Supporting information for article:

On the correlation between hydrogen bonding and melting points in the inositols

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Electronic Supporting Information

S1. Elemental analysis

Calculated for C₆H₁₂O₆ (%): C, 40.00; H, 6.71.
Found for D-1-A: C, 39.74; H, 6.37.
Found for rac-1: C, 39.70; H, 6.72.
Found for 2-A: C, 40.08; H, 6.80.
Found for 5-E: C, 39.76; H, 6.58.
Found for 7-C: C, 39.92; H, 6.61.

S2. Rietveld refinements

The isostructurality (bar a reflection) of the crystal structure of D-(+)-chiro-inositol with that of L-(-)-chiro-inositol was confirmed through comparison of the experimental powder diffraction pattern of D-1-A with the powder pattern simulated from the single crystal structure of L-1-A. A crystal structure for D-1-A was obtained by starting from the single crystal structure of L-1-A and multiplying all atomic coordinates by -1. The resulting crystal structure was Rietveld refined with TOPAS-Academic 4.1. The positions of the hydrogen atoms were energy-optimised with a dispersion-corrected density functional theory method keeping the positions of the non-hydrogen atoms and the unit cell fixed.

The Rietveld plot for D-1-A is given in Fig. S1. The cif file for the crystal structure is part of the ESI of this paper.
Figure S1  Rietveld plot of D-1-A: observed (black), calculated (red) and difference (blue) profiles and tick marks (green). At about 36° in 2θ the scale changes by a factor of 5.
Figure S2  Rietveld plot of rac-1: observed (black), calculated (red) and difference (blue) profiles and tick marks for rac-1 (green) and D/L-1·⅓H₂O (magenta). At about 32° in 2θ the scale changes by a factor of 3.
Figure S3  Rietveld plot of 5-A: observed (black), calculated (red) and difference (blue) profiles and tick marks (green). At about $36^\circ$ in $2\theta$ the scale changes by a factor of 5.
**Figure S4** Rietveld plot of 5-D: observed (black), calculated (red) and difference (blue) profiles and tick marks (green). At about 36° in 2θ the scale changes by a factor of 7.
**Figure S5** Rietveld plot of 5-E: observed (black), calculated (red) and difference (blue) profiles and tick marks (green). At about 36° in 2θ the scale changes by a factor of 5.
Figure S6  Rietveld plot of 7-C: observed (black), calculated (red) and difference (blue) profiles and tick marks (green). At about 36° in 2θ the scale changes by a factor of 10.

S3. Pawley refinements on the rotator phases L-1-B, D-1-B, 5-C, 6-B and 5-B

All phases were measured with Cu-Kα1 radiation (λ = 1.5406 Å) in the range 2θ = 2-80° (the mixture of 5-C and 5-B was measured in the range 2-60°). All phases have chemical formula C₆H₁₂O₆, Mᵣ = 180.16 g/mol. The Pawley fits, carried out with TOPAS 4.1, converged well for D-1-B: \( F^* \), \( a = 9.31568 \) Å, \( V = 808.432 \) Å³, \( Z = 4 \), measurement at 500 K, \( R_{wp} = 0.0304 \), \( R_p = 0.0233 \), \( R_{exp} = 0.0280 \) (before background subtraction), \( R'_{wp} = 0.1584 \), \( R'_p = 0.1925 \), \( R'_{exp} = 0.1460 \) (after background subtraction), \( \chi^2 = 1.085 \), for L-1-B: \( F^* \), \( a = 9.31210 \) Å, \( V = 807.501 \) Å³, \( Z = 4 \), measurement at 500 K, \( R_{wp} = 0.0254 \), \( R_p = 0.0190 \), \( R_{exp} = 0.0190 \) (before background subtraction), \( R'_{wp} = 0.2013 \), \( R'_p = 0.2191 \), \( R'_{exp} = 0.1506 \) (after background subtraction), \( \chi^2 = 1.786 \), for 5-C: \( F^* \), \( a = 9.33440 \) Å, \( V = 813.316 \) Å³, \( Z = 4 \), measurement at 500 K, \( R_{wp} = 0.0601 \), \( R_p = 0.0461 \), \( R_{exp} = 0.0635 \) (before background subtraction), \( R'_{wp} = 0.2018 \), \( R'_p = 0.2947 \), \( R'_{exp} = 0.2132 \) (after background subtraction), \( \chi^2 = 0.947 \) and for 6-B: \( F^* \), \( a = 9.26836 \) Å, \( V = 796.175 \) Å³, \( Z = 4 \), measurement at 473 K, \( R_{wp} = 0.0404 \), \( R_p = 0.0304 \), \( R_{exp} = 0.0344 \) (before background subtraction), \( R'_{wp} = 0.1925 \), \( R'_p = 0.2689 \), \( R'_{exp} = 0.1624 \) (after background subtraction), \( \chi^2 = 1.185 \). For 5-B: \( P3^*/P6^* \), \( a = 6.57509 \) Å, \( c = 10.5818 \) Å, \( V = 396.181 \) Å³, \( Z = 2 \), measurement at 473 K, \( R_{wp} = \)
0.0296, $R_p = 0.0225$, $R_{exp} = 0.0263$ (before background subtraction), $R'_{wp} = 0.1369$, $R'_p = 0.1663$, $R'_{exp} = 0.1214$ (after background subtraction), $\chi^2 = 1.127$.

The Pawley plots for D-1-B, L-1-B, 5-C, 6-B and 5-B are given in Fig. S7, Fig. S8, Fig. S9, Fig. S10 and Fig. S11, respectively.

**Figure S7** Pawley plot of D-1-B: observed (black), calculated (red) and difference (blue) profiles and tick marks (green).
Figure S8  Pawley plot of L-1-B: observed (black), calculated (red) and difference (blue) profiles and tick marks (green).
Figure S9 Pawley plot of 5-C with 5-B present: observed (black), calculated (red) and difference (blue) profiles and tick marks for 5-B (green) and 5-C (magenta).
Figure S10 Pawley plot of 6-B: observed (black), calculated (red) and difference (blue) profiles and tick marks (green).
Figure S11 Pawley plot of 5-B: observed (black), calculated (red) and difference (blue) profiles and tick marks (green).

S4. Stability of 7-C

XRPD measurements after one, two and three months revealed that 7-C is not stable at room temperature and slowly transforms back to 7-A (see Fig. S12). As shown in Fig. S12 there are four clearly free reflections (021 reflection at 15.4°, 111 at 17.4°, 102 at 18.7° and 112 at 20.1°) which indicate the increase of 7-A in 7-C over a period of three months. After one month a ratio of approximately 7:1 between 7-C and 7-A can be observed, after two months the ratio increases to 3:1 and after three months the ratio increases to 1:5. Therefore it can be assumed that after a longer period of time 7-C converts back to 7-A completely and that 7-C is a meta-stable polymorph of 7. Therefore no thermal effect could be observed during the cool-down process in the DSC (see Fig. 18 in the paper). Additional DSC and T-XRPD measurements on 7 up to 250 °C yielded only a partial conversion of 7-A to 7-C. Therefore the crystal structure of 7-C was determined with a sample from DSC measurements heated up to 280 °C and cooled down to 20 °C.
**Figure S12** Overlay of the X-ray powder diffraction traces of myo-inositol, 7, showing the reference trace of 7-C (black) and 7-A (red), 7-C after one month (blue), two months (green) and three months (violet) stored at room temperature. Black asterisks indicate the reflections of interest.
Figure S13 DSC trace of myo-inositol, 7, measured from 280 down to 20 °C showing the recrystallisation of 7-A from the melt at 186 °C.