

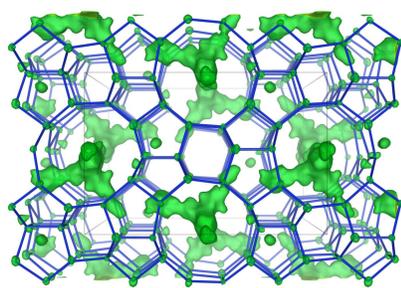
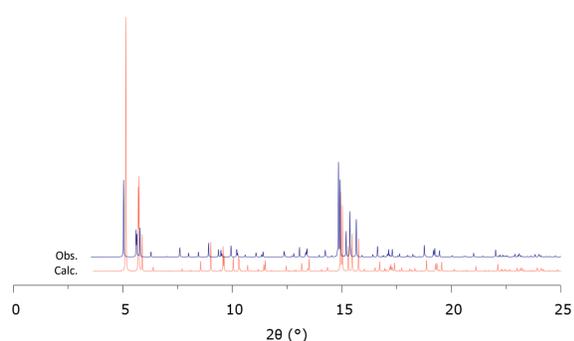
LOCATING ORGANIC GUESTS IN INORGANIC HOST MATERIALS FROM X-RAY POWDER DIFFRACTION DATA

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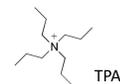
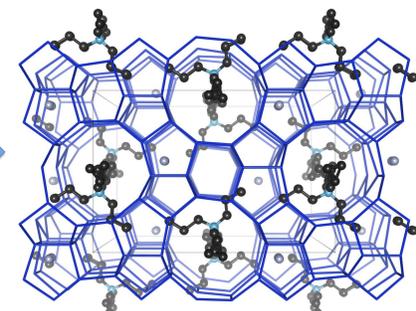
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Determining the location of the organic structure-directing agent (SDA) inside the channel system of a zeolite is a long-standing problem in zeolite structural science. We have developed a method that can be applied systematically to determine the location of the organic guest in inorganic host materials. [1]

Method



Simulated annealing



Start with structure of host material

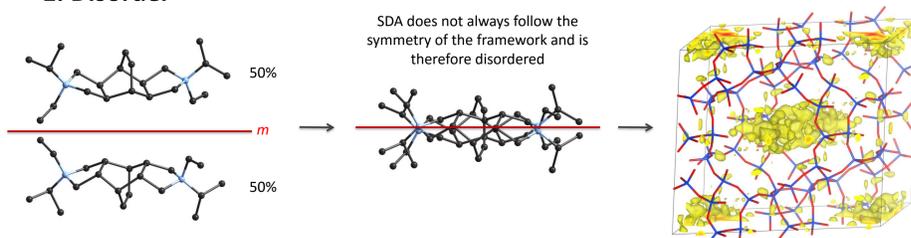
1. Estimate scale using high-angle data only
2. Difference map reveals rough location of SDA

3. Introduce rigid-body model of SDA

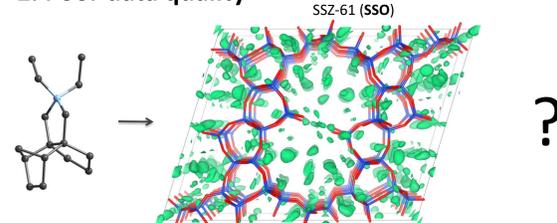
4. Optimize location/orientation with simulated annealing
5. Use this location as a starting point for Rietveld refinement

Obstacles in locating the SDA

1. Disorder



2. Poor data quality

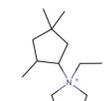
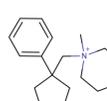
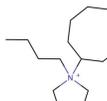
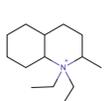
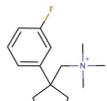
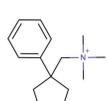


Can simulated annealing be applied systematically?

Six borosilicate zeolites studied:

- Known frameworks
- Different, flexible SDAs
- Molecular modeling data for SDA location available

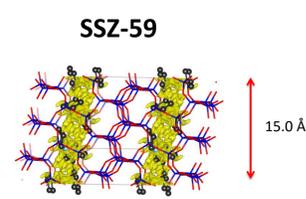
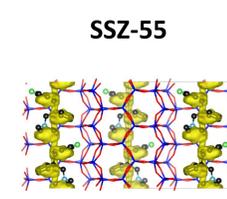
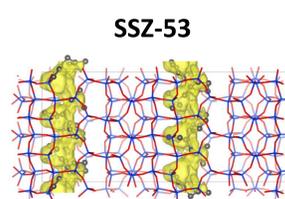
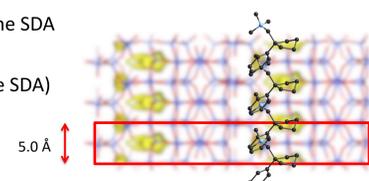
| ftc | Spgr. | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) |
|--------|-------|--------------------|-------|-------|-------|-------|-------|
| SSZ-53 | SFH | C2/c | 5.02 | 33.74 | 21.17 | 90.5 | |
| SSZ-55 | ATS | Cmc2 ₁ | 12.95 | 21.85 | 5.08 | | |
| SSZ-56 | SFS | P2 ₁ /m | 13.95 | 19.90 | 12.36 | 106.7 | |
| SSZ-58 | SFG | Pmma | 25.11 | 12.50 | 12.86 | | |
| SSZ-59 | SFN | P-1 | 5.02 | 12.74 | 14.72 | 103.4 | 90.5 |
| SSZ-60 | SSY | P2 ₁ | 21.95 | 13.70 | 5.01 | | |



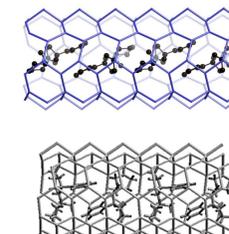
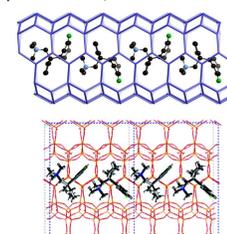
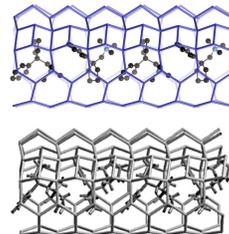
Sometimes it takes a bit of thinking

1D channel system (with 5Å repeat distance) impedes procedure as SDAs do not fit unit cell

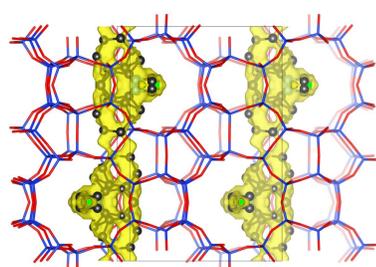
1. Expand unit cell (here x3) to allow full ordering of the SDA
2. Locate SDA with simulated annealing
3. Reduce unit cell to original size (keep location of the SDA)
4. Refine structure using restraints



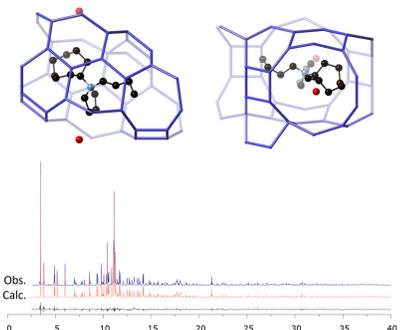
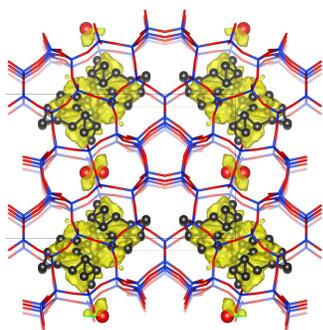
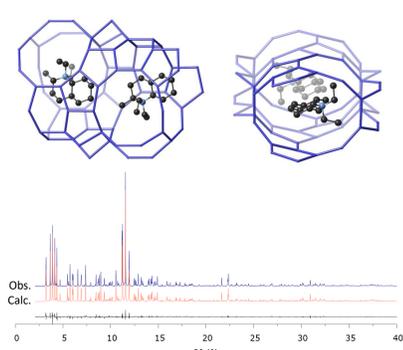
Comparison to molecular modeling
(top: refinement, bottom: modeling [2])



Sometimes the procedure is straightforward

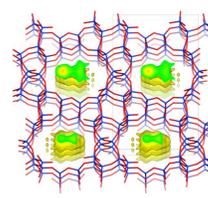


Difference map with optimized SDA

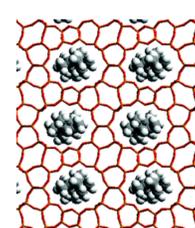


Sometimes the data are just not good enough

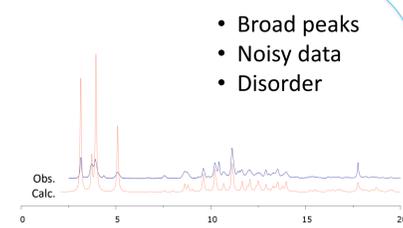
SSZ-60



Difference map



Molecular modeling [3]



- Broad peaks
- Noisy data
- Disorder

References

- [1] S. Smeets, *et al.*, *J. Am. Chem. Soc.*, 2016, doi:10.1021/jacs.6b02953, 2016
- [2] A. Burton, *et al.*, *Chem.-Eur. J.* 9(23), 5737, 2003;
A. Burton, *et al.*, *J. Phys. Chem. B* 110(11), 5273, 2006
- [3] A. Burton, S. Elomari, *Chem. Commun.*, 2618, 2004