Polymorphism in molecular magnetism:

relevance and prediction employing a new-generation of intermolecular potentials

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Outline of this presentation

1. Motivation for this work

2. Polymorphism and Molecular Magnetic Materials

3. Why PIXEL intermolecular potentials are interesting?

4. Polymorph prediction using PIXEL potentials
   a) The PIXCRYPAR program
   b) Crystal structure optimization with PIXEL
   c) Polymorph prediction with PIXEL

5. Acknowledgments

1. MOTIVATION FOR THIS WORK

GEM2's main research line

Crystal engineering of molecular crystals presenting technological properties (magnetism, conductivity, superconductivity) using accurate (quantum mechanical) methods

Key facts

1.- The technological properties of crystals depend on the crystal packing

Consequence: one has to learn

a) how to predict and control their crystal packing (Crystal Engineering)

b) what orientations present the desired electronic property

2.- Many of the approximate popular theories used to explain the packing or electronic properties of crystals (magnetism) are too approximate and do not always work properly.

Therefore, there are two group reasearch sublines:

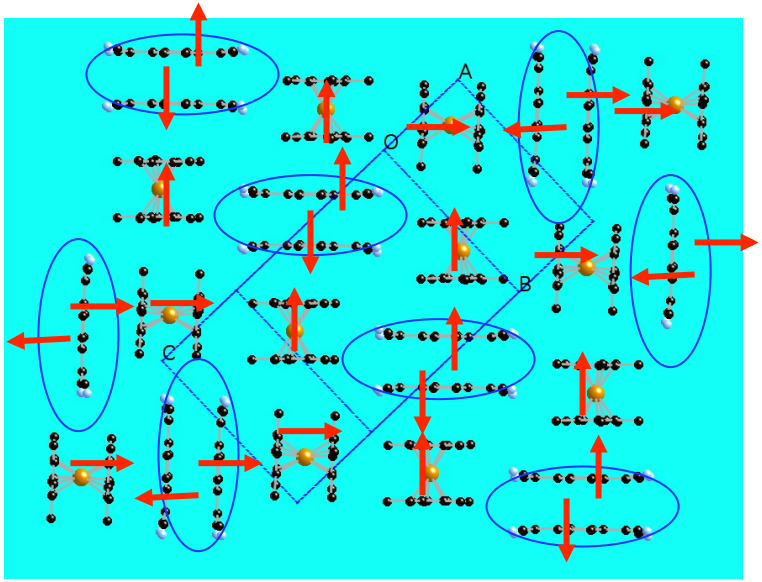
1) Theoretical studies on crystal packing and polymorph prediction

2) Theoretical studies on the mechanism of magnetic interaction

1) Magnetism and crystal packing : $Fe(Cp^*)_2$-TCNQ

the first molecule-based bulk ferromagnet [Miller et al. JACS, 109, 769 (1987)]
*$Fe(Cp^*)_2^+$ and $TCNQ^-$ both are **stable radicals** (doublets)*

I



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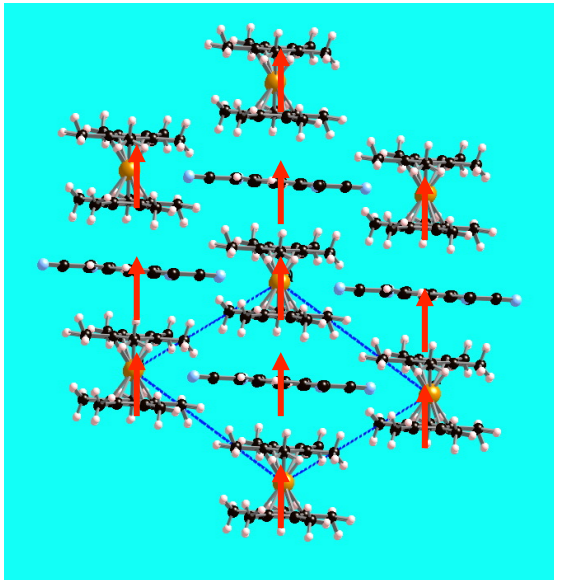

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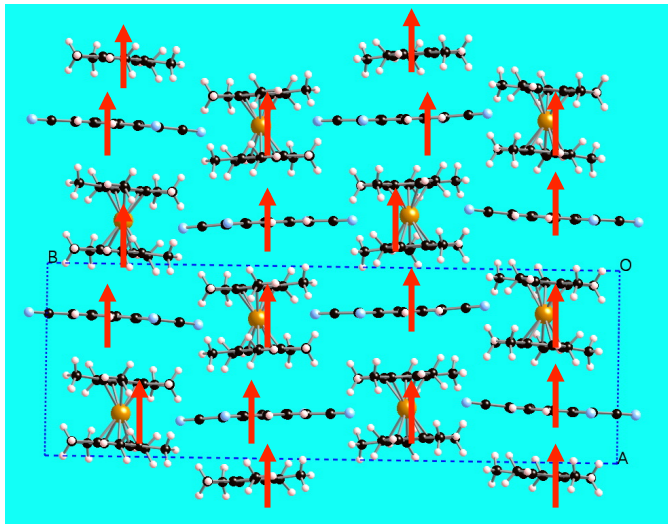


I: **paramagnet**, *thermodynamic crystal form*

II: **metamagnet**, *kinetic form*

III: **bulk ferromagnet (T_c=3K)**, *kinetic form*

2. POLYMORPHISM AND MOLECULAR MAGNETIC MATERIALS

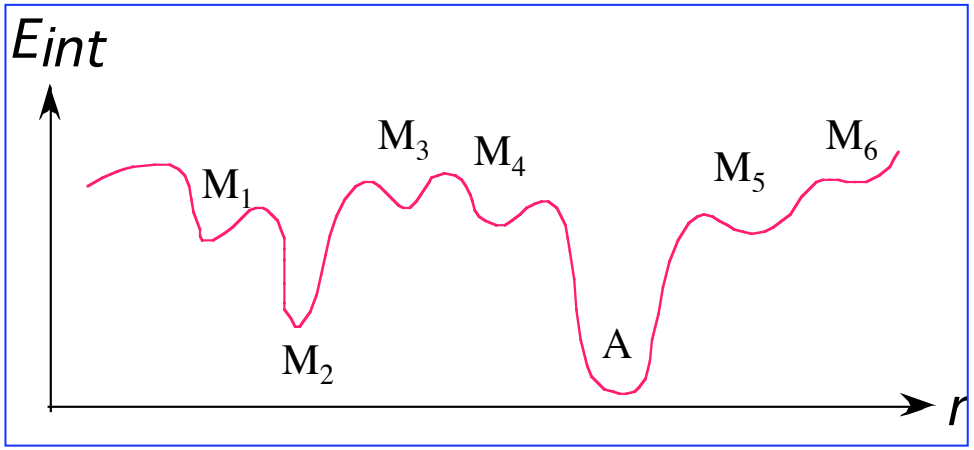
Basic principles of polymorphism: QM view

Each polymorph is a minimum on the $\Delta G = \Delta U - T\,\Delta S$ energy surface of the crystal

There is an absolute minimum (A) and many metaestable minima (M_1, …)

Absolute: obtained under "thermodynamic conditions"
(slow growth, giving time to relax the structure),
Metaestable: obtained under "kinetic conditions"
(fast growth, energetic conditions: high T or P)

The minima are not always interconnected (Ostwald Law; A → M_2).
Consequence: Some crystals have to be disolved/melted to go from one polymorph to another.



It is possible to extend all QM concepts developed for intramolecular reactivity to supramolecular reactivity

2) Magnetism: rigorous description

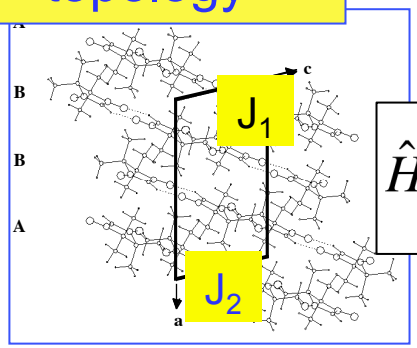
The first principles *bottom-up* (FPBU) methodology

General procedure to connect micro and macro magnetic properties in an unbiased, accurate, and physically meaningful way

First-principles:
J_{AB} are computed using first principles
No assumptions

Bottom-up:
From radicals to macroscopic properties

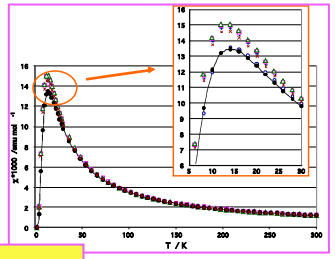
MICRO
$\{J_i\}$
+
magnetic topology



$$\hat{H} = \sum_{A<B}^{N} -2J_{AB}\hat{S}_A\hat{S}_B$$

Deumal, Robb, Novoa, et al. *J. Phys. Chem. A*, **106**, 1299 (2002)

Statistical Thermodynamics on known magnetic topologies



MACRO
Macroscopic properties
(χ, C_p, M, …)

How to connect the microscopic and macroscopic magnetic worlds?

Using Statistical Mechanics (rigorous form)

macro
χ, ...

$$\chi = \frac{Ng^2\mu_B^2}{3k_BT}\mu_o \left[\frac{\sum_n S_n(S_n+1)(2S_n+1)\exp\left[-(E_n - E_o)/k_BT\right]}{\sum_n (2S_n+1)\exp\left[-(E_n - E_o)/k_BT\right]} \right]$$

Diagonalize the matrix representation of the Heisenberg Hamiltonian to obtain *all* $\{E_i\}$:

$$\langle i|\hat{H}|j\rangle = \langle i| - \sum_{A,B}^{N} J_{AB}\left(2\hat{S}_A\hat{S}_B + \frac{1}{2}\hat{I}\right)|j\rangle$$

Same $\{E_i\}$ than

$$\hat{H} = \sum_{A<B}^{N} -2J_{AB}\hat{S}_A\hat{S}_B$$

micro
J_{AB}

J_{AB} = radical-radical magnetic interactions

N = all the spin-configurations of the crystal (N = ∞)

NEED OF A PROPER FINITE MODEL OF THE CRYSTAL

Four-steps implementation of the first-principles *bottom-up* procedure

1. Locate all unique (microscopic) *radical-radical pairs* and compute the strength of their magnetic interactions (J_{AB}):

a) Crystal packing analysis to locate all unique radical-radical pairs,

b) Compute J_{AB} for all unique radical-radical pairs (from the energy difference between states of different spin multiplicity, computed using first-principles methods).

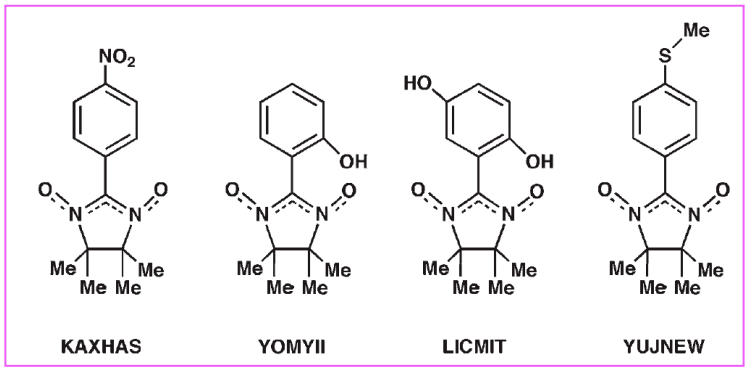
2. Define the *magnetic topology* of the J_{AB} interactions (network conectivities that the J_{AB} make among the radicals of the crystal)

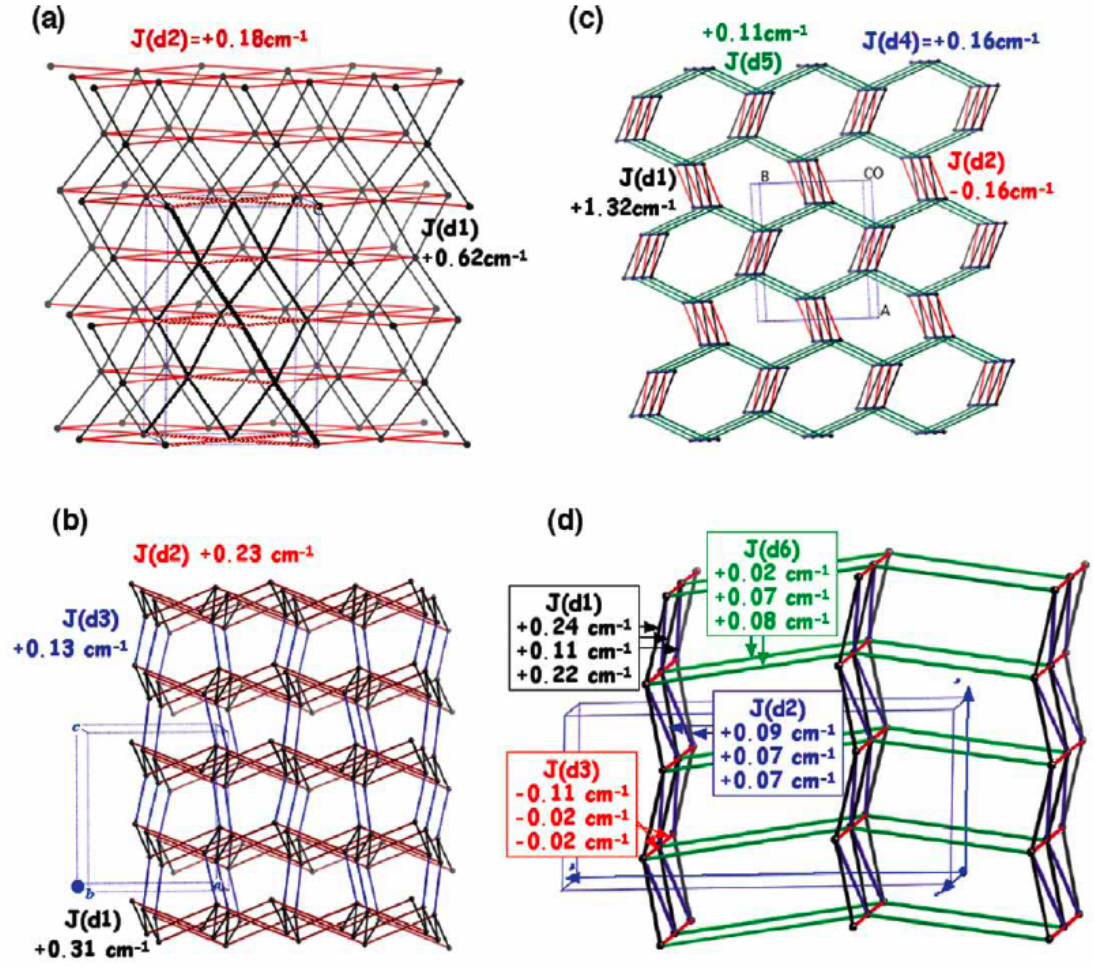
3. Look for the *minimal magnetic model* that describes the magnetic topology in an even form (must reproduce the full crystal by translation)

4. Compute matrix representation and the *energy of all the magnetic states* in the minimal magnetic model space spin functions. Use these values to compute the *macroscopic magnetic properties* (Statistical Mechanics expressions).

FPBU example: bulk-FM nitronyl nitroxides (1)

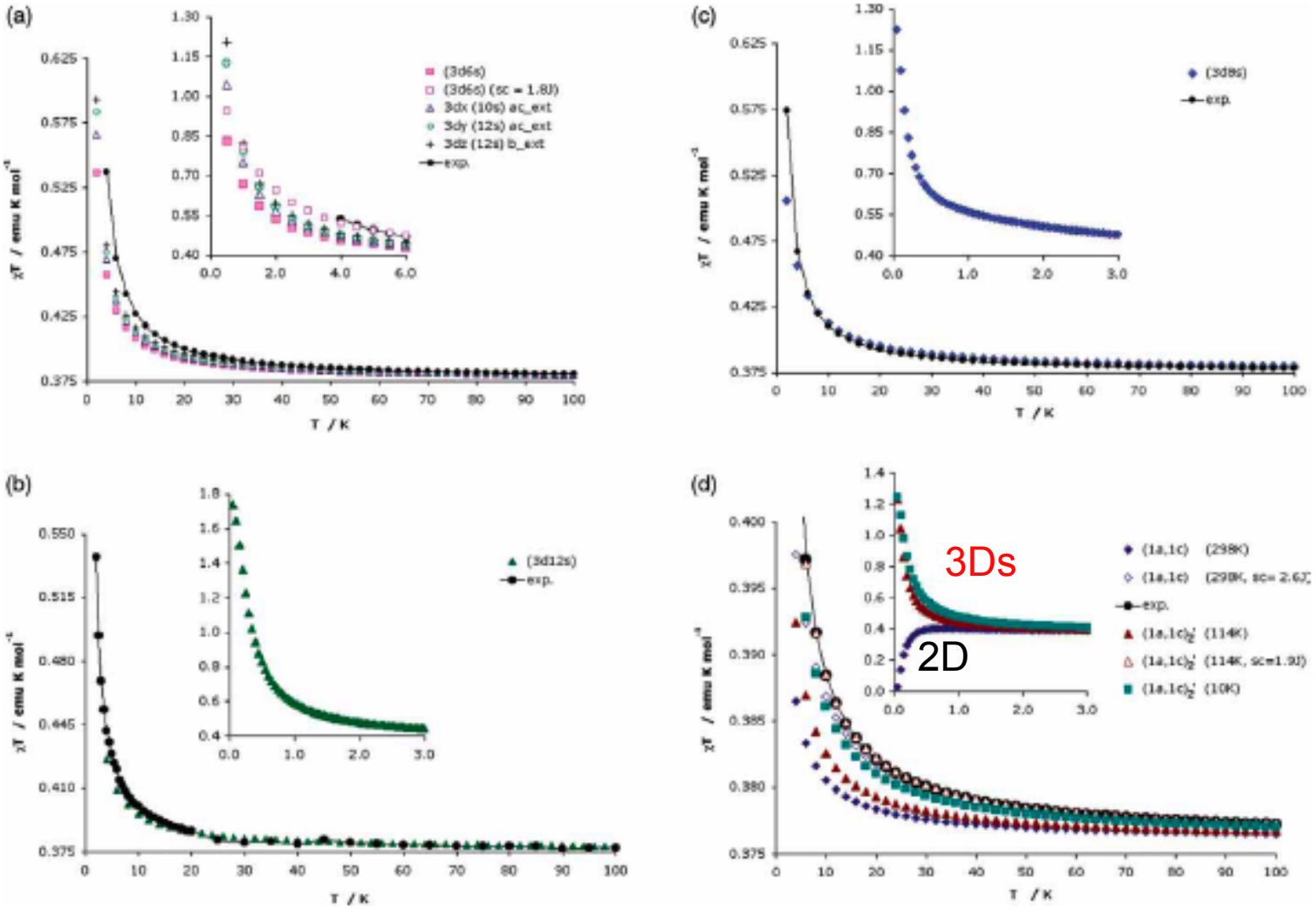
Four known member (among many crystals)





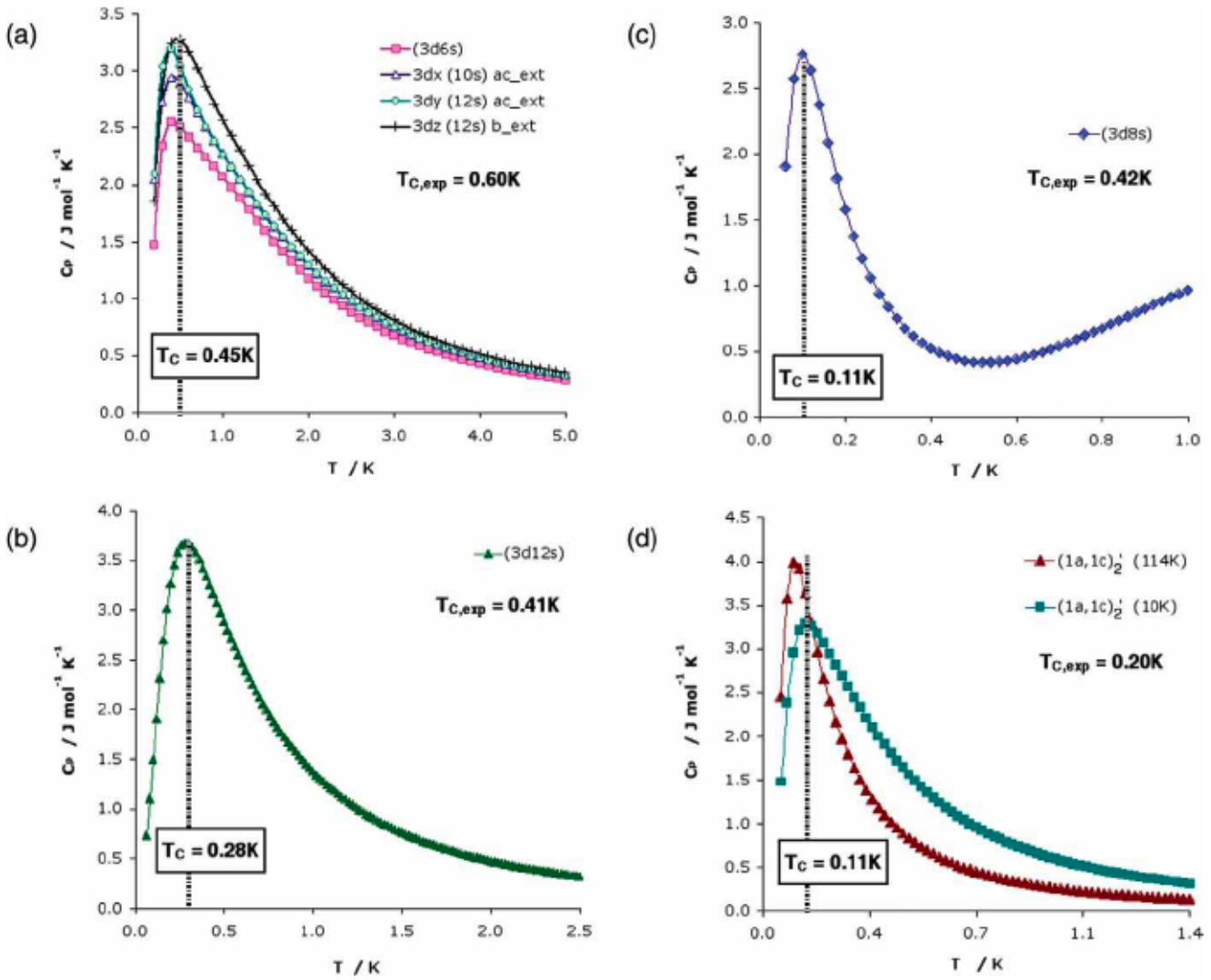
3D: bulk-FM nitronyl nitroxides (2)

Theoretical vs experimental magnetic susceptibility curves



3D: bulk-FM nitronyl nitroxides (3)

Theoretical vs experimental heat capacity curves



Conclusion

By doing FPBU calculations we can

Reproduce

Understand

and, then,

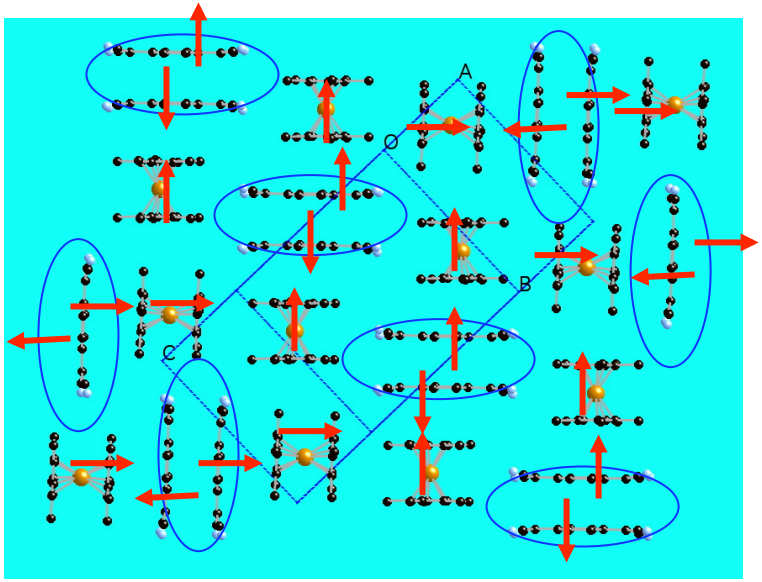
Predict

the magnetic properties of molecular magnets

Why different magnetic behaviors: $Fe(Cp^*)_2$-TCNQ

the first molecule-based bulk ferromagnet [Miller et al. JACS, 109, 769 (1987)]
$Fe(Cp^*)_2^+$ and $TCNQ^-$ both are stable open-shell radicals (doublets)

I



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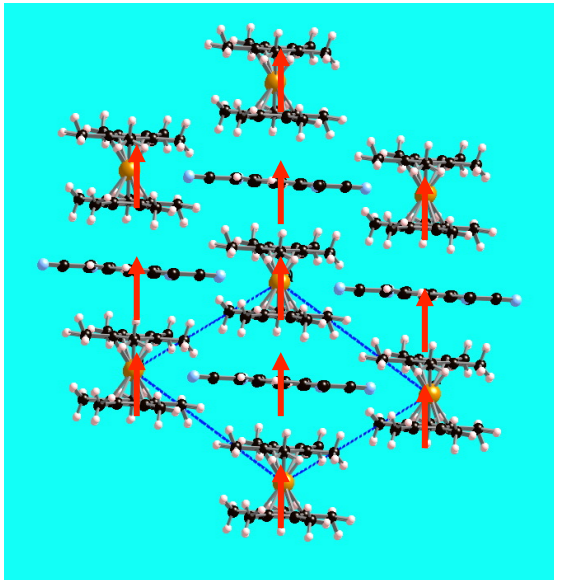

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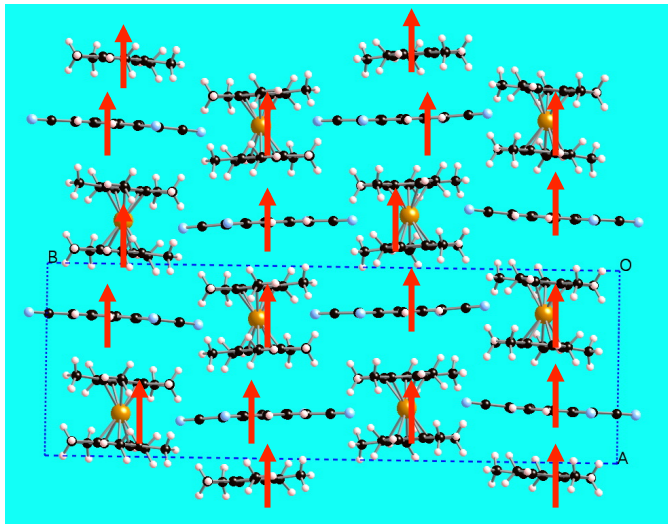


I: **paramagnet**, *thermodynamic form*
formation of $(TCNQ^-)_2$ diamagnetic dimers
$Fe(Cp^*)_2^+$ radicals are then isolated

II: **metamagnet**, *kinetic form*
$(TCNQ^-)(Fe(Cp^*)_2^+)$ chains (calculation)

III: **bulk ferromagnet** ($\mathbf{T_c}$**=3K**), *kinetic form*
$(TCNQ^-)(Fe(Cp^*)_2^+)$ chains (calculation)

Form I: $TCNQ^{\cdot -}\cdots TCNQ^{\cdot -}$ dimerization

Two $TCNQ^{\cdot -}$ anion-radicals at ~3 Å, despite being energetically repulsive, form a long-distance covalent-like bond (**yes**, at C-C ≈ 3 Å !!!)

I. Garcia-Yoldi, J. S. Miller, JJN, J. Phys. Chem. A, **2009,** *113*, 7124

$(TCNQ^{\cdot -})_2$ dimers become diamagnetic (closed-shell singlet ground state)

Similar behavior than also found in $TCNE^{\cdot -}$, $cyanil^{\cdot -}$, $TTF^{\cdot +}$, …

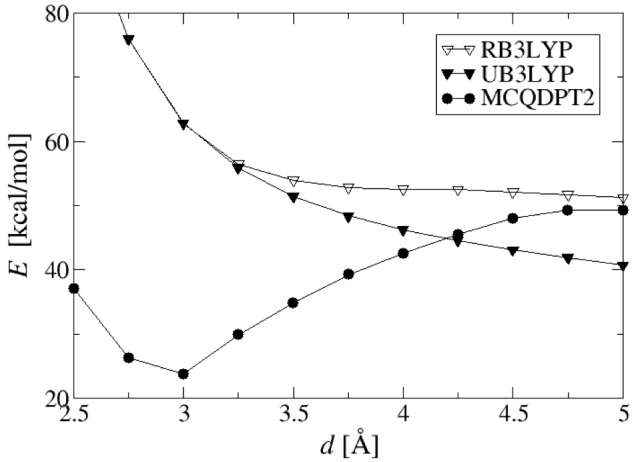
JJN, P. Lafuente, RE Del Sesto, JS Miller, *Angew. Chem. Int.. Ed.* **2001**, *40*, 2540.

RE Del Sesto, JS Miller, JJN, P Lafuente, *Chem. Eur. J.* **2002**, *8*, 4894.

JS Miller, JJN, *Acc. Chem. Res.* **2007**, *40*, 189.

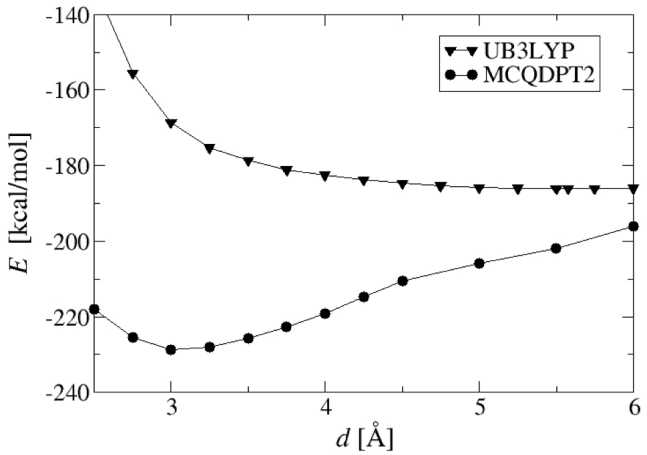
JS Miller, JJN, et al. *J. Am. Chem. Soc.* **2009,** *113*, 9070

E>0



Isolated $(TCNQ^{\cdot -})_2$ dimers

E<0



$(TCNQ^{\cdot -})_2$ dimers in K_2TCNQ_2

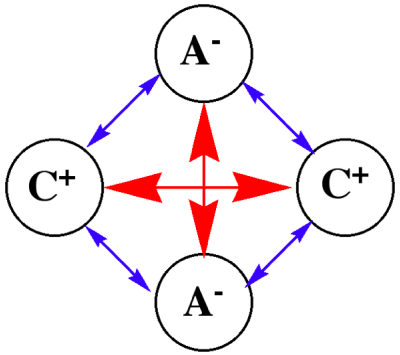
Why a long-distance bond in $(TCNQ^{\cdot -})_2$ dimers?

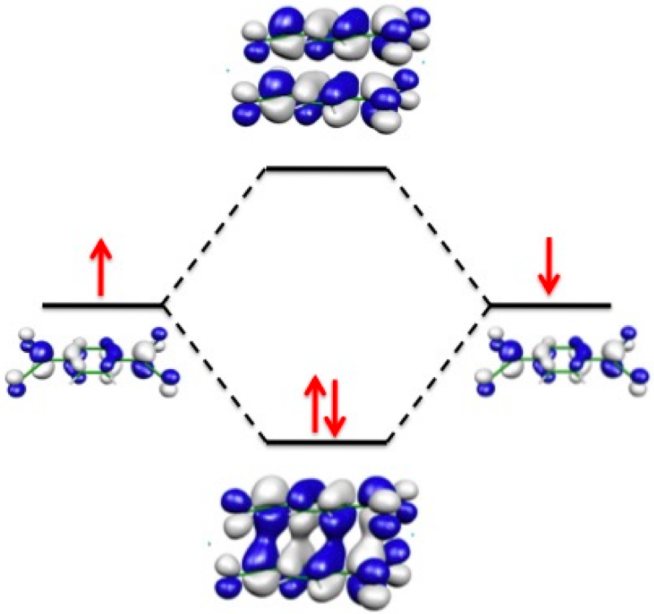
1) Due to the cation···anion interactions the $TCNQ^{\cdot -}$ SOMOs overlap

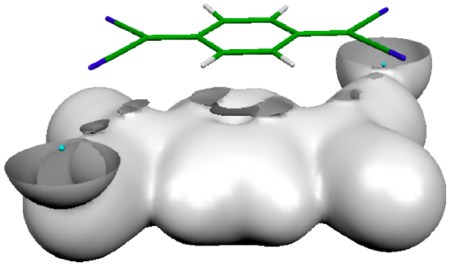
2) Thus, the same electronic structure than conventional covalent bonds

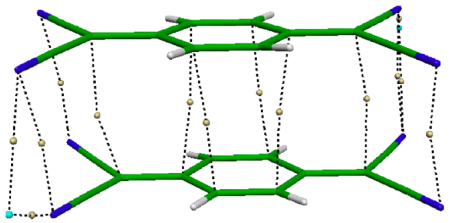
3) Thus, bond critical points in the electron density are generated

K_2TCNQ_2







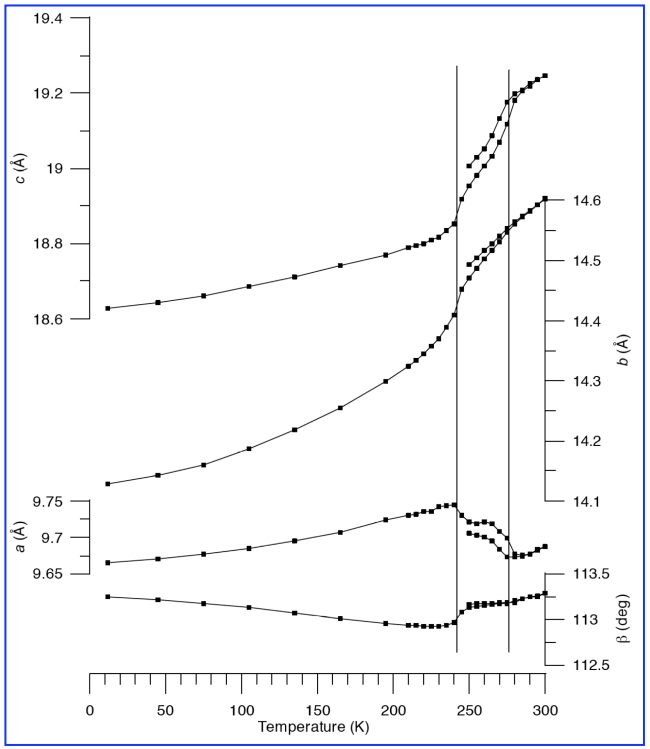


Forms II and III: different magnetic topology

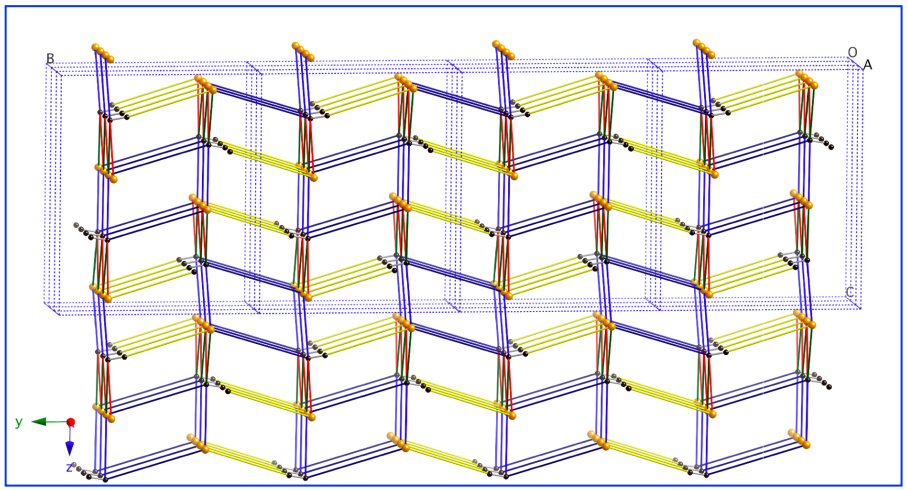
Bulk-FM requires a 3D magnetic topology

A proper study of this topology requires a very-low T crystal structure and these crystals:

- Are not easy to grow as large-enough single crystals
- Show complex phase transformations when T is decreased
- Solution: syncrotron studies at ~10 K (still under work)



Fe(Cp*)$_2$-TCNE (similar to from III)



P Stevens, JS Miller, JJN, et al. *Inorg. Chem*. **2009**, *48*, 3296
Forum Issue on Molecular Magnetism

3. WHY PIXEL INTERMOLECULAR POTENTIALS ARE INTERESTING?

Polymorph prediction key points

Compute in a systematic way all energetically likely crystal structures

Currently mostly done using empirical atom-atom potentials

Results are far from reliable

Need for more reliable potentials

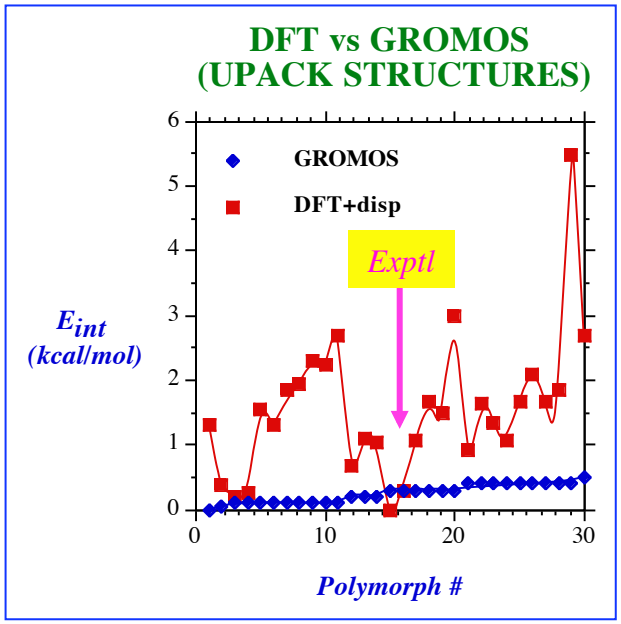
Computational polymorph prediction

Currently:

Full Ab initio (DFT+disp): accurate, but too expensive

Atom-atom potentials: reasonably & cheap but not always accurate enough

Assessing the accuracy of atom-atom potential crystal predictions on acetic acid
C. Rovira, JJN, *J. Phys. Chem.B*, **105**, 1710 (2001).



Need for good intermolecular potentials in crystal predictions

Acetic acid polymorph prediction

Only two Pna21 but wrong order and motif in a-a

TABLE 1: Structures Included in the Subset of the 30 Most Stable Polymorphs Computed Using the UPACK Program and the GROMOS Force Field[a]

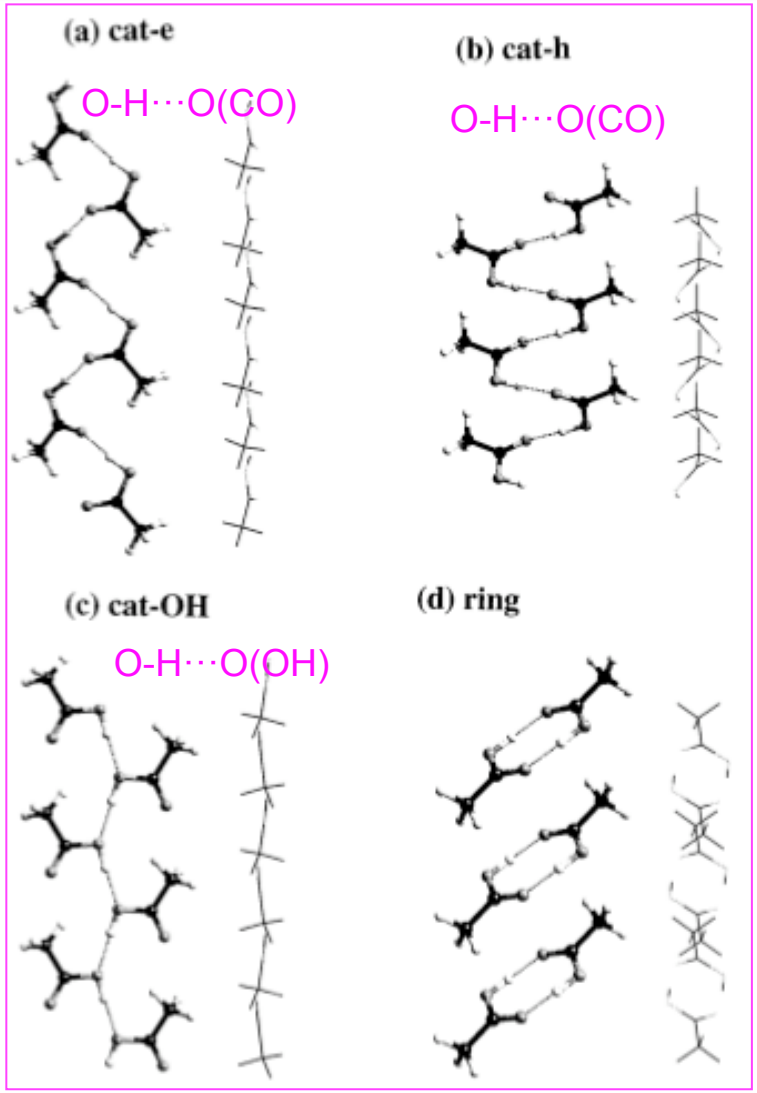
	number	sp group	motif	GROMOS energy[b]
	715	*C2/c*	cat-e	0.
	494	*P21/c*	cat-h	0.04
	9	*P212121*	cat-h	0.1
	14	*P21*	cat-h	0.1
	119	*P21/c*	cat-h	0.1
7	76	*Pna21*	cat-h	0.1 ←
	45	*P21/c*	cat-e	0.1
	4	*Pbca*	cat-e	0.1
	13'	*C2/c*	cat-e	0.1
	125	*P-1*	ring	0.1
	362	*P21/c*	cat-e	0.1
	116	*P21/c*	ring	0.2
	815	*P21/c*	cat-h	0.2
	31	*P21/c*	ring	0.2
15	13	*Pna21*	cat-e	0.3 ←

(same cell p. and fr. coordinates)

right results with DFT+disp

TABLE 3: Interaction Energy (in kcal/mol) Computed at the Ab Initio Level for the 30 Structures of the First Subset (Table 1)[a]

	number	sp group	motif	*E*(BP)	*E*(disp)	*E*(BP−disp)
1	13	*Pna21*	cat-e	−1.21	−12.75	−13.96 ←
	9	*P212121*	cat-h	−1.01	−12.75	−13.76
	14	*P21*	cat-h	−0.91	−12.78	−13.69
	50	*P21/C*	ring	−0.81	−12.85	−13.66
	494	*P21/C*	cat-h	−0.71	−12.86	−13.57
	116	*P21/C*	ring	−0.21	−13.07	−13.28
	815	*P21/C*	cat-h	−0.01	−12.86	−12.87
	31	*P21/C*	ring	+0.19	−13.11	−12.92
	973	*P21/C*	ring	+0.39	−13.43	−13.04
	97	*P212121*	cat-e	+0.39	−12.70	−12.31
	119	*P21/C*	cat-h	+0.39	−12.81	−12.42
12	76	*Pna21*	cat-h	+0.49	−13.14	−12.65 ←
	Exp.	*Pna21*	cat-e	−7.32	−9.30	−16.62



-13.96 → -16.62 kJ/mol: crystal DFT reoptimization

The experimental structure, not reproduced by atom-atom potentials, is fully reproduced by ab initio theory

Looking for better intermolecular potentials

Atom-atom potentials

1- Atom-atom potentials without specific Coulombic terms

2- Add specific q_1q_2/r_{12} Coulombic terms

3- Add an empirical dispersion term

4- DMA expansion of the electrostatic component

Not much space left for improvements after this level

Molecule-molecule potentials

Various proposals in the literature (Clementi, …)

Pixel potentials (Gavezzotti) seems a very promissing approach

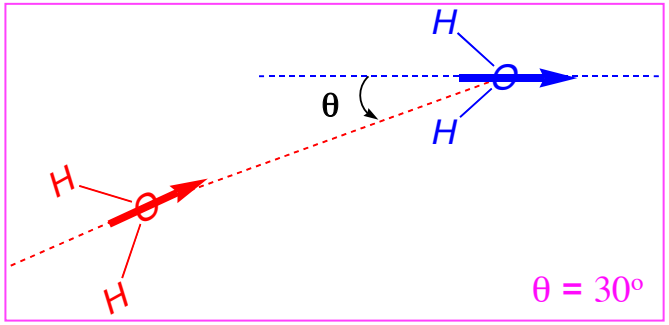
Why PIXEL potential are promising?: Understanding intermolecular interactions and bonds

***Intermolecular interactions**: the driving force behind supramolecular aggregates (and, thus, crystal packing)*

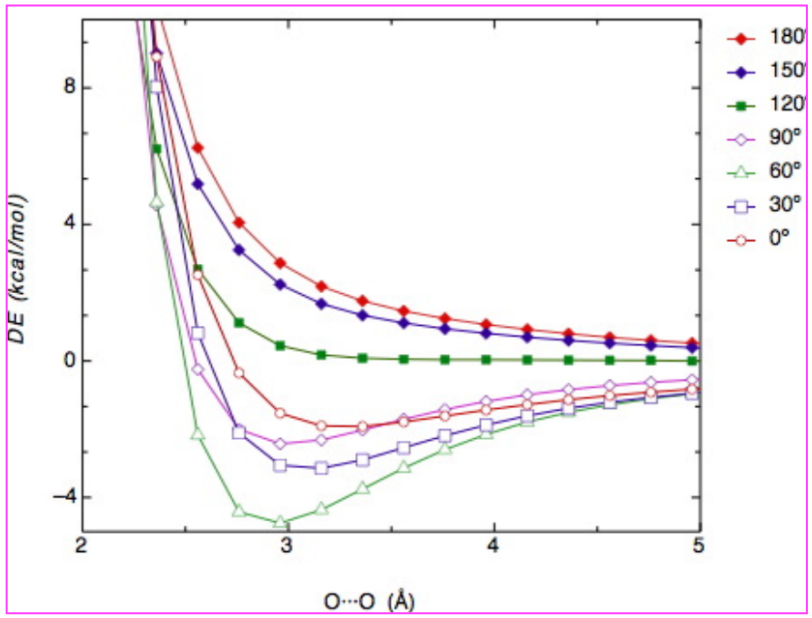
Their properties not fully understood yet

Interactions ≠ bonds ≠ contacts

They can be attractive or repulsive



Repulsive > 120º



Nature of the intermolecular interactions

Intermolecular perturbation theory (IMPT) calculations (Stone)
(rigorous QM method valid when the intermolecular overlap is small)

$$E_{int} = E_{er} + E_{elec} + E_{ind} + E_{ct} + E_{disp} \approx E_{er} + E_{elec} + E_{disp}$$

E_{er} = exchange-repulsion (Pauli Exclussion + exchange) > 0
E_{elec} = electrostatic (permanent-permanent multipoles) < 0
E_{ind} = induction (permanent-induced multipoles) < 0 small
E_{ct} = charge-transfer (transfer of charge due to overlap) < 0 small
E_{disp} = dispersion (instantaneous e^- interactions) < 0

Open-shell molecules: + E_{bond}

$$E_{int} \approx E_{er} + E_{elec} + E_{disp}$$

E_{er}: Kitaigorodskii, Dunitz&Gavezzoti

At large distance IMPT agrees with the results of the
classical multipole expansion model + repulsion + dispersion

Classical multipole expansion + repulsion + dispersion

The large distance limit of quantum calculations

Closed-shell molecules

$\mathbf{E_{int} = E_{er} + E_{elec} + E_{ind} + E_{disp}}$ $\mathbf{(E_{ct} = 0)}$

$\mathbf{E_r}$ = repulsion (Pauli Exclussion + exchange) > 0 → rep. wall

$\mathbf{E_{elec}}$ = electrostatic (permanent-permanent multipoles) < 0

$\mathbf{E_{ind}}$ = induction (perm-induced + ind-ind multipoles < 0

$\mathbf{E_{disp}}$ = dispersion (instantaneous e^- interactions) < 0

→ The only attractive components

Open-shell molecules: + E_{bond}

$\mathbf{E_r} = K S_{AB} \approx \exp(1/r_{ij})$

$\mathbf{E_{elec}} = E(q,q) + E(q,\mu) + E(\mu,\mu) + \ldots$

$\mathbf{E_{ind}} = E(q,\alpha q) + E(q,\alpha\mu) + E(\mu,\alpha\mu) + \ldots$

$\mathbf{E_{disp}} = k\alpha_A\alpha_B/r^6$

1. $E_{elec} >> E_{ind} >> E_{disp}$ *(look at the electrostatic component !)*
2. $E(q,q) >> E(q,\mu) >> E(\mu,\mu)$

Energy components for representative intermolecular interactions

System	r_{opt}	E_{el}	E_{er}	E_p	E_{ct}	E_{disp}	E_{tot}	E_{MP2}[a]
				ionic interactions				
$Na^+\cdots Cl^-$	2.412	-142.3	25.4	-10.5	-1.4	-35.5	-164.3	-128.0
$HC_2O_4^-\cdots HC_2O_4^-$	1.537	25.4	31.4	-7.7	-4.2	-11.6	+33.2	+40.9[b]
				hydrogen bonded interactions				
$NH_3CH_2COOH^+\cdots SO_4^-$	1.520	-155.1	31.4	-14.4	-6.2	-12.4	-156.6	-160.0
$H_3O^+\cdots H_2O$	1.202	-45.5	54.3	-27.4	-9.6	-31.7	-59.9	-31.8
$H_2O\cdots F^-$	1.415	-38.3	30.6	-10.1	-4.3	-8.5	-30.6	-25.3
$CH_4\cdots F$-	1.873	-8.3	13.7	-6.7	-1.4	-4.0	-6.8	-5.8
$FH\cdots H_2O$	1.716	-16.3	12.2	-1.0	-0.6	-3.2	-8.9	-7.9
$H_2O\cdots H_2O$	1.990	-6.7	5.0	-0.7	-0.5	-2.0	-3.9	-4.2
$C_2H_2\cdots H_2O$	2.174	-4.1	2.6	-0.4	-0.2	-1.4	-3.5	-2.7
$CH_4\cdots H_2O$	2.553	-0.9	1.5	-0.2	-0.1	-0.9	-0.6	-0.4
$FH\cdots Ar$	2.634	-0.1	0.5	-0.2	-0.1	-0.4	-0.3	-0.4
				van der Waals				
$Ar\cdots Ar$	3.842	-0.04	0.15	0.00	0.00	-0.28	-0.16	-0.16
$CO_2\cdots CO_2$	3.058	-1.7	1.9	-0.2	-0.1	-1.8	-1.8	-1.0
$C_6H_6\cdots C_6H_6$	3.800[c]	1.2	2.7	-0.2	-0.2	-5.2	-1.7	-1.8

a BSSE corrected values.

b The interaction is repulsive, and therefore cannot be a bond. It is only shown here for illustrative purposes.

c Value obtained after a partial geometry optimization using frozen fragments.

PIXEL potentials

Pixel basic ideas

A. Gavezzotti, *CrystEngComm* **5**, 429 (2003)

a) Represent the electron density of the interacting molecule by sets of pixels

b) E_{int} as in IMPT

$$E_{int} = E_{er} + E_{el} + E_{pol} + E_{ct} + E_{disp}$$

c) Each energetic component expanded as a summatory over all relevant pixels

Results similar to those found in IMPT calculations
Nowadays is an analytical tool for the analysis of crystal structures
Reason: *COMPUTATIONALLY DEMANDING IN 1 CPU MACHINES*

4. POLYMORPH PREDICTION USING PIXEL POTENTIALS

a) The PIXCRYPAR program

b) Validation: I, Crystal structure optimization

c) Validation: II, Polymorph prediction

a) The PIXCRYPAR program

Parallel code for the optimization of crystal structures and the prediction of polymorphs employing PIXEL potentials

Runs about 100 times faster than 1 CPU computers
(it can run even faster, if needed, using higher levels or parallelism)

Parallelism implemented at the do-loop level,
using MPI architecture

With the technical support of David Vicente
(BSC, **B**arcelona **S**upercomputer **C**enter)

CPU Time

COND LEVEL	TIME		CYCLES	
	Steep. Des.	Simplex	Steep. Desc.	Simplex
3	1:48:53	8:00	12	109
4	38:02	1:46	18	109
5	19:33	0:35	32	110
6	15:32	0:30	72	200

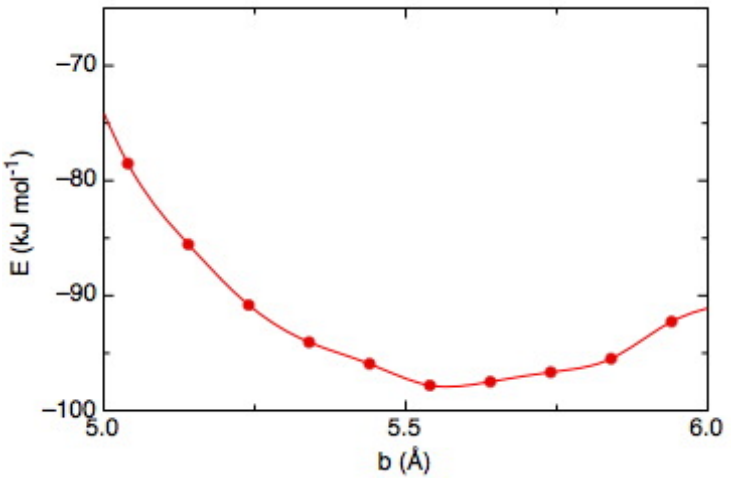
Running on 128 processors

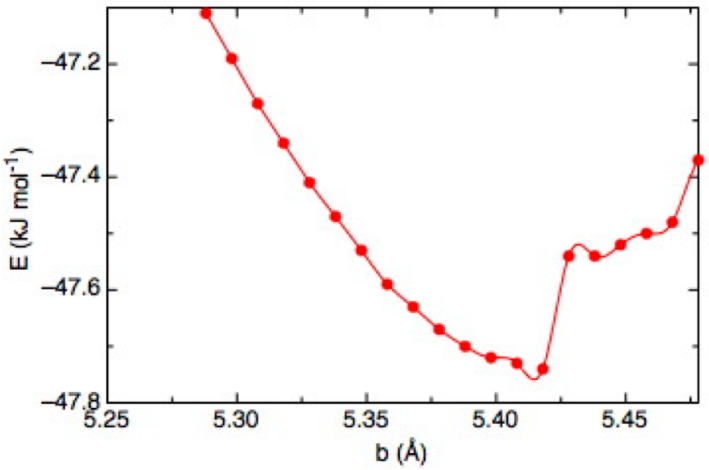
MARENOSTRUM
10240 IBM Power PC 970MP processors at 2.3 GHz (2560 JS21 blades)
with a final calculation capacity of 94.21 Teraflops

b) Validation: I, Crystal structure optimization:

1) Dichlorobenzene

Complex potential energy surfaces

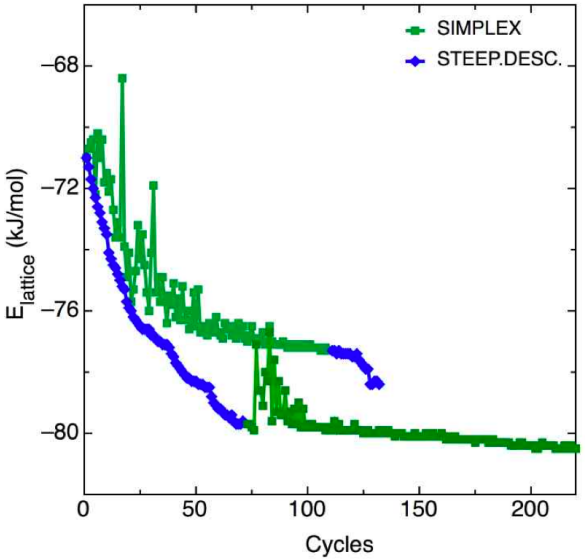


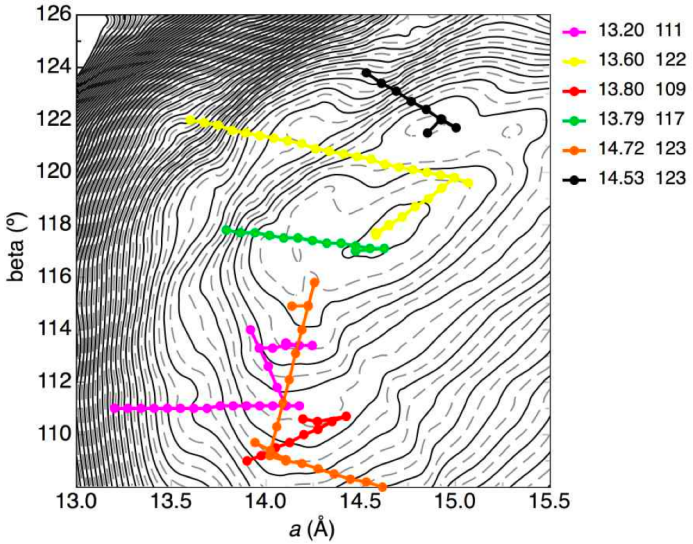


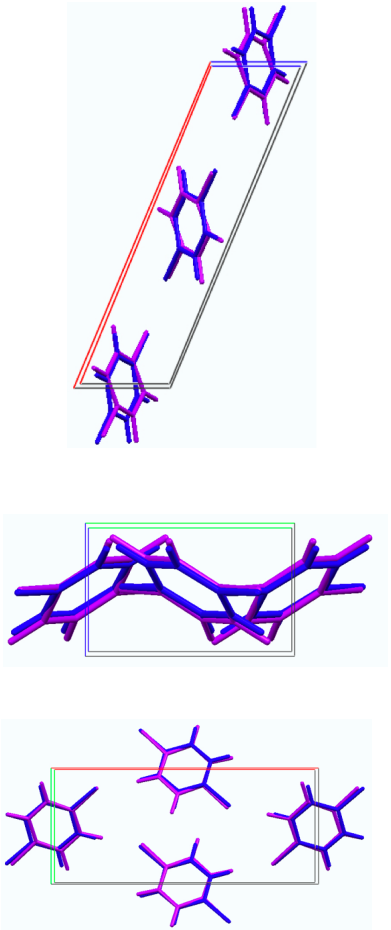
Optimization algorithms: Simplex & Steepest descent

Simplex & Steepest descent: Accuracy

Dichlorobenzene



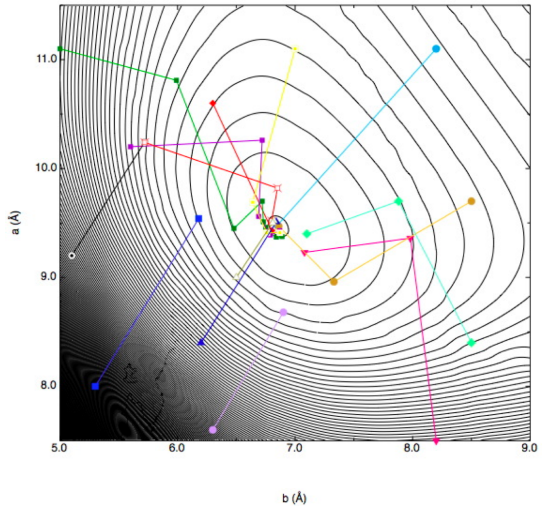




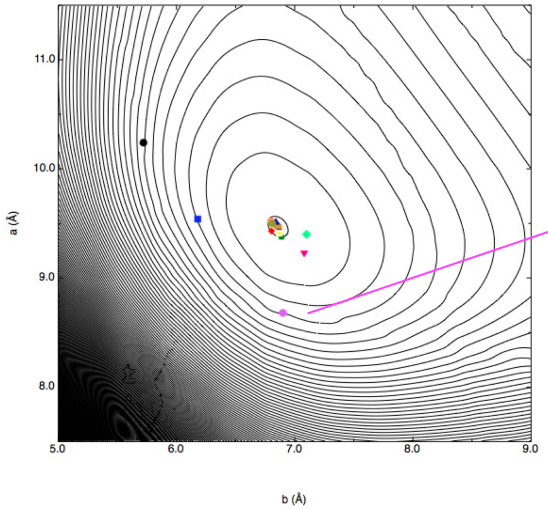
Violet = theor / blue = exp.

2) Benzene (BENZEN)

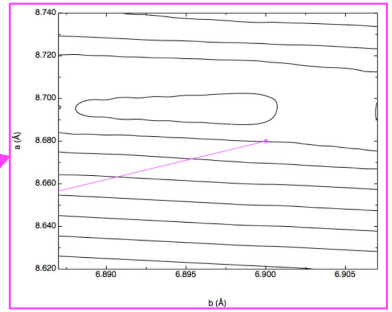
Optimization trajectories



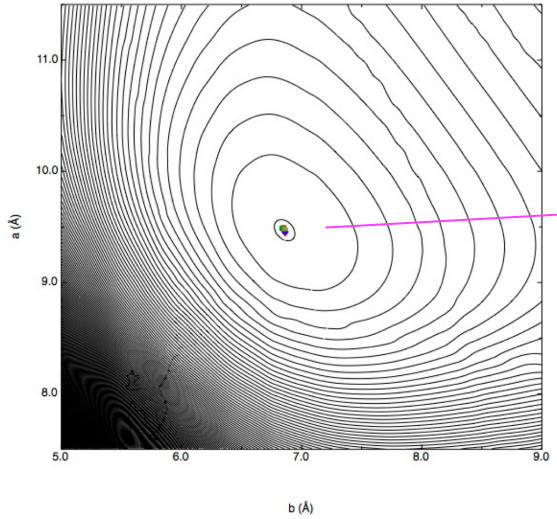
Optimization end

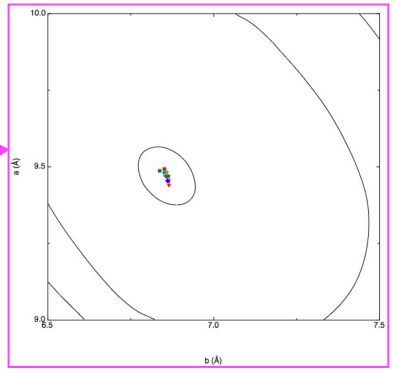


Metaestable Minimum !!!

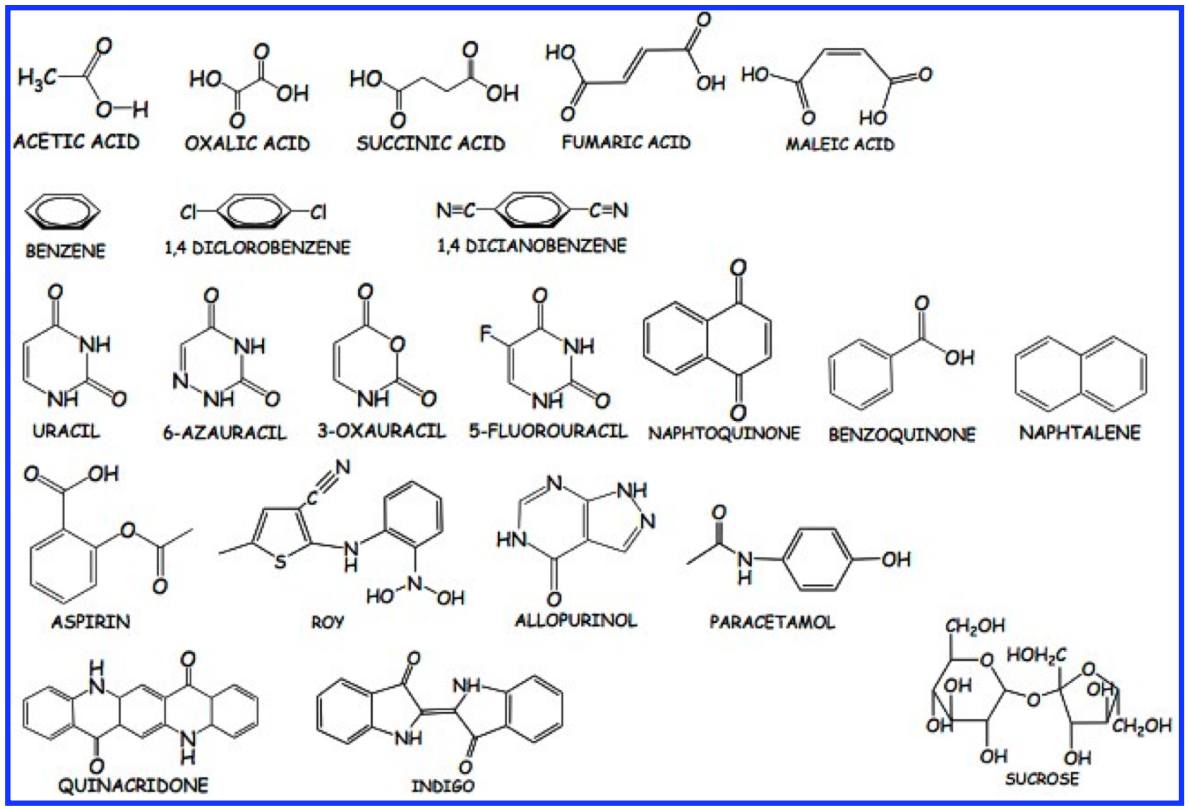


New optimization algorithm:
Steepest descent + more accurate gradients + “shaking”





3) Subset of 35 crystal structures (from 22 molecules)



The experimental crystal structure is always properly reproduced
The mean error with PIXEL is smaller than with atom-atom potentials

Mean value of standard deviation with respect to experimental data of optimization (both atom-atom and Pixel) results. *a*, *b* and *c* in Å, angles in degree, volume in Å^3 and energies in kJ/mol.

	a	*b*	*c*	α	β	γ	V	E
at-at	0.023	-0.113	-0.080	-2.092	0.012	1.406	21.784	11.146
Pixel	0.00036	0.017	-0.0052	-0.0015	0.0025	0.0034	0.423	-7.324
	0.00076	**0.00029**	**0.020**	**-0.67**	**-0.65**	**-1.80**	**2.792**	**-4.436**

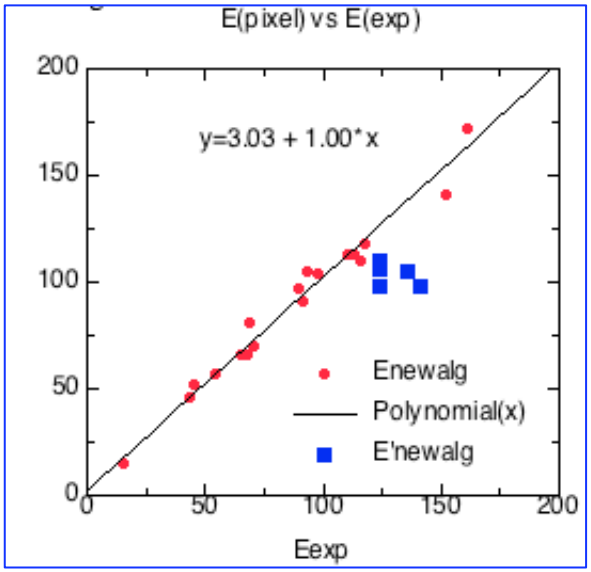
Initial

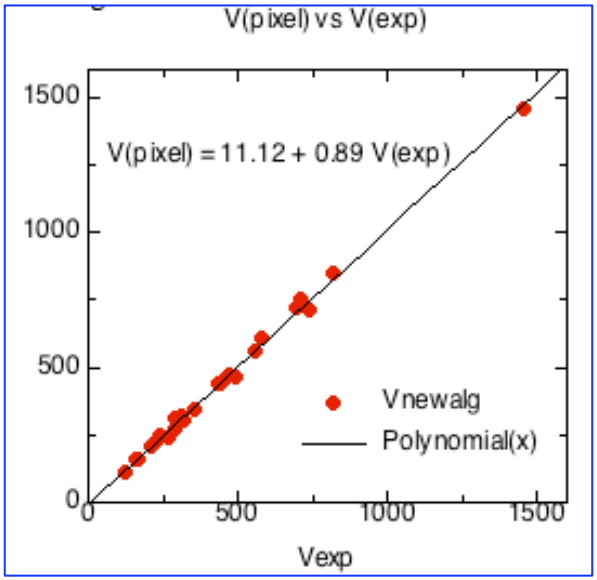
new

Old & new PIXEL optimization algorithm

In all cases the experimental structure is reproduced

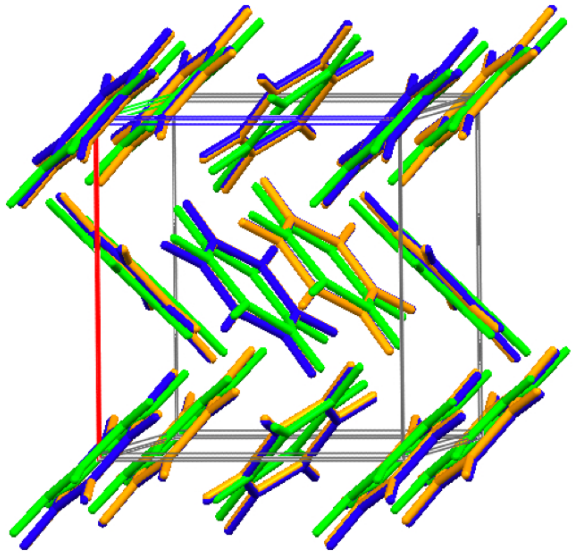
REFCODE	V_{exp}	V_{old}	V_{newalg}	E_{exp}	E_{old}	E_{newalg}
ACETAC05	289.2	291.4	310.1		62.4	64.7
ACETAC09	289.4	281.8	270.1	67.3	64.4	66.3
ACSALA05	816.0	822.1	846.6		97.7	101.6
ALOPUR	553.3	547.1	559.2		119.9	122.5
AZURAC01	429.9	435.3	436.8	141.0	97.6	97.8
AZURAC10	431.2	431.2	442.4		92.2	94.2
BENZEN	491.6	468.0	467.54	45.1	52.5	52.5
BENZEN03	206.2	208.2	210.5	53.9	56.3	57.0
BNZQUI03	262.9	246.0	242.3	68.5	80.1	81.1
DCLBEN01	320.6	306.4	304.5	64.8	66.0	66.1
FUMAAC	709.3	719.8	750.9	123.6	100.1	105.9
FUMAAC01	119.3	116.7	115.1	123.6	109.1	110.2
FURACL03	470.7	470.7	472.3		80.8	81.4
HXACAN08	1458.0	1458.0	1458.0	117.9	118.3	118.3
INDIGO03	580.5	607.5	610.0	136.0	103.3	105.3
MALIAC13	232.1	231.7	234.2	110.0	113.0	113.4
NAPHQU	741.2	725.8	712.2	91.0	89.2	90.6
NAPHTA10	355.3	353.3	345.1	70.4	69.3	70.3
OXALAC04	156.6	161.1	163.6	93.4	104.4	104.7
OXALAC05	307.0	322.1	319.8	97.9	103.4	104.0
QARVOV	437.3	434.5	439.3		98.2	98.4
QNACRD04	691.5	717.0	723.7		143.0	144.5
SUCACB03	239.3	248.7	248.8	113.2	112.7	112.9
TEPNIT11	165.6	165.1	159.5	89.7	95.6	96.6
URACIL	463.4	463.4	465.7	115.5	108.5	109.8





Geometry: Pixel / atom-atom / experimental

acetic acid
ACETAC05



Benzene
BENZEN

c) Polymorph prediction using PIXEL

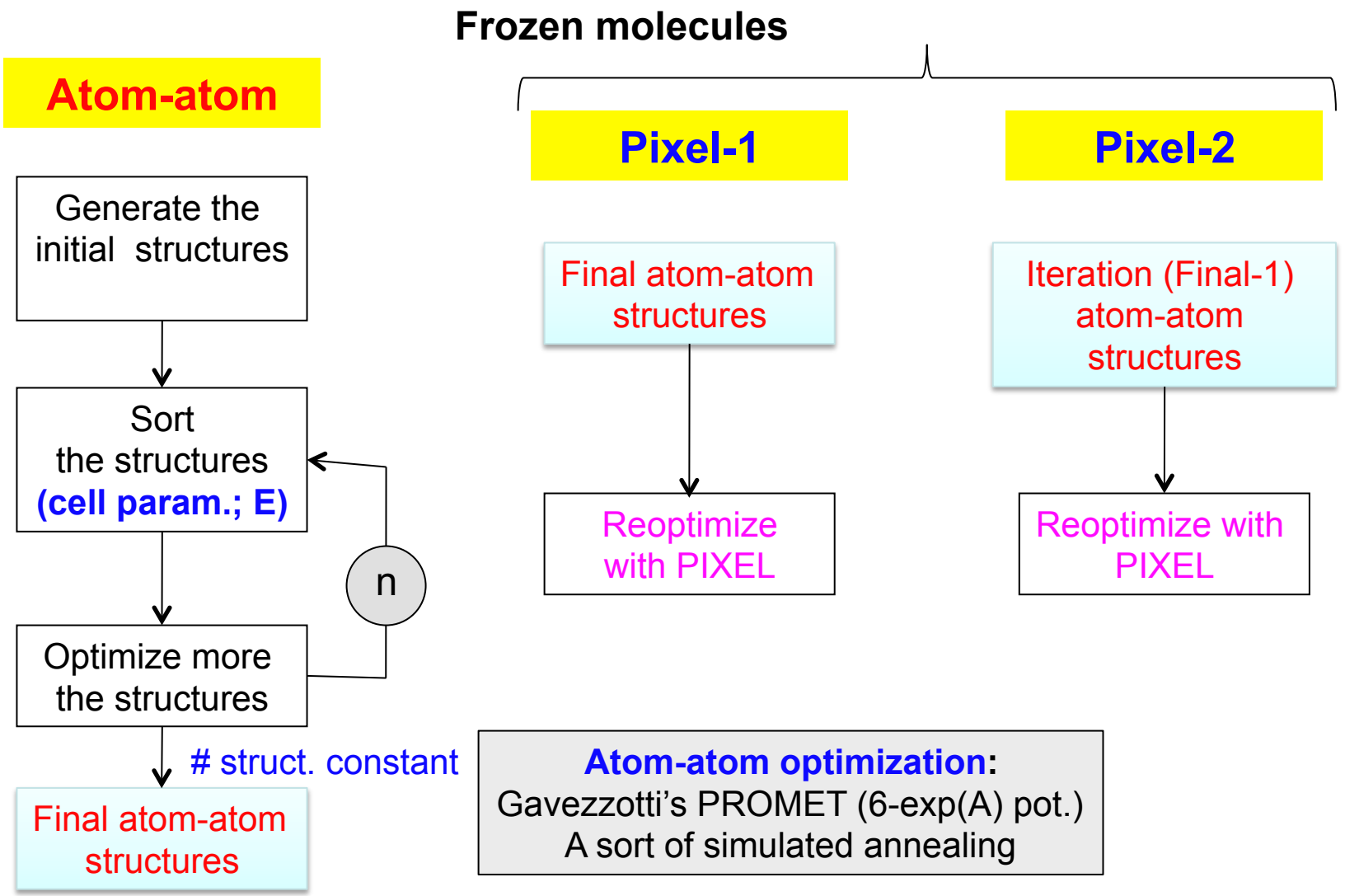
First basic idea:

Hypothesis:
atom-atom potentials predict a reasonable experimental structure, but the energy scale is incorrect and the geometry has to be reoptimized

Algorithm:
reoptimize with PIXEL the lowest energy atom-atom polymorphs

PIXEL polymorph prediction algorithm

Atom-atom + (**Pixel-1** or **Pixel-2**)



1) Benzene polymorph prediction

Well studied polymorphism with multiple phases (only two fully characterized, i.e., with fractional coordinates, **I** and **III**)

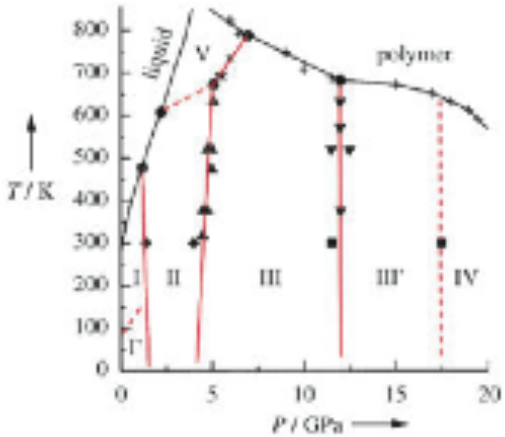
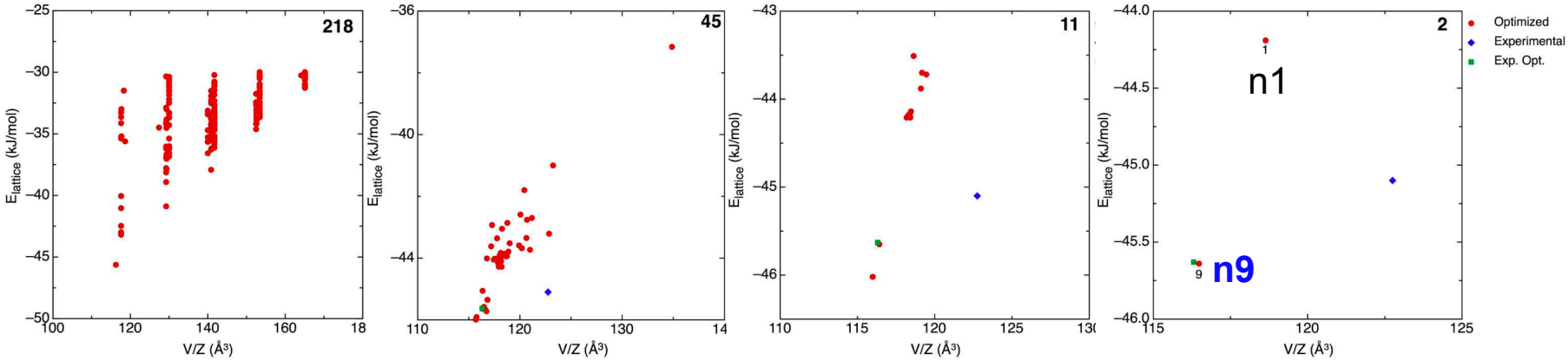


Figure 1. Proposed phase diagram of solid benzene. For phases I, II, III, III', and IV we follow the nomenclature of ref. [15]. As a consequence phase IV of ref. [16] becomes here phase V. The liquid–solid boundary and all the points reported in the picture are taken from refs. [15,16]. Hypothetical phase boundaries are represented with dashed lines.

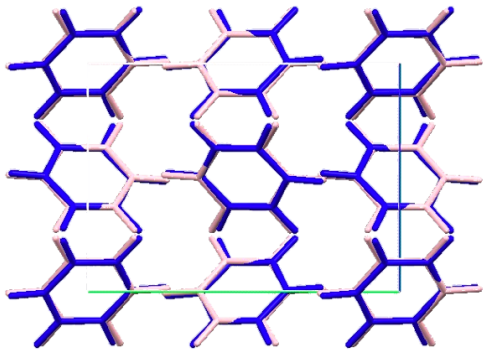
I = *Pbca*
III = $P2_1/c$

Atom-atom prediction for **I** (Pbca)

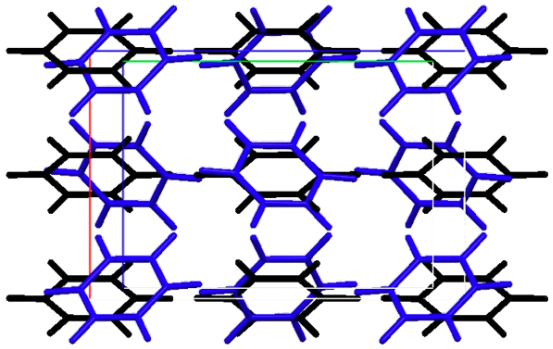


cycle 1 → cycle 2 → cycle 3 → cycle 4 (final)

n9



n1

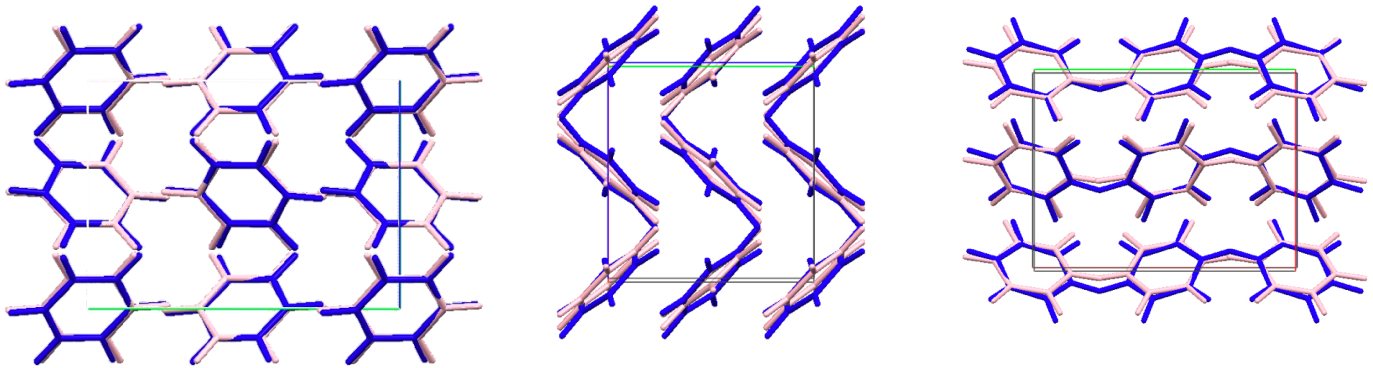


Values of the parameters (Å), total volume (Å^3) and the lattice energies (kJ/mol) for the two structures resulting from the prediction in the Pbca space group. The values of the Exp.Opt. and Exp. structures are also with the aim of comparison.

	a	*b*	*c*	*V*	*E*
1	7.870	5.419	11.096	118.31	-44.18
9	7.097	9.552	6.870	116.41	-45.65
Exp.Opt.	7.110	9.560	6.840	116.31	-45.63
Exp.	7.440	9.550	6.920	122.75	-45.10

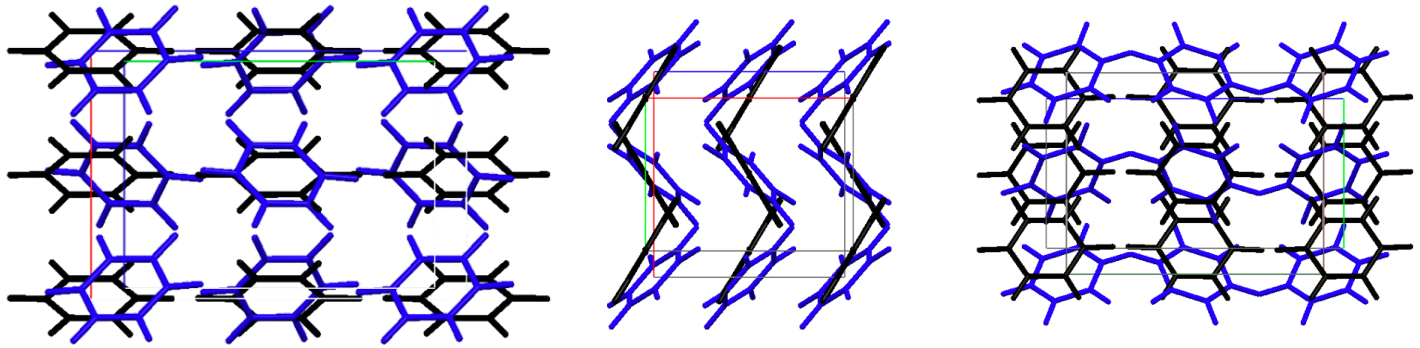
Pixel-1 prediction for form I (Pbca)

n9



experimental; pixel n9; pixel n1

n1



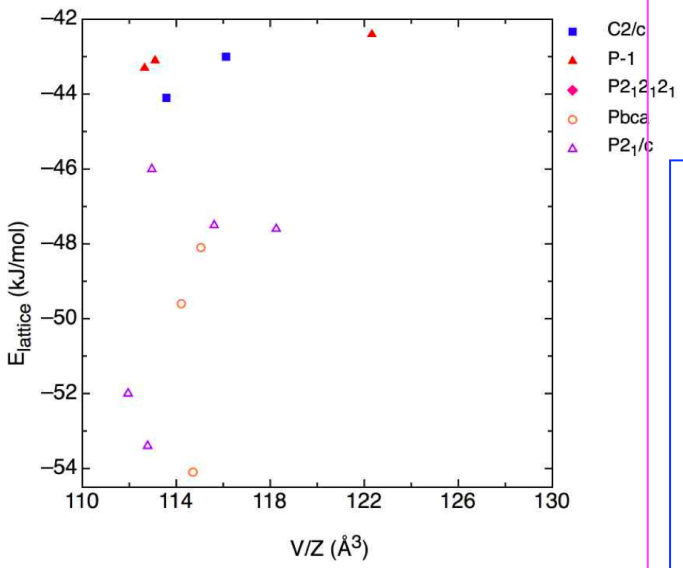
Values of the parameters (Å), total volume (Å^3) and the lattice energies (kJ/mol) for the two structures resulting from the prediction in the Pbca space group, when the last step of the prediction is carried out using PIXCRYPAR. The values of the Exp.Opt. (optimized with PIXCRYPAR) and Exp. structures are also with the aim of comparison.

	a	*b*	*c*	*V/Z*	*E pixel*
1	7.787	5.475	10.715	114.21	-49.60
9	7.066	6.839	9.495	114.71	-54.10
Exp.Opt.	7.320	9.383	6.815	117.03	-52.49
Exp.	7.440	9.550	6.920	122.75	-45.10

Pixel-2 predicts the same structures

BENZEN polymorph energy landscape

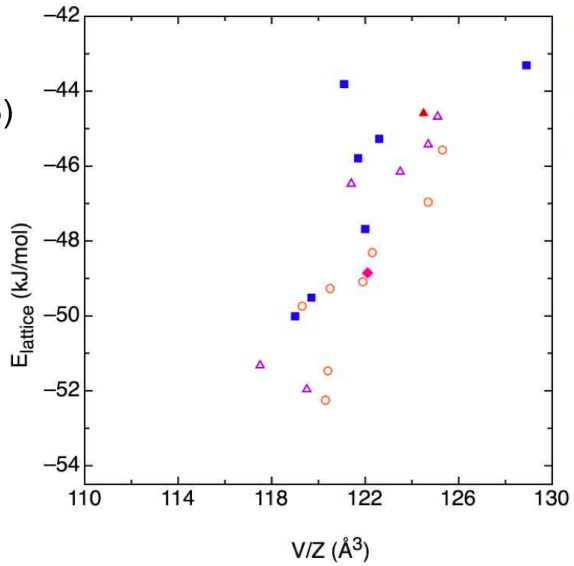
Pixel



Atom-atom

(van Eijck et al.)

Acta Cryst. B54, 291 (**1998**)



Pixel in BENZEN:

a) Less polymorphic forms

b) More dense structures

c) Similar E scale

d) More accurate structures

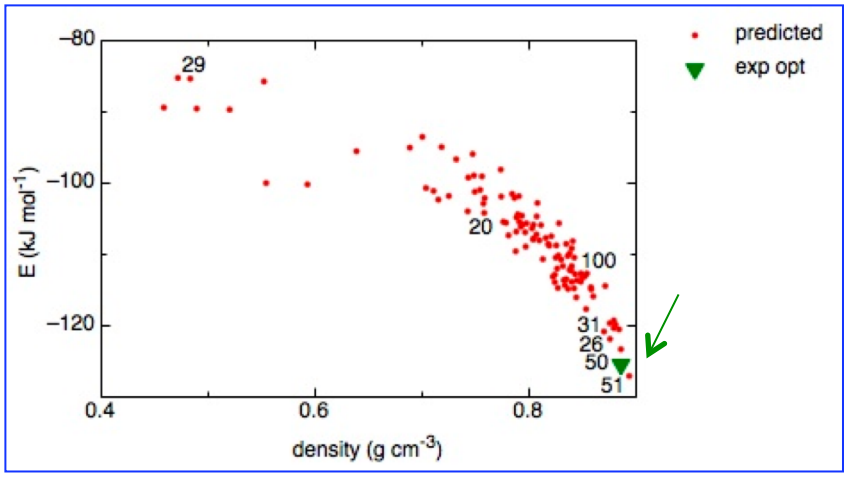
Other polymorph predictions

ACSALA05	(P21/c, Z=4)	S
BENZEN03	(P21/c, Z=2)	S
OXALAC05	(Pbca, Z=4)	S
PAHYON01	(C2/c, Z=8)	S
XULDUD	(Pbca, Z=8)	S
QUAVOV	(P21/c, Z=4)	F

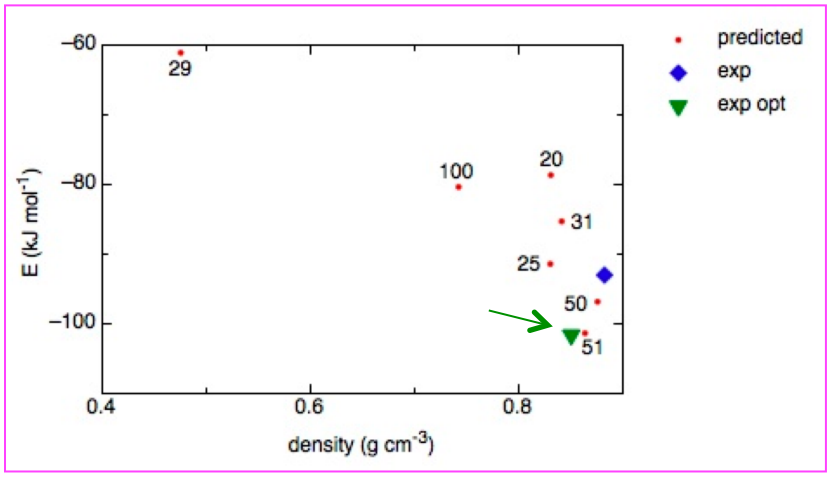
S

ACSALA05 (P21/c, Z=4) polymorph prediction

Atom-atom prediction



PIXEL prediction

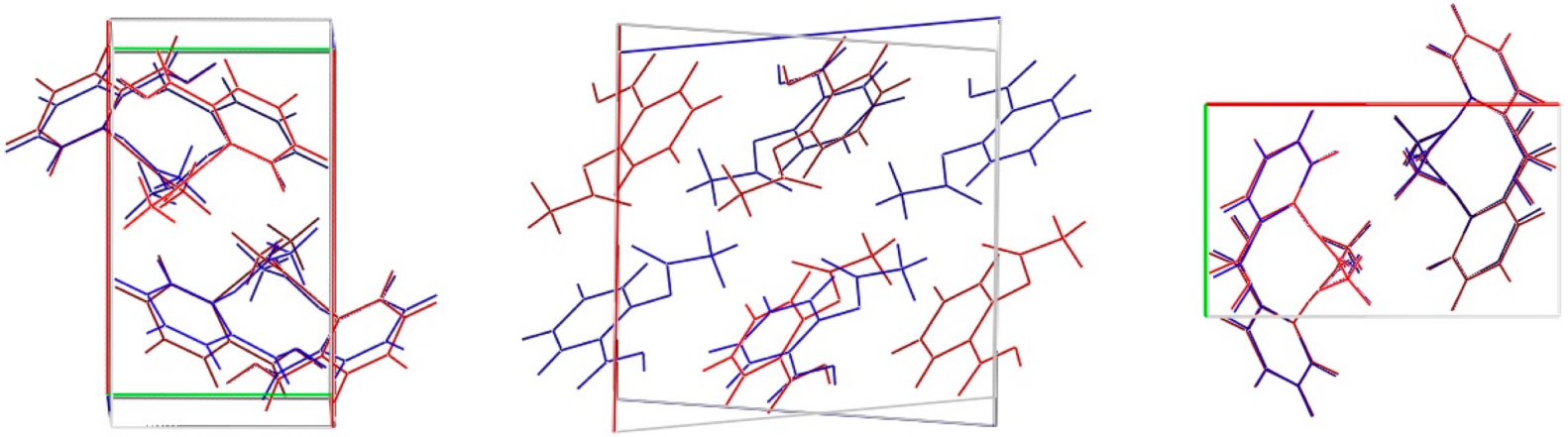


N	a	b	c	al	be	ga	ro	E FF	Epixel	diff
exp	11.186	6.540	11.217	90.00	96.10	90.00	0.88	-117.30	-93.00	
exp minop	11.196	6.532	11.210	90.00	97.45	90.00	0.89	-125.47		
20 minop	11.768	5.747	13.729	90.00	100.84	90.00	0.79	-104.35		0.200
26 minop	9.412	7.521	12.873	90.00	63.36	90.00	0.88	-120.50		0.040
29 minop	18.071	5.074	16.282	90.00	93.20	90.00	0.48	-85.32		0.556
31 minop	9.909	5.516	15.983	90.00	110.37	90.00	0.88	-120.32		0.042
50 minop	11.027	6.613	11.169	90.00	93.53	90.00	0.89	-123.29		0.017
51 minop	11.919	6.436	11.205	90.00	110.38	90.00	0.89	-127.05		0.015
100 minop	7.233	15.043	7.856	90.00	81.20	90.00	0.85	-112.95		0.107
exp pixel	11.474	6.558	11.312	90.00	95.94	90.00	0.85	-113.20	-101.60	
20 pixel	11.996	5.969	13.794	90.00	100.82	90.00	0.74	-90.70	-80.35	0.245
26 pixel	9.454	7.779	13.161	90.00	63.63	90.00	0.83	-106.00	-91.41	0.103
29 pixel	18.071	5.160	16.265	90.00	92.95	90.00	0.48	-74.50	-61.09	0.595
31 pixel	10.048	5.684	15.995	90.00	110.47	90.00	0.84	-104.60	-85.29	0.161
50 pixel	11.054	6.658	11.192	90.00	93.53	90.00	0.88	-112.80	-96.82	0.056
51 pixel	12.063	6.557	11.242	90.00	110.35	90.00	0.86	-114.80	-101.34	0.016
100 pixel	7.244	15.060	8.039	90.00	81.17	90.00	0.83	-96.90	-78.65	0.227

Atom-atom = PIXEL

ACSALA05 (exp vs 51, RMS=2.37)

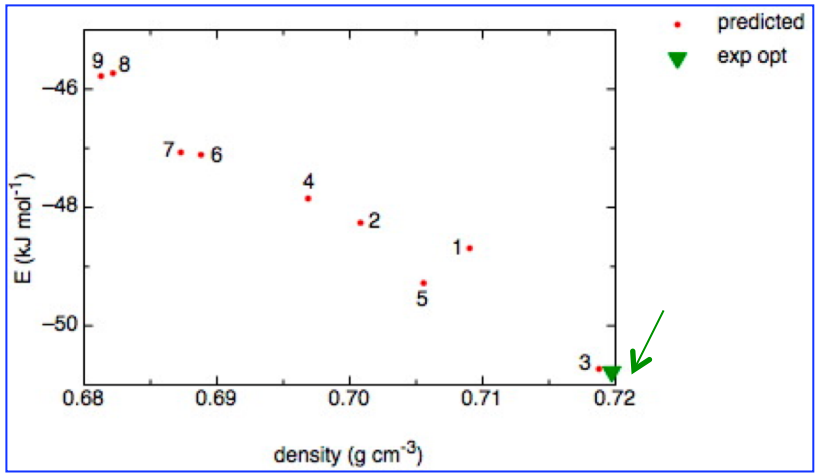
RMS obtained from a new sorting algorithm
Chisholm, JA; Motherwell, S. *J. Appl. Cryst. (2005).* ***38, 228-231***



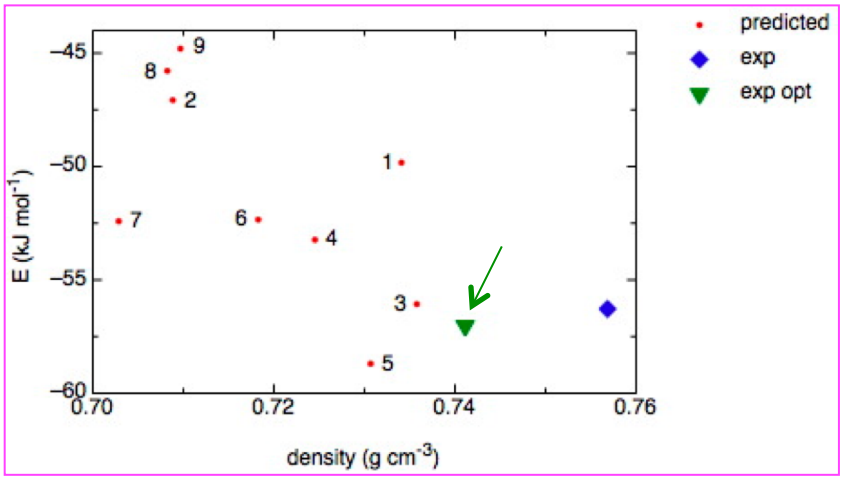
S

BENZEN03 (P21/c, Z=2) polymorph prediction

Atom-atom prediction



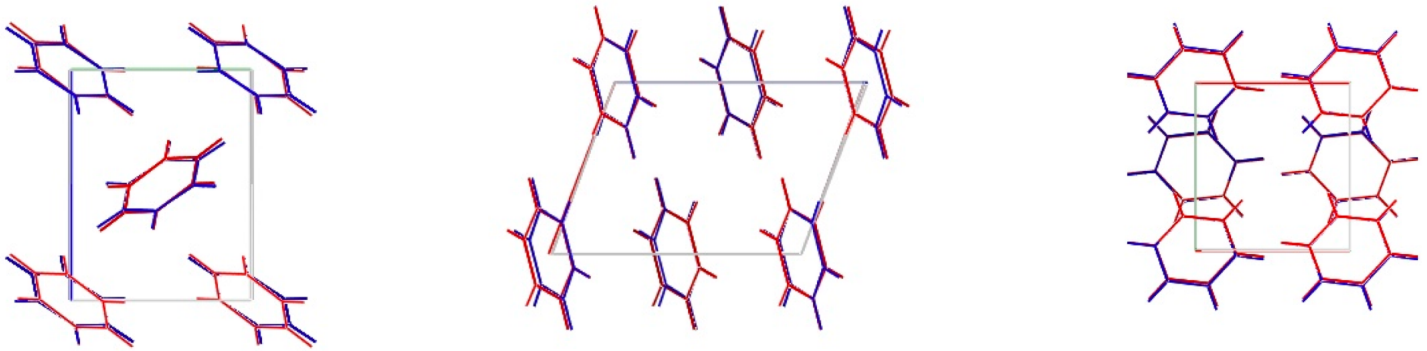
PIXEL prediction



N	a	b	c	al	be	ga	ro	E FF	Epixel	diff
exp	5.417	5.376	7.532	90.00	110.00	90.00	0.76	-46.90	-56.28	
exp minop	5.589	5.492	7.500	90.00	109.68	90.00	0.72	-50.78		
1 minop	5.855	3.720	11.289	90.00	116.51	90.00	0.71	-48.69		0.044
2 minop	6.446	3.521	11.780	90.00	123.62	90.00	0.70	-48.26		0.056
3 minop	5.608	5.513	7.455	90.00	70.34	90.00	0.72	-50.73		1.982e-3
4 minop	6.635	5.780	7.126	90.00	55.00	90.00	0.70	-47.85		0.066
5 minop	5.671	6.745	6.949	90.00	56.29	90.00	0.71	-49.28		0.036
6 minop	6.182	7.035	5.833	90.00	63.21	90.00	0.69	-47.11		0.084
7 minop	6.221	7.351	5.537	90.00	63.71	90.00	0.69	-47.07		0.086
8 minop	3.659	10.648	6.133	90.00	73.15	90.00	0.68	-45.73		0.112
9 minop	3.661	10.792	5.942	90.00	77.29	90.00	0.68	-45.78		0.112
exp pixel	5.460	5.479	7.545	90.00	111.17	90.00	0.74	-47.31	-57.03	
1 pixel	5.770	3.872	10.769	90.00	117.96	90.00	0.73	-43.50	-49.83	0.127
2 pixel	6.205	3.734	11.421	90.00	123.73	90.00	0.71	-42.10	-47.07	0.180
3 pixel	5.440	5.573	7.450	90.00	69.84	90.00	0.74	-47.16	-56.07	0.018
4 pixel	6.662	5.683	7.237	90.00	51.79	90.00	0.72	-45.15	-53.23	0.070
5 pixel	5.636	6.647	6.902	90.00	55.66	90.00	0.73	-46.10	-58.70	0.032
6 pixel	6.004	7.082	5.727	90.00	63.10	90.00	0.72	-43.83	-52.34	0.087
7 pixel	6.072	7.359	5.546	90.00	63.59	90.00	0.70	-44.76	-52.41	0.095
8 pixel	3.832	10.328	5.832	90.00	72.62	90.00	0.71	-40.12	-45.78	0.202
9 pixel	3.749	10.647	5.650	90.00	77.08	90.00	0.71	-40.68	-44.80	0.218

Atom-atom = PIXEL

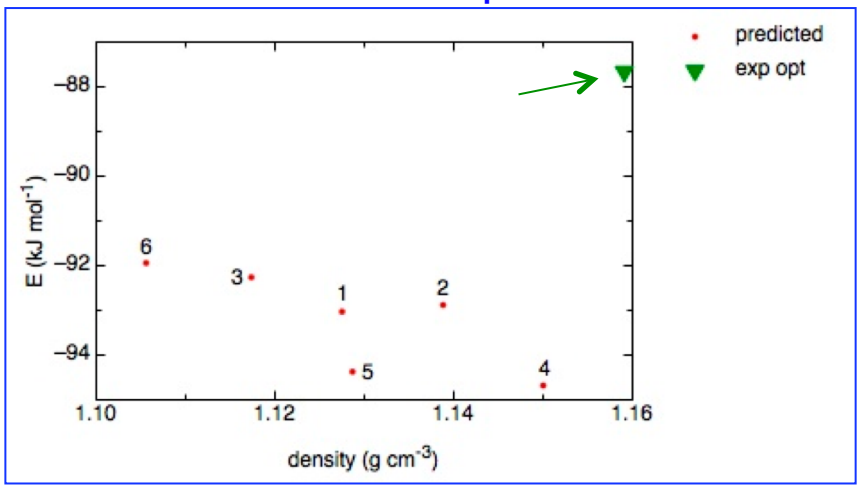
BENZEN03 (exp vs 3, RMS=0.21)



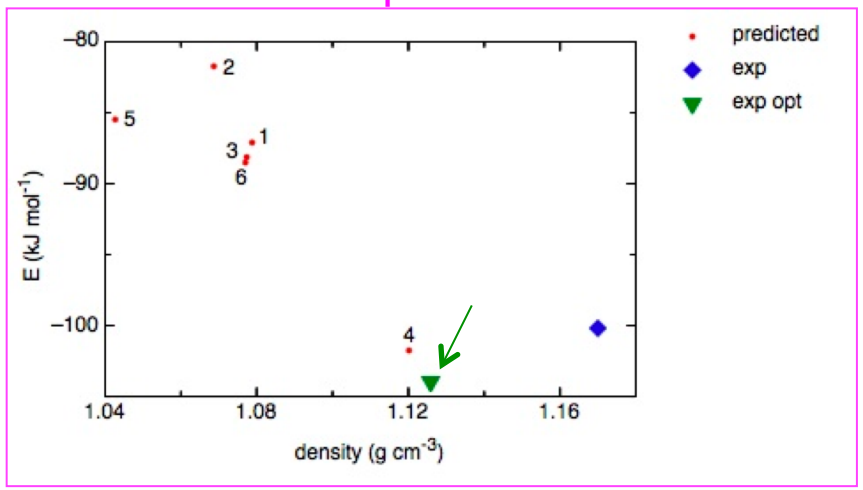
S

OXALAC05 (Pbca, Z=4) polymorph prediction

Atom-atom prediction



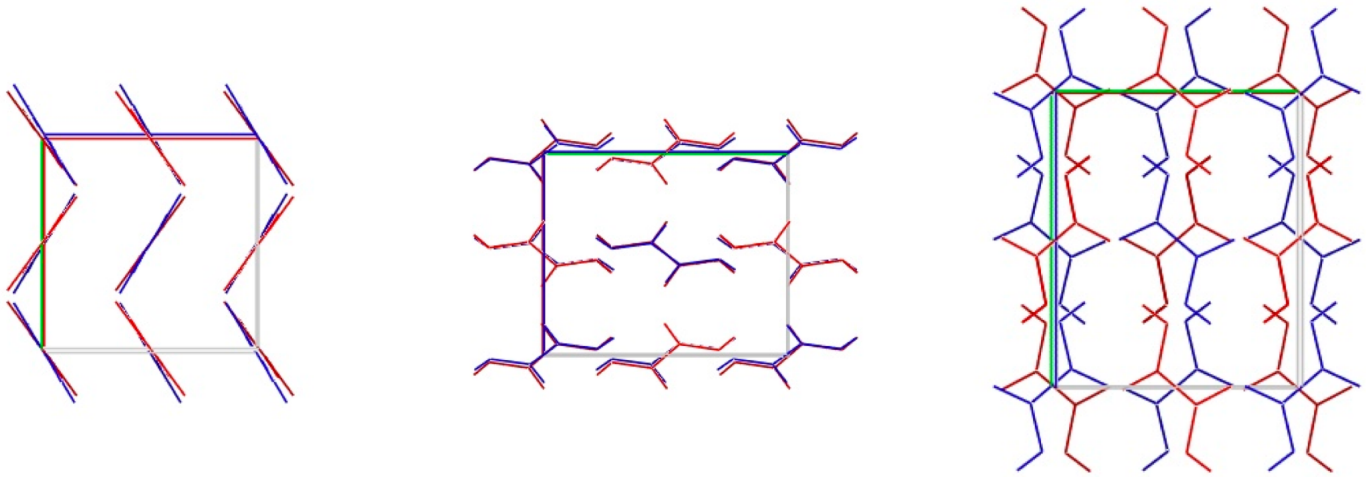
PIXEL prediction



N	a	b	c	ro	E FF	E pixel	diff
exp	6.493	6.060	7.803	1.17	-46.89	-100.19	
exp minop	7.440	6.265	6.663	1.16	-87.66		
1 minop	10.011	5.139	6.206	1.13	-93.03		0.067
2 minop	8.924	3.687	9.607	1.14	-92.88		0.062
3 minop	7.358	4.331	10.111	1.12	-92.26		0.064
4 minop	7.360	6.500	6.543	1.15	-94.68		0.080
5 minop	6.384	8.439	5.920	1.13	-94.37		0.081
6 minop	5.903	7.953	6.936	1.11	-91.94		0.067
exp pixel	6.493	6.302	7.814	1.13	-66.40	-103.97	
1 pixel	10.396	5.288	6.071	1.08	-79.80	-87.10	0.168
2 pixel	5.209	6.459	10.013	1.07	-49.70	-81.73	0.220
3 pixel	7.020	4.536	10.493	1.08	-78.70	-88.13	0.158
4 pixel	6.554	7.714	6.357	1.12	-71.20	-101.76	0.022
5 pixel	6.582	8.753	5.994	1.04	-81.50	-85.48	0.193
6 pixel	6.080	8.199	6.705	1.08	-81.10	-88.51	0.155

Atom-atom wrong E
PIXEL right

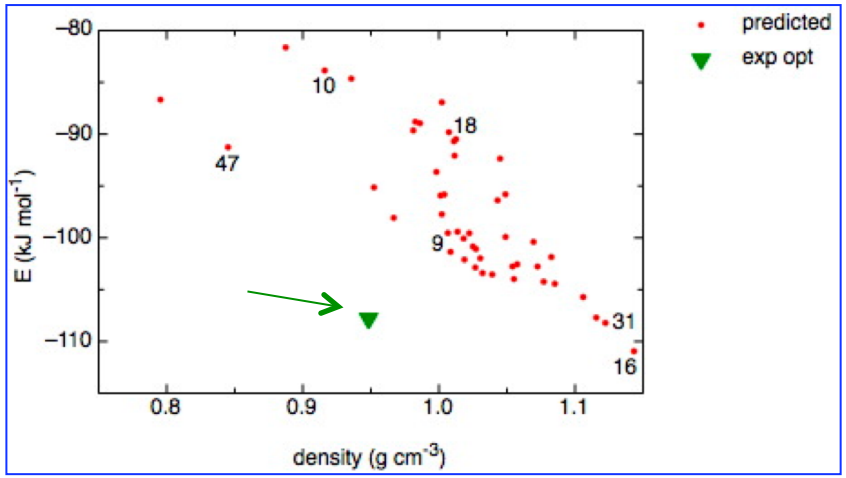
OXALAC05 (exp vs 4, RMS=1.30)



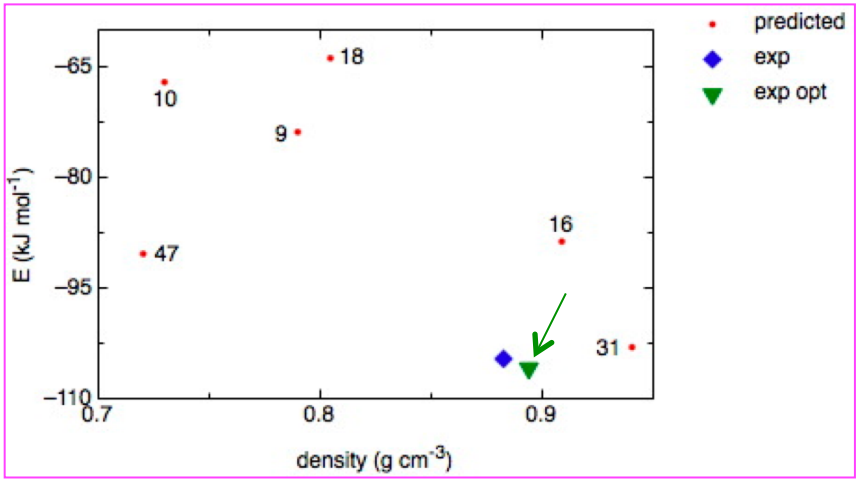
S

PAHYON01 (C2/c, Z=8) polymorph prediction

Atom-atom prediction



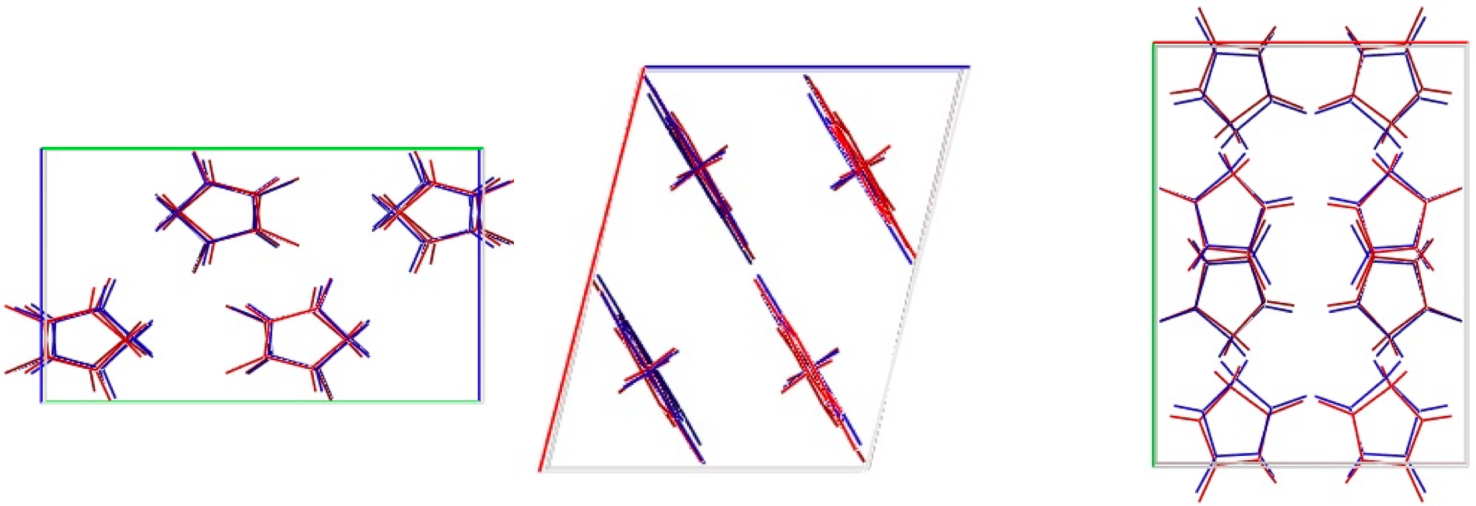
PIXEL prediction



N	a	b	c	al	be	ga	ro	E FF	E pixel	diff
exp	9.354	12.176	7.229	90.00	104.59	90.00	0.88	-96.70	-104.61	
exp minop	8.913	12.082	7.086	90.00	103.40	90.00	0.95	-107.80		
9 minop	9.035	8.465	10.432	90.00	97.21	90.00	1.02	-100.08		0.10133
10 minop	8.435	8.851	13.930	90.00	55.03	90.00	0.92	-83.86		0.22493
16 minop	7.691	10.045	10.945	90.00	59.24	90.00	1.14	-110.95		0.20560
18 minop	8.114	10.712	10.244	90.00	61.94	90.00	1.01	-90.49		0.17355
31 minop	8.977	11.878	7.087	90.00	76.71	90.00	1.12	-108.21		0.18143
47 minop	12.748	13.337	6.354	90.00	58.82	90.00	0.85	-91.26		0.18906
exp pixel	9.276	12.135	7.228	90.00	104.54	90.00	0.89	-98.52	-105.88	
9 pixel	9.482	8.829	10.728	90.00	97.03	90.00	0.79	-87.15	-73.85	0.32277
10 pixel	9.607	8.488	14.716	90.00	53.50	90.00	0.73	-71.30	-67.08	0.40827
16 pixel	7.909	10.296	11.073	90.00	59.21	90.00	0.91	-100.12	-88.70	0.16363
18 pixel	8.442	11.064	10.629	90.00	61.81	90.00	0.80	-81.15	-63.83	0.40859
31 pixel	9.088	11.890	7.117	90.00	76.77	90.00	0.94	-99.02	-103.02	0.06278
47 pixel	12.919	13.441	6.570	90.00	58.96	90.00	0.72	-85.19	-90.37	0.24055

Atom-atom wrong E
PIXEL right

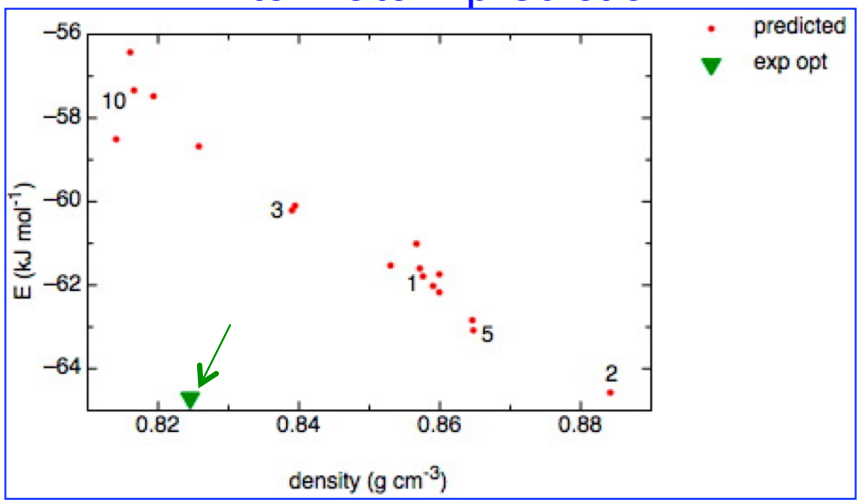
PAHYON01 (exp vs 31, RMS=0.39)



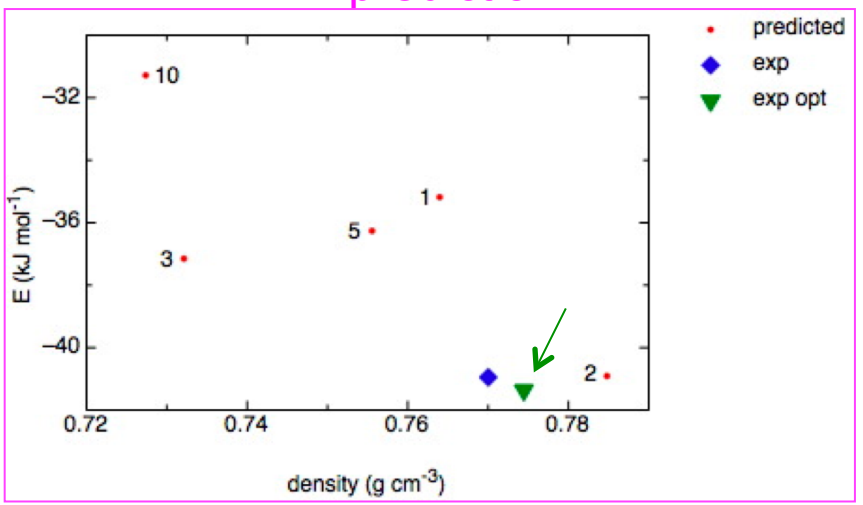
S

XULDUD (Pbca, Z=8) polymorph prediction

Atom-atom prediction



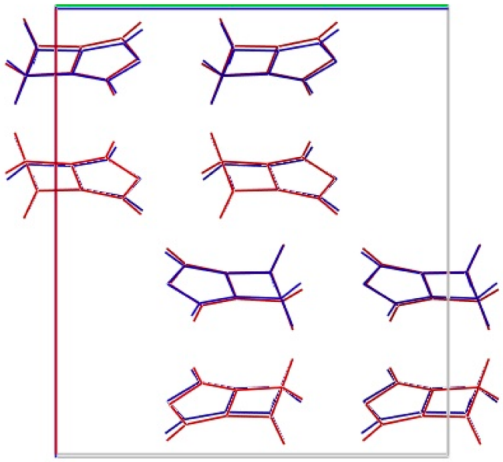
PIXEL prediction

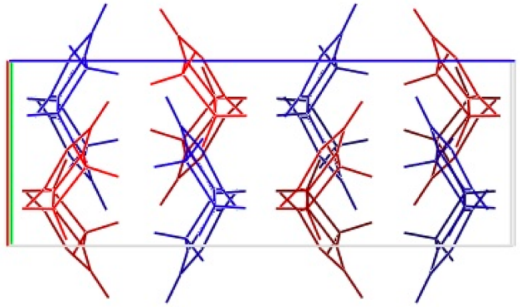


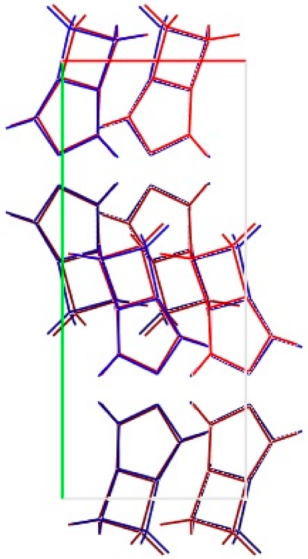
N	a	b	c	ro	E FF	E pixel	diff
exp	5.309	12.648	14.544	0.77	-59.40	-40.95	
exp minop	5.128	12.441	14.295	0.82	-64.70		
1 minop	14.281	5.221	12.589	0.86	-61.79		0.064
2 minop	14.236	5.143	12.498	0.88	-64.57		0.078
3 minop	12.555	5.691	13.380	0.84	-60.10		0.075
5 minop	9.989	7.159	13.042	0.86	-63.08		0.060
10 minop	15.106	7.069	9.134	0.82	-57.48		0.112
exp pixel	5.298	12.601	14.545	0.77	-59.54	-41.36	
1 pixel	14.386	5.393	12.687	0.76	-57.73	-35.18	0.150
2 pixel	14.323	5.309	12.600	0.78	-60.70	-40.91	0.022
3 pixel	12.628	5.814	13.991	0.73	-54.80	-37.15	0.113
5 pixel	10.236	7.348	13.233	0.76	-58.51	-36.26	0.125
10 pixel	15.803	7.291	8.973	0.73	-52.78	-31.28	0.250

Atom-atom wrong E
PIXEL right

XULDUD (exp vs 2, **RMS =10.0 !!!**)

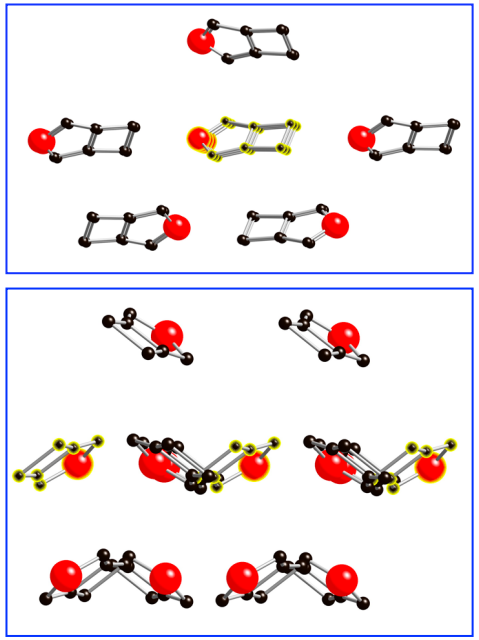


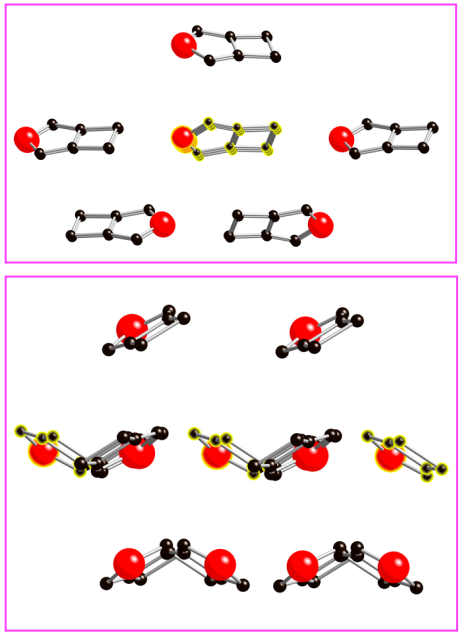




The theoretical and experimental crystals are racemic

theoretical



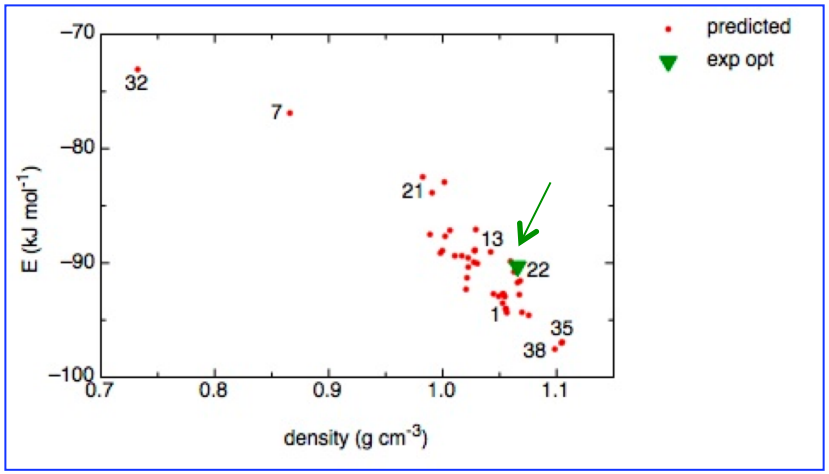


experimental

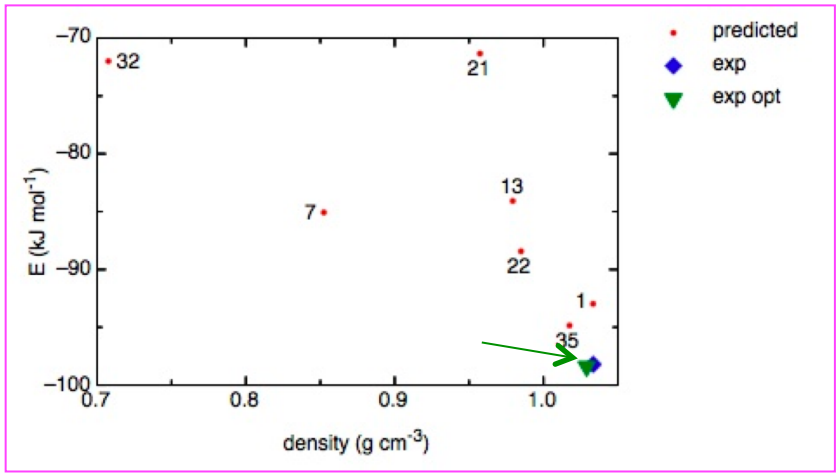
F

QARVOV (P21/c, Z=4) polymorph prediction

Atom-atom prediction



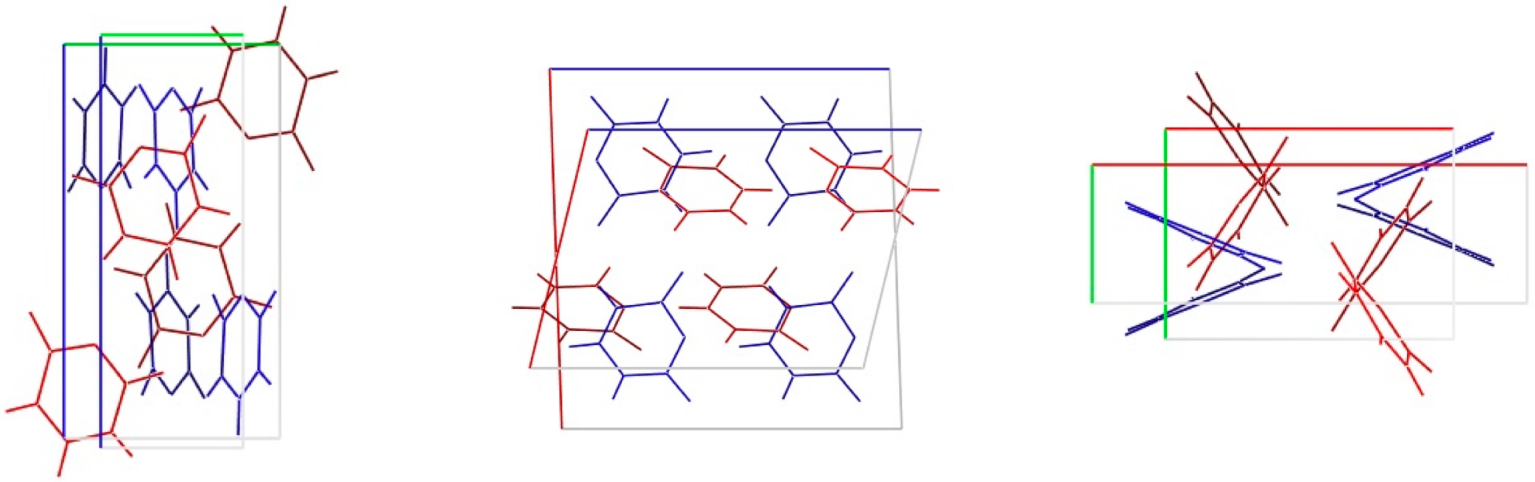
PIXEL prediction



N	a	b	c	al	be	ga	ro	E FF	E pixel	diff
exp	7.741	5.540	10.493	90.00	103.60	90.00	1.03	-70.40	-98.21	
exp minop	7.984	5.653	10.077	90.00	111.18	90.00	1.07	-90.31		
1 minop	6.744	5.498	11.591	90.00	85.09	90.00	1.06	-94.07		0.04
7 minop	9.845	5.456	11.863	90.00	125.00	90.00	0.87	-76.89		0.24
13 minop	6.619	6.160	11.853	90.00	114.52	90.00	1.03	-88.94		0.04
21 minop	6.648	8.043	10.416	90.00	125.00	90.00	0.99	-83.86		0.10
22 minop	6.955	9.954	6.489	90.00	71.24	90.00	1.06	-90.78		5.99e-3
32 minop	10.876	5.505	12.585	90.00	125.00	90.00	0.73	-73.07		0.37
35 minop	11.237	3.531	10.325	90.00	87.75	90.00	1.10	-97.00		0.08
38 minop	12.328	3.334	10.011	90.00	90.60	90.00	1.10	-97.54		0.09
exp pixel	7.780	5.541	10.484	90.00	103.58	90.00	1.03	-71.00	-98.39	
1 pixel	6.466	5.798	11.720	90.00	84.51	90.00	1.03	-77.20	-92.97	0.06
7 pixel	9.532	5.792	11.736	90.00	125.07	90.00	0.85	-63.60	-85.07	0.22
13 pixel	6.258	6.612	12.535	90.00	117.14	90.00	0.98	-66.00	-84.08	0.15
21 pixel	6.988	8.258	10.037	90.00	125.41	90.00	0.96	-76.40	-71.34	0.28
22 pixel	7.291	10.000	6.646	90.00	71.29	90.00	0.98	-79.70	-88.43	0.11
32 pixel	10.854	5.685	12.658	90.00	125.14	90.00	0.71	-65.20	-71.99	0.41
35 pixel	11.417	3.645	10.680	90.00	88.07	90.00	1.02	-86.50	-94.85	0.04

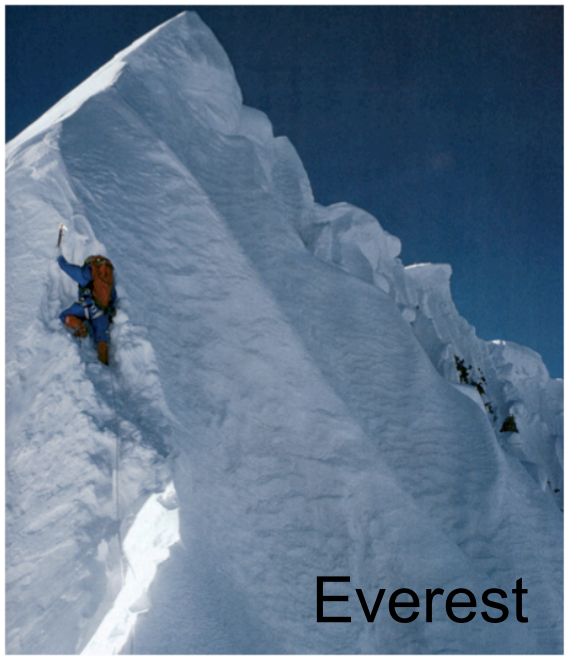
Atom-atom wrong E
PIXEL right

QARVOV (exp vs 35, RMS =10.0)



Concluding remarks

- It is possible to perform crystal optimization with PIXEL with better accuracy that atom-atom based methods
- Accurate PIXEL polymorph prediction is also possible
- Still space for improvement
  - Better atom-atom potentials (1st step)
  - Better generation algorithm (unlikely)
  - Better sorting algorithm (already done!)
  - Better general approach



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CESCA
Barcelona Supercomputer Center (BSC)

Group picture