Structure Comparison, Analysis and Validation

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Overview

This lecture lists and discusses the various tools and descriptors that are available for the analysis and validation of a single crystal study as implemented in the PLATON program.

Structure Analysis

- Analysis of the Intra-molecular Geometry
- Analysis of the Inter-molecular Geometry
- Analysis of the Coordination Geometry
- Bond Valence Model (Brown et al.)
- 'CALC ALL' - LISTING

Intra-molecular Geometry

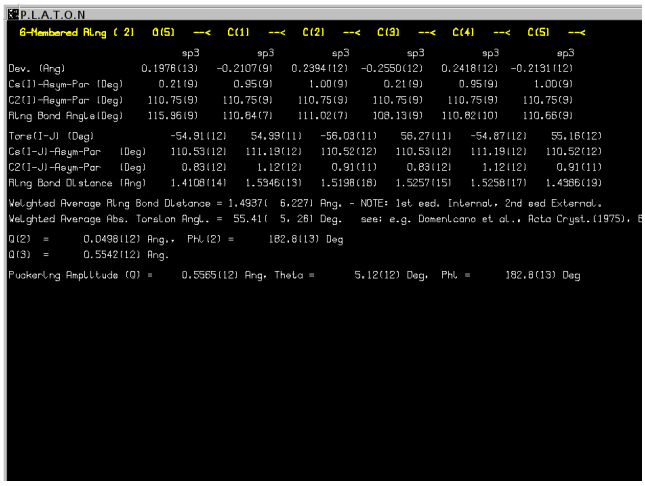
- Generation of the symmetry expended Connected Set on the basis covalent radii plus a tolerance..
- Special tolerances are applied for certain types of X-Y bonds/contacts, either to include or avoid them.
- Residues grow from a starting atom by recursive spherical expansion.

Intra-molecular Geometry

- Detection of residues and derivation of the Moiety formula, Z and Z'.
- Bond distances, Bond Angles, Torsion Angles.
- Automatic ring search,automatic seach of planar parts in the structure

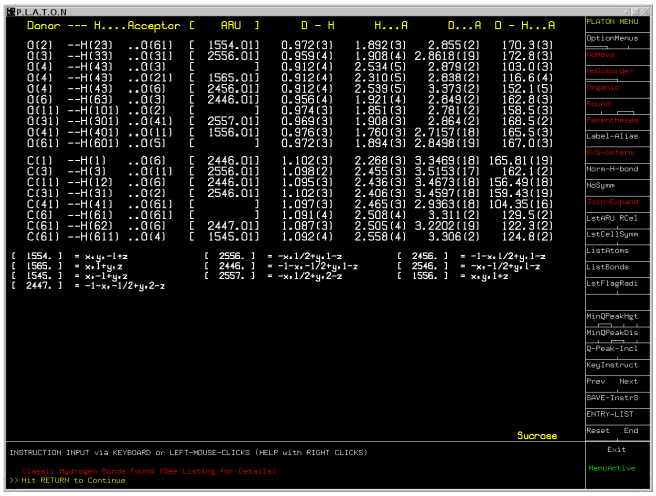
Intra-Molecular (Continued)

- Determination of the hybridization, R/S assignments and ‘topology numbers’.
- Listing of the plane-plane and bond-plane angles.
- Ring puckering analysis (Cremer & Pople)



Inter-Molecular

- Hydrogen Bonds (linear, bi- and trifurcated)
- Automatic analysis in terms of 1, 2 and 3-D networks (aggregates or cooperative)
- Search for pi-pi and C-H..pi interactions

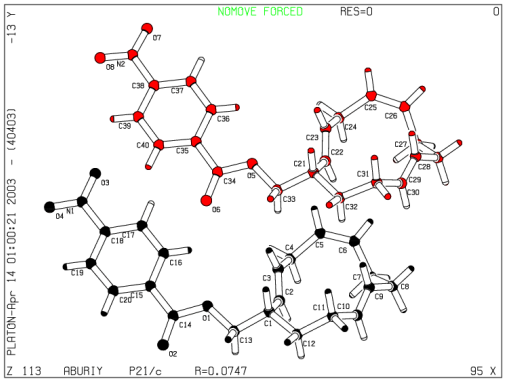


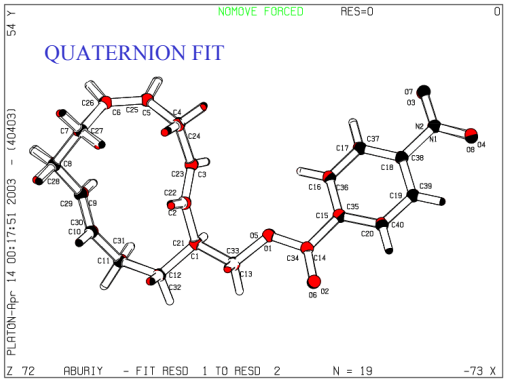
Structure Comparison

- Quaternion Fitting
  - Modified version of A.L.Mackay (1984), A40,165-166 (Note: 180 degree singularity)
  - Alternative: S.K.Kearsley (1989), A45, 208-210.
- Comparison of Simulated Powder Patterns
- StructureTidy (Inorganics)

QUATERNION FIT

- In many cases, an automatic molecule fit can be performed
- A) Identical atom numbering
- B) Sufficient number of Unique Atoms
- C) By manual picking of a few atom pairs



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==============================================================================
Molfit with Quaternion Method (A.L. Mackay, Acta Cryst.(1984), A40, 165-166)
==============================================================================

Fit Rotation angle about (Pseudo)axis [l,m,n] =        3.29 Degree
Direction Cosines with Orthogonal Cell l,m,n  =    0.436719  0.830383  0.346553
Components in crystal system                       0.394049  1.000000  0.083576

Transf. Orthogonal Coord. Mol1     Orth. Coord. Mol2 with Resp. to C.G. Dist (A)
------------------------------------------------------------------------------
 O(1)      1.224  -0.879  -1.850   O(5)      1.198  -0.889  -1.868       0.033
 O(2)      3.035  -1.529  -2.978   O(6)      3.008  -1.572  -2.964       0.052
 N(1)     -0.456   1.596  -7.411   N(2)     -0.369   1.657  -7.412       0.106
 C(1)      0.535  -1.424   0.352   C(21)     0.498  -1.430   0.337       0.041
 C(2)      0.325   0.021   0.707   C(22)     0.253   0.000   0.695       0.076
 C(3)     -0.645   0.793   0.325   C(23)    -0.743   0.741   0.291       0.116
 C(4)     -0.844   2.220   0.754   C(24)    -0.972   2.175   0.700       0.146
 C(5)     -2.124   2.389   1.499   C(25)    -2.203   2.340   1.516       0.095
 C(6)     -2.269   2.324   2.800   C(26)    -2.291   2.305   2.823       0.037
 C(7)     -1.239   2.048   3.830   C(27)    -1.178   2.089   3.790       0.084
 C(8)     -1.452   0.723   4.578   C(28)    -1.303   0.782   4.602       0.162
 C(9)     -1.384  -0.460   3.664   C(29)    -1.310  -0.424   3.725       0.102

                              ... etc ...

:: Weighted and Unit Weight RMS-Fit =     0.08729   0.08194 Angstrom
```

Cg1 0.946 0.234 0.592

Cg2 0.441 0.253 0.581

```
                                                                        "ABURI
==============================================================================
Comparison of the Bonds of the Fitted Residues
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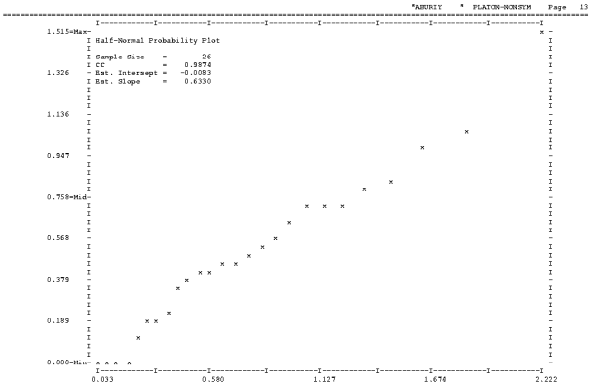
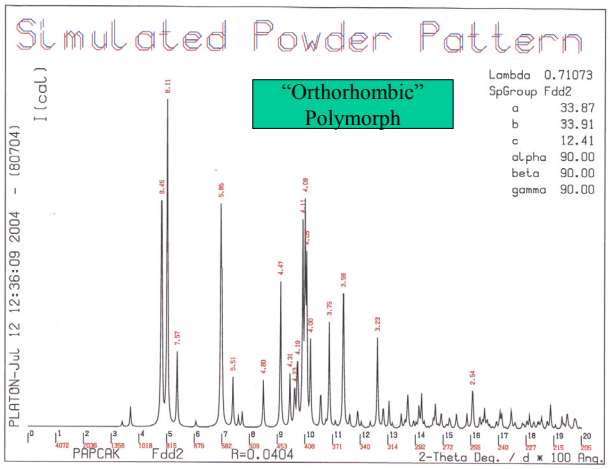
Resd#1              Resd#2                Dist#1        Dist#2      Diff  Diff/Sig
------------------------------------------------------------------------------
O(1)    -C(13)      O(5)    -C(33)      1.449(6)      1.440(6)    0.0090    1.0607
O(1)    -C(14)      O(5)    -C(34)      1.326(6)      1.320(6)    0.0060    0.7071
O(2)    -C(14)      O(6)    -C(34)      1.198(7)      1.198(6)         0         0
O(3)    -N(1)       O(7)    -N(2)       1.225(7)      1.210(7)    0.0150    1.5152
O(4)    -N(1)       O(8)    -N(2)       1.217(7)      1.210(7)    0.0070    0.7071
N(1)    -C(18)      N(2)    -C(38)      1.477(8)      1.475(7)    0.0020    0.1881
C(1)    -C(2)       C(21)   -C(22)      1.502(7)      1.494(7)    0.0080    0.8081
C(1)    -C(12)      C(21)   -C(32)      1.523(7)      1.530(7)   -0.0070   -0.7071
C(1)    -C(13)      C(21)   -C(33)      1.504(7)      1.507(6)   -0.0030   -0.3254
C(2)    -C(3)       C(22)   -C(23)      1.297(7)      1.306(6)   -0.0090   -0.9762
C(3)    -C(4)       C(23)   -C(24)      1.503(7)      1.508(7)   -0.0050   -0.5051
C(4)    -C(5)       C(24)   -C(25)      1.491(8)      1.487(7)    0.0040    0.3763
C(5)    -C(6)       C(25)   -C(26)      1.311(9)      1.311(8)         0         0
C(6)    -C(7)       C(26)   -C(27)      1.483(8)      1.489(8)   -0.0060   -0.5303
C(7)    -C(8)       C(27)   -C(28)      1.537(8)      1.544(7)   -0.0070   -0.6585
C(8)    -C(9)       C(28)   -C(29)      1.496(8)      1.491(8)    0.0050    0.4419
C(9)    -C(10)      C(29)   -C(30)      1.284(8)      1.284(8)         0         0
C(10)   -C(11)      C(30)   -C(31)      1.496(8)      1.501(7)   -0.0050   -0.4704
C(11)   -C(12)      C(31)   -C(32)      1.520(8)      1.526(7)   -0.0060   -0.5644
C(14)   -C(15)      C(34)   -C(35)      1.483(7)      1.483(7)         0         0
C(15)   -C(16)      C(35)   -C(36)      1.393(7)      1.395(6)   -0.0020   -0.2169
C(15)   -C(20)      C(35)   -C(40)      1.387(7)      1.383(7)    0.0040    0.4041
C(16)   -C(17)      C(36)   -C(37)      1.375(7)      1.374(7)    0.0010    0.1010
C(17)   -C(18)      C(37)   -C(38)      1.383(8)      1.374(7)    0.0090    0.8467
C(18)   -C(19)      C(38)   -C(39)      1.374(7)      1.372(7)    0.0020    0.2020
C(19)   -C(20)      C(39)   -C(40)      1.378(7)      1.374(7)    0.0040    0.4041

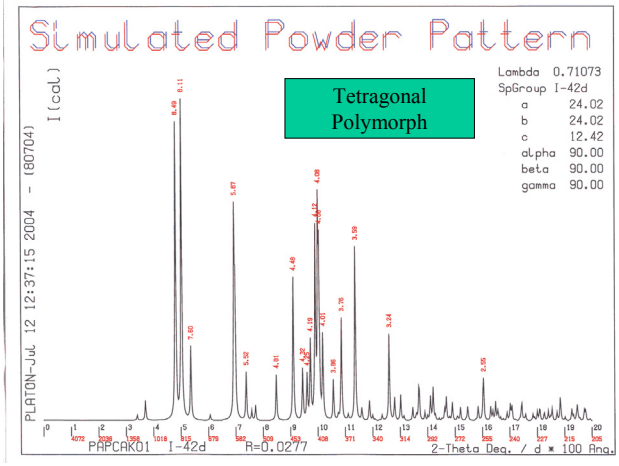
:: RMS Bond Fit =      0.0060 Ang.
```

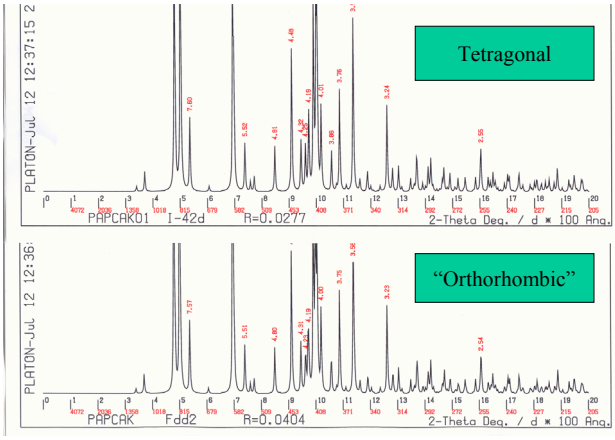


Simulated Powder Patterns

- It is not always apparent that two crystal structures are identical. The assigned unit cell or space group can differ.
- Comparison of the associated calculated powder patterns should solve the issue.
- Example for the CSD:

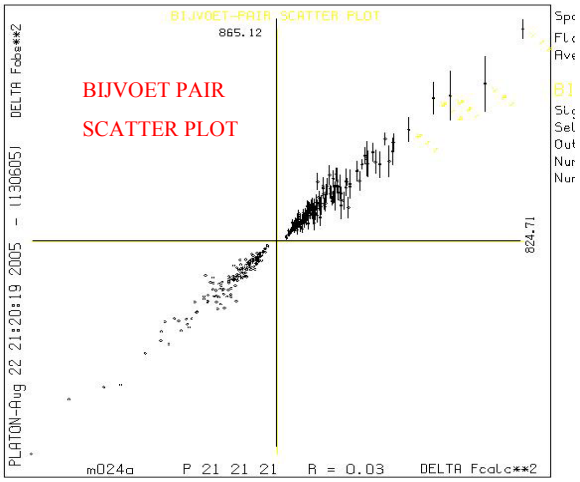






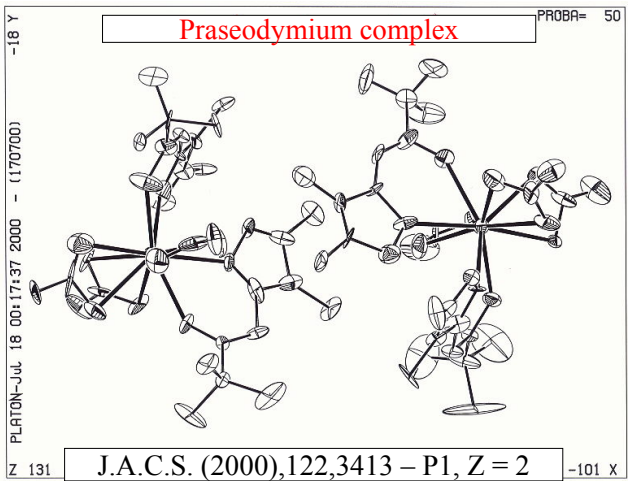
Absolute Structure

- The absolute structure of a compound is normally determined with the refinement of the Flack parameter.
- The value of the Flack parameter can be inconclusive in view of a high su.
- A detailed scatter-plot may be more conclusive.

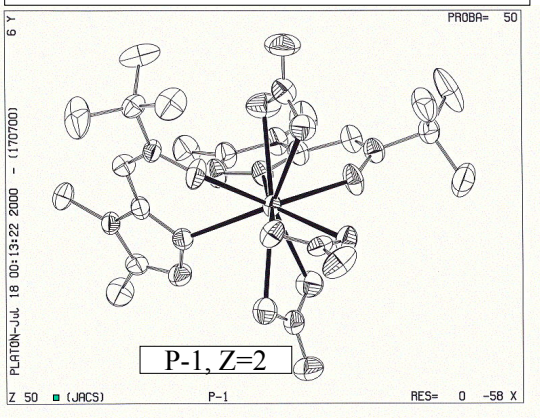


Validation

- ORTEP
- IUCr – CHECKCIF Structure Validation
- FCF- Validation (Completeness & Twinning)



CORRECTLY REFINED STRUCTURE



STRUCTURE VALIDATION

Single crystal structure validation addresses three important questions:

1 – Is the reported information complete?
2 – What is the quality of the analysis?
3 – Is the Structure Correct?

IUCR-CHECKCIF

IUCR-TESTS:
- MISSING DATA, PROPER PROCEDURE, QUALITY

PLATON TESTS:
- SYMMETRY, GEOMETRY, DISPLACEMENT PARAMETERS

ALERT LEVELS:
- ALERT A - SERIOUS PROBLEM
- ALERT B - POTENTIALLY SERIOUS PROBLEM
- ALERT C - CHECK & EXPLAIN

Problems Addressed by PLATON

- Missed Higher Space Group Symmetry
- Solvent Accessible Voids in the Structure
- Unusual Displacement Parameters
- Hirshfeld Rigid Bond test
- Miss-assigned Atom Type
- Population/Occupancy Parameters
- Mono Coordinated/Bonded Metals
- Isolated Atoms

Problems Addressed by PLATON

- Too Many Hydrogen Atoms on an Atom
- Missing Hydrogen Atoms
- Valence & Hybridization
- Short Intra/Inter-Molecular Contacts
- O-H without Acceptor
- Unusual Bond Length/Angle
- CH3 Moiety Geometry

Validation with PLATON

- Details: www.cryst.chem.uu.nl/platon
- Driven by the file **CHECK.DEF** with criteria, ALERT messages and advice.
- Use: **platon –u structure.cif**
- Result on file: **structure.chk**
- Applicable on CIF's and CCDC-FDAT
- FCF-Valid: **platon –V structure.cif**

BAMYEU

Dalton Trans
2003,134-140

Cc

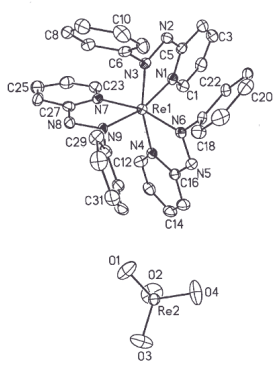
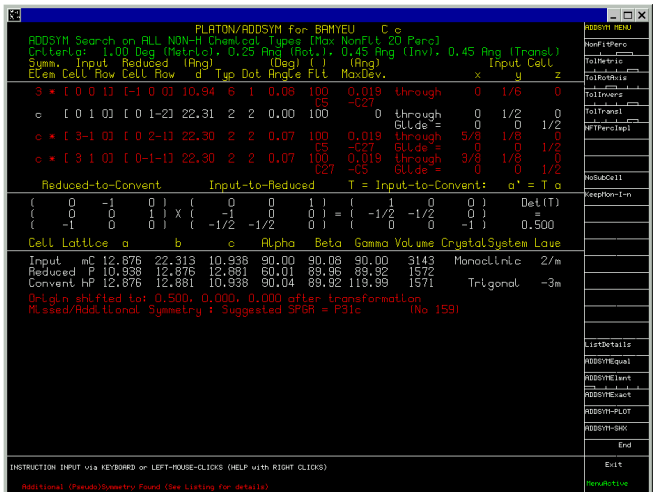
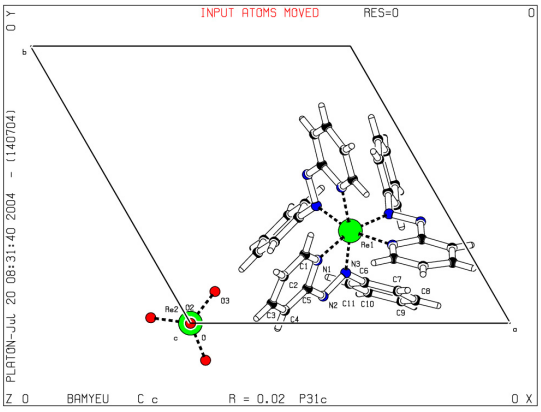


Fig. 4 A perspective view of $[Re(L^3)_2]ReO_4$ **4a**. The atoms are represented by their 30% thermal probability ellipsoids.

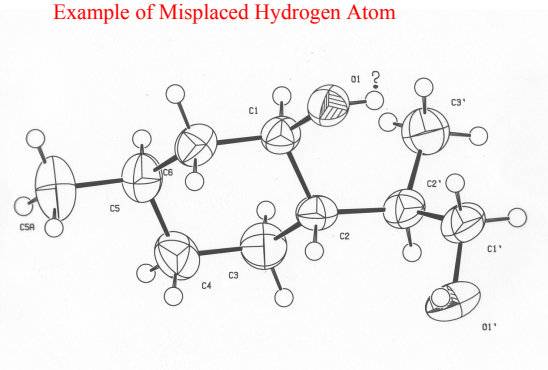




Misoriented O-H

- The O-H moiety is generally, with very few exceptions, part of a D-H..A system.
- An investigation of structures in the CSD brings up many 'exceptions'.
- Closer analysis shows that misplacement of the O-H hydrogen atom is in general the cause.

Example of Misplaced Hydrogen Atom



Two ALERTS related to the misplaced Hydrogen Atom

```
#==============================================================================
# PLATON/CHECK run versus check.def version of 21/06/00       for entry:I
# Data From: publ.cif - Data Type: CIF

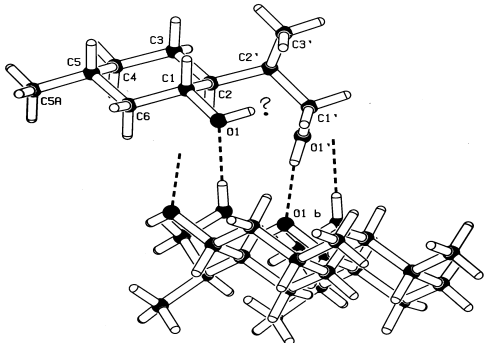
# CELL   0.71069    8.571    6.466    9.850   90.00  106.78   90.00    522.69
# SpaceGroup P21                  Rep: P 21
# MoietyFormula C10 H20 O2
#       Reported ?
# SumFormula C10 H20 O2    Rep: C10 H20 O2
# Mr          =     172.26[Calc],     172.26[Rep]
# Dx,gcm-3    =       1.094[Calc],      1.094[Rep]
# Z           =           2[Calc],          2[Rep]
# Mu (mm-1)   =       0.074[Calc],      0.074[Rep]
# Calculated T limits: Tmin=0.993 Tmin'=0.978  Tmax=0.996
# Reported   Hmax= 10, Kmax=  7, Lmax= 11, Nref= 1935       , Th(max)= 25.76
# Calculated Hmax= 10, Kmax=  7, Lmax= 12, Nref= 1090( 1991), Ratio= 1.78( 0.97)
# R= 0.0500( 1299), wR2= 0.1870( 1935), S = 0.721, Npar= 112
#==============================================================================

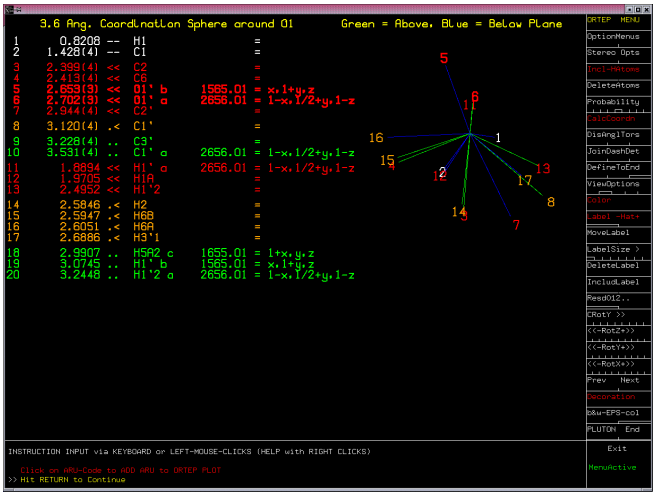
>>> The Following ALERTS were generated <<<

420_ALERT B D-H without acceptor       O(1)   -    H(1)              ?         <<
#==============================================================================
048_ALERT C MoietyFormula not Given ......................          ?
084_ALERT C High R2 value ................................       0.19
086_ALERT C Unsatisfactory S value (Too Low or not given)        0.72
142_ALERT C su on b - axis small or missing (x 100000) ...         30 Ang.
145_ALERT C su on beta      small or missing  (x 10000) ...        30 Deg.
414_ALERT C Short intra D-H..H-X      H(1)    ..  H(12') =       1.93 Ang.   <<
708_ALERT C D-H..A  Calc    170.5(5), Rep    170.00, Dev.       1.05 Sigma
         O1'   -H1'   -O1      1.555   1.555   2.646

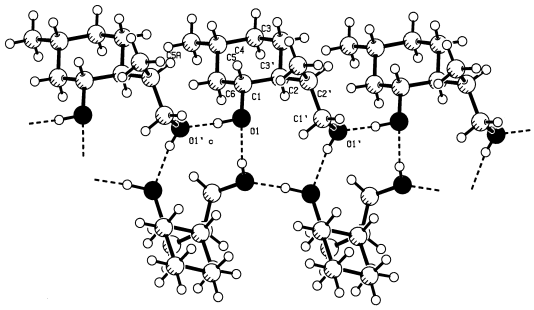
  1 ALERT Level B = Potentially Serious Problem
  7 ALERT Level C = Check & Explain
#==============================================================================
```

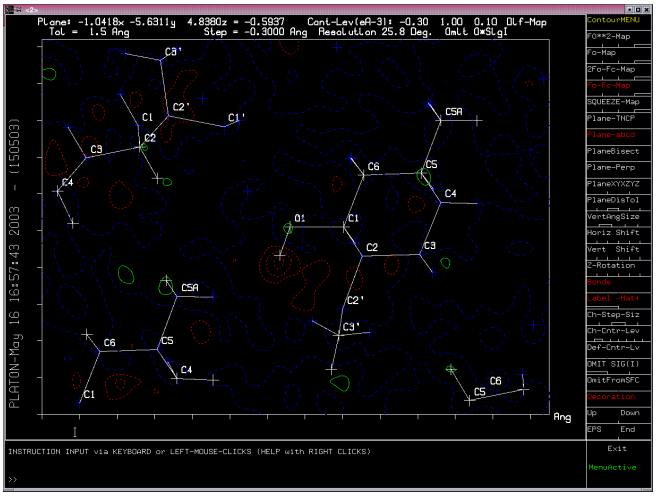
Unsatisfactory Hydrogen Bond Network

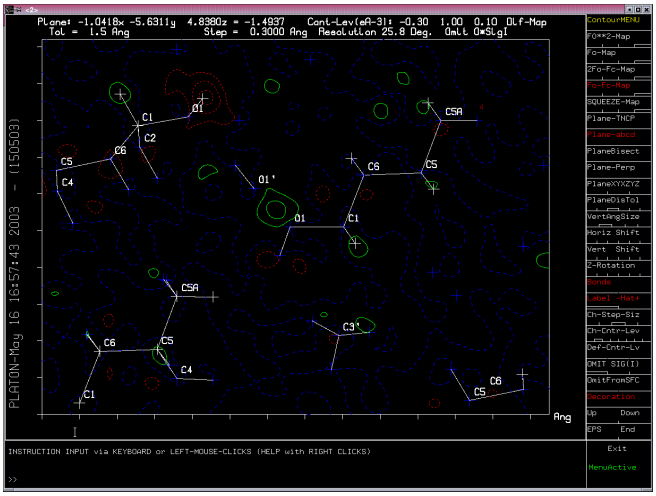




Satisfactory Hydrogen Bond Network with new H-position



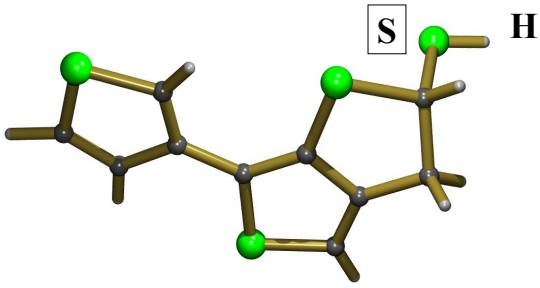




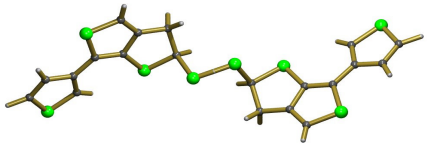
Consult the CSD

- It is a good idea to always consult the CSD for previous reports on structures related to the one at hand.
- The statistics provided by VISTA (CCDC) can be very helpful for this.
- However, such an analysis often shows outliers. Many of those appear to be errors.

Entry from the CAD



But with Space Group Symmetry



=> Different structure with S-S Bond !

Concluding Remarks

- Automatic Validation both ALERTS for potential errors and for interesting features in a structure to be discussed.
- Detailed analysis of intermolecular interactions appears often to be ignored in a service setting.