

FullProf Tutorial

How to use restraints and the rigid body description of molecular fragments in the program FullProf.

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Restraints in FullProf

$$M = M_{ex} + M_{res} = \sum_i w_i \{y_i(obs) - y_i(calc)\}^2 + \chi^2 \left(\sum_j \left\{ \frac{D_j(obs) - D_j(calc)}{\sigma_j} \right\}^2 \right)$$

$$\chi^2 = \frac{1}{N - P} \sum_i w_i \{y_i(obs) - y_i(calc)\}^2$$

The first term corresponds always to experimental data. The observations $y_i(obs)$ may be profile intensities of a powder pattern (or several powder patterns), square of structure factors of single crystal diffraction data, flipping ratios obtained with polarised neutrons, etc.

Restraints in FullProf

$$M = M_{ex} + M_{res} = \sum_i w_i \{y_i(obs) - y_i(calc)\}^2 + \chi^2 \left(\sum_j \left\{ \frac{D_j(obs) - D_j(calc)}{\sigma_j} \right\}^2 \right)$$

$$\chi^2 = \frac{1}{N-P} \sum_i w_i \{y_i(obs) - y_i(calc)\}^2$$

The variables $D_j(obs)$ are provided by the user and correspond to different things: expected distances between pairs of atoms, expected bond angles between triplets of atoms or any linear combination of refined parameters having a prescribed value defined by the user. The corresponding calculated values use a certain number of the P free parameters of the model under study. The standard deviations of the restraints are controlled by the user and may be changed at will. A small standard deviation means a high weight to the particular restraint.

Distance and Angles Restraints in FullProf

$$M_{res} = \chi^2 \left(\sum_j \left\{ \frac{d_j(obs) - d_j(calc)}{\sigma_{dj}} \right\}^2 + \sum_k \left\{ \frac{\theta_k(obs) - \theta_k(calc)}{\sigma_{\theta k}} \right\}^2 \right)$$

Each **Distance** restraint is formed by a line with the following content:

CATOD1 CATOD2 ITnum T1 T2 T3 Dist Sigma

The variables **CATOD1** and **CATOD2** correspond to names of atoms of the asymmetric unit, they should be strictly given with the same names as those appearing in the list of atoms. **ITnum** is the number of a rotational symmetry operator (given in the manual of FullProf) and (**T1**, **T2**, **T3**) corresponds to the associated translational part of the symmetry operator. This symmetry operator is applied to the position (as given in the list) of the second atom to calculate the distance to the first atom. **Dist** is the prescribed distance and **Sigma** is the user supplied standard deviation.

Distance and Angles Restraints in FullProf

$$M_{res} = \chi^2 \left(\sum_j \left\{ \frac{d_j(obs) - d_j(calc)}{\sigma_{dj}} \right\}^2 + \sum_k \left\{ \frac{\theta_k(obs) - \theta_k(calc)}{\sigma_{\theta k}} \right\}^2 \right)$$

The restraints on angles have to be provided in the PCR file after the restraints on distances. Each Angle restraint is formed by a line with the following content:

CATOD1 CATOD2 CATOD3 ITnum1 ITnum2 T1 T2 T3 t1 t2 t3 Angl Sigma

The central atom for the angle calculation is CATOD2. The meaning of the symbols is similar to those of the distance restraint line.

Distance and Angles Restraints in FullProf

An example of the relevant part of a PCR file is shown below.

```
.....
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
1.00000 0.00000 0.09553 0.03018 0.00000 0.00000 0.00000 0.00000
0.00 0.00 701.00 721.00 0.00 0.00 0.00 0.00
! Soft distance constraints:
Ow3 Hw1 3 1.50000 0.50000 0.50000 0.99100 0.00200
Ow3 Hw2 3 1.50000 0.50000 1.50000 0.99100 0.00200
C1 C3 1 0.00000 0.00000 0.00000 1.56000 0.00200
C2 C2 -1 1.00000 1.00000 0.00000 1.56000 0.00200
! Soft angle constraints:
Hw1 Ow3 Hw2 3 1 1.5000-0.5000 0.5000 0.0000 0.0000-1.0000 105.50 0.30
O2 C1 O5 1 1 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 127.44 0.30
O1 C3 O7 1 1 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 127.44 0.30
O4 C2 O6 1 1 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 127.44 0.30
! 2Th1/TOF1 2Th2/TOF2 Pattern # 1
.....
```

Distance and Angles Restraints in FullProf

In the course of the refinement the position parameters of the concerned atoms should satisfy the new user-provided restraints (“additional observations”).

Progressively the prescription is approached depending on the “hardness” of the restraint.

```

CYCLE 1      (Chi2 before: 2.36, RB= 3.78)
=> Distance restraints:      Dobs      Dcalc diff/sigma
(Ow3 - Hw1 ) :      0.99100    1.01588   -12.43862
(Ow3 - Hw2 ) :      0.99100    1.01707   -13.03562
(C1 - C3 ) :      1.56000    1.56089    -0.44292
(C2 - C2 ) :      1.56000    1.52922   15.38748
=> Angle restraints:      Ang_obs Ang_calc diff/sigma
(Hw1 - Ow3 - Hw2 ) :      105.50   104.24    4.20001
(O2 - C1 - O5 ) :      127.44   128.42   -3.28155
(O1 - C3 - O7 ) :      127.44   126.95    1.64124
(O4 - C2 - O6 ) :      127.44   126.42    3.38842

CYCLE 2      (Chi2 after cyc1: 3.21, RB= 6.51)
=> Distance restraints:      Dobs      Dcalc diff/sigma
(Ow3 - Hw1 ) :      0.99100    0.99342   -1.21140
(Ow3 - Hw2 ) :      0.99100    0.97895    6.02278
(C1 - C3 ) :      1.56000    1.56117   -0.58573
(C2 - C2 ) :      1.56000    1.58074  -10.37055
=> Angle restraints:      Ang_obs Ang_calc diff/sigma
(Hw1 - Ow3 - Hw2 ) :      105.50   106.46   -3.20012
(O2 - C1 - O5 ) :      127.44   128.29   -2.83493
(O1 - C3 - O7 ) :      127.44   127.13    1.04340
(O4 - C2 - O6 ) :      127.44   128.51   -3.56923

CYCLE 3      (Chi2 after cyc2: 2.39, RB= 3.93)
CYCLE 4      (Chi2 after cyc3: 2.42, RB= 4.29)
CYCLE 5      (Chi2 after cyc4: 2.34, RB= 3.77)
CYCLE 16     (final Chi2 : 2.34, RB= 3.77)
=> Distance restraints:      Dobs      Dcalc diff/sigma
(Ow3 - Hw1 ) :      0.99100    0.99078    0.11191
(Ow3 - Hw2 ) :      0.99100    0.99203   -0.51472
(C1 - C3 ) :      1.56000    1.56106   -0.52935
(C2 - C2 ) :      1.56000    1.55722    1.39117
=> Angle restraints:      Ang_obs Ang_calc diff/sigma
(Hw1 - Ow3 - Hw2 ) :      105.50   105.69   -0.64191
(O2 - C1 - O5 ) :      127.44   128.34   -3.01193
(O1 - C3 - O7 ) :      127.44   127.07    1.24980
(O4 - C2 - O6 ) :      127.44   127.65   -0.71131

```

Distance and Angles Restraints in FullProf

For creating the strings of distance and angle restraints one can use the program **Bond_Str** or calculate the distance and angles from **FullProf**.

In both cases a file named **CFML_Restraints.tpcr** contains the calculated distances and angles for a particular compound presented exactly as needed for the file PCR. One has to select the appropriate restraint and modify the desired value and sigma.

General Linear Restraints in FullProf

A series of linear restraints corresponds to a set of equations of the form:

$$\sum_i c_i^{(j)} p_{n[i]} = v^{(j)} \pm \sigma^{(j)}$$

In which the **c**-coefficients are fixed by the user, $p_{n[i]}$ correspond to the value of the parameter with number $n[i]$ in the list of free parameters, $v^{(j)}$ is the expected value of the restraint j to be satisfied approximately within the standard deviation $\sigma^{(j)}$.

The meaning of the above set of equations is that the restraint term in the global cost function to be minimised has the form:

$$M_{res} = \chi^2 \sum_j \left\{ \frac{v^{(j)} - \sum_i c_i^{(j)} p_{n[i]}}{\sigma^{(j)}} \right\}^2$$

General Linear Restraints in FullProf

A series of linear restraints corresponds to a set of equations of the form:

$$\sum_i c_i^{(j)} p_{n[i]} = v^{(j)} \pm \sigma^{(j)}$$

Introducing general linear restraints in **FullProf** can be done using the flag **NLI** and adding additional information at the end of the PCR file.

The flag **NLI** corresponds to the number of linear restraints provided by the user.

If **NLI>0**, the program expect to read additional information just after the list given for **Nre** relations (parameters to be constrained in a box) in the PCR file, or after the simulated annealing mode items. This additional information is constituted by the following items:

NLI pairs of lines containing

First line: Name of the restraint (up to 8 characters), number of coefficients, (maximum 10), value of the restraint, sigma of the restraint.

Second line: Up to 10 pairs of (coefficient, parameter number) values.

General Linear Restraints in FullProf

$$\sum_i c_i^{(j)} p_{n[i]} = v^{(j)} \pm \sigma^{(j)}$$

Ti atoms doping a ferrite may be distributed in **3 sites**. The refinement codes of the occupation parameters are: **231.0, 241.0 and 251.0**.

The other element in presence is Fe with codes for the same sites **261.0, 271.0 and 281.0**.

We can introduce **three restraints** corresponding to **full occupancy of the different sites** (**0.375, 1.00 and 0.125**) and another to fix the chemical composition (**0.45 for Ti**).

```
!Set of 4 linear restraints named Site_a, Site_b, Site_c and ChemComp:
!Identifier, number of coeff., value,sigma/List of coeff & Parameters
Site_a      2      0.375000      0.000100
1.0000  23  1.0000  26
Site_b      2      1.000000      0.000100
1.0000  24  1.0000  27
Site_c      2      0.125000      0.000100
1.0000  25  1.0000  28
Chemcomp    3      0.450000      0.000100
1.0000  23  1.0000  24  1.0000  25
```

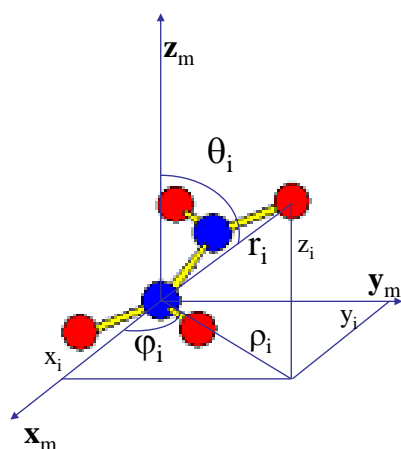
Rigid Bodies in FullProf

The atoms positions of a known molecular fragment are not independent variables. The whole object may be treated as a rigid body, so that we need only six free parameters for defining completely its position in the unit cell.

We have two Cartesian reference frames:

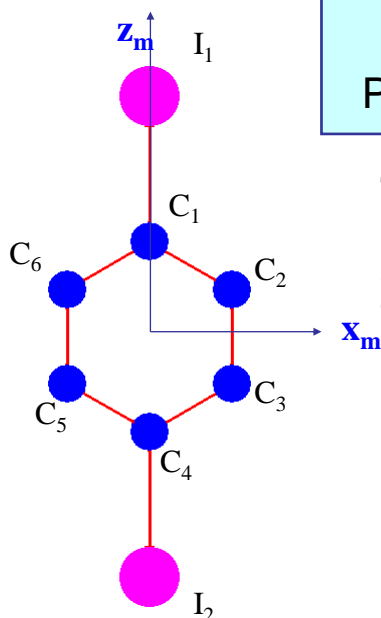
- (1) Internal: it may be arbitrarily defined
- (2) Crystallographic: related to crystallographic the unit cell

Rigid Bodies in FullProf: Molecular reference frame



The internal coordinates of the atoms constituting the rigid group can be given in the following ways (all distances are given in Å and angles in radians or degrees):

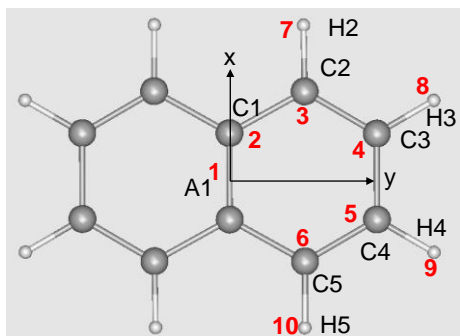
- 1: Spherical coordinates: (r_i, θ_i, ϕ_i)
- 2: Cartesian coordinates (x_i, y_i, z_i)
- 3: Cylindrical coordinates (ρ_i, ϕ_i, z_i)
- 4: Z-matrix formulation



Example: Para-di-Iodo-Benzene

The internal coordinates of the atoms constituting the rigid group given in spherical coordinates: (r_i, θ_i, ϕ_i)

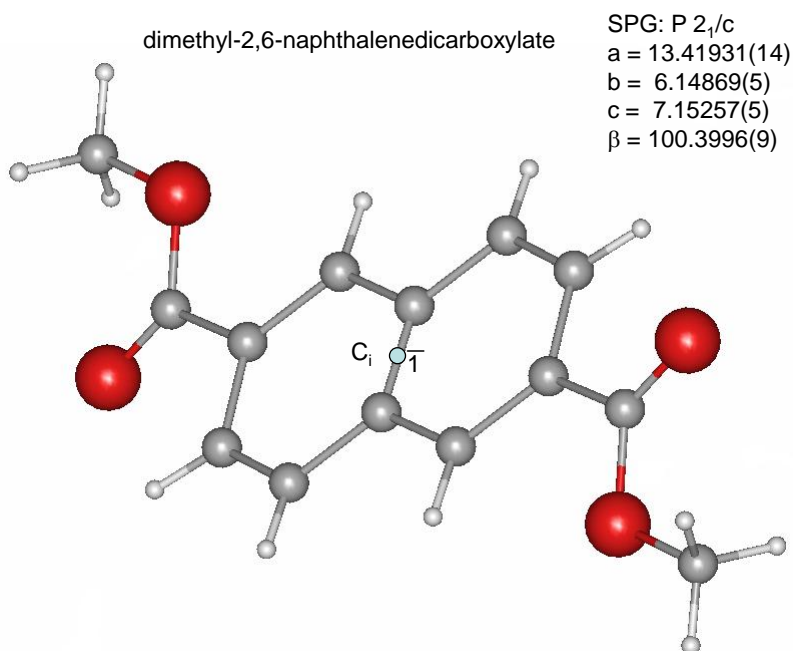
	$(r_i,$	$\theta_i,$	$\phi_i)$
I_1	: (3.500,	0.0000,	0.00)
C_1	: (1.394,	0.0000,	0.00)
C_2	: (1.394,	$1.0472(\pi/3),$	0.00)
C_3	: (1.394,	$2.0944(2\pi/3),$	0.00)
I_2	: (3.500,	$3.1416(\pi),$	0.00)
....			

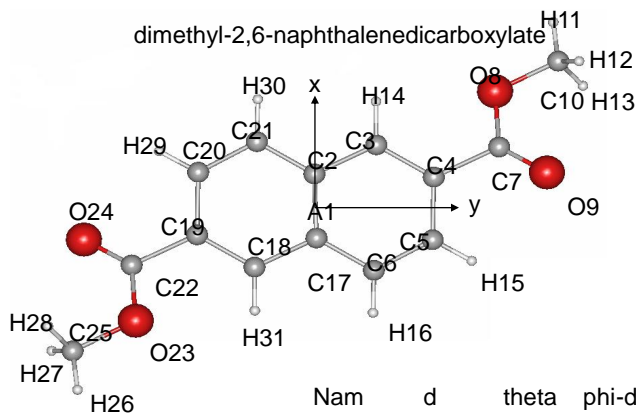
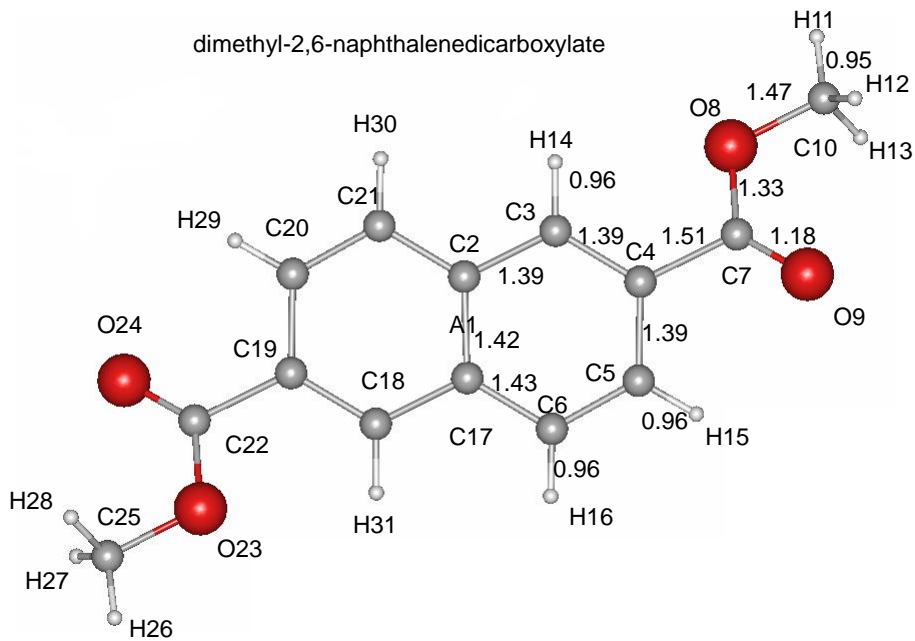


Centro-symmetric molecule
Only half molecule is needed
 $d=1.4$, $d'=1.1$

Z-matrix

#	Nam	dist	theta	dihedral	N1	N2	N3
1	A1	0	0	0	0	0	0
2	C1	d/2	0	0	1	0	0
3	C2	d	120	0	2	1	0
4	C3	d	120	0	3	2	1
5	C4	d	120	0	4	3	2
6	C5	d	120	0	5	4	3
7	H2	d'	120	180	3	2	1
8	H3	d'	120	180	4	3	2
9	H4	d'	120	180	5	4	3
10	H5	d'	120	180	6	5	4



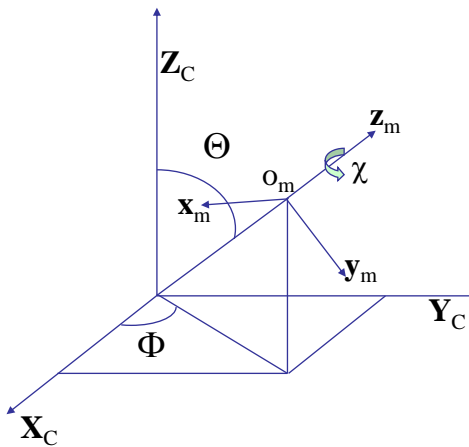


Z-matrix

Centro-symmetric molecule
Only half molecule is needed
d=1.4, d'=1.50, d''=1.30

Nam	d	theta	phi-dih	N1	N2	N3
A1	0	0	0	0	0	0
C2	d/2	0	0	1	0	0
C3	d	120	0	2	1	0
C4	d	120	0	3	2	1
C5	d	120	0	4	3	2
C6	d	120	0	5	4	3
C7	d'	120	180	4	3	2
O8	d''	120	0	7	4	3
O9	d''	120	180	7	4	3
C10	d'	120	0	8	7	9

Rigid Bodies in FullProf: Crystal reference frame



The molecular reference frame is placed in the crystal reference frame as shown in the figure.

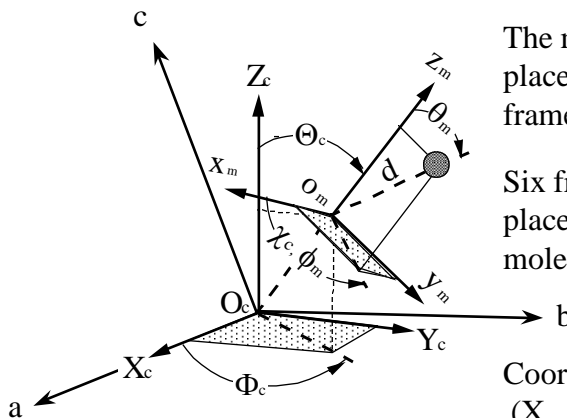
Six free parameters are needed to place in an arbitrary position the molecular frame.

Coordinates of the origin:

Cartesian Fractional
 $(x_o, y_o, z_o) \Rightarrow (X_o, Y_o, Z_o)$

(Θ, Φ, χ) Pseudo-Euler angles

Rigid Bodies in FullProf: Crystal reference frame



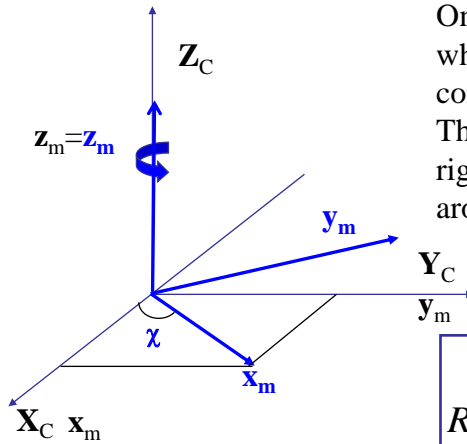
The molecular reference frame is placed in the crystal reference frame as shown in the figure.

Six free parameters are needed to place in an arbitrary position the molecular frame.

Coordinates of the origin:
 (X_o, Y_o, Z_o) Cartesian or
 Fractional coordinates

(Θ, Φ, χ) Euler angles

Rigid Bodies in FullProf: Interpretation of the Euler angles

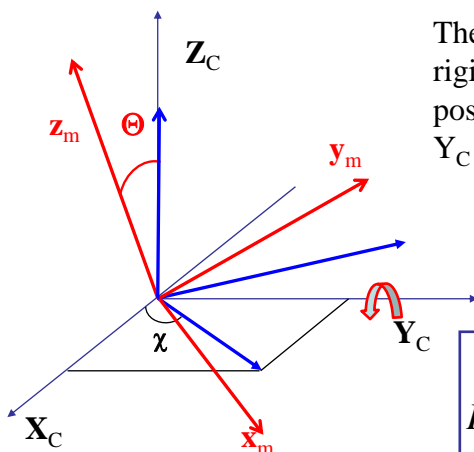


One can consider an initial position where the two Cartesian frames coincide.

The first rotation, χ , applied to the rigid body rotates the internal frame around the Z_C axis

$$R_{\chi}(Z_C) = \begin{pmatrix} \cos \chi & -\sin \chi & 0 \\ \sin \chi & \cos \chi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

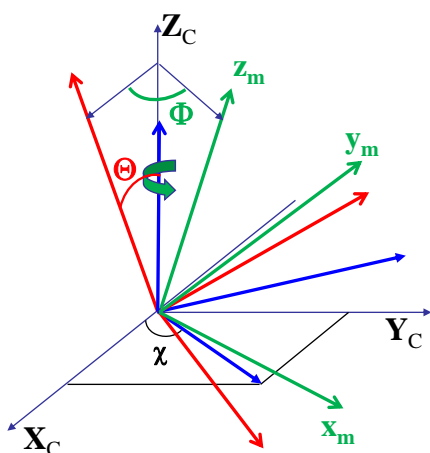
Rigid Bodies in FullProf: Interpretation of the Euler angles



The second rotation, Θ , applied to the rigid body rotates the previous position of the rigid body around the Y_C axis

$$R_{\Theta}(Y_C) = \begin{pmatrix} \cos \Theta & 0 & \sin \Theta \\ 0 & 1 & 0 \\ -\sin \Theta & 0 & \cos \Theta \end{pmatrix}$$

Rigid Bodies in FullProf: Interpretation of the Euler angles



The third rotation, Φ , applied to the rigid body rotates the previous position of the rigid body around the Z_C axis

$$R_{\Phi}(Z_C) = \begin{pmatrix} \cos \Phi & -\sin \Phi & 0 \\ \sin \Phi & \cos \Phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Rigid Bodies in FullProf PCR file

To access the rigid body formulation one must put **JBT=4**

A free atom must not contain numbers in the label

A rigid body group has the same two letters label plus a number from 1 to 99

Rigid Bodies in FullProf: PCR file

```

Naphthalene D9
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
10 0 0 0.0 0.0 1.0 4 4 0 0 0 0.0 0 0 0
!
P 21/a
!Atom Typ x y z B Occ P6 THETA PHI Spc
! dist Bond-ang Torsion-ang X0 Y0 Z0 CHI Connectiv DEG KIND
NA1 ZE 0.00000 0.00000 0.00000 0.50000 1.00000 4.00000 111.260 -152.972 0
0.00000 0.00 0.00 0.00 0.00 0.00 0.00 11.00 21.00 3
0.00000 0.00 0.00 0.00 0.00 0.00 0.00 31.00
NA2 C 0.04763 -0.10530 0.03761 0.31749 1.00000 1 0 0 0
0.71000 0.000 0.000
0.00 0.00 0.00
NA3 C 0.11120 -0.16730 0.22264 0.44746 1.00000 2 1 0 0
0.00 0.00 0.00 71.00 0.00
1.42000 120.000 0.000
0.00 0.00 0.00
NA4 C 0.07955 -0.01869 0.33247 0.61211 1.00000 3 2 1 0
0.00 0.00 0.00 81.00 0.00
1.42000 120.000 0.000
0.00 0.00 0.00
NA5 C -0.01565 0.19194 0.25729 0.59487 1.00000 4 3 2 0
0.00 0.00 0.00 91.00 0.00
1.42000 120.000 0.000
0.00 0.00 0.00
. . . . .

```

Rigid Bodies in FullProf: PCR file

```

Naphthalene D9 (Rigid Body Spherical coordinates)
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
10 0 0 0.0 0.0 1.0 4 4 0 0 0 256.348 0 0 1
!
P 21/a
!Atom Typ x y z B Occ P6 THETA PHI Spc
! r/xc/rho the/yc/phi phi/zc/z X0 Y0 Z0 CHI P16:SAT DEG KIND
NA1 ZE 0.00000 0.00000 0.00000 0.50000 1.00000 1.00000 110.720 -153.026 0
0.00 0.00 0.00 0.00 0.00 0.00 0.00 11.00 21.00 0
0.00000 0.00 0.00 0.00 0.00 0.00 0.00 31.00
NA2 C 0.04848 0.00000 0.03792 0.42742 1.00000 0 0 0 0
0.71879 90.000 0.000
0.00 0.00 0.00
NA3 C 0.11318 0.16653 0.22257 0.57700 1.00000 0 0 0 0
0.00 0.00 0.00 71.00 0.00
1.87412 90.000 40.893
0.00 0.00 0.00
NA4 C 0.08224 -0.01794 0.32981 0.65930 1.00000 0 0 0 0
0.00 0.00 0.00 81.00 0.00
2.52915 90.000 73.898
0.00 0.00 0.00
NA5 C -0.01238 0.18997 0.25581 0.60049 1.00000 0 0 0 0
0.00 0.00 0.00 91.00 0.00
2.52915 90.000 106.102
0.00 0.00 0.00
. . . . .

```

Rigid Bodies in FullProf: PCR file

```

!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ      Nvk Npr More
  6  0  0  1.0 0.0 0.0  4  0  0  0  12      1335.628  0  5  0

!
P b c a
!Atom Typ      x      y      z      B      Occ      P6      THETA      PHI      Spc
!      d      theta      phi      X0      Y0      Z0      CHI      P16:SAT
Pi1  I      0.17416  0.04667  0.31061  0.00000  1.00000  -5.00000  1.00200  0.11300  0
      0.00      0.00      0.00      0.00      0.00      0.00      0.00      185.00      195.00
      3.50000  0.00000  0.00000  0.00000  0.00000  0.00000  -0.44622  0.00000
      0.00      0.00      0.00      0.00      0.00      0.00      205.00
Pi2  C      0.06937  0.01859  0.12371  0.00000  1.00000
      0.00      0.00      0.00      0.00      0.00
      1.39400  0.00000  0.00000
      0.00      0.00      0.00
Pi3  C      0.07282  -0.05408  -0.08933  0.00000  1.00000
      0.00      0.00      0.00      0.00      0.00
      1.39400  1.04720  0.00000
      0.00      0.00      0.00
Pi4  C      0.00345  -0.07266  -0.21304  0.00000  1.00000
      0.00      0.00      0.00      0.00      0.00
      1.39400  2.09440  0.00000
      0.00      0.00      0.00
Pi5  D      0.13007  -0.09659  -0.15956  0.00000  1.00000
      0.00      0.00      0.00      0.00      0.00
      2.49000  1.04720  0.00000
      0.00      0.00      0.00
Pi6  D      0.00616  -0.12979  -0.38054  0.00000  1.00000
      0.00      0.00      0.00      0.00      0.00
      2.49000  2.09440  0.00000
      0.00      0.00      0.00
  
```

```

Para-di-Iodo-Benzene (Sim.Annealing)
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ      Nvk Npr More
  6  0  0  1.0 0.0 0.0  4  4  0  0  0      0.00  0  0  0

!
P b c a
!Atom Typ      x      y      z      B      Occ      P6      THETA      PHI      Spc
!      d      theta      phi      X0      Y0      Z0      CHI      P16:SAT
Pi1  I      0.17439  0.04548  -0.30989  0.00000  1.00000  1.00000  2.05548  0.06590  0
      0.00      0.00      0.00      0.00      0.00      0.00      0.00      11.00      21.00
      3.50000  -0.09100  -0.09100  0.00000  0.00000  0.00000  -2.62905  0.00000
      0.00      0.00      0.00      0.00      0.00      0.00      31.00
Pi2  C      0.06946  0.01811  -0.12342  0.00000  1.00000
      0.00      0.00      0.00      0.00      0.00
      1.39400  -0.09100  -0.09100
      0.00      0.00      0.00
. . . . .

! Limits for selected parameters (+ steps & BoundCond for SA):
  1  0.0000  3.1416  0.5000  1  Theta
  2 -3.1416  3.1416  0.5000  1  Phi
  3 -3.1416  3.1416  0.5000  1  Chi
! T_ini  Anneal  Accept  NumTemps  NumThCyc  InitConf
  8.000  0.900  0.020  80  0  0
! NCyclM  Nsolu  Num_Ref  Nscalef  NAlgor
  200  1  71  1  1
  
```

Part of a PCR file showing the use of the simulated annealing method to determine the orientation of the molecule of $I_2C_6D_4$. The center of the molecule is at the origin and only three angles are needed to fix the position of the molecule in the unit cell.

```

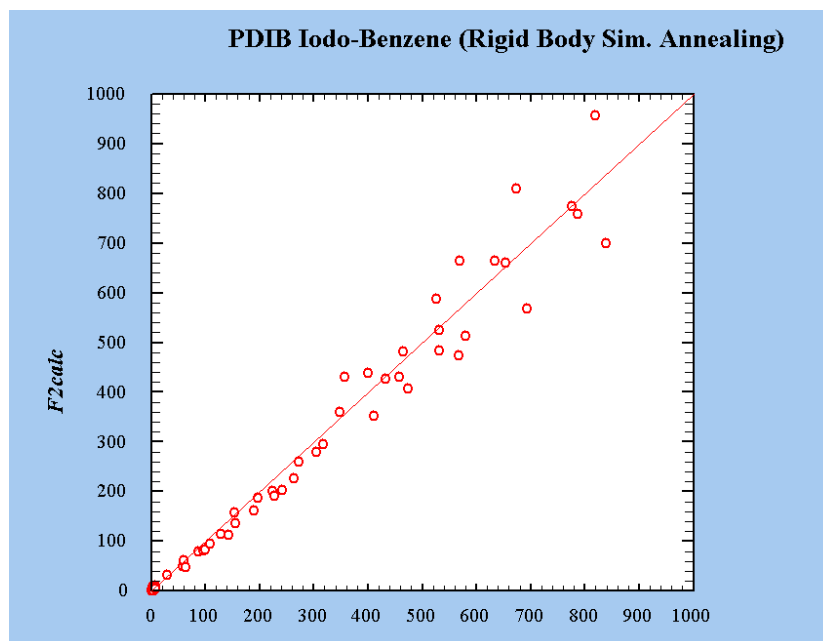
=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****
=> Initial configuration cost:      77.53
=> Initial configuration state vector:
=>      Theta      Phi      Chi
=>      1          2          3
=>      1.3807      2.4672     -3.0110
=> NT:  1 Temp:  8.00 (%Acc): 23.50 <Step>:  5.2360 <R-factor>: 44.4302
=> NT:  6 Temp:  4.72 (%Acc): 30.50 <Step>:  0.3496 <R-factor>: 23.8774
=> NT: 11 Temp:  2.79 (%Acc): 39.33 <Step>:  0.1440 <R-factor>: 13.4990
=> NT: 21 Temp:  0.97 (%Acc): 38.50 <Step>:  0.0530 <R-factor>:  6.3417
=> NT: 33 Temp:  0.27 (%Acc): 36.17 <Step>:  0.0179 <R-factor>:  4.3854

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:      1
=> -> Configuration parameters (      71 reflections):
=> Sol#: 1 RF2=      3.928 ::
=>      Theta      Phi      Chi
=>      1          2          3
=>      0.9401      0.1464      2.7477

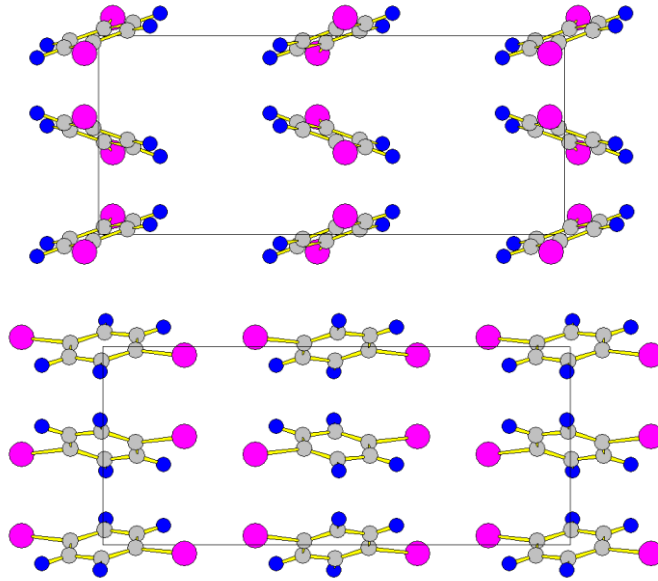
=>      CPU Time:      25.177 seconds
=>      0.420 minutes

```

Simplified screen capture of the *FullProf* output when running in the simulating annealing mode for the example of figure 3. The first picture of the structure corresponds to the starting configuration. The final result is also displayed.



Initial configuration: RF= 77.53%



Final configuration: RF = 3.93%