

DELOCALISATION ERROR: THE NEXT FRONTIER MAGDALENE COLLEGE JRF

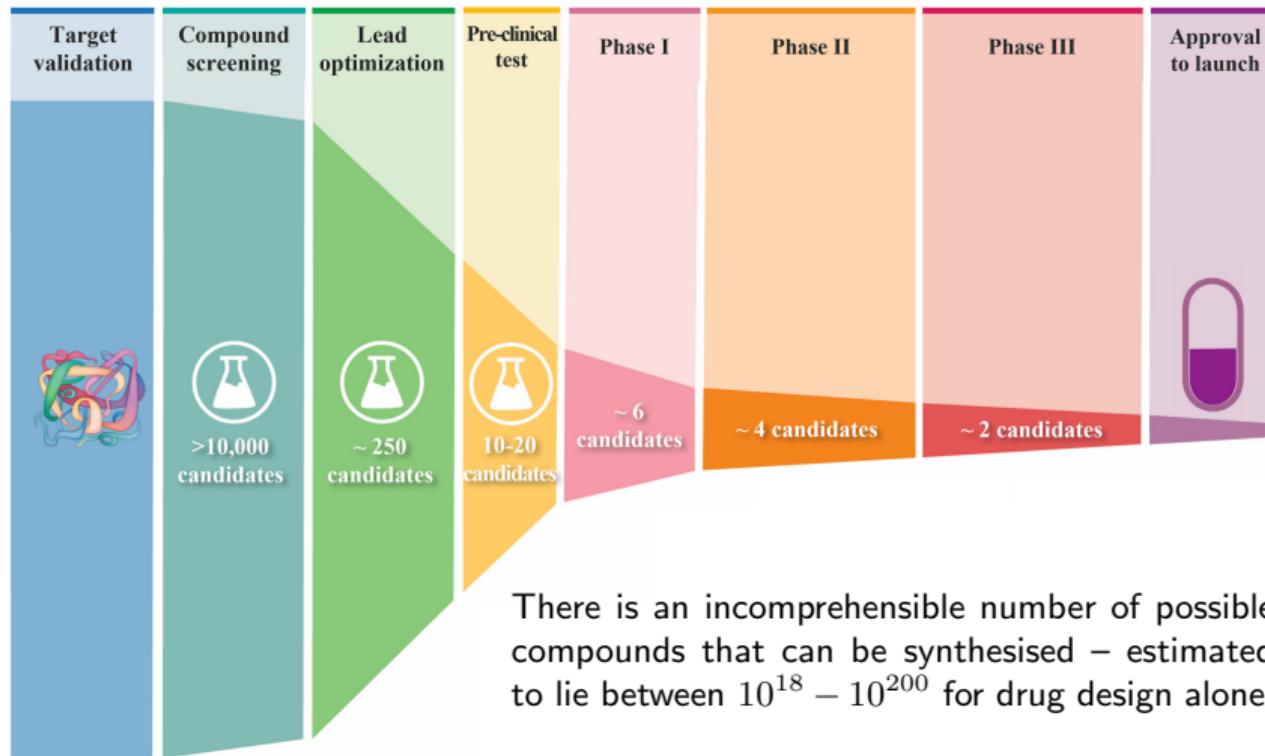


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Chemical Space and Drug Discovery



What is Computational Chemistry?

Traditionally computational chemistry has been used to interpret experimental results.

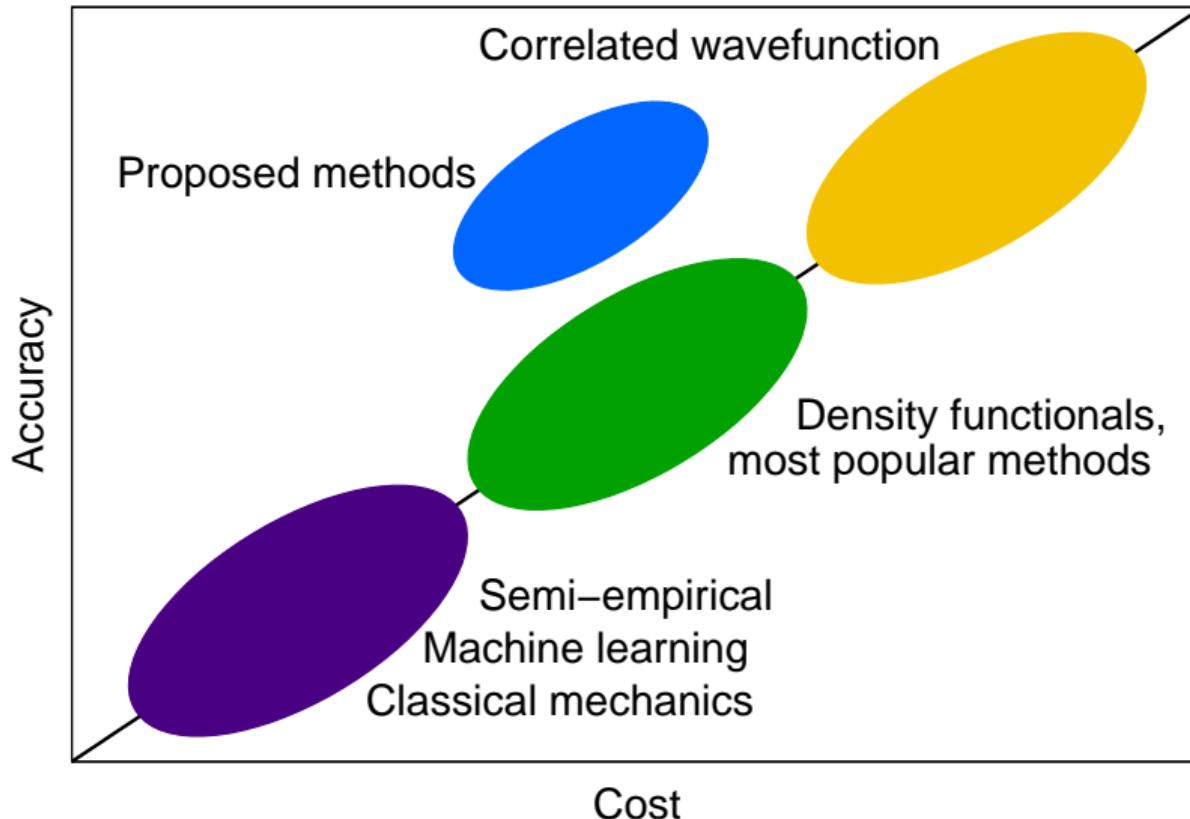


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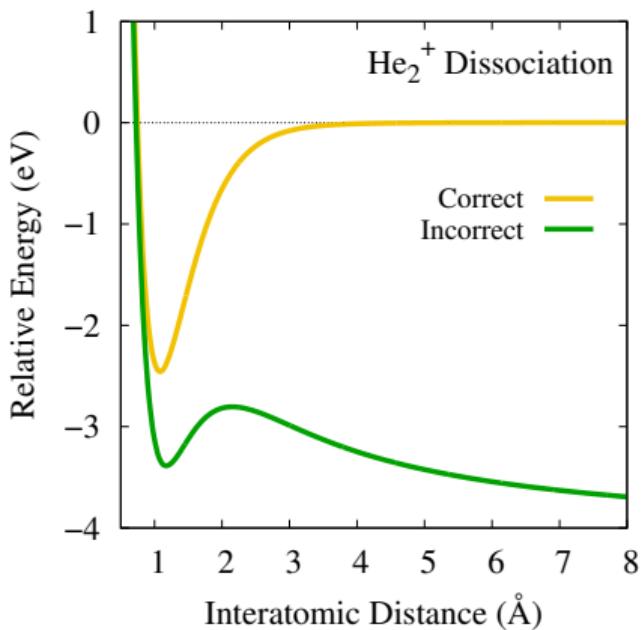
The long-term goal is to use computational chemistry in a predictive way, to drive experimental design and compound discovery.

Cost versus Accuracy



Delocalisation Error

- Prevents mid-cost methods with high accuracy
- Popular density-based methods 'over-share' charge
- This affects computational modelling of systems like
 - water and ice
 - electrolytes used in batteries
 - semi-conductors used in electronics
 - organic co-crystals and salts used in drugs
- Current solutions involve parameterisation and are not general
- I will work towards resolving this problem



Overlap with Cambridge Researchers



Professor Angelos Michaelides FRS

Collaborate on modelling various phases of water ice. Bulk water is an exceedingly stringent challenge for computational methods due to delocalisation error.



Dr Alex Thom

Collaborate on categorising the problems found within existing methods and building a benchmark of delocalisation error targets for testing new methods.

Overlap with Cambridge Researchers



Professor Chris J Pickard

Collaborate on application of proposed methods to *ab initio* random searching for materials structure prediction. This would lead to improved accuracy for theory-driven materials discovery.

CCDC

The Cambridge Crystallographic Data Centre

Interested in the development and direct application of accurate and efficient methods for crystal structure prediction, which are assessed through the CCDC's blind test competitions.

Plan for Functional Development

The B05 functional is the first correlation model that correctly integrates 100% exact exchange.

$$E_{XC} = E_X^{\text{HF}} + a_{\text{NC}}^{\text{opp}} U_{\text{NC}}^{\text{opp}} + a_{\text{NC}}^{\text{par}} U_{\text{NC}}^{\text{par}} + a_{\text{DC}}^{\text{opp}} E_{\text{DC}}^{\text{opp}} + a_{\text{DC}}^{\text{par}} E_{\text{DC}}^{\text{par}}$$

- includes energy terms for different correlation types – non-dynamical (NC) and dynamical (DC) – and whether electrons have opposite or parallel spins
- $a_{\text{NC}}^{\text{opp}}, a_{\text{NC}}^{\text{par}} \approx 0.5$ (virial theorem), $a_{\text{DC}}^{\text{opp}}, a_{\text{DC}}^{\text{par}} \approx 1$
- Correlation terms depend on ρ , $\nabla\rho$, $\nabla^2\rho$, τ , and the exact exchange-energy density.

B05 correctly dissociates H_2^+ , H_2 , He_2^+ , He_2 – notable since H_2^+ and He_2^+ are dramatic examples of delocalisation error.

Much development must be still done to allow self-consistent calculations and extension to solids.

Becke. J. Chem. Phys., 122, 064202 (2005), Dale, et al. J. Chem. Phys., 147, 154103 (2017)

Numerical Atom-Centered Orbitals and FHI-aims

Gaussian basis functions commonly used in molecular calculations, while planewave basis sets are commonly used for periodic solids.

Computing the exact exchange energy is intractable for large systems with planewaves, while Gaussian basis sets pose challenges for self-consistent implementation of B05 due to the correlation terms.

Our solution is to use numerical atom-centered orbitals. These are basis functions of the form:

$$\varphi_{nlm}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\theta, \phi)$$

- ✓ Routine use of hybrids for solids
- ✓ $\mathcal{O}(N)$ scaling
- ✓ correct exponential orbital shapes



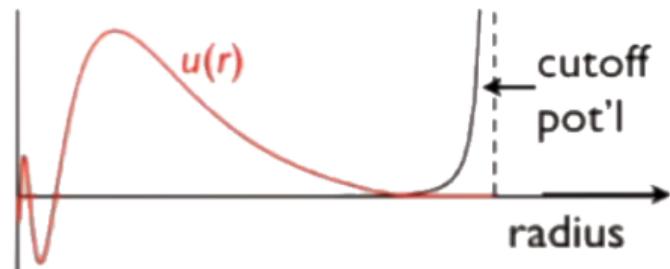
NAO Efficiency

Within FHI-aims, $u(r)$ is constructed to satisfy the single-particle, Schrödinger-like equation

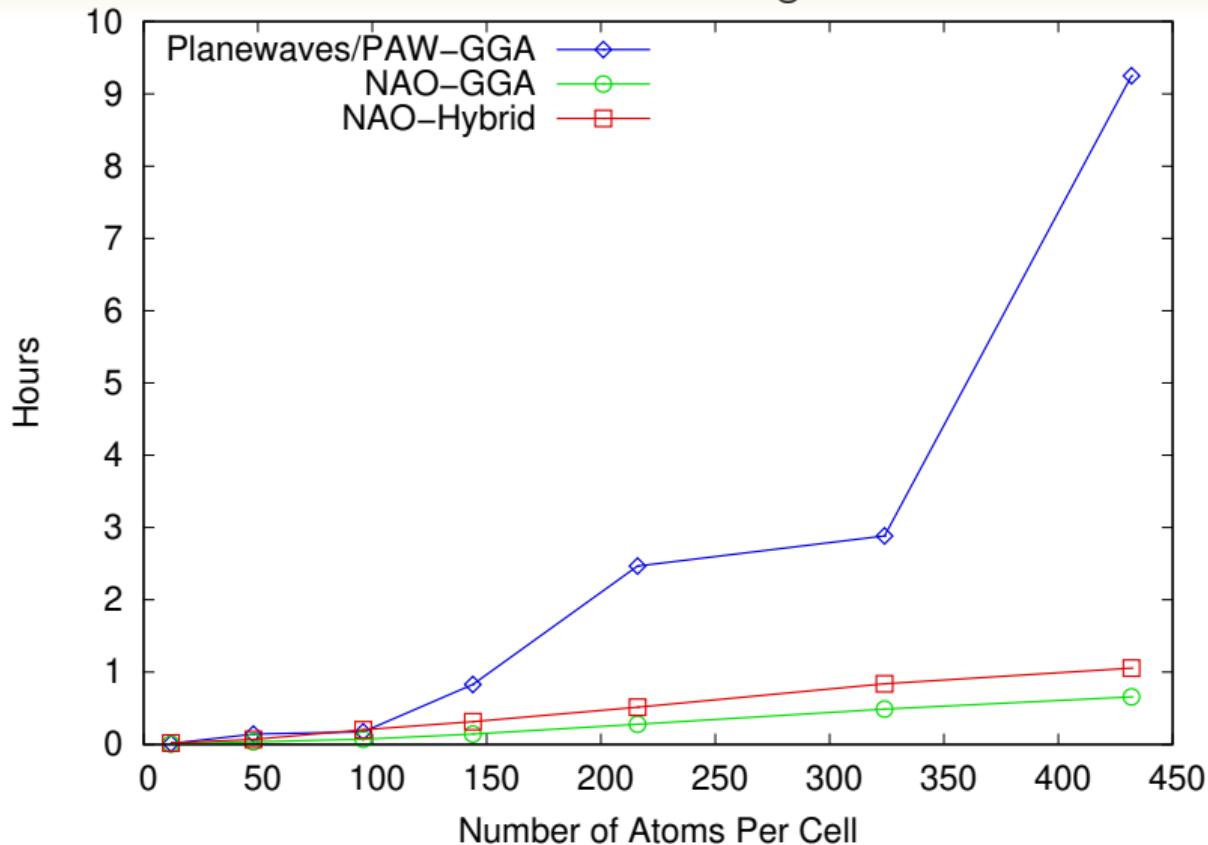
$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}(r) \right] u_i(r) = \varepsilon_i u_i(r)$$

The NAOs are strictly localised by the confining potential, $v_{\text{cut}}(r)$, which cuts off the slowly decaying tails:

$$v_{\text{cut}}(r) = \begin{cases} 0 & r \leq r_{\text{onset}} \\ \frac{s}{(r-r_{\text{cut}})^2} \exp\left(\frac{-w}{r-r_{\text{onset}}}\right) & r_{\text{onset}} < r < r_{\text{cut}} \\ \infty & r \geq r_{\text{cut}} \end{cases}$$



Low Cost and Favourable Scaling of FHI-aims

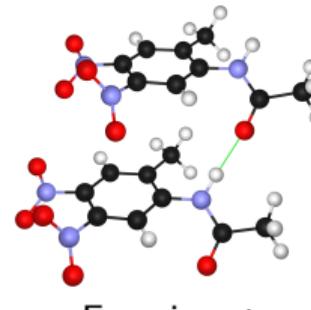


Importance of Hybrid DFT for Molecular Crystals: Compound X from the 3rd CSP Blind Test

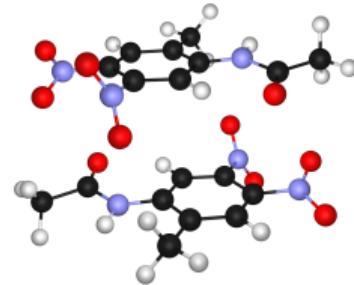
Delocalisation error favours extended conjugation, rather than intermolecular H-bonding.

A MP2 monomer energy correction improves the B86bPBE-XDM energy ranking:

Structure	ΔE_{DFT}	$\Delta E_{\text{DFT}+\Delta \text{MP2}}$
Experiment	0.00	0.00
vanEijck-3	-0.44	0.24

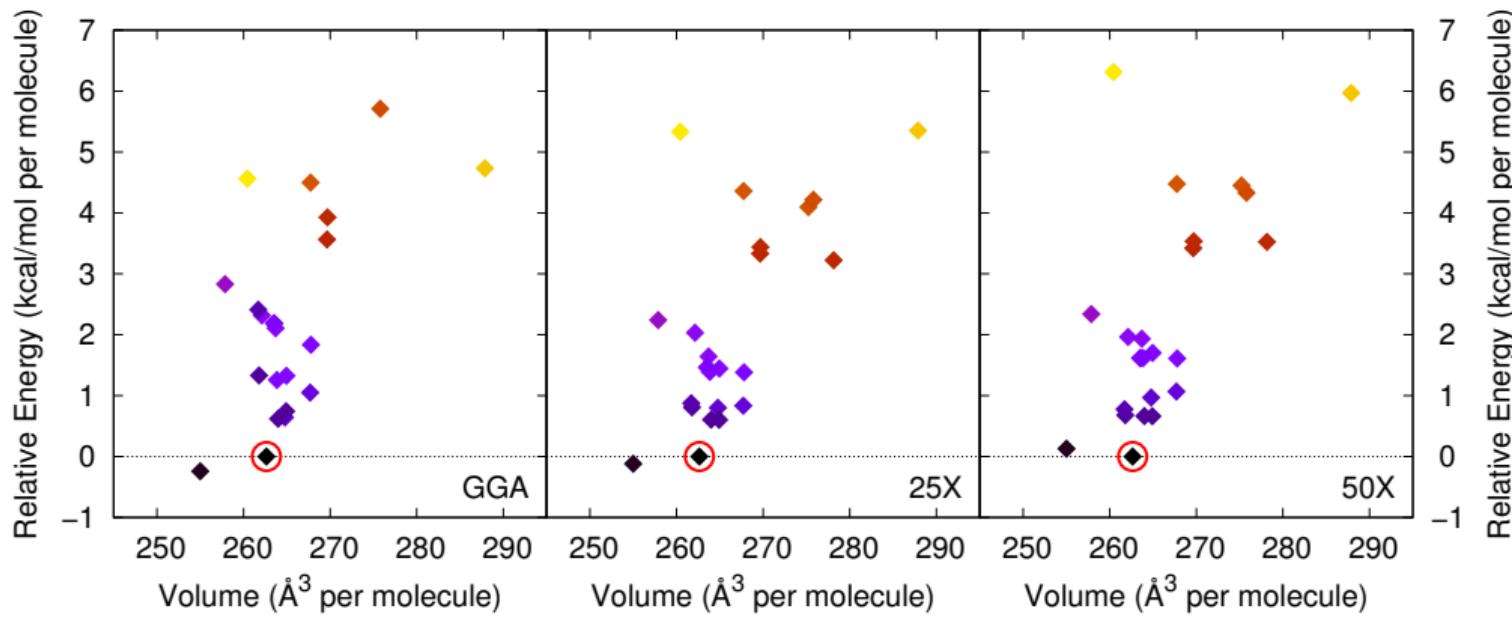
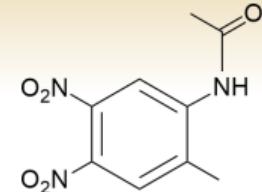


Experiment

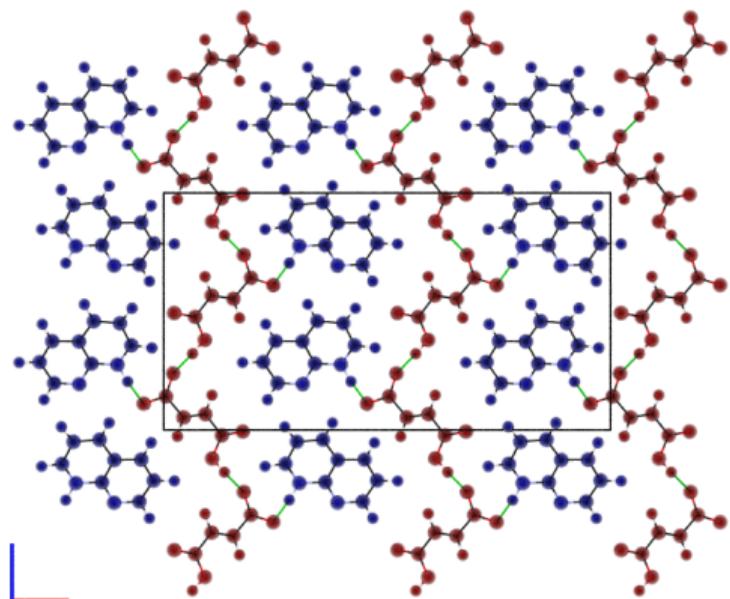
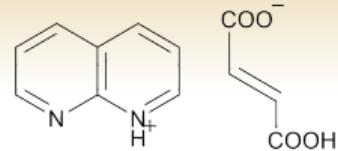


vanEijck-3

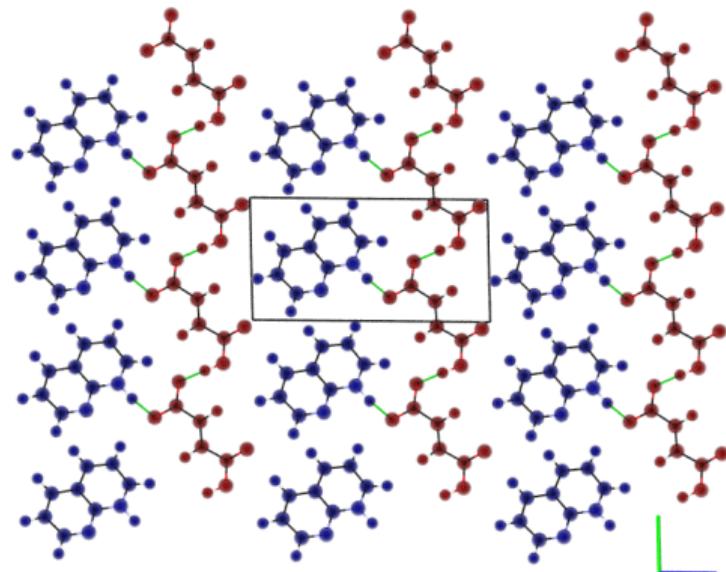
CSP Landscapes for Compound X



Compound XIX from the 5th CSP Blind Test

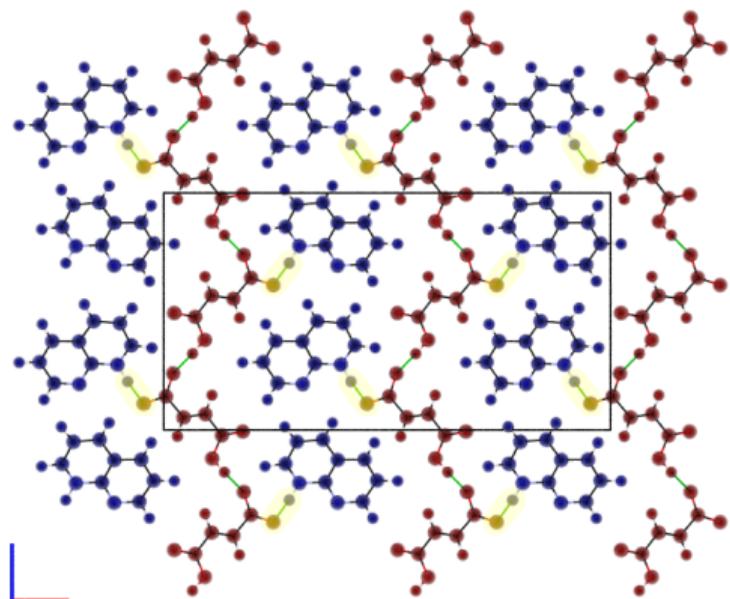
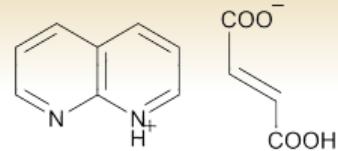


Experimental structure

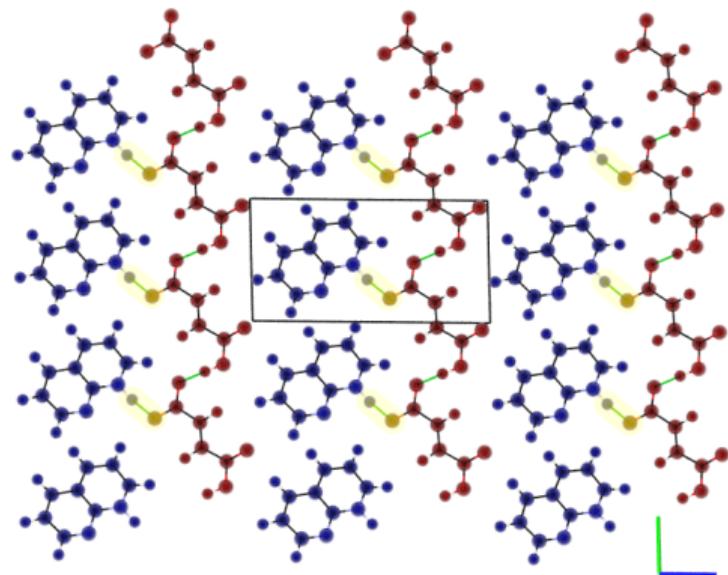


GGA-favoured structure

Compound XIX from the 5th CSP Blind Test



Experimental structure



GGA-favoured structure

CSP Landscapes for Compound XIX

