QUESTIONNAIRE FOR STRUCTURE DETERMINATION BY POWDER DIFFRACTOMETRY ROUND ROBIN

Submitted by

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Only the solution of the second sample has been attempted. The quality of the experimental data is sufficient to solve the crystal structure.

1. Preliminary work

1.1 Did you obtain additional information from the chemical formula ? - No

Remark: The molecular formula was taken from transparency 30 of A. Le Bail's talk on trends in SDPD (http://www.cristal.org/iniref/ecm18/t30.gif)

1.2 Did you obtain additional information from the powder pattern ? - Yes

The program Powder Fit was used to determine accurate lattice parameters, profile parameters and background coefficients from the synchrotron powder pattern. Powder Fit is part of the Cerius2 software package.

1.3 Did you extract the structure factors ? - No

2 Structure solution

2.1 Did you use direct methods ? - No

2.2 Did you use Patterson methods ? - No

2.3 Did you use another method ? - Yes

2.3.1 If yes, which method(s) ?

The structure was solved using a direct space approach and a Monte Carlo/simulated annealing method. Molecules are treated as rigid bodies with a limited number of internal torsional degrees of freedom. The quality of the model structure is determined by a full profile comparison with the experimental powder diffraction pattern. Minima of the Rwp factor are located by rigid body Rietveld refinement, thus allowing for relatively high temperatures in the simulated annealing procedure.

In a first step, the structure was solved with a total of 11 degrees of freedom. The initial temperature was chosen high enough to overcome all barriers on the Rwp hypersurface. The comparison with the synchrotron powder pattern was carried out in the angular range from 2.12° to 17°, covering a total of 133 reflections. Hydrogen atoms were ignored in the calculation of the peak intensities. The best Rwp factor obtained had a value of 6.04% (All cited Rwp values have been calculated without background subtraction.). In a second step, the solution was improved by searching the Rwp hypersurface in the vincinity of the minimum located in the first step. For this purpose, some of the intramolecular bonds were cut and the numbers of torsional degrees of freedom was increased. A Monte Carlo/simulated annealing run at low temperature with a small Monte Carlo step width and a total of 27 degrees of freedom resulted in an Rwp factor of 2.87%. The comparison with the experimental powder spectrum was performed for the full

angular range from 2.12° to 40.0°. Hydrogen atoms were now taken into account in the calculation of the diffraction intensities.

2.3.2 Which program(s) did you use ?

The structure was solved using the program Powder Solve, implemented in the Cerius2 software package.

2.4 Did you first locate the whole structure – Yes
2.4.3 Was the initial model derived from the molecular formula ? – Yes

The initial molecular geometry was derived from the molecular formula by force field and semi-empirical calculations. Energy minimisations were carried out using the Dreiding 2.21 force field, the COMPASS force field and the PM3 hamiltonian, leading to three different starting geometries. The crystal structure was solved with the result of the Mopac PM3 calculation as a starting point.

2.4.4 Were the initial atomic coordinates taken from a known structure ? – No

3 Structure completion

Since the whole structure was located in the structure solution step, structure completion was not necessary.

4 Final refinement

Three alternations of rigid body Rietveld refinement and lattice energy minimisation were used in the final refinement step. The rigid body refinement was carried out with Powder Solve using 5 rigid bodies with a total of 11 internal torsional degrees of freedom. The lattice energy minimisations based on the COMPASS forcefield were limited to a small number of minimisation steps, thus assuring a compromise between a low Rwp factor and reasonable bond lengths and bond angles. The last Rietveld refinement step produced a Rwp factor of 2.42%. The subsequent lattice energy minimisation was stopped when the Rwp factor reached a value of 2.67%. Finally, the hydrogen bonded network was analysed. Some of the torsion angles defining the orientation of the OH groups were slightly adjusted to obtain a more favorable orientation for hydrogen bonding. This modification led to a final Rwp factor of 2.70% (Rp=2.0%).
At the present stage, Powder Solve does not allow the refinement of thermal parameters and the calculation of standard deviations. All thermal parameters were set to zero. The following atomic coordinates were obtained:

NAME	X	Y	Z
C1	0.66562	0.12218	-0.39185
C2	0.56719	0.19782	-0.37715
C3	0.46574	0.16839	-0.32059
C4	0.48365	0.07626	-0.26126
C5	0.52054	-0.01593	-0.31407
C6	0.62879	0.01030	-0.37581
C7	0.36954	0.05111	-0.20873
C8	0.29390	-0.03113	-0.22477
C9	0.31668	-0.11241	-0.29584
C10	0.41303	-0.07088	-0.35872
C11	0.18122	-0.04754	-0.17332
C12	0.10320	-0.13919	-0.19698
C13	0.10974	-0.18298	-0.27782
C14	0.19814	-0.13769	-0.34321
C15	0.01895	-0.17597	-0.13737

C16	-0.05442	-0.26014	-0.15697
C17	-0.04676	-0.30567	-0.23637
C18	0.03382	-0.26669	-0.29641
C19	0.21009	-0.21028	-0.42090
C20	0.56525	0.29162	-0.41612
C21	0.80850	-0.01680	-0.27748
C22	0.71608	-0.16433	-0.36146
O1	0.00132	-0.13085	-0.05839
O2	0.15712	-0.04022	-0.37577
O3	0.14787	0.01176	-0.11693
O4	0.34471	0.11668	-0.14195
O5	0.36794	0.21544	-0.31471
O6	0.58297	0.10232	-0.20556
O7	0.76187	0.13836	-0.42857
O8	0.46541	0.35105	-0.41288
N1	0.65508	0.33576	-0.46066
N2	0.74387	-0.05052	-0.35670
H1	0.21760	-0.29338	-0.40522
H2	0.28773	-0.19002	-0.46189
H3	0.12884	-0.20105	-0.46095
H4	0.08807	-0.05209	-0.41011
H5	-0.12044	-0.28934	-0.11047
H6	-0.10801	-0.37029	-0.25207
H7	0.40524	0.11026	-0.09822
H8	0.36758	-0.02116	-0.40665
H9	0.85330	0.05789	-0.29099
H10	0.87622	-0.07639	-0.26248
H11	0.74397	-0.00888	-0.22490
H12	0.80114	-0.20787	-0.35462
H13	0.67468	-0.17899	-0.42401
H14	0.65168	-0.18541	-0.31133
H15	0.47828	0.41115	-0.44744
H16	0.65055	0.40842	-0.48355
H17	0.55624	0.09247	-0.14730
H18	0.03362	-0.30295	-0.35968
H19	0.03105	-0.06157	-0.06244
H20	0.54873	-0.07041	-0.26385
H21	0.35283	-0.18457	-0.26691
H22	0.44976	-0.13789	-0.39438
H23	0.60596	-0.01311	-0.44167
H24	0.72902	0.29816	-0.48253
H25	0.80589	-0.03518	-0.40802
CL1	-0.42735	-0.92106	-0.00103

At this stage, the refined structure was compared to the structure shown on transparency 30 of A. Le Bail's talk on trends in SDPD, and it was noticed that the (OH)C(NH2) group of the refined structure was rotated by 180° with respect to the depicted one. Indeed, turning the (OH)C(NH2) group by 180° significantly improved the Rwp factor, and after one step of rigid body Rietveld refinement, lattice energy minimisation and adjustment of the OH torsion angles a final Rwp factor of 2.15% was obtained (Rw=1.66%). The corresponding atomic coordinates are presented below.

NAME	X	Y	Z
C1	0.66040	0.12422	-0.39107
C2	0.56103	0.19937	-0.37554
C3	0.46084	0.16846	-0.31900
C4	0.48227	0.07579	-0.26131
C5	0.52133	-0.01644	-0.31387
C6	0.62902	0.01130	-0.37525
C7	0.36966	0.04916	-0.20876

C8	0.29366	-0.03209	-0.22552
C9	0.31567	-0.11177	-0.29736
C10	0.41359	-0.07079	-0.35934
C11	0.18172	-0.04821	-0.17355
C12	0.10422	-0.13973	-0.19782
C13	0.11044	-0.18326	-0.27875
C14	0.19694	-0.13715	-0.34475
C15	0.02189	-0.17756	-0.13731
C16	-0.05019	-0.26283	-0.15643
C17	-0.04325	-0.30772	-0.23617
C18	0.03542	-0.26758	-0.29694
C19	0.20933	-0.20914	-0.42263
C20	0.56051	0.29254	-0.41541
C21	0.81095	-0.01770	-0.27809
C22	0.71765	-0.16355	-0.36357
O1	0.00432	-0.13289	-0.05847
O2	0.15176	-0.03886	-0.37321
O3	0.15017	0.00849	-0.11507
O4	0.34318	0.11461	-0.14261
O5	0.36221	0.21452	-0.31193
O6	0.58327	0.10140	-0.20677
O7	0.75457	0.14346	-0.42925
O8	0.65587	0.32826	-0.45965
N1	0.46572	0.35784	-0.41500
N2	0.74533	-0.04954	-0.35751
H1	0.21521	-0.29231	-0.40687
H2	0.28783	-0.18927	-0.46295
H3	0.12878	-0.19885	-0.46316
H4	0.08932	-0.05138	-0.41518
H5	-0.11447	-0.29351	-0.10915
H6	-0.10352	-0.37334	-0.25114
H7	0.39976	0.10598	-0.09727
H8	0.36867	-0.01992	-0.40665
H9	0.86470	0.05200	-0.29319
H10	0.87105	-0.08193	-0.25995
H11	0.74580	-0.00184	-0.22708
H12	0.79839	-0.20772	-0.34461
H13	0.69354	-0.17988	-0.43008
H14	0.64048	-0.18277	-0.32247
H15	0.72088	0.27963	-0.45540
H16	0.46502	0.42475	-0.44853
H17	0.55797	0.09855	-0.14837
H18	0.03466	-0.30361	-0.36024
H19	0.03762	-0.06457	-0.06170
H20	0.55070	-0.07199	-0.26470
H21	0.35190	-0.18326	-0.26730
H22	0.44877	-0.13808	-0.39541
H23	0.60666	-0.01096	-0.44139
H24	0.38740	0.34826	-0.38386
H25	0.80691	-0.03343	-0.40901
CL1	-0.42807	-0.92052	-0.00195

It has to be pointed out that the right orientation of the (OH)C(NH2) group has been missed due to the small amount of time spend on the final structure refinement. The hydroxy group and the amino group carry the same number of electrons and have comparable distances to the central carbon atom. Therefore it was an oversight not to calculate the Rwp factor as a function of the torsion angle of the (OH)C(NH2) group, and the right orientation could have easily been found. The Monte Carlo / Simulated annealing run that solved the structure did not find the correct orientation, because the end temperature was significantly higher than the difference of the Rwp factors of both orientations. The

subsequent low temperature Monte Carlo / Simulated annealing run missed out the right orientation, because the temperature was not high enough to pass the barrier between the two conformations on the Rwp hypersurface. This example demonstrates the power of fully automated and integrated software for structure solution and refinement, but it also shows the importance of chemical and crystallographic expertise in applying such software.

5 CPU requirements

The high temperature simulated annealing run was performed on a Silicon graphics O2 workstation with a R5000 processor running at 180 MHz. With the molecular geometry determined by a MOPAC calculation, the structure solution took a couple of hours.

The low temperaturesimulated annealing run was carried out on a Silicon graphics Indigo2 workstation with a R10000 processor running at 195 MHz. The run took several hours.