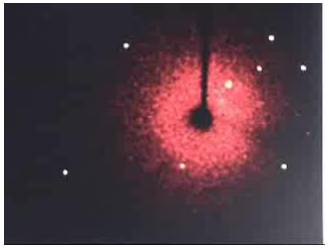
George L. Clark X-ray Laboratory

3M Materials Chemistry Facility



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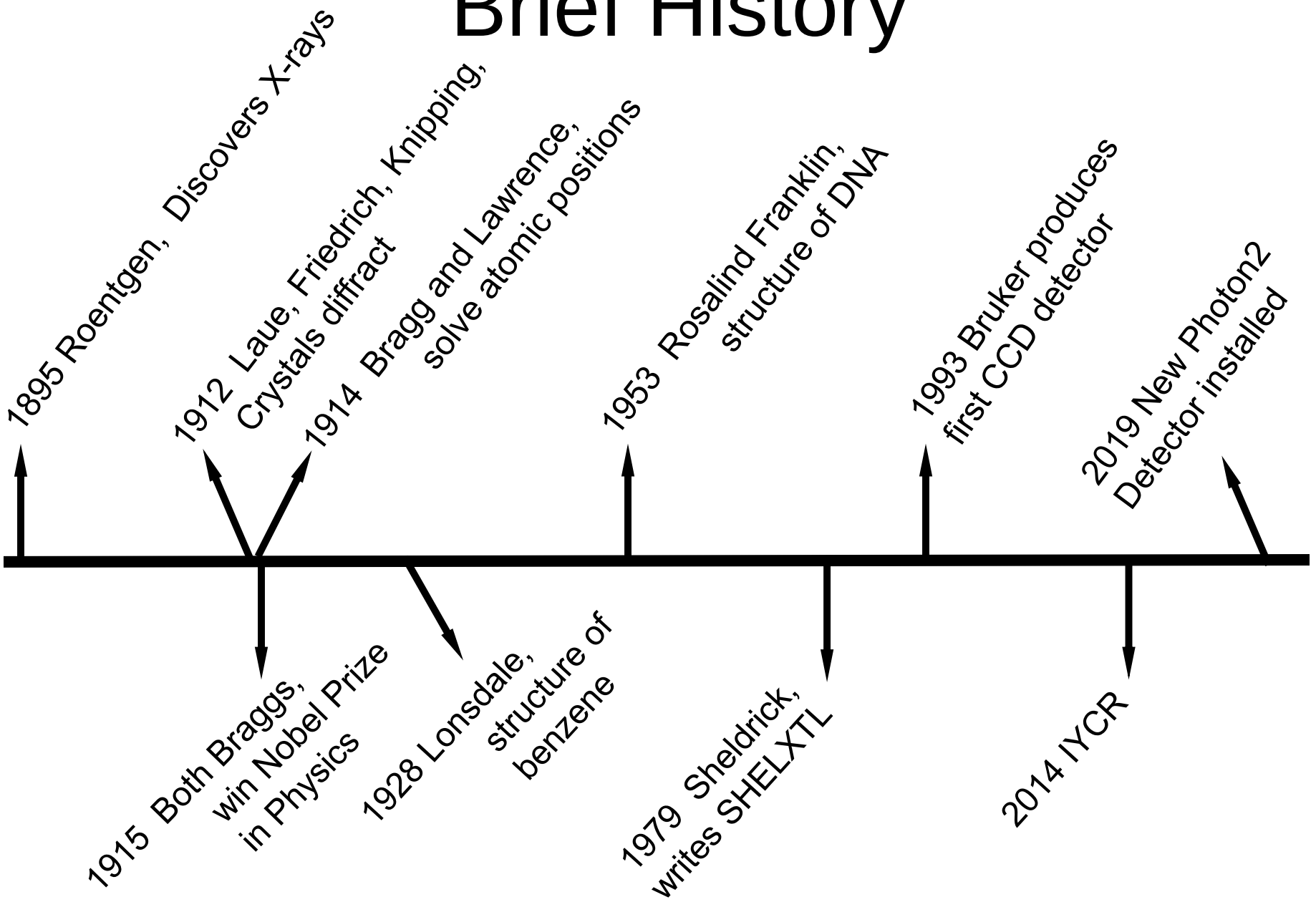
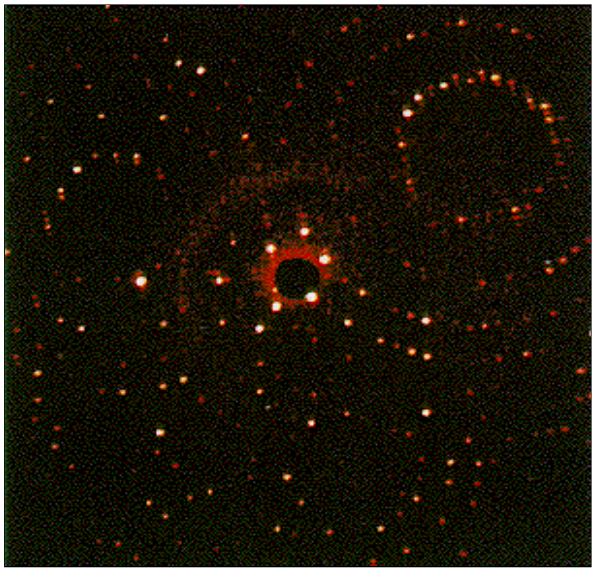
Business Hours	8:30a - 12:00p and 1:00p - 4:30p	Monday - Friday
Consulting Hours	10:00a - 11:00a and 2:00p - 3:00p	Monday - Friday
Laboratory Entry	Northeast Ground Floor Noyes, Room 60	

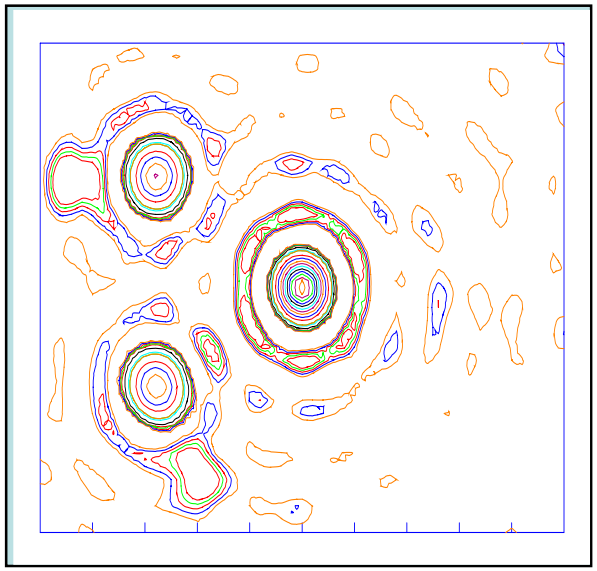
Brief History



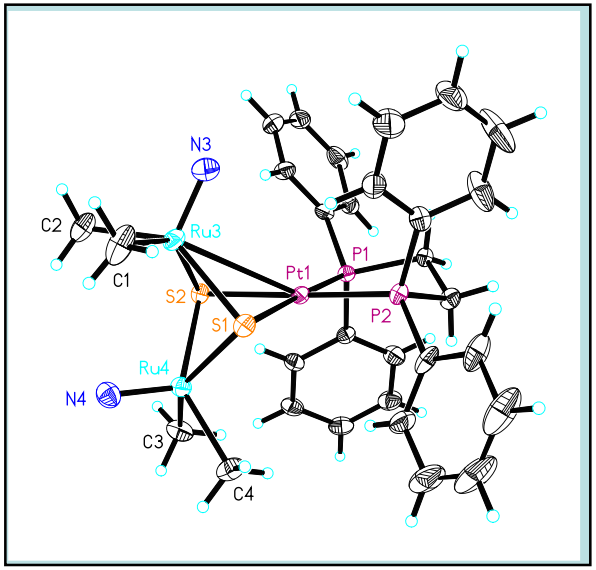
Overview



SHELXTL
XPREP
XS
XP

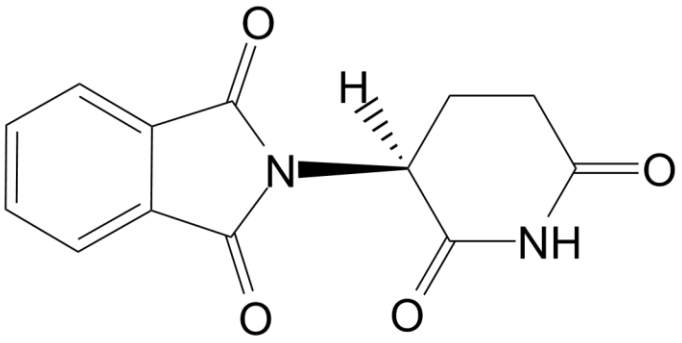


P 21/n
a = 23.3481(4)
b = 12.3868(2)
c = 23.8191(1)
beta = 92.756(1)

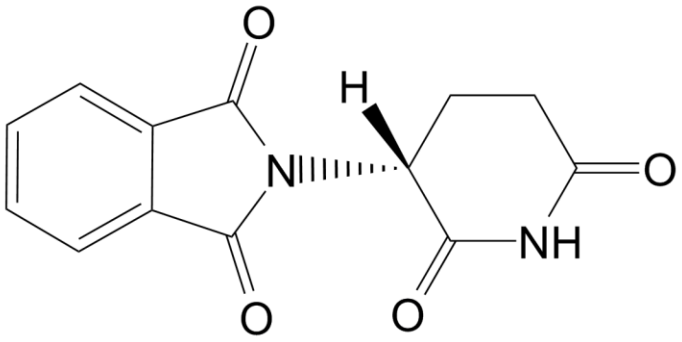


Chemistry
XL

Organic Chemistry and Crystallography it matters



(*S*)-thalidomide, identified as the teratogenic agent



(*R*)-thalidomide, the therapeutic agent for the treatment of morning sickness

Absolute structure without a heavy atom

1. Crystallize the compound with a component of known stereochemistry
2. Bijvoet Pairs (h k l and -h -k -l) need to be examined for anomalous scattering effects

Centrosymmetric vs. Non-centrosymmetric

$F_{hkl} = F_{-h-k-l}$ $F_{hkl} \neq F_{-h-k-l}$

Flack and/or Hooft

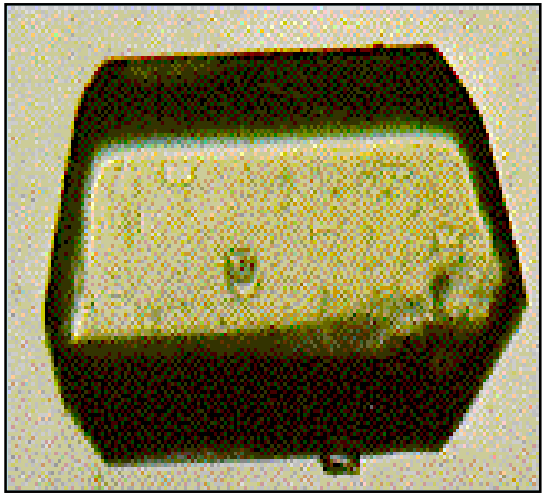
Analysis

In order to measure anomalous scattering effects you must be using a radiation near the absorption edge of the atom types. You **MUST** have Cu radiation for light atom structures!

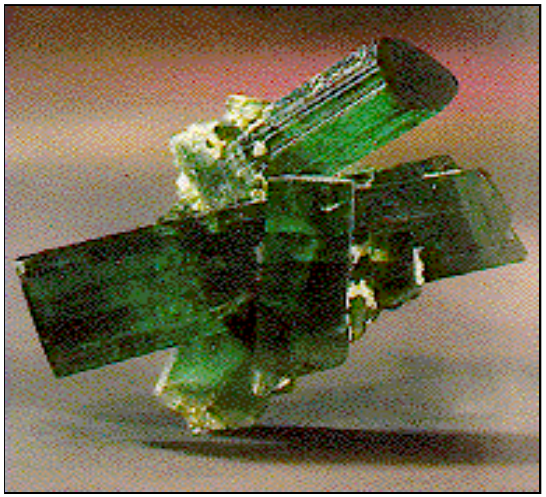
The main pitfall of absolute structures

- Is the crystal examined a representative of the bulk crystals?
  - Racemic mixtures can crystallize
    1. As a centrosymmetric crystal
    2. As a non-centrosymmetric crystal that is twinned
    3. Each individually as non-centrosymetric crystals
  - Circular dichroism or enantioselective chromatography to test if crystal is the same as bulk

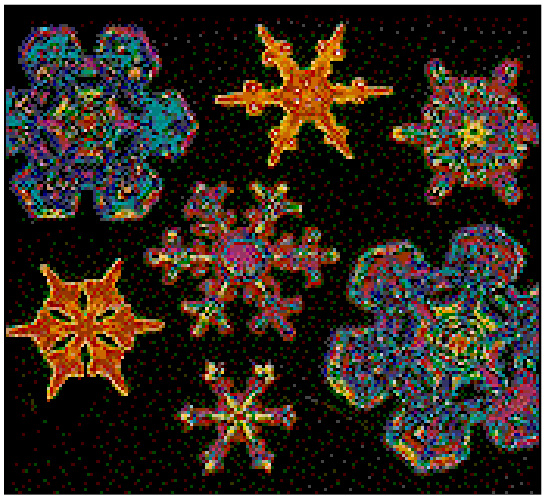
Crystal Quality is Essential



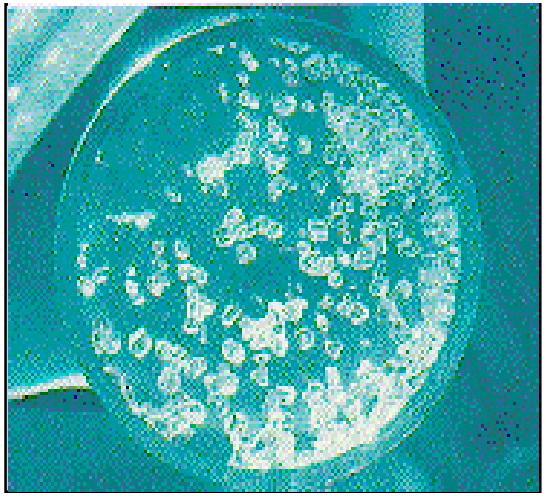
YES

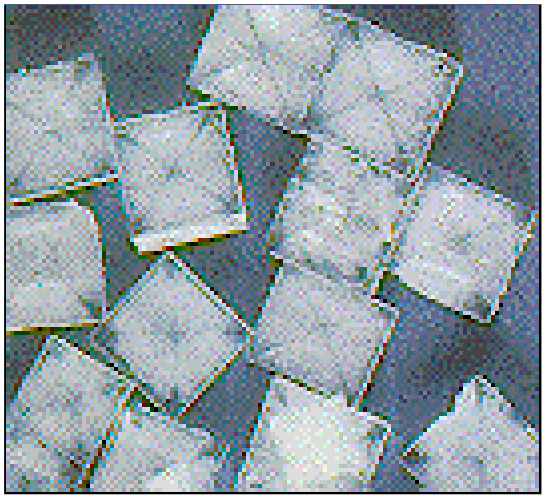


MAYBE



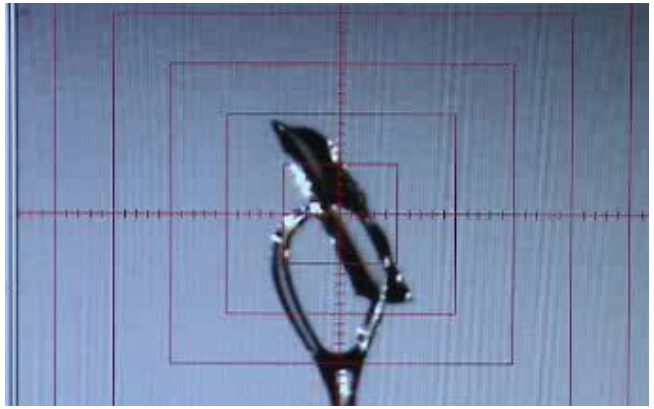
NO





The Ideal Sample

The ideal sample, like this 40 x 70 x 360 μm crystal mounted on a 300 μm cryo-loop, is attached using an inert oil, frozen in place using a cold gas stream, and recovered after the diffraction experiment is finished.



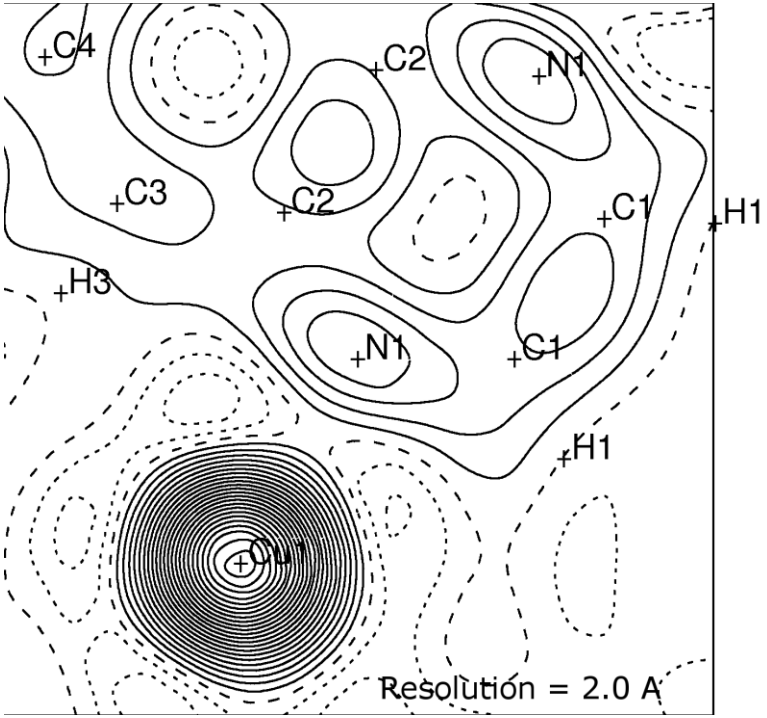
Like many spectroscopic techniques, the overall amplitude of the diffraction pattern is proportional to sample volume. There are no limits on crystal morphology, but the practical range of linear dimensions is 5 to 500 μm. Air, temperature, and light sensitive samples are routinely used.

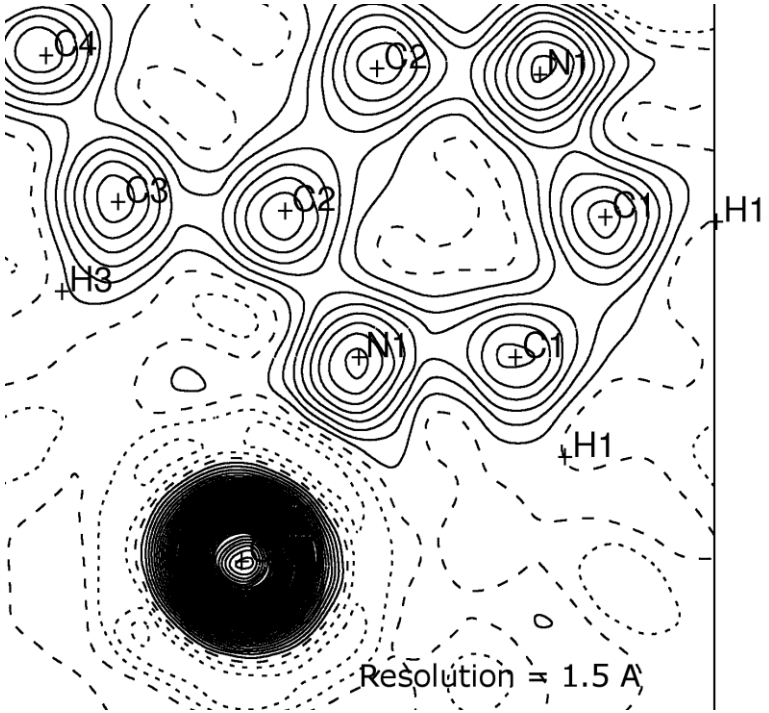
Growing “good” crystals

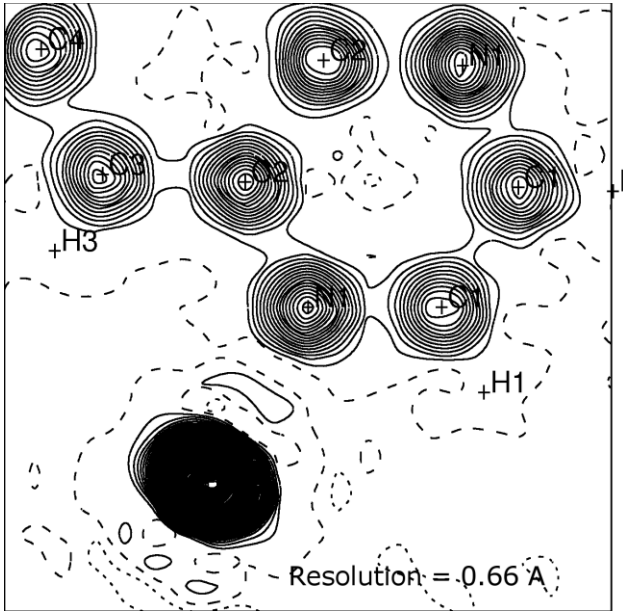
- Solvent Cooling
- Solvent Evaporation
- Layering Liquid/Liquid diffusion
- Vapor Diffusion
- Sublimation

No matter how you grow the crystals, bring them to the X-ray facility the way you grew them!

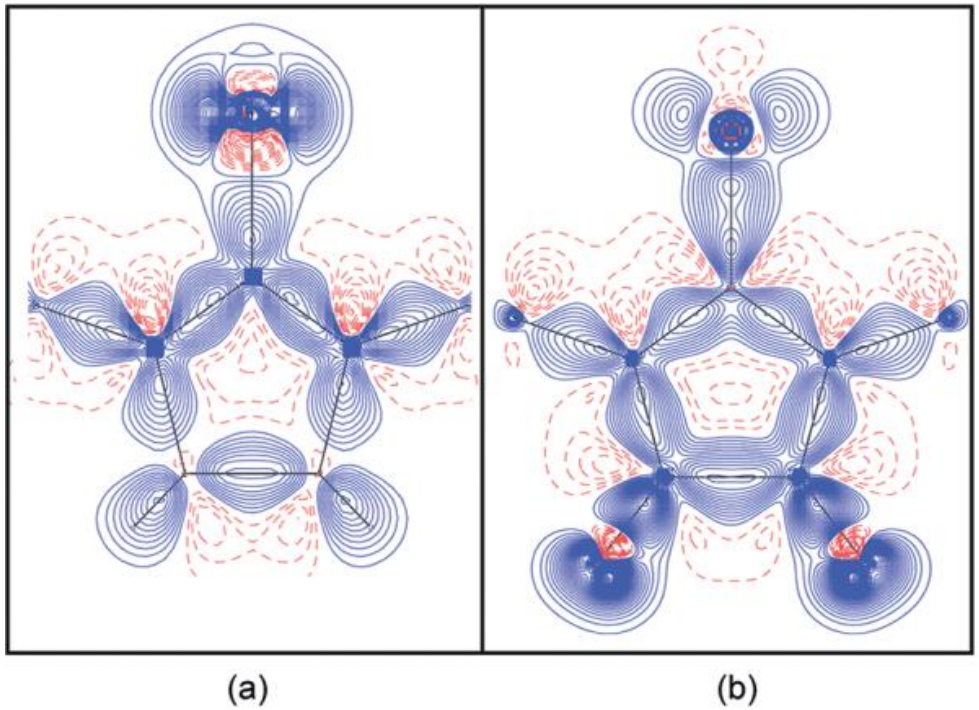
DO NOT REMOVE THE SOLVENT!

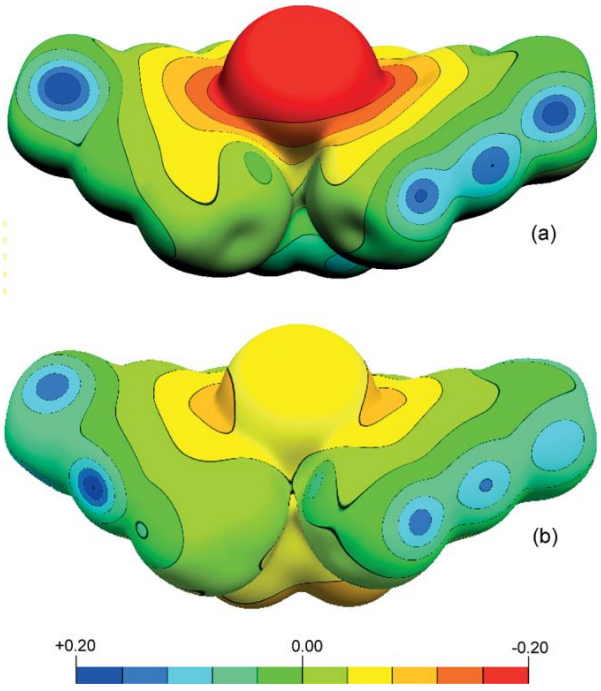

C4
C2
N1
C3
C2
C1
H1
H3
N1
C1
H1
Cu1
Resolution = 2.0 A


C4
C2
N1
C3
C2
C1
H1
H3
N1
C1
H1
Resolution = 1.5 A


C4
C2
N1
C3
C2
C1
H1
H3
N1
C1
H1
Resolution = 0.66 A

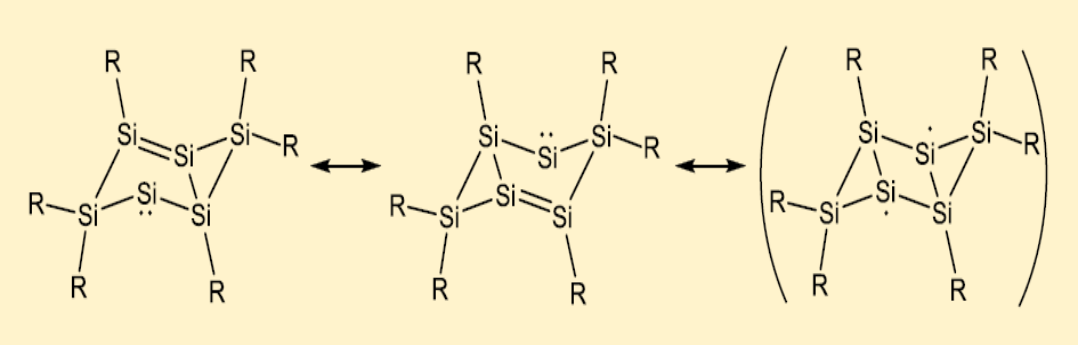
Static deformation density map:
Essentially the total electron density minus spherical core electron density

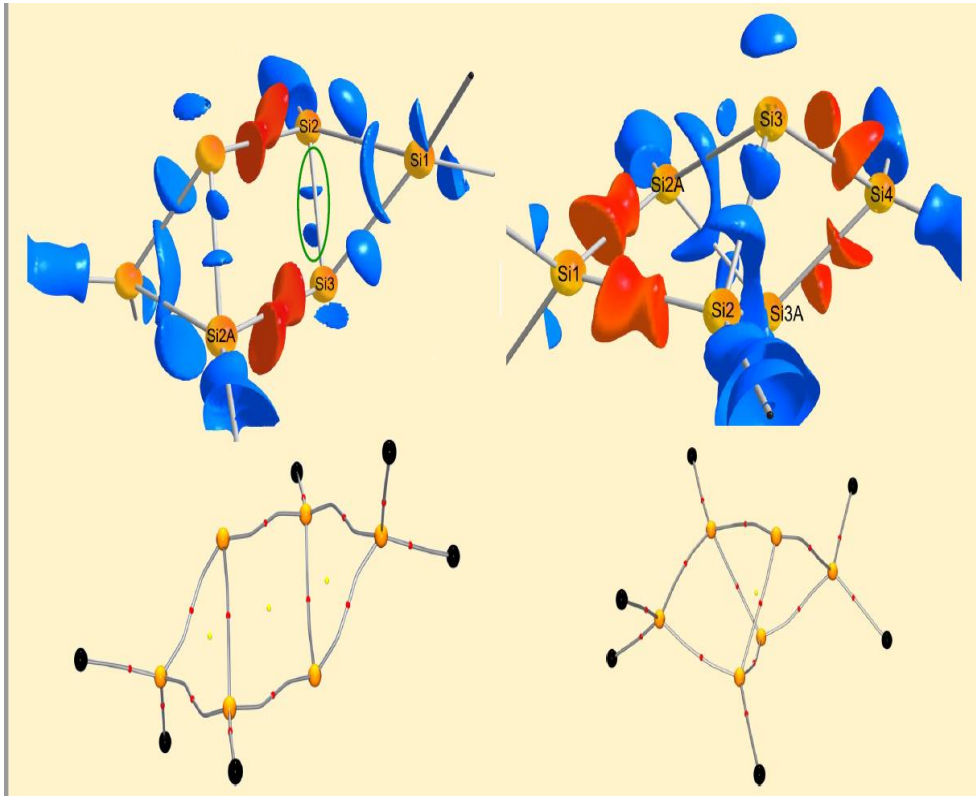




Electrostatic Potential Maps:
Same idea as an ESP map generated by a DFT calculation but it is derived from experimental information
(same Se complexes as on previous slide)

Hexasilabenzene

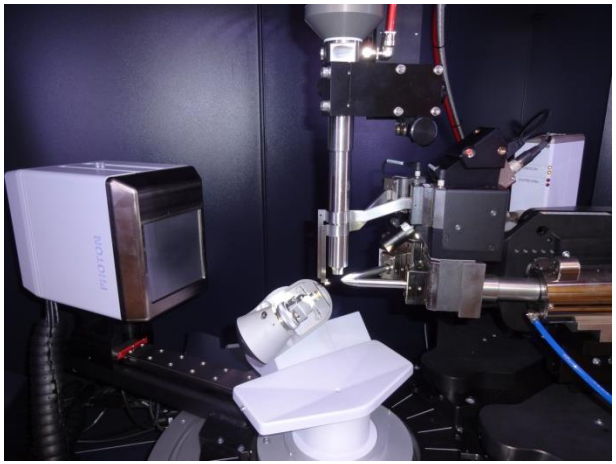




Which resonance structure is correct, or is the system an average of the three?

Bond paths (gray lines) and bond critical points (red spheres) provide an experimentally observable definition of a “bonding interaction”

You too can learn to collect and solve your own structures!



- How to pick a good crystal
- How to collect a data set
- How to integrate a data set
- How to solve a structure using OLEX2/SHELX

	User run	Staff run
Screening the crystals (Unit Cell)	$33.71	$57.26
Data Set	$103.36	$175.58
Structure Solution	$212.30	$360.64

Charge Density Analysis Price TBD