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Supporting information for article:

A new crystalline form of αβ-d-lactose prepared by oven drying a concentrated aqueous solution of d-lactose

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Table S1 Lattice parameters for the monoclinic form of αβ-D-lactose reported in this work (αβ-L_M, $P2_1$, T = 100 K) and the previously reported triclinic form (αβ-L_T, $P1$, T = 120 K).

	a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	V (Å^3)
αβ-L_M	5.0044(3)	38.6364(14)	7.6007(4)	90	106.200(5)	90	1411.26(13)
αβ-L_T	5.030(3)	7.593(5)	19.374(12)	81.026(10)	85.044(9)	74.247(9)	702.7(8)

S1. Pawley refinement of low-T single-crystal lattice parameters against room-temperature PXRD data

A frequently encountered scenario in powder diffraction is one where PXRD data have been collected at room temperature and the experimentalist wishes to fit that data using either a Pawley or Rietveld refinement of the lattice parameters / atomic coordinates of a known single-crystal structure. If the single-crystal structure was determined at room temperature, then this is usually a straightforward process. If however, as is more usually the case, the single-crystal structure was obtained at low temperature (typically T < 150 K) then the refinement of the lattice parameters can often get trapped in a local minimum; the thermal expansion of the lattice means that observed PXRD peaks can occur at some distance from the 2θ positions predicted from the single-crystal lattice constants. Further complications can arise, as was the case in this work, where the PXRD data are not phase pure.

We have found that an effective approach to overcoming the "local minimum" problem is to employ multiple random start points for the Pawley refinement, where those random start points are clustered around the single-crystal lattice parameters. This can easily be achieved in the *TOPAS* software package by utilising the `continue_after_convergence` command in combination with the `val_on_continue` command. This is most easily illustrated by comparing the commands needed for lattice parameter refinement in a conventional Pawley fit, with those for the random start point approach.

Conventional Pawley refinement

```
hkl_Is              ' specifies Pawley run with variable reflection intensity values
      phase_name "Lactose new monoclinic form"
      a @  5.0044 ' the @ sign indicates a variable parameter in the refinement
      b @  38.6364
      c @  7.6007
      al 90.000
      be @  106.200
      ga 90.000
```

This input instructs TOPAS to perform a least-squares refinement of the lattice parameters, allowing reflection intensities to vary as is normal in a Pawley refinement. The refinement converges to the nearest minimum in parameter space. If the fit to the data is poor, it is possible that the lattice parameter refinement is trapped in a local minimum, due to the magnitude of the differences between the low-T and room temperature lattice constants.

Random start point approach

```
continue_after_convergence
hkl_Is
       phase_name "Lactose monoclinic"
       a @  5.0044         val_on_continue = Rand(4.8, 6.2);
       b @  38.6364        val_on_continue = Rand(38.4, 38.8);
       c @  7.6007         val_on_continue = Rand(7.4, 7.8);
       al 90.000
       be @  106.200       val_on_continue = Rand(105, 107);
       ga 90.000
```

This input instructs *TOPAS* to perform a least-squares refinement of the lattice parameters, allowing reflection intensities to vary as is normal in a Pawley refinement. The refinement converges to the nearest minimum in parameter space, but then (a) as a consequence of the inclusion of the `continue_after_convergence` command, it restarts using a new set of values for *a*, *b*, *c* and β specified by (b) the `val_on_continue` command, with the exact values generated at random from within the ranges specified by the `Rand` command.

This next refinement then proceeds to the nearest minimum in parameter space, and the process repeats until interrupted by the user. *TOPAS* keeps track of the lowest R_{wp} value obtained in this series of Pawley refinements and when interrupted, returns the corresponding best set of lattice parameters and the associated plot of the fit to the data. It is then a simple matter to ascertain if the fit is sufficiently good to conclude that the lattice parameters have refined to their correct room temperature values. Some experimentation may be required in terms of the width of the ranges that are sampled, in order to achieve a satisfactory fit to the data.