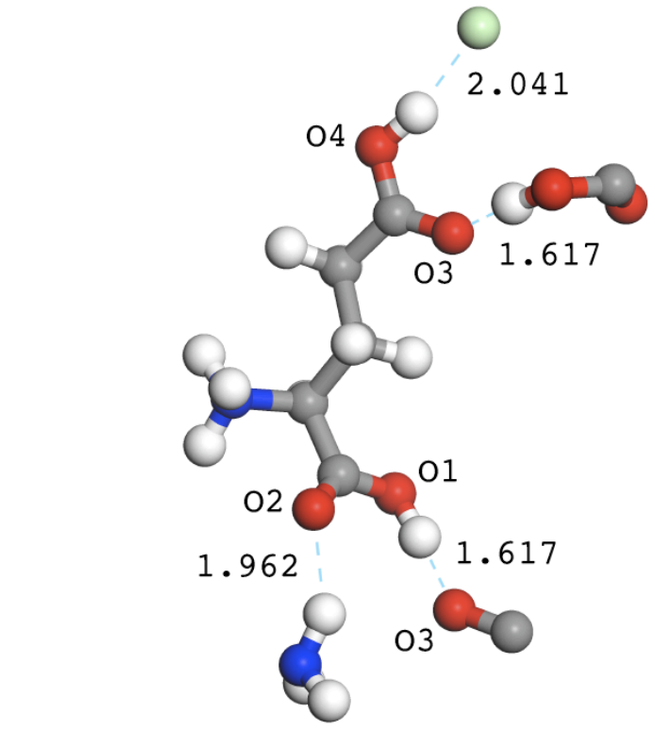
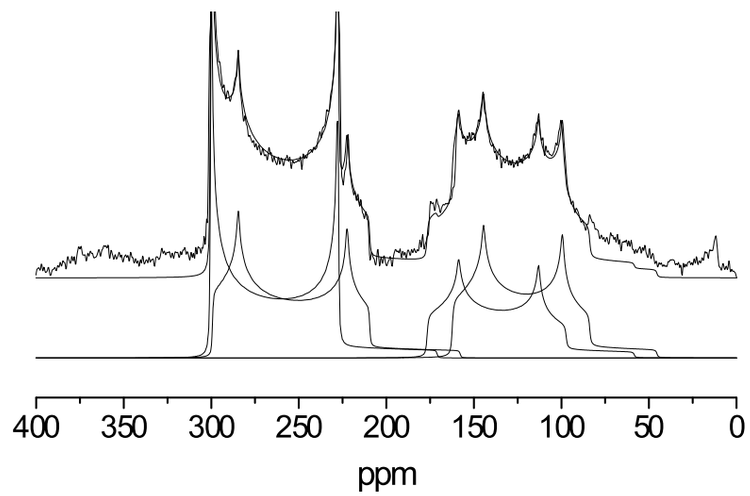
Materials Modelling Laboratory, Oxford Materials

Oxygen-17 NMR

Ray Dupree (Warwick)

^{17}O MAS Glutamic Acid . HCl





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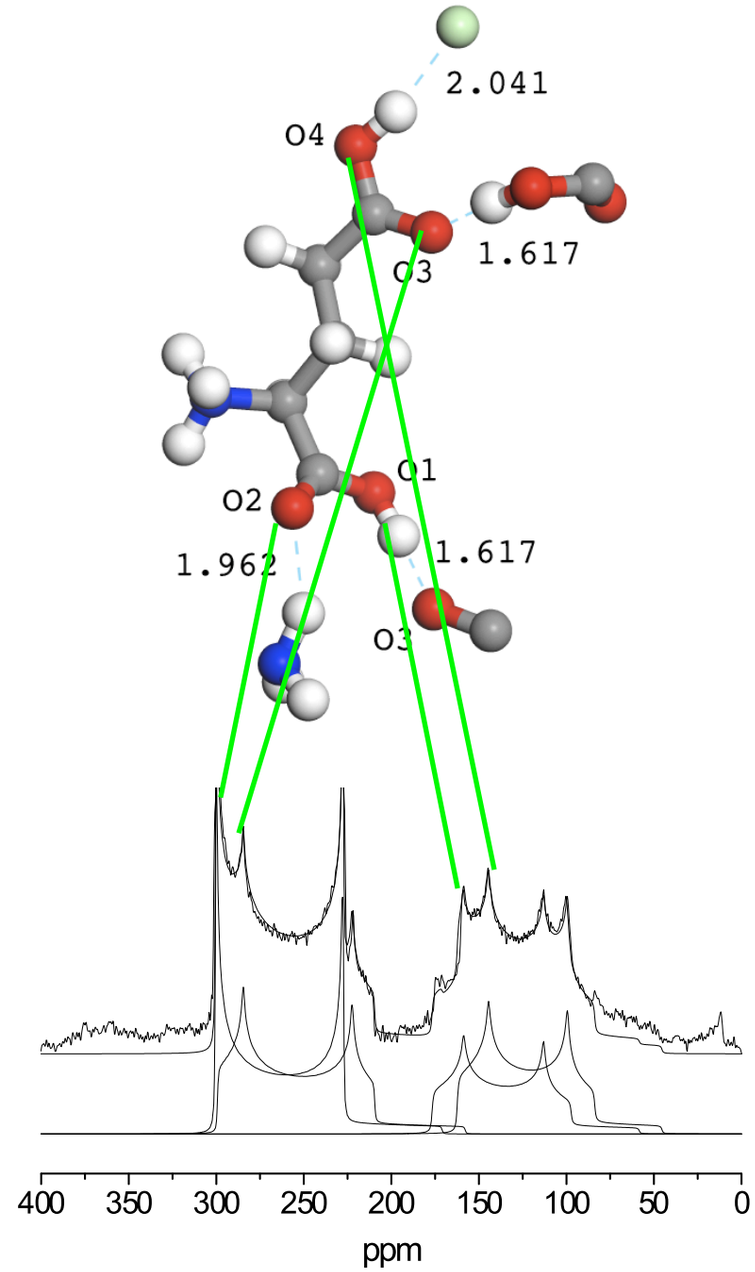
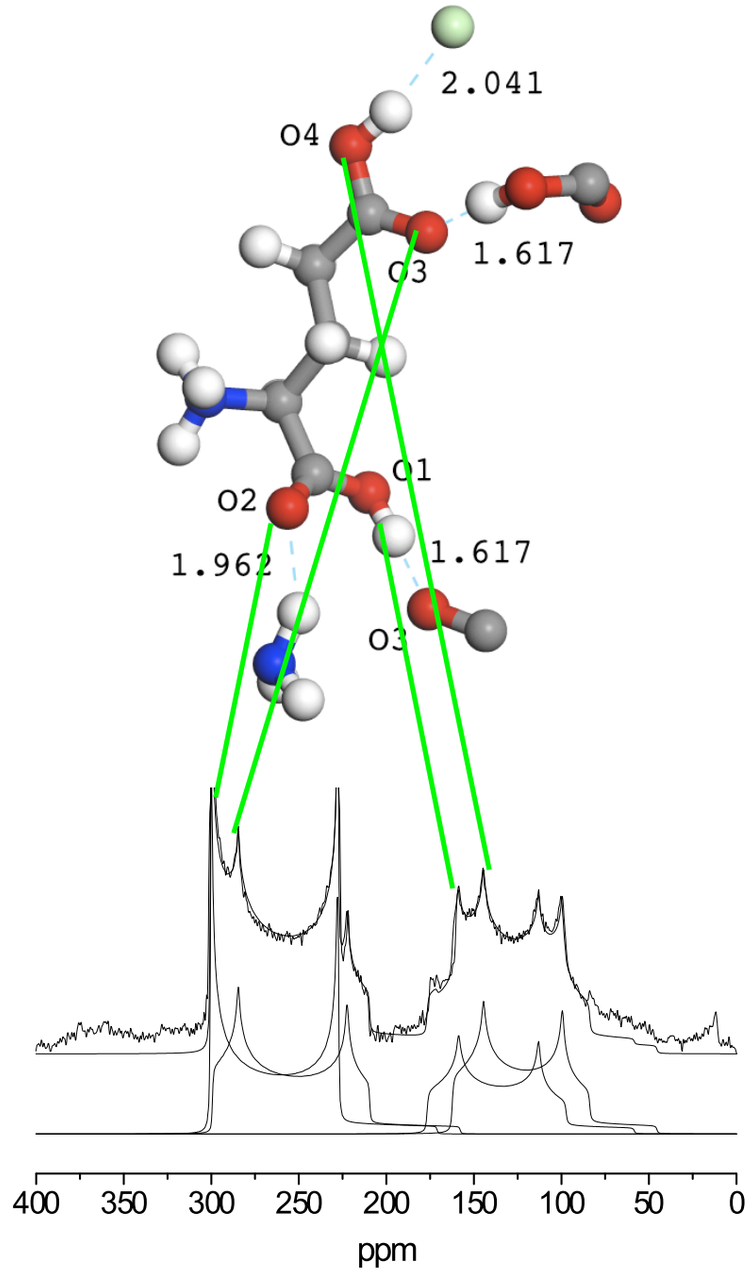


Oxygen-17 NMR

Ray Dupree (Warwick)

^{17}O MAS Glutamic Acid . HCl

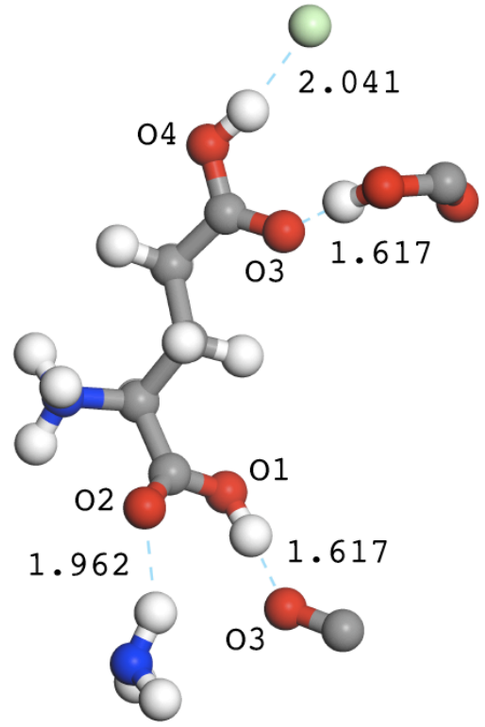
Site	Calculation			Experiment		
	δ_{iso}(ppm)	C_Q(MHz)	η_Q	δ_{iso}(pm)	C_Q(MHz)	η_Q
O1	177.6	7.72	0.22	172.5	7.45	0.25
O2	316.9	8.61	0.12	322	8.16	0.0
O3	311.0	8.90	0.23	315	8.31	0.17
O4	198.0	8.13	0.21	187	7.49	0.25



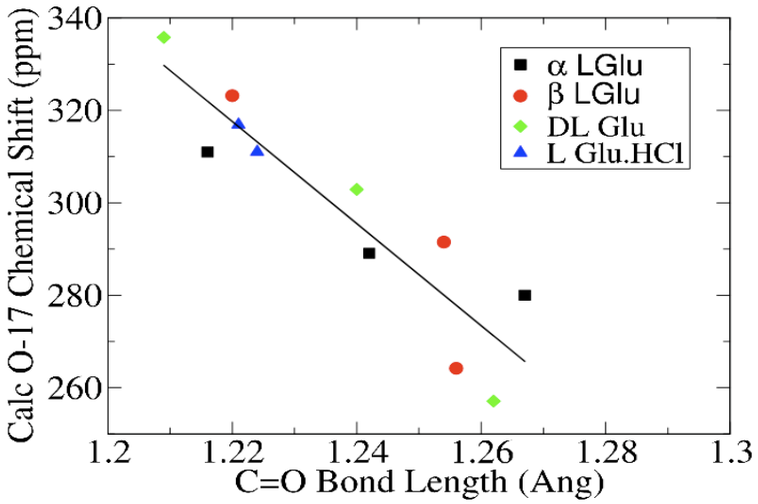
Glutamic Acid Polymorphs

- We find correlations between NMR parameters and hydrogen-bond strength

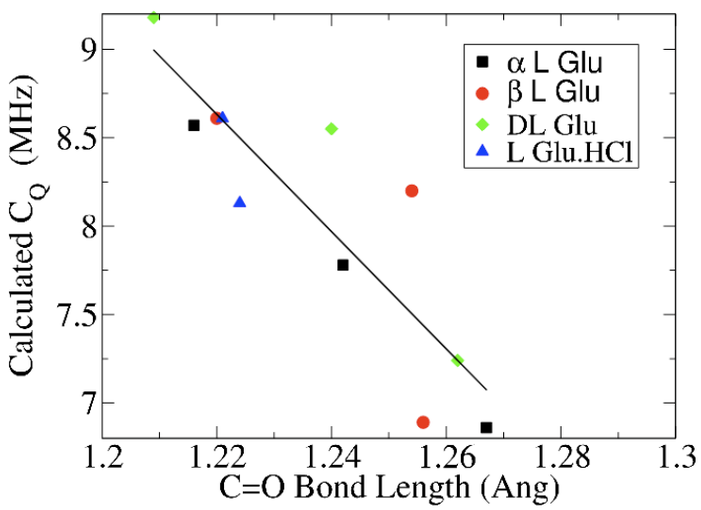
  Yates *et al* J.Phys. Chem. A 108 6032 (2004)



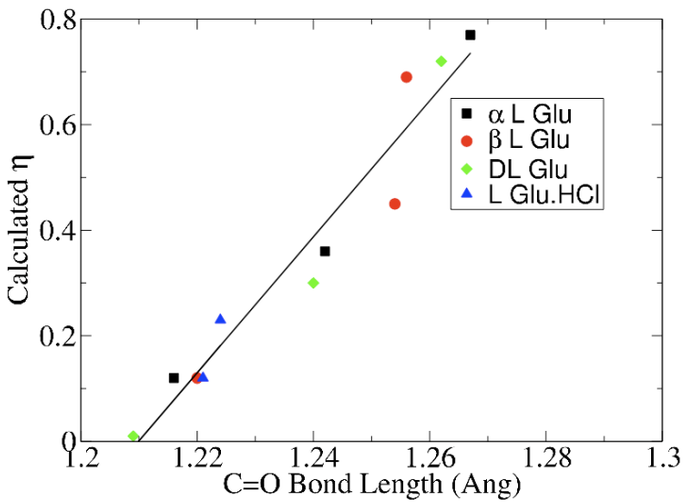
Chemical Shift



Quadrupolar Coupling



Asymmetry



Extended to wide range of amino-acids

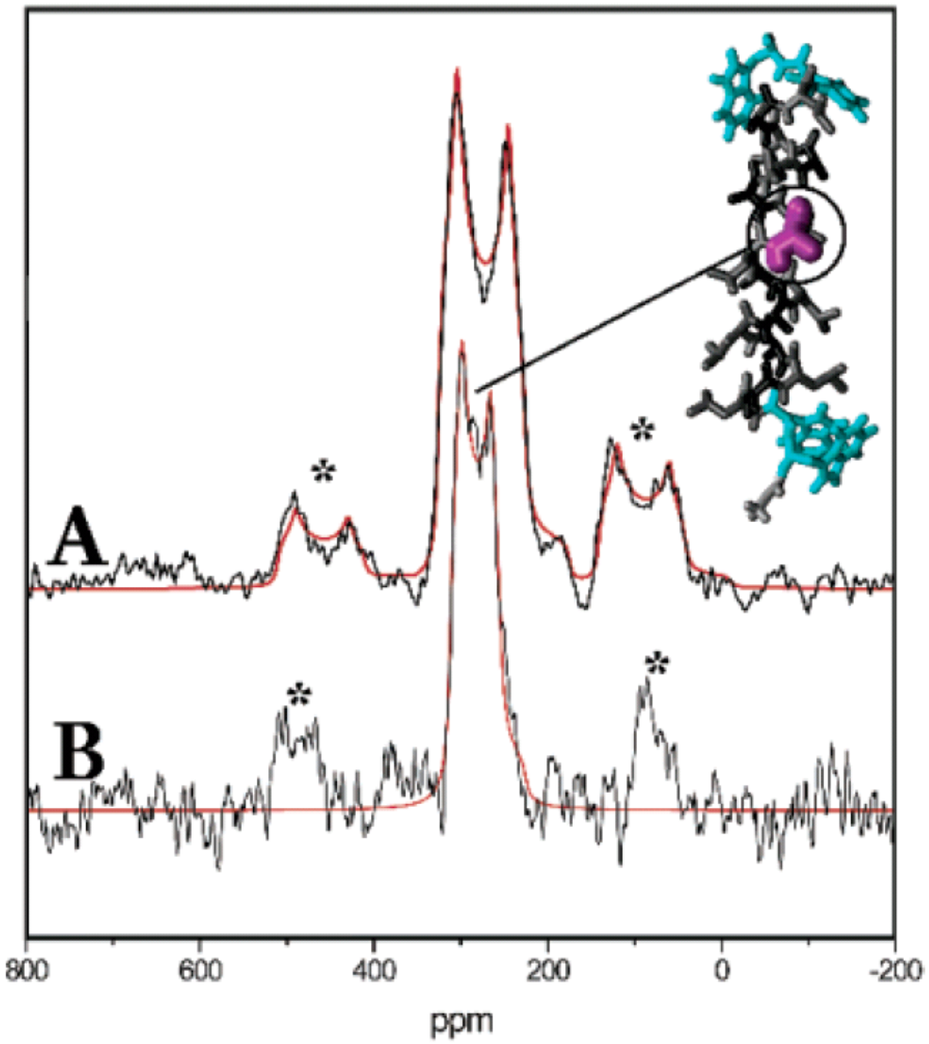
Combined first-principles computational and experimental multinuclear solid-state NMR investigation of amino acids
Gervais, C; Dupree, R; Pike, KJ; Bonhomme, C; Profeta, M; Pickard, CJ; Mauri, F,
J. Phys. Chem. A, 109 (31), 6960 -6969, 2005.

Oxygen-17 NMR Future Perspectives

Transmembrane proteins

^{17}O-[Ala12]-WALP23 synthetic peptide

- Chemical shift decreases ~1200ppm/Å with C=O bond length



WALP23 in DSPC Vesicle

δ_{iso}=311±1ppm C=O 1.217Å

WALP23 in Hydrated DSPC Vesicle

δ_{iso}=315±1ppm C=O 1.223Å

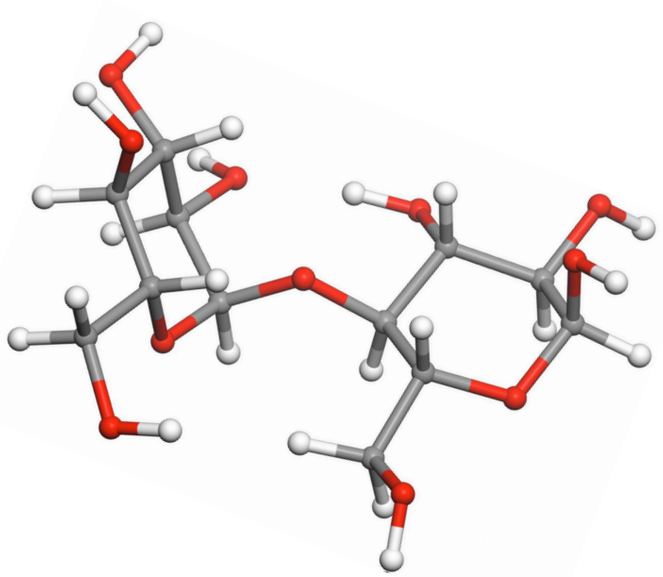
Solid-State ^{17}O NMR as a Probe for Structural Studies of Proteins in Biomembranes
V. Lemaitre, M.R.R. de Planque, A.P. Howes, M.E. Smith, R. Dupree, A. Watts
J. Am. Chem. Soc.; 2004; 126(47); 15320

J-Resolved Solid-State NMR

Steven Brown (Warwick)

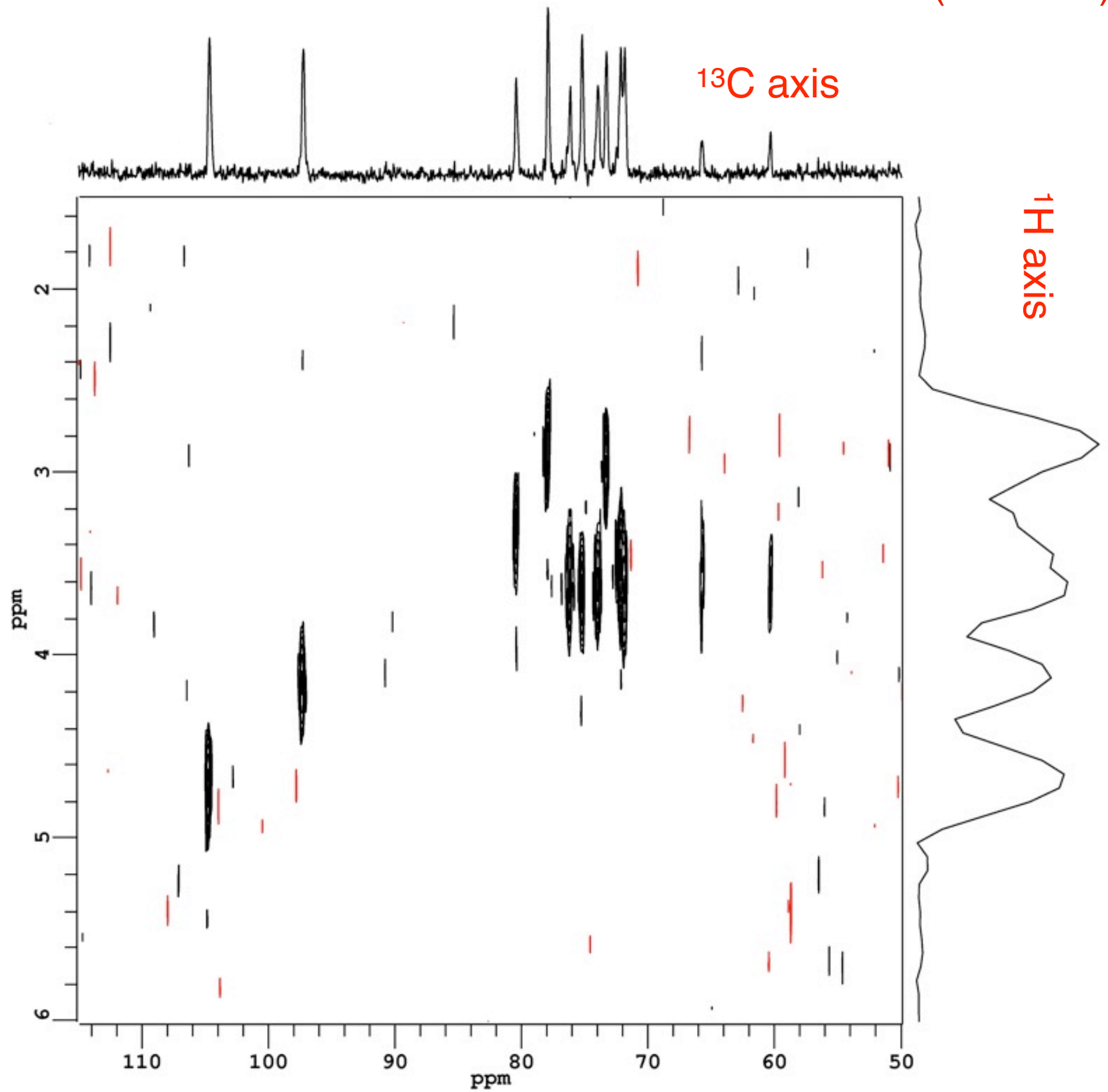
Maltose

sugar used in brewing

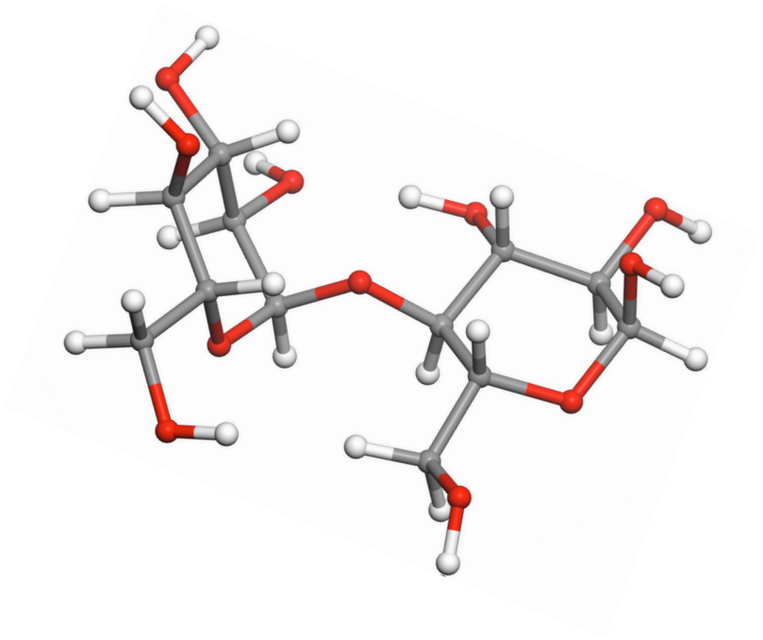


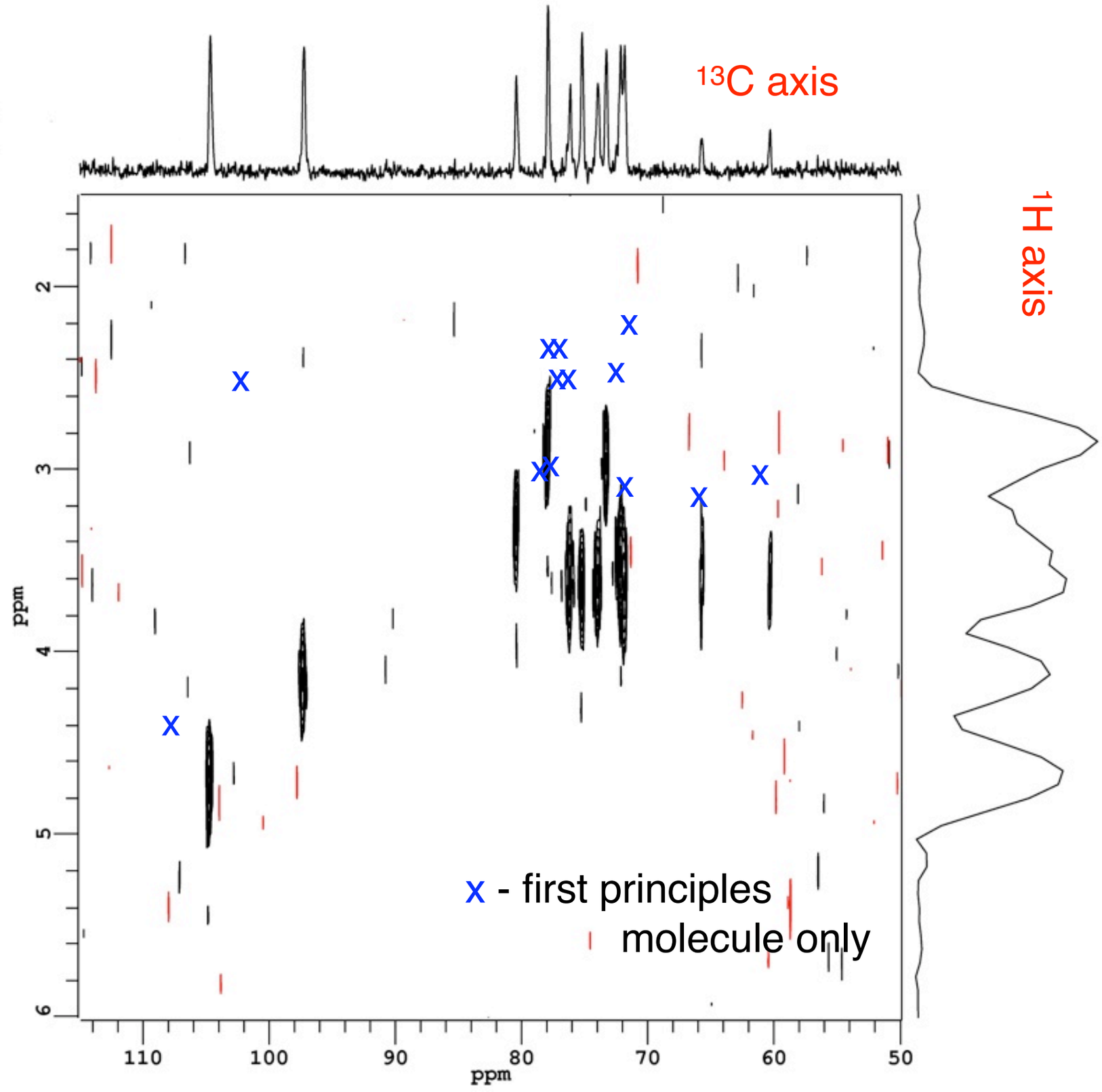
Cross-peaks when J-coupling between spins: -
C-H “bonds”

MAS–J–HMQC

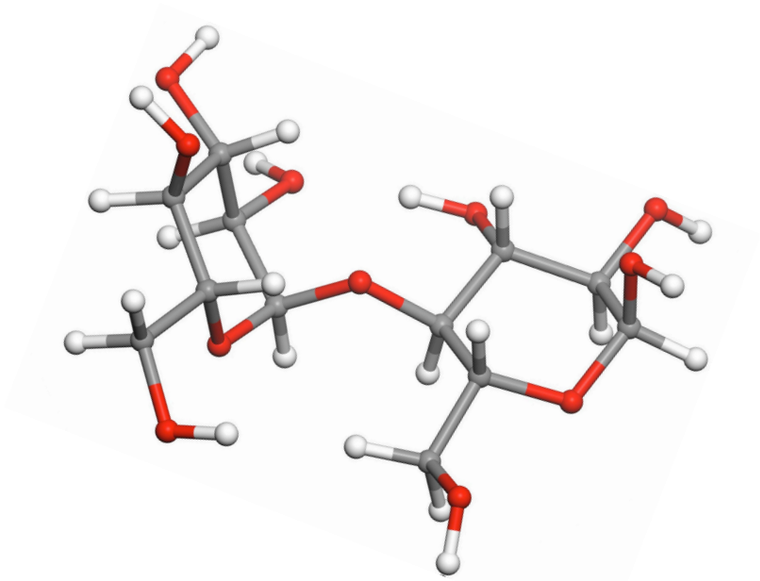


J-Resolved Solid-State NMR



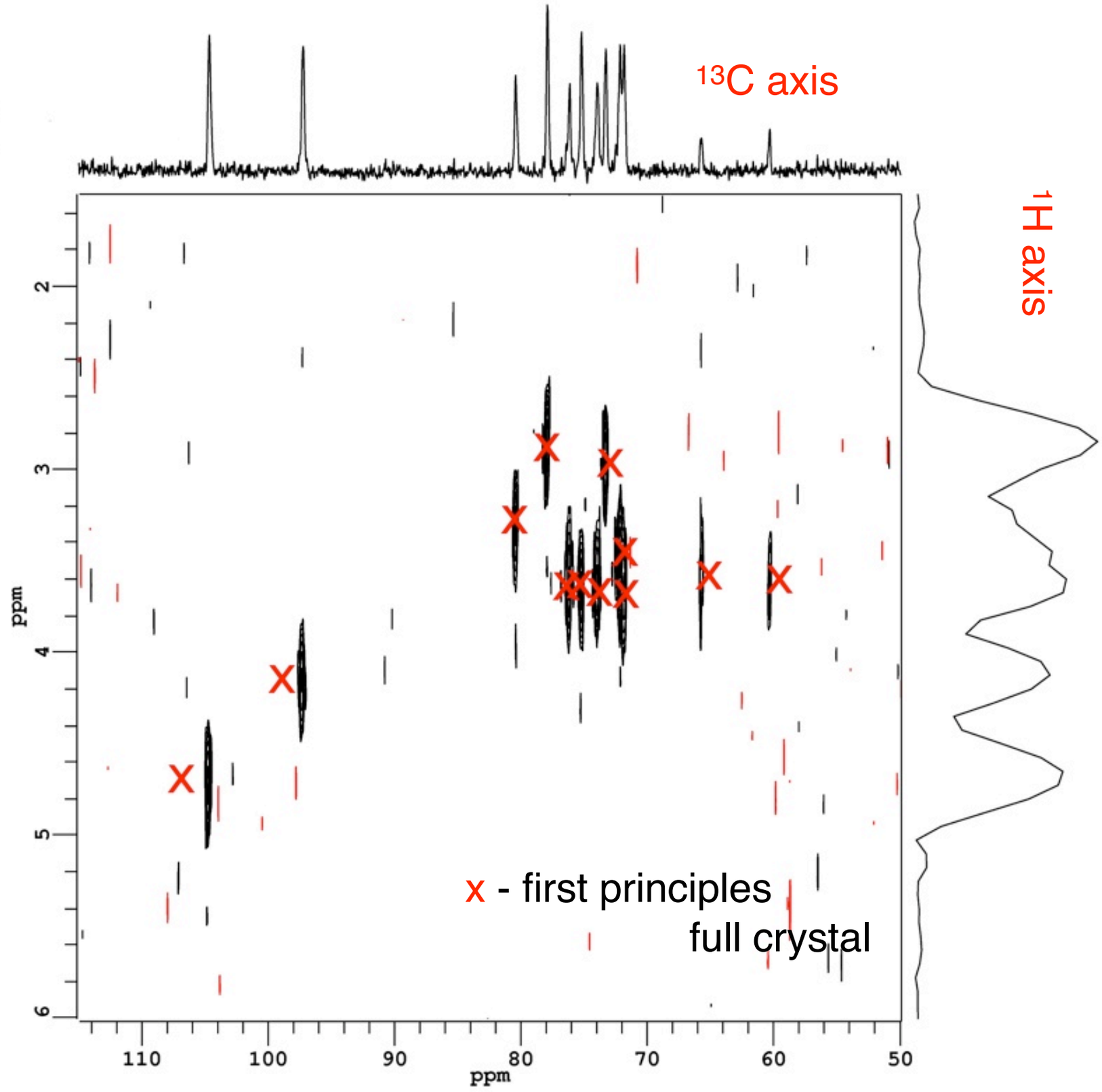


J-Resolved Solid-State NMR



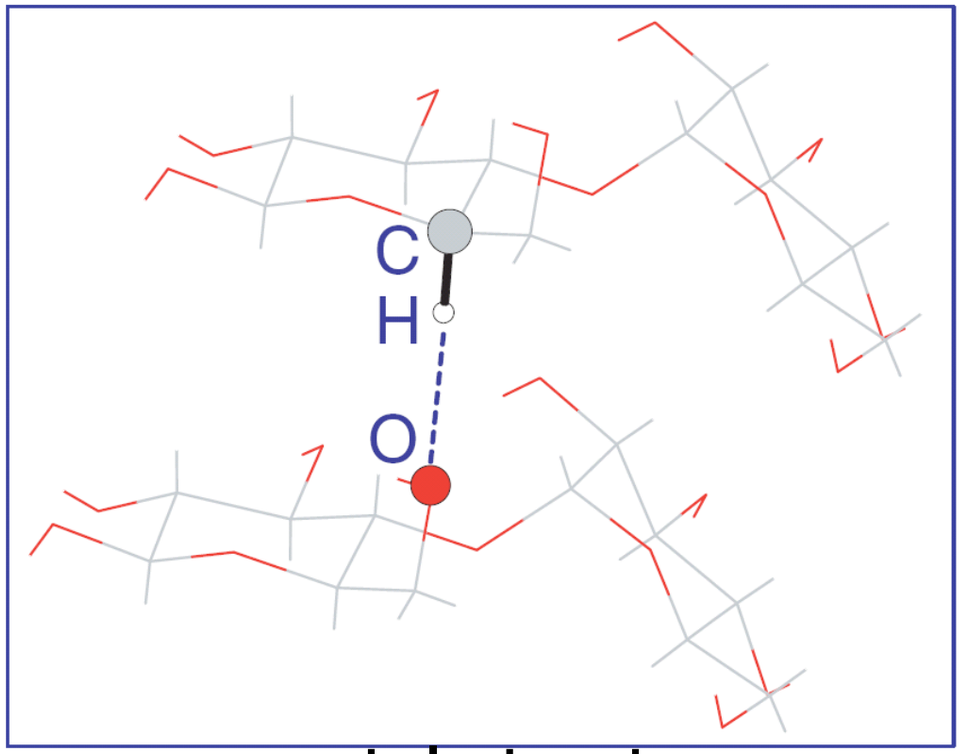
Molecule to solid variation due to intermolecular interactions (weak hydrogen bonds)

J. Am. Chem. Soc. 127 10216 (2005)
J. Am. Chem. Soc. 130 945 (2008)



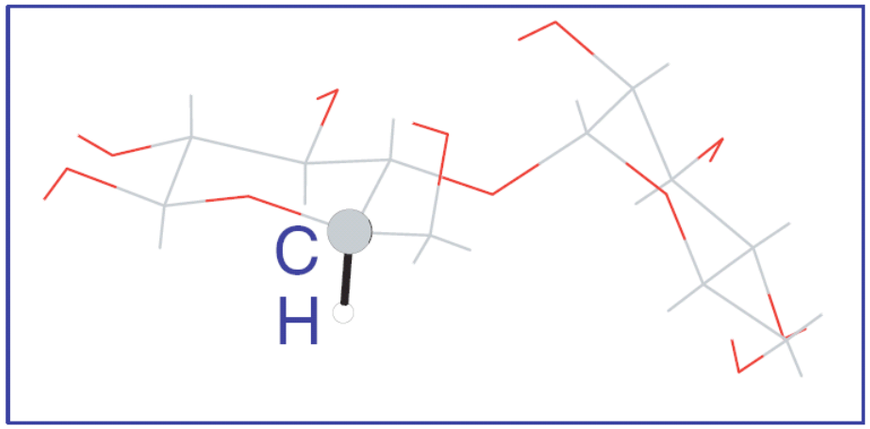
Maltose

anhydrous α–maltose: H4’ proton



crystal structure

$\delta_{iso}(^1H; cryst) = 3.66$ ppm

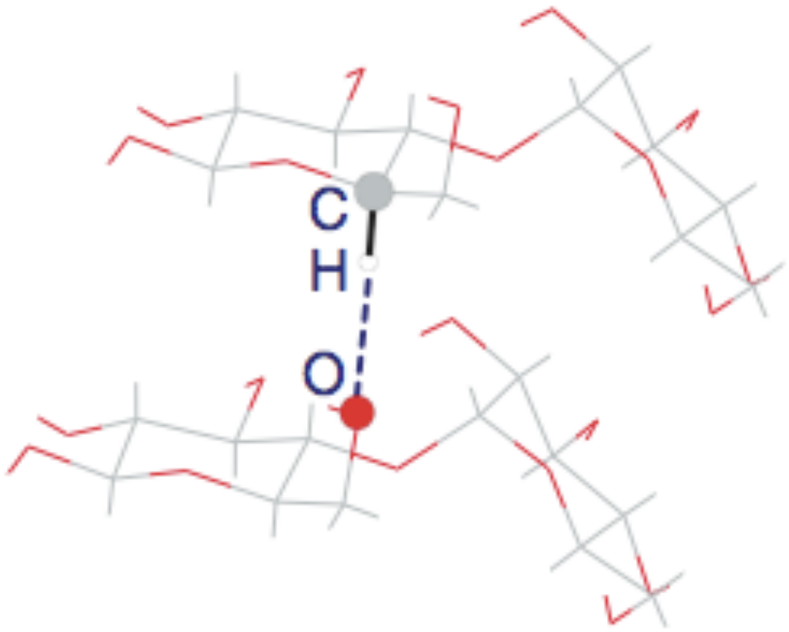


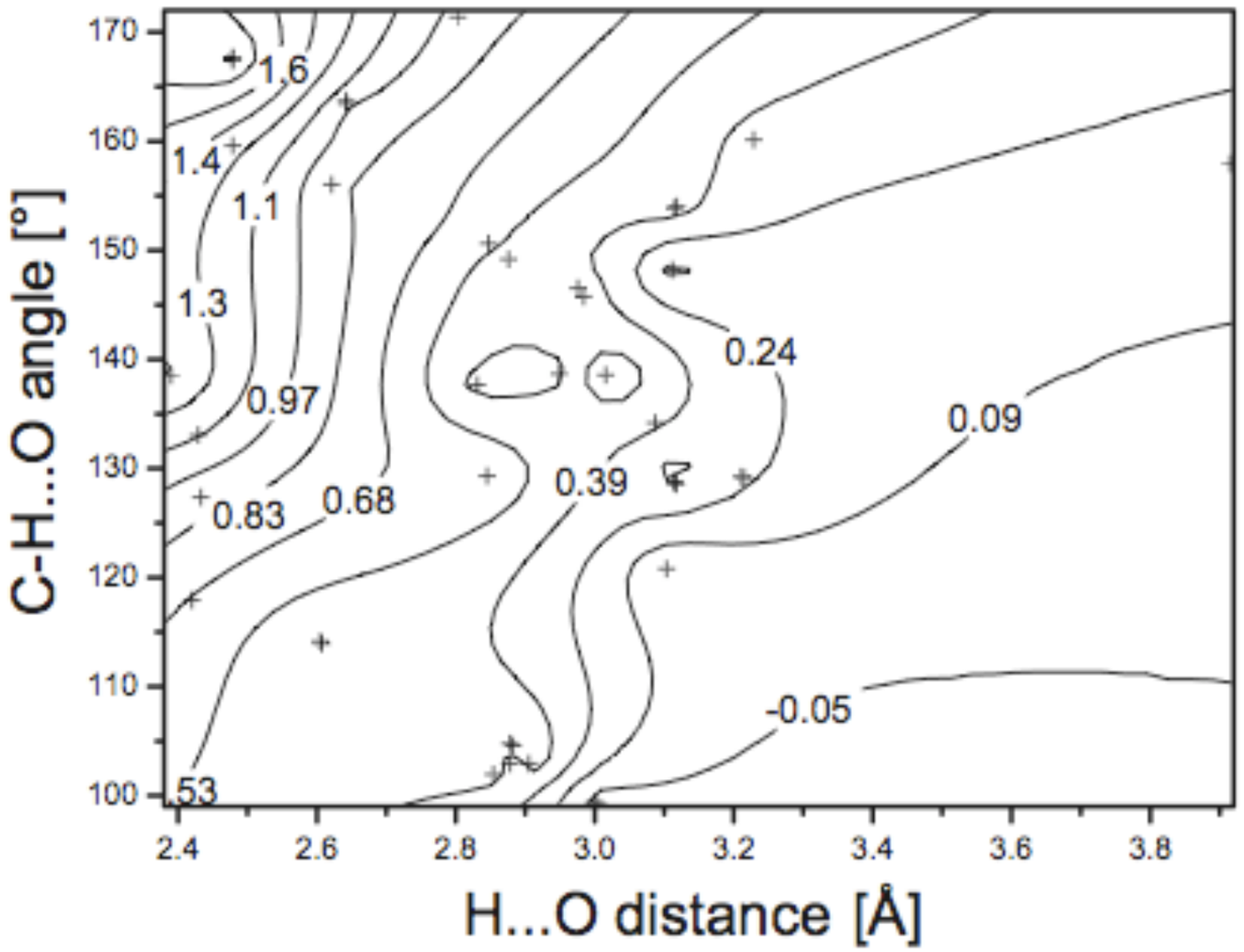
isolated molecule

$\delta_{iso}(^1H; mol) = 1.76$ ppm

$\Delta\delta_{iso}(^1H; mol\ to\ crys) = 1.90$ ppm

Intermolecular “Weak” Hydrogen bonds

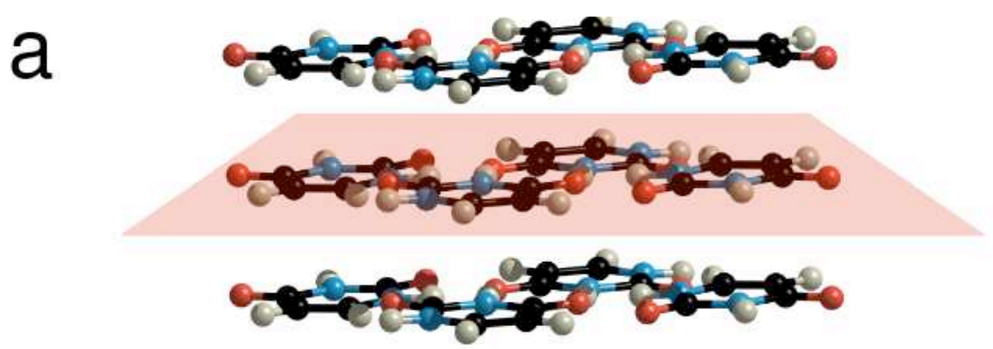




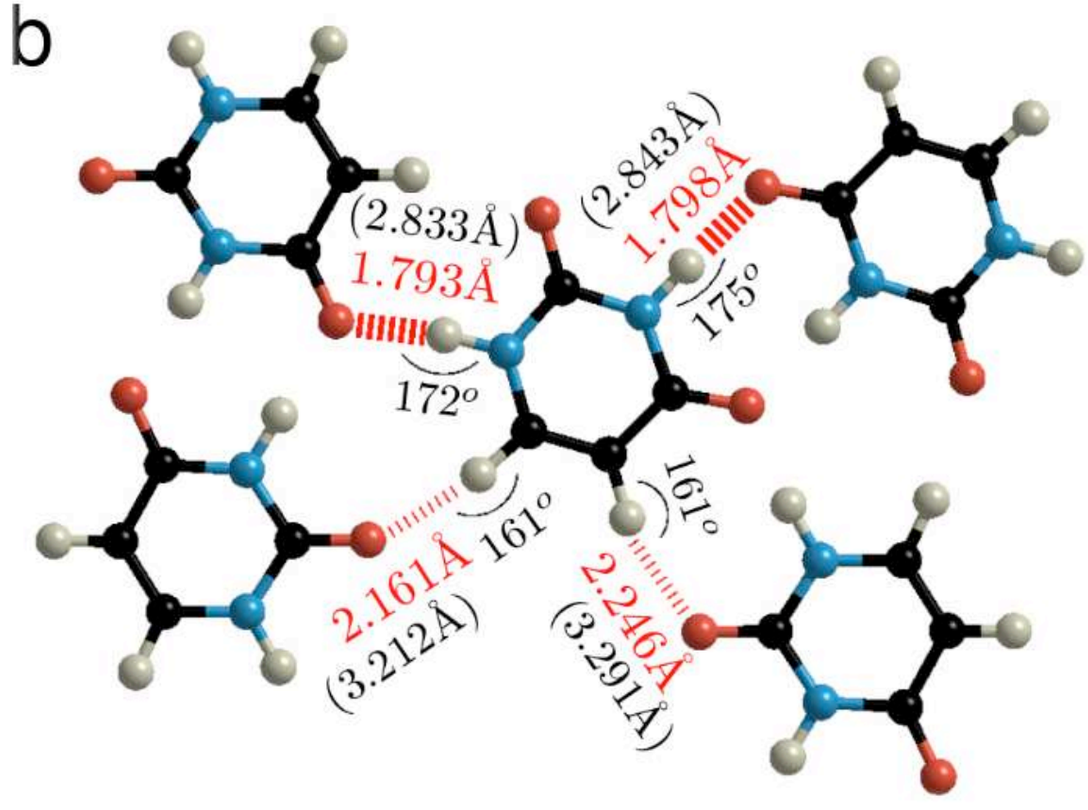
Correlation between a large calculated $\Delta\delta_{iso}(^1H$; mol to crys) and
a short H...O intermolecular distance (<2.7)
and a CHO bond angle greater than 130 degrees

Yates et-al J. Am. Chem. Soc. 127 10216 (2005)

Uracil



Isolate H-bonding from ring currents



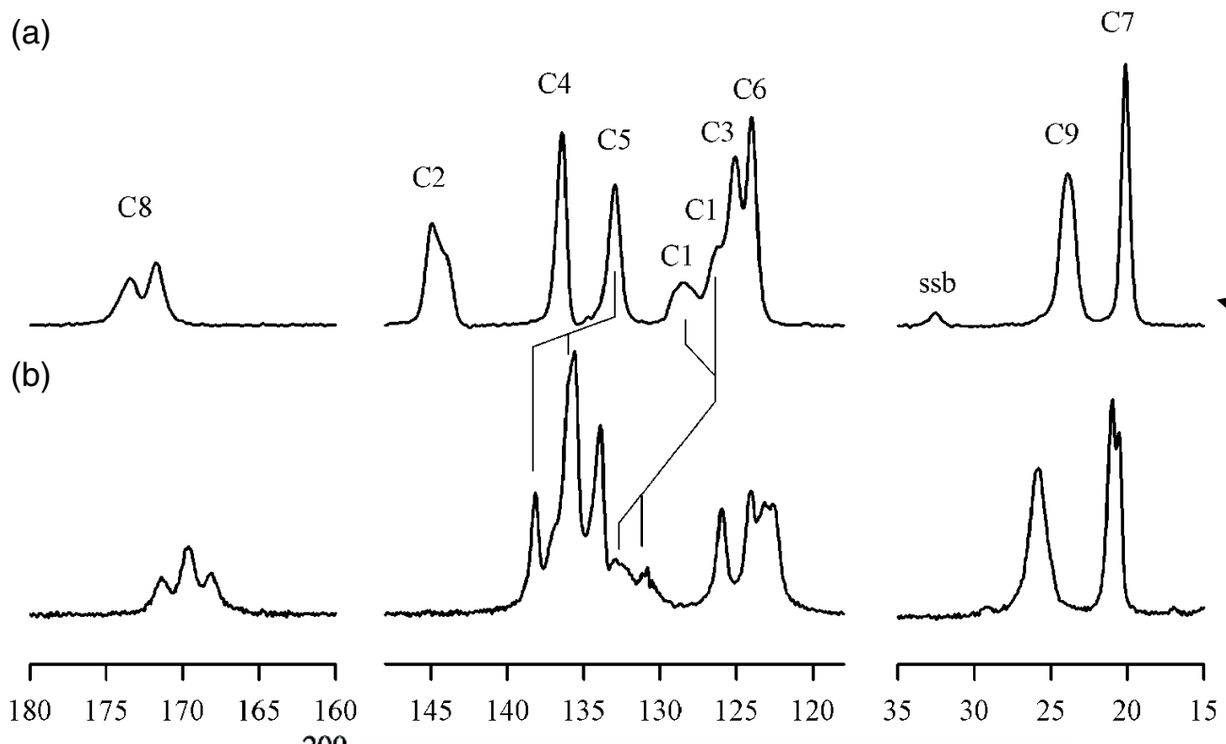
Doner	Δδ(Mol-Xal)
N-H	5.1
N-H	5.4
C-H	2.0
C-H	2.2

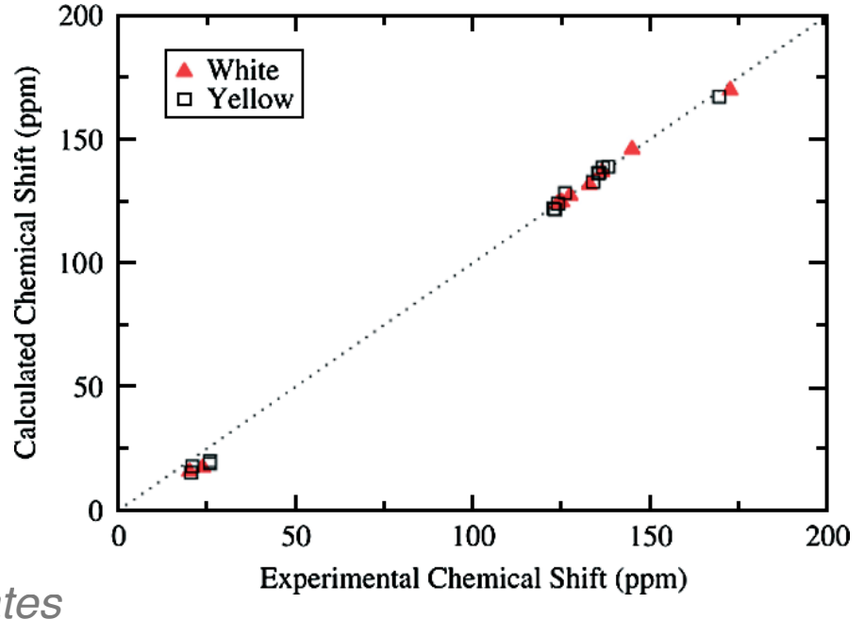
J. Am. Chem. Soc. 130 945 (2008)

NMR Crystallography

Regulatory requirement to identify polymorphic forms of new pharmaceuticals

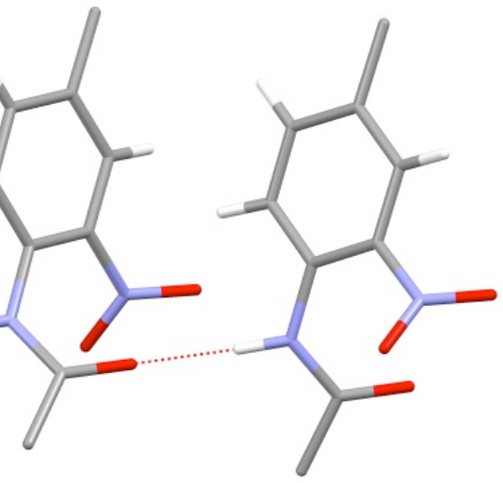
4-Methyl-2-nitroacetanilide (MNA)



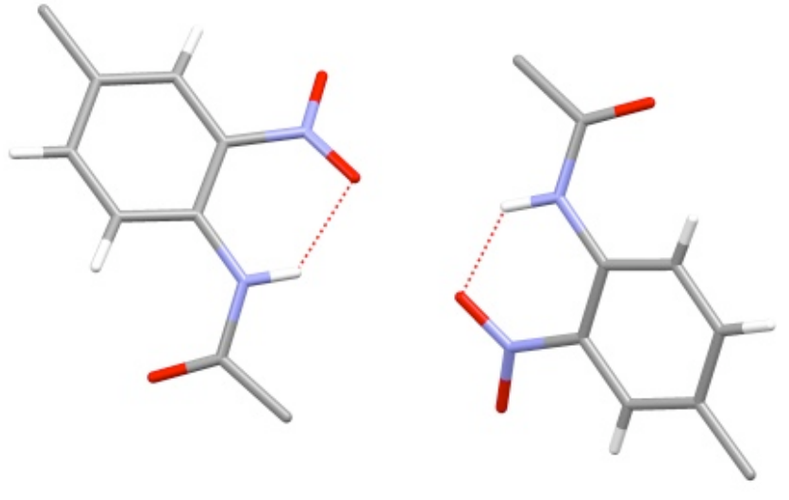


Magn. Reson. Chem. 44 325-333 (2006)

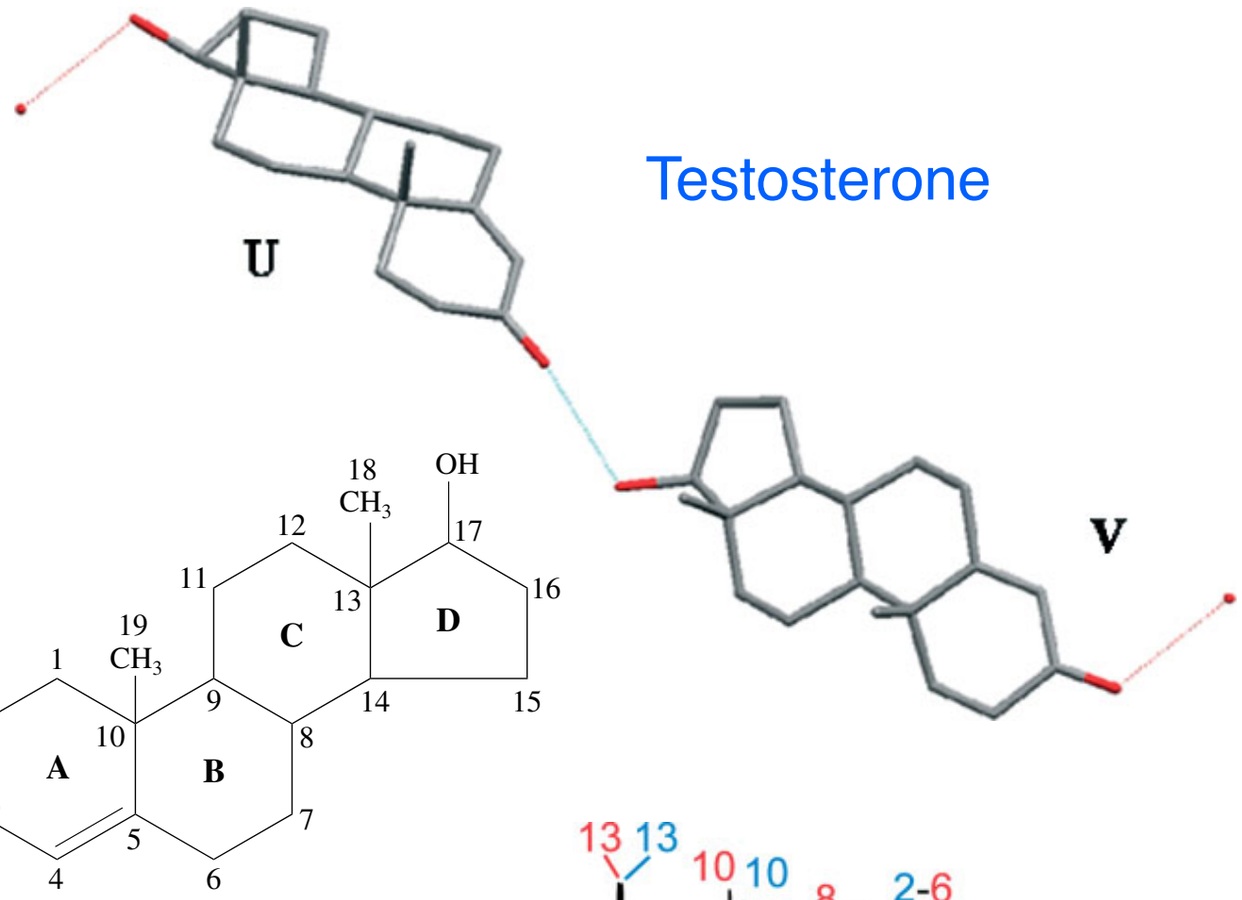
"white" MNA



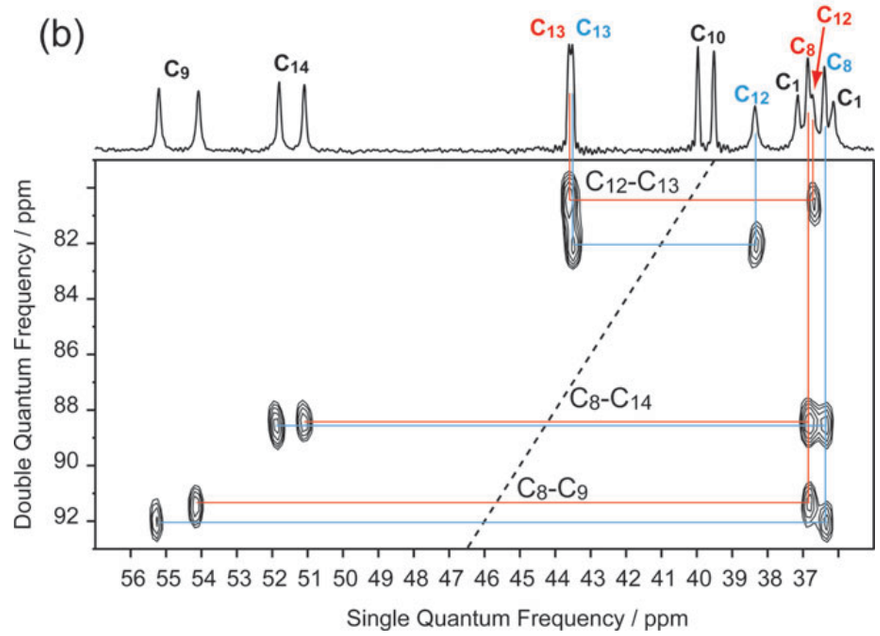
"yellow" MNA



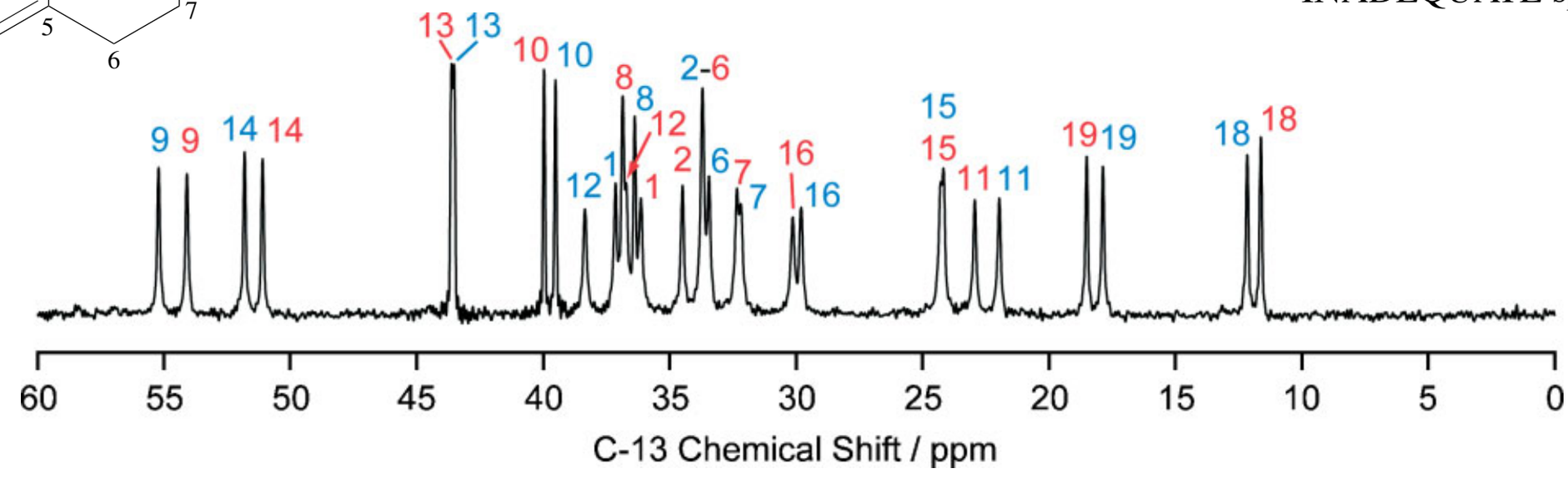
Two molecules in Asymmetric Unit



Testosterone



INADEQUATE spectrum

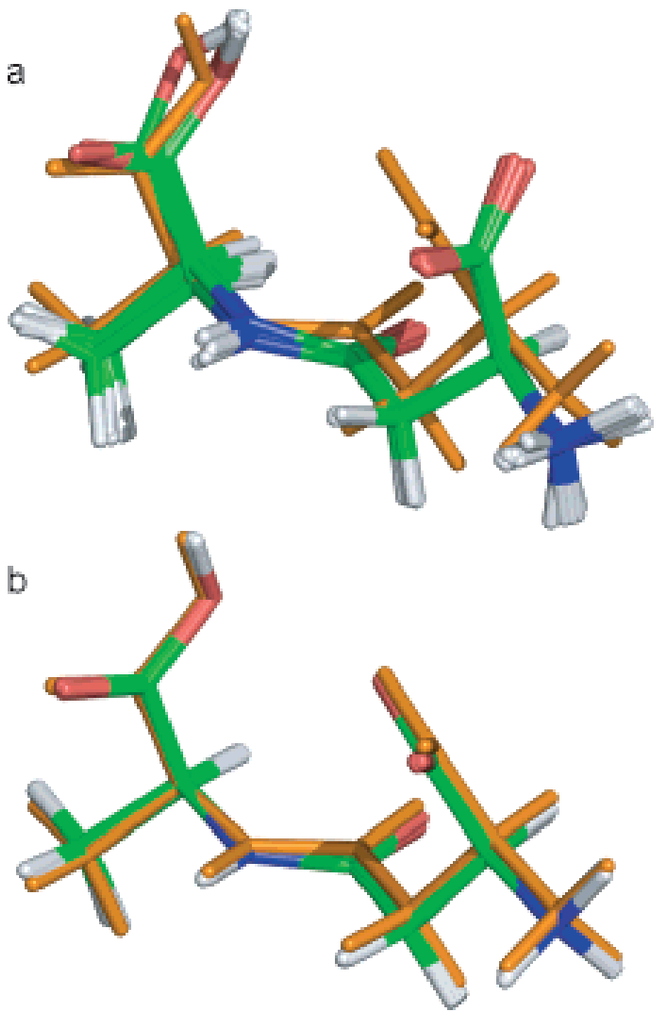


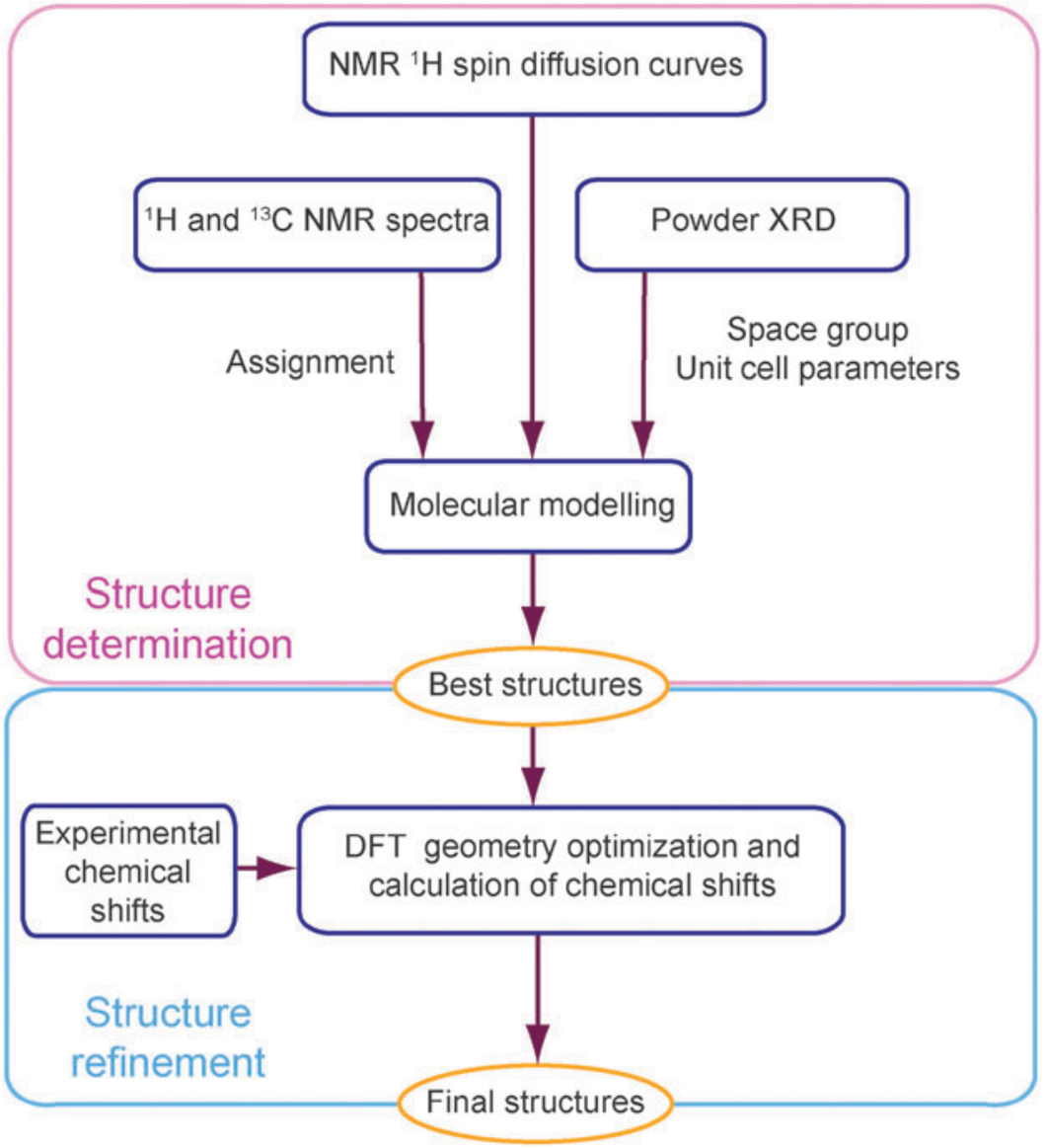
Robin K. Harris, Sian A. Joyce, Chris J. Pickard, Sylvian Cadars and Lyndon Emsley
Phys. Chem. Chem. Phys., 2006, 8, 137

NMR Crystallography

Elodie Salager, Robin S. Stein, Chris J. Pickard, Benedicte Elena and Lyndon Emsley
Phys. Chem. Chem. Phys. , 2009, 11, 2610

Chris J. Pickard, Elodie Salager, Guido Pintacuda, Benedicte Elena, and Lyndon Emsley,
J . Am. Chem. Soc., 129 (29), 8932 -8933, 2007

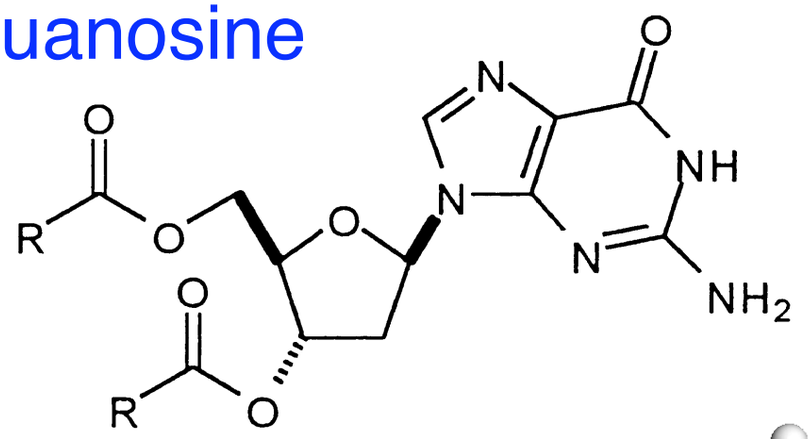




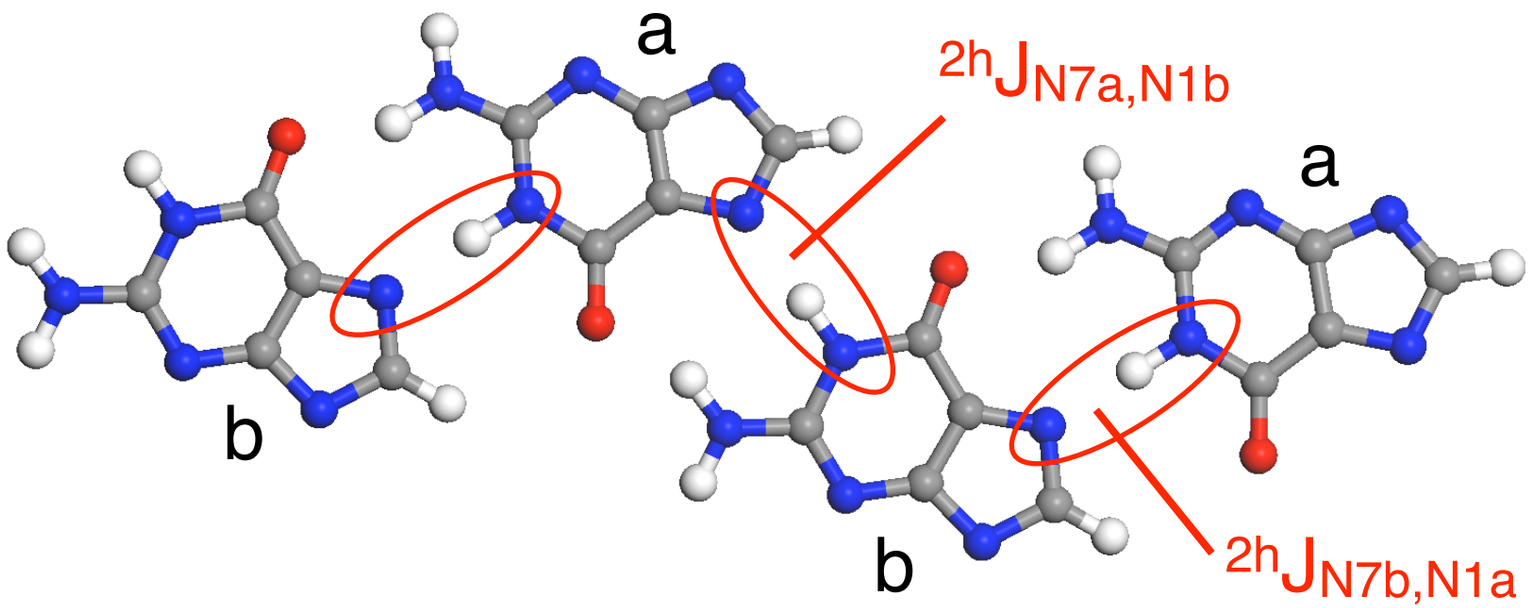
DNA bases

Steven Brown (Warwick)

Guanosine



self-assembles into ribbons
molecular electronics (FET)



$^{2h}J_{N7b,N1a}$ = 6.2±0.4 Hz (expt)
6.5 Hz (calc)

$^{2h}J_{N7a,N1b}$ = 7.4±0.4 Hz (expt)
7.7 Hz (calc)

J. Am. Chem. Soc. (2008) doi:10.1021/ja800419m

Predictions

$^{2h}J_{O6a,N2b}$ = 5.7 Hz
$^{1}J_{O6a,C1a}$ = 22.0 Hz

^{17}O - ^{15}N J-couplings

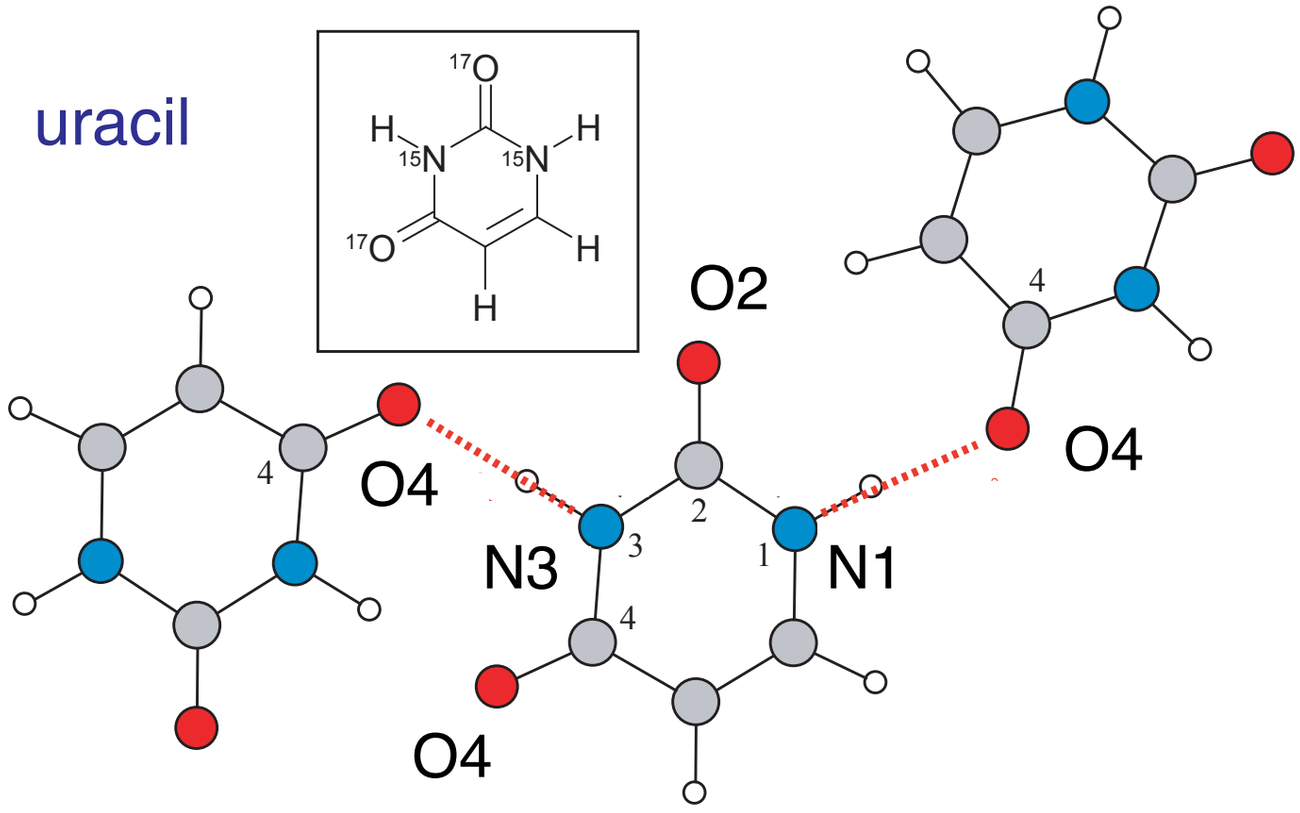
Steven Brown (Warwick)

Observing ^{15}N spin-echo

$^{2h}J_{NO}$	Expt	Calc
N1-O4:	6.7± 0.4 Hz	6.1 Hz
N3-O4:	4.8± 0.5 Hz	4.6 Hz

$^{2}J_{NN}$

N1-N3: 2.7± 0.1 Hz 2.7 Hz



Observing ^{17}O spin-echo

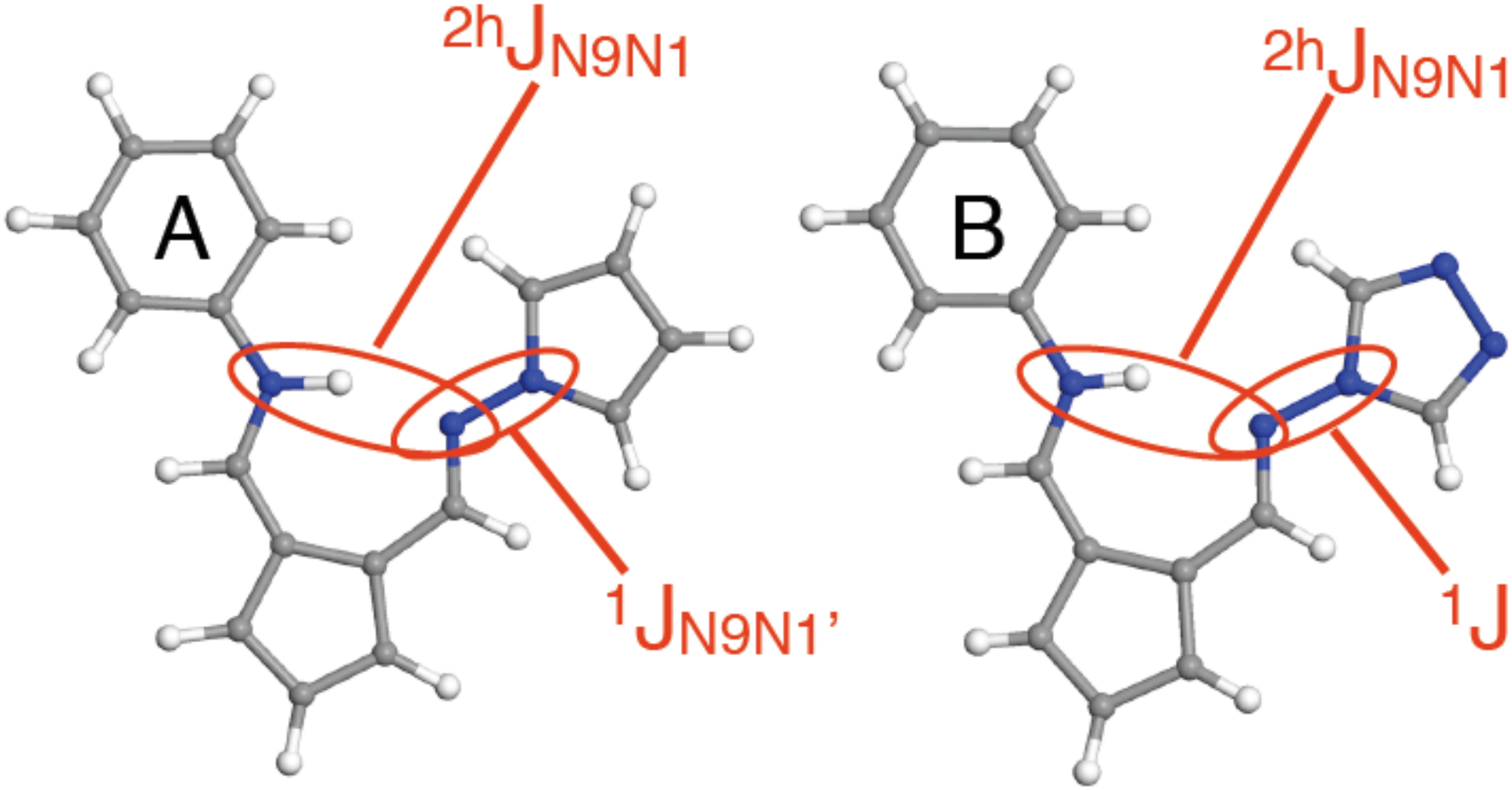
$^{2}J_{ON}$

O4-N1/3: 5.1± 0.5 Hz 5.4 Hz

J. Am. Chem. Soc. ***131*** *1820 (2009)*

Intra-molecular H-bonds

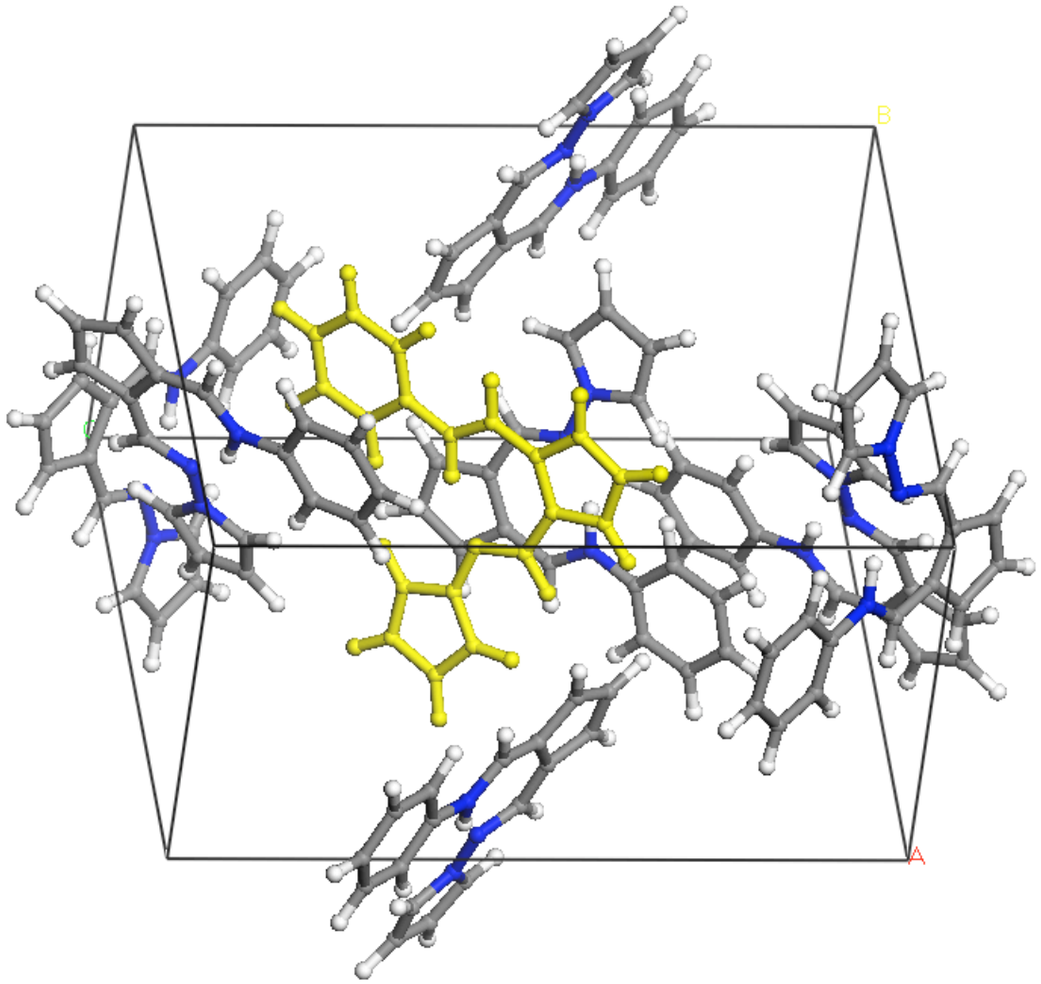
Steven Brown (Warwick)



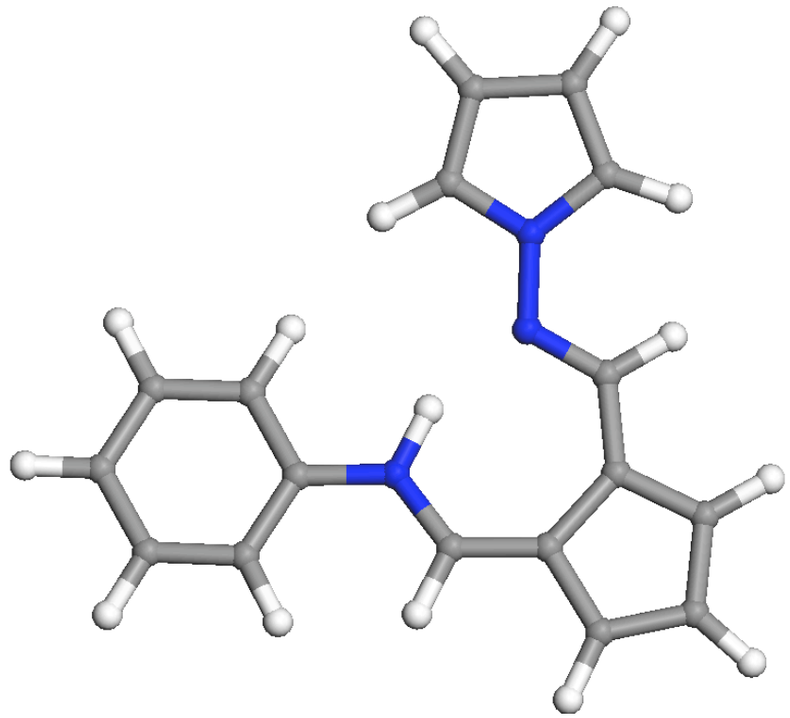
	Pyrrole (A)		Triazole (B)	
	$^{2h}J_{N9N1}$	$^{1}J_{N9N1'}$	$^{2h}J_{N9N1}$	$^{1}J_{N9N1'}$
Calculation[7]	8.1	-9.8	7.4	-11.4
Experiment[6]	8.0±0.3	10.2±0.4	7.2±0.1	12.0±0.1

J. Am. Chem. Soc., 130, 12663 (2008)

Effect of Crystal Lattice



full crystal



isolated molecule

Intra-molecular H-bonds

	$^{2h}J_{N9N1}$	$^{1}J_{N9N1'}$	
Solid-state	8.1	-9.8	J computed for a perfect crystal of (A)
Electrostatic	0.5	0.4	change in J due to effect of crystal lattice (isolated molecule at crystal geometry)
Structural	1.2	0.0	change in J due to subsequent relaxation of isolated molecule
Molecular	9.8	-9.4	J computed for isolated molecule (in vacuum)

Intra-molecular H-bonds

	$^{2h}J_{N9N1}$	$^{1}J_{N9N1'}$	
Solid-state	8.1	-9.8	J computed for a perfect crystal of (A)
Electrostatic	0.5	0.4	change in J due to effect of crystal lattice (isolated molecule at crystal geometry)
Structural	1.2	0.0	change in J due to subsequent relaxation of isolated molecule
Molecular	9.8	-9.4	J computed for isolated molecule (in vacuum)
Solution-state	9.0	10.3	Experimental result (note: systematic 0.9 Hz error due to neglect of solvation)

J. Am. Chem. Soc., 130, 12663 (2008)