2-(1-Hydroxy-2-methyl-propyl)-2,5-dihydro-furan-2-carboxylic acid diisopropylamide: A study of a phase transition to a pseudosymmetrical *Z′*=2 structure

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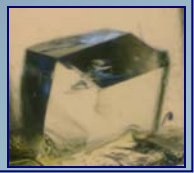
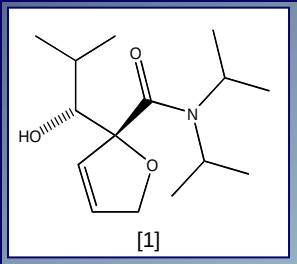
The Structure

The structure of 2-(1-hydroxy-2-methyl-propyl)-2,5-dihydro-furan-2-carboxylic acid diisopropyl-amide [1] has been solved at two temperatures, 150K and 250K. The high temperature structure has *Z′* = 1, but at low temperature *Z′* = 2, with the two non-crystallographically equivalent molecules related by a pseudotranslation of ½ along the *c*-axis. Between these two temperatures, the crystal undergoes a reversible second order phase change, which is clearly seen in diffraction patterns produced within that temperature range.





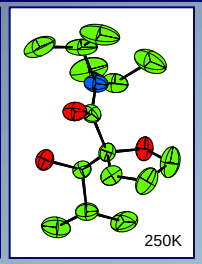


Fig 1. ***Left****: 2-D diagram of [1].* ***Right****: Thermal ellipsoids of the high temperature structure.*

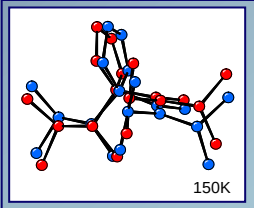


Fig 2. Comparison of the pseudotranslation with a true translation of c/2, viewed down the b*-axis, with the two molecules in the asymmetric unit are superimposed. The centroids of the two molecules thus overlaid are separated by 0.2331Å.*

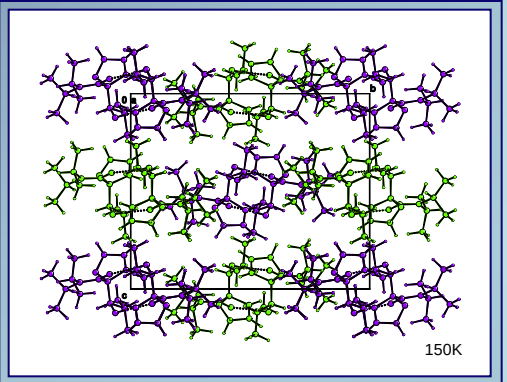
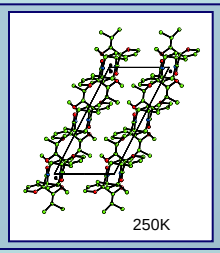
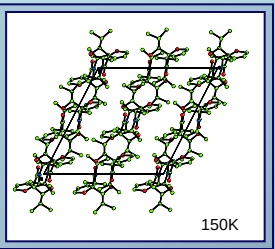


Fig 3. Hydrogen bonding, shown as dotted lines, in the low temperature structure of [1] viewed down the a*-axis. The two asymmetric molecules are differentially coloured. H-bonds of 1.86Å occur between pairs of crystallographically-identical molecules.*

Fig 4. Views down the b*-axis.*
Right*: High temperature structure.*
Cell parameters: a = *7.6713 Å,* b = *16.6108 Å,* c = *14.9651 Å;* b = *118.02º; V = 1683.41 Å³.*
Space group is $P2_1/a$.
Far right*: Low temperature structure.*
Cell parameters: a = *14.8538 Å,* b = *16.5425 Å,* c = *15.2857 Å;* β = *117.92º; V = 3318.87 Å³.*
Space group is $P2_1/n$.
Both structures have been set in non-standard space groups to ease direct comparison.





Acknowledgments

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References

1. A. Xia, J.P. Slegue, A. Carrillo, B.O. Patrick, S. Parkin, C.P. Brock, *Acta Cryst.*, 2001, **B57**, 507.

The Phase Change

The cell volume and cell parameters were studied as a function of temperature, first cooling the crystal, then heating it back up. The crystal exhibits a second order phase transition over the temperature range 166-206K. This phase change is seen most clearly by examining a series of diffraction patterns over a range of temperatures.

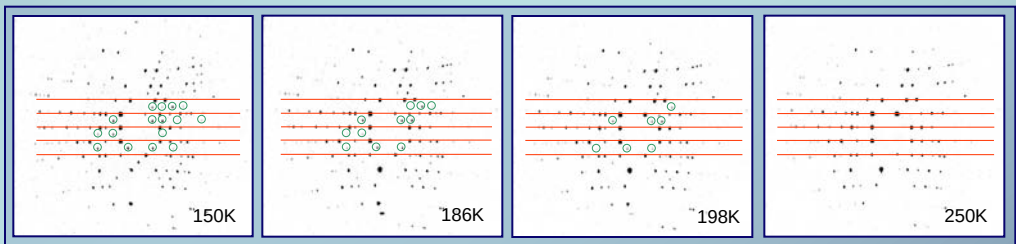

Fig 5. Diffraction patterns obtained at a range of temperatures on heating. These are composite images produced from 10 x 1º scans, with the background removed. Rows of l *are horizontal in these images. At 150K, there are large numbers of closely spaced spots. As the temperature is increased, peaks gradually disappear in lines corresponding to odd values of* l*. Red lines drawn on the images above, labelled according to their* l *value at low temperature, make the disappearance of these peaks easier to see. Green circles indicate reflections at odd values of* l *in the range -3 ≤ l ≤ +3.*

Wilson plots

Wilson plots are generally used in order to find an average value of the scale and temperature factors. However they can also provide a quantitative comparison of the intensities of strong and weak reflections, here by plotting odd and even *l* reflections separately[1].

The average values of $|E^2\text{-}1|$ differ between high and low temperature structures. $\langle|E^2\text{-}1|\rangle$ measures the absolute deviation of E^2 from its average value of unity. The more variation there is in E^2, the larger the value of $\langle|E^2\text{-}1|\rangle$. For centric distributions, $\langle|E^2\text{-}1|\rangle$ is ideally 0.97. At 250K $\langle|E^2\text{-}1|\rangle$ = 0.871 and at 150K $\langle|E^2\text{-}1|\rangle$ = 0.955. This indicates a larger spread in the low temperature data. This is unsurprising as *E* attaches greater weight to high angle data and at higher resolution the differences between the two asymmetric molecules become more important.

Fig 6.

Top: *Wilson plot for odd, even and all* l *reflections for the low temperature structure. $(\sin\theta/\lambda)^2$ bins are overlapping to minimise sampling errors. In the high temperature case (not shown), there is no appreciable difference between the odd and even* l *reflections. However in the low temperature structure there is a marked difference in the gradients of the graphs for odd and even* l *values. The odd* l *reflections are systematically weak due to the translation along the* c*-axis although the differences in intensity of odd and even reflections are much smaller at high resolution. All of the high angle data contain more detail about the differences in the structures of the two molecules in the asymmetric unit relative to the low angle data.*

Bottom: *Plot of $\langle E\rangle$ for odd and even reflections of* l *at 150K. Note that they are not independent of one another. At low angle, it is the even reflections that contribute the most structural information, at high angle it is the odd data.*