

# A Disappearing Polymorph

## A Classical Example of a Disappearing Polymorph and the Shortest Intermolecular H...H Separation Ever Found in an Organic Crystal Structure\*\*

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One of the best documented examples of a “disappearing polymorph”<sup>[1–7]</sup> concerns 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose.<sup>[8–17]</sup> Following its first preparation in 1947,<sup>[8]</sup> polymorph *A* was routinely obtained in different laboratories over several years.<sup>[9,13]</sup> By 1954 this polymorph had “disappeared”<sup>[12–14]</sup> in favor of a more stable, higher melting polymorph *B*.<sup>[10,11,15,16]</sup> Attempts to obtain polymorph *A* in Europe,<sup>[10,11,13]</sup> Australia,<sup>[15]</sup> and the United States<sup>[12,14,16]</sup> were unsuccessful. In 1981 polymorph *A* reappeared in Budapest,<sup>[17]</sup> and, thanks to strict precautions against contamination, it has been possible to preserve it over many years. The initial X-ray study has now been followed up by low-temperature X-ray and neutron diffraction analyses of both polymorphs, which reveal significant differences in the crystal packing and molecular conformation. At 110 K and below, unstable polymorph *A* contains the shortest intermolecular H...H contact ever found in an organic crystal structure.

In recent years, the study of polymorphism<sup>[6,18–20]</sup> has gained considerable impetus as its scientific, industrial and commercial significance has been recognized.

Several cases are documented<sup>[1,3,6]</sup> where, after nucleation of a more stable crystal form, a previously obtained polymorph became unobtainable. Such loss of control over the crystallization process<sup>[1]</sup> is not only disturbing but may also make industrial processes intractable.<sup>[21]</sup> More sophisticated techniques,<sup>[22–25]</sup> such as the addition of tailor-made additives, conformational mimicry, or solvent-mediated transformations, have been introduced to influence the crystallization process to preferentially produce a particular polymorph.

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

Studies of the polymorphism of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose have a long history.<sup>[1,4,5,7]</sup> The compound is used as starting material for nucleoside synthesis. The preparation of the lower melting unstable form *A* was described in 1947 (m.p. 58 °C,  $[\alpha]_D^{15} = +20^\circ$  in chloroform)<sup>[8]</sup> and in 1948 (m.p. 56 °C,  $[\alpha]_D^{20} = -3.6^\circ$  in methanol).<sup>[9]</sup> The higher melting stable form *B* (m.p. 82 °C,  $[\alpha]_D^{24} = -12.6^\circ$  in chloroform,  $[\alpha]_D^{20} = -15.4^\circ$  in methanol)<sup>[10]</sup> apparently appeared only in 1950.

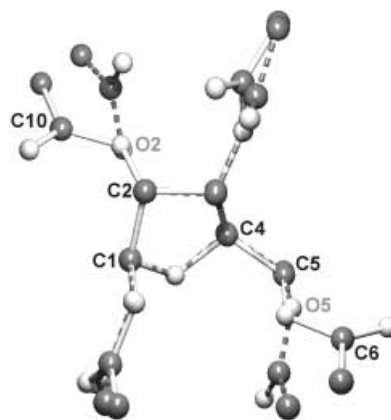
The phase transition of this compound and the catalytic effect of form *B* in this transformation were recognized in July 1952.<sup>[12]</sup> However, the nature of the difference between the two forms was not clear and they were alluded to as isomers. In November 1952, Farrar<sup>[13]</sup> recorded that the dissolved crystals of both forms showed no significant change in specific rotation and thus concluded that structural isomerism was unlikely.

The first X-ray diffraction results and at the same time the apparently last occurrence of the unstable form *A* were reported in 1954 by Patterson and Groshens.<sup>[14]</sup> The cell parameters, crystal system, and space group of both dimorphs were determined and the transformation in the solid state was examined by Laue photographs.

The difficulty of reproducing the lower melting form<sup>[1,4,7,10–14]</sup> has long prevented further study of this remarkable polymorphism. Although the room-temperature crystal structure of the stable form *B* was reported in 1973<sup>[15]</sup> and again in 1976,<sup>[16]</sup> form *A* seems to have “disappeared” until in 1981, 27 years after its last reported occurrence, it reappeared in Budapest.<sup>[17]</sup> Its melting point, space group and cell constants agreed with those given by Patterson and Groshens,<sup>[14]</sup> and its optical rotation in chloroform matched that of the stable form *B*, in agreement with Farrar's observation.<sup>[13]</sup> Czugler et al. reported the single-crystal X-ray diffraction measurement at room temperature.<sup>[17]</sup> The structure analysis showed that although the crystal packing is quite different, the puckering of the furanose rings is essentially the same. However, the conformations of two of the four acetyl groups differ significantly ( $C4-C5-O5-C6 \Delta\tau = 92.5^\circ$ ,  $C1-C2-O2-C10 \Delta\tau = 70.0^\circ$ ), which indicates conformational dimorphism of *A* and *B* (Figure 1). It was also apparent that some intermolecular H···H contacts (see Table 1 in the Supporting Information) in the unstable form *A* are markedly shorter than 2.4 Å, the sum of the van der Waals radii (even if the “classical” van der Waals radius of 1.20 Å for hydrogen<sup>[26]</sup> is found to be overestimated by about 0.1 Å<sup>[27]</sup>), whereas no such short contacts are present in form *B*. It seemed to us possible that this type of close intermolecular contact might be responsible for the relative instability of form *A*.<sup>[28,29]</sup>

To estimate the role of crystal forces on the molecular conformation, the intramolecular nonbonded potential energy was minimized for both the *A* and *B* molecular geometries with empirical atom-pair potential functions.<sup>[17]</sup> The computed intramolecular potential energy of the molecule in form *B* was higher by 15.7 kJ mol<sup>−1</sup>, which suggests that the greater stability of this polymorph must be a result, not of intramolecular, but of intermolecular effects.

In an attempt to improve the room-temperature X-ray model, especially in regard of the hydrogen atoms, we

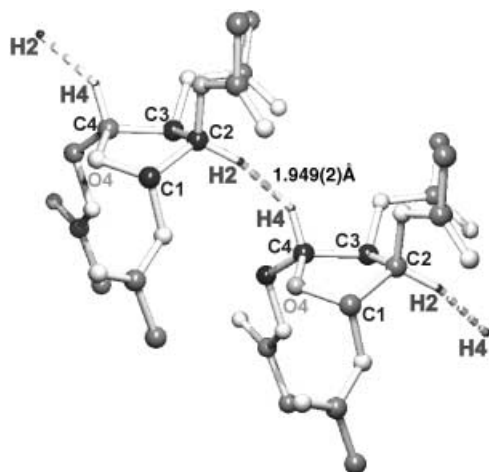


**Figure 1.** Superposition of the 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose molecule in the unstable form *A* (solid) and the stable form *B* (dotted), as determined by neutron diffraction at 25 K.

undertook low-temperature X-ray analyses of both crystal forms<sup>[30]</sup> (Figure 1). Careful recrystallization from ethanol yielded large (8–9 mm long, 2–3 mm thick) columns of the unstable form *A* suitable for neutron diffraction measurement (Figure 1 in the Supporting Information). Large plates (2.6–3.0 mm long, 1 mm thick) of form *B* were obtained by controlled evaporation of a methanol solution. During the whole experimental period various precautions were taken to preserve the unstable polymorph *A*, crystals of which were stored in sealed ampoules over many years. Each experiment was done first with form *A*, then with form *B*, with strict adherence to protocol. The differential scanning calorimetry (DSC) measurements were made in hermetically sealed sample pans. After crystallization of the stable form *B*, the laboratory was repainted and every piece of furniture, equipment was cleaned. Labcoats, towels, and clothing were washed after working with this form to prevent contamination by it. New glassware was used whenever the unstable form *A* was handled.

The neutron diffraction experiments were carried out at 25.0 K (Figure 1).<sup>[32]</sup> The low-temperature X-ray structures were used as starting models in the neutron-data refinement (Supporting Information Figures 2 and 3), which included anisotropic displacement parameters of hydrogen atoms. The hydrogen positions derived from the X-ray model at 110 K agreed well with those from the neutron diffraction results, the largest difference in O=C–C–H torsion angle is 6.5°. Re-refinement of the room-temperature model<sup>[17]</sup> of form *A* with up-to-date computing techniques led to remarkable differences in methyl hydrogen positions but no major variations compared with the low-temperature X-ray and neutron diffraction structure models.

The neutron diffraction study shows the presence of a remarkably short intermolecular C–H···H–C distance ( $H2\cdots H4$  1.949(7) Å) between ribose H atoms in the unstable form *A* (Figure 2) and its absence ( $H2\cdots H4$  3.70(1) Å) in the stable form *B*. With C–H bond distances fixed at 1.08 Å, the  $H2\cdots H4$  distance is 1.95(9) Å at 110 K and 2.10(7) Å at 298 K. Thus, even at room temperature the distance in question is extremely short.<sup>[27,33]</sup> Over the whole temperature range, and



**Figure 2.** The shortest intermolecular H...H distance C2-H2...H4-C4 (1.949(7) Å) to be found in an organic crystal structure. It occurs in the unstable form *A* of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose. It is seen that the approach of the two hydrogen atoms is nearly head on. Other hydrogen atoms are omitted for clarity.

especially at low temperature, this intermolecular contact must correspond to a strong repulsive force in the crystal structure *A*, which is, of course balanced by the resultant of all the other, mainly attractive forces.<sup>[33]</sup> The repulsive H2...H4 interaction is nearly parallel to the crystallographic *b* axis. On cooling the crystal from room temperature to 110 K, the *b* axis contracts by 0.12 Å, but on further cooling to 25 K, it does not contract any more.

There are three other short H...H distances within the sum of the van der Waals radii (2.4 Å) between C-H moieties in both crystals (form *A*: H1...H11A 2.257(8), H7A...H13C 2.342(7), H5B...H7B 2.377(8) Å (Supporting Information: Figure 4) and form *B*: H2...H5A 2.25(1), H4...H7C 2.38(2), H5B...H9B 2.35(2) Å, not shown) in which at least one of the atoms is from a terminal methyl group, with more conformational freedom than a methylene or a skeletal hydrogen atom. Five attractive C-H...O interactions shorter than 2.6 Å (average length is 2.52(5) Å) may help to balance the repulsive H...H approaches in the unstable form *A*. In the stable form *B* there are eight intermolecular C-H...O hydrogen bonds with the average length of 2.45(9) Å (Supporting Information: Table 1).

With the help of the Cambridge Crystallographic Database,<sup>[34]</sup> intermolecular H...H distances between 1.9 and 2.2 Å in all crystal structures determined by neutron diffraction were collected. We find that form *A* of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose at 25 K contains the shortest intermolecular H...H distance (1.949(7) Å) ever observed in an organic crystal. This distance corresponds to the strong repulsive region of the potential energy curve obtained in an ab initio calculation for CH<sub>4</sub>...CH<sub>4</sub> as a function of C-C separation and relative orientation.<sup>[36]</sup>

The phase transition was examined by placing a small crystal of form *B* on top of a 2–3 mm size block of crystal *A* at room temperature. Crystal *A* became opaque within an hour but its outward shape was unchanged after four days. On placing crystals of form *A* and *B* in a drop of saturated

solution, rapid recrystallization was observed; the less soluble form *B* grew at the expense of the more soluble form *A* within minutes, which confirms that *B* is the stable dimorph.

The phase transition cannot be generated by grinding the crystals or by changing the temperature within the range –150 to +100°C, as shown by cooling and heating samples of forms *A* and *B* separately in a DSC apparatus. The phase transition occurs only after inoculation of form *A* with even a minute amount of form *B*. Immediate heating in the temperature range 12 to 100°C then shows endothermic melting of form *A* at 55–56°C, followed by fast exothermic recrystallization of the liquid drop on the crystal of *B*, and, finally, melting of form *B* at 81–82°C (Supporting Information: Figure 5). The phase transition also takes place in the solid phase at room temperature; 26 h after seeding form *A*, form *B* was present almost exclusively, as shown by the melting point and enthalpy of melting (Supporting Information: Figure 6). Since the phase transformation is a slow exothermic process, the DSC signal tends to fade into the baseline. The lower melting enthalpy of unstable form *A* (91 J g<sup>–1</sup>) relative to the higher value of stable form *B* (102 J g<sup>–1</sup>) indicates<sup>[37]</sup> that the 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose polymorph system is monotropic.

The unit-cell volume per molecule is higher for the stable form *B* than for the unstable form *A* at the same temperature. Thus, the stable crystal is less densely packed in a higher-symmetry space group than the unstable crystal (packing coefficients<sup>[38]</sup> are *A*: 73.2%, *B*: 71.8%). Usually it is the other way round.<sup>[18,33,39,40]</sup> It is an example of the limitation of the close-packing principle: the more tightly packed polymorph, may have lower free energy,<sup>[33]</sup> as a balance of the repulsive H...H and the only occurring attractive C-H...O forces. Also unusual is the behavior of form *A* on cooling from 110 K to 25 K. The unit cell volume *increases* by 5.4(7) Å<sup>3</sup> (0.7%). The *b* and *c* axial lengths do not change while the *a* axis increases by 0.077 Å.

Our structural study of the unstable polymorph *A* of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose has shown that this crystal contains the shortest intermolecular H...H distance ever found in an organic crystal structure. The repulsive interaction associated with this distance may be decisive for the crystal stability as determined by the fine-tuning of intra- and intermolecular crystal forces.

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- [32] a) Neutron diffraction measurements at 25 K, scan mode  $\omega$ - $\theta$ ; Lorentz and polarization correction, least-squares structure refinement on  $F$  by DUPALS<sup>[32b]</sup> form A:  $\lambda = 1.215 \text{ \AA}$ , crystal dimensions:  $2 \times 4 \times 4 \text{ mm}$ ,  $a = 12.592(4)$ ,  $b = 5.463(2)$ ,  $c = 10.867(4) \text{ \AA}$ ,  $\beta = 96.355(1)^\circ$ ,  $V = 742.9(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.423 \text{ g cm}^{-3}$ , 1666 collected reflection, 1512 independent reflections, 1450 reflections  $I > 3\sigma$ ,  $\theta_{\text{max}} = 60.00^\circ$ , parameters 251,  $\mu = 0.2055$ , analytical absorption correction,  $T_{\text{min}} = 0.3587$ ,  $T_{\text{max}} = 0.7013$ ,  $R = 0.031$ ; form B:  $\lambda = 1.207 \text{ \AA}$ , crystal dimensions:  $1 \times 2.6 \times 3 \text{ mm}$ ,  $a = 7.291(4)$ ,  $b = 13.577(4)$ ,  $c = 15.117(9) \text{ \AA}$ ,  $V = 1496.4(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.412 \text{ g cm}^{-3}$ , 2237 collected reflection, 2033 independent reflections, 1430 reflections  $I > 2\sigma$ ,  $\theta_{\text{max}} = 51.09^\circ$ , parameters 252,  $\mu = 0.233$ , analytical absorption correction,  $T_{\text{min}} = 0.6262$ ,  $T_{\text{max}} = 0.8032$ ,  $R = 0.059$ ; b) T. Gustafsson, DUPALS, A Full-matrix Least-squares Refinement Program, Uppsala University, **1993**.
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