[11] P. Bandyopadhyay, V. Janout, L. Zhang, S. L. Regen, *J. Am. Chem. Soc.* **2001**, *123*, 7691 – 7696.
[12] J. F. Barry, A. P. Davis, M. N. Pérez-Payan, M. R. J. Elsegood, R. F. W. Jackson, C. Gennari, U. Piarulli, M. Gude, *Tetrahedron Lett.* **1999**, *40*, 2849 – 2852.
[13] Y. R. Vandenburg, B. D. Smith, M. N. Pérez-Payán, A. P. Davis, *J. Am. Chem. Soc.* **2000**, *122*, 3252 – 3253.
[14] C. Li, A. S. Peters, E. L. Meredith, G. W. Allman, P. B. Savage, *J. Am. Chem. Soc.* **1998**, *120*, 2961 – 2962.
[15] S. Broderick, A. P. Davis, R. P. Williams, *Tetrahedron Lett.* **1998**, *39*, 6083 – 6086.
[16] U. Taotafa, D. B. McMullin, S. C. Lee, L. D. Hansen, P. B. Savage, *Org. Lett.* **2000**, *2*, 4117 – 4120.
[17] J. Haldar, V. K. Aswal, P. S. Goyal, S. Bhattacharya, *Angew. Chem.* **2001**, *113*, 1278 – 1282; *Angew. Chem. Int. Ed.* **2001**, *40*, 1228 – 1232.
[18] D. M. Small in *The Bile Acids, Vol. 1* (Eds.: P. P. Nair, D. Kritchevsky), Plenum, New York, **1971**, pp. 249 – 356.
[19] C. Li, L. P. Budge, C. D. Driscoll, B. M. Willardson, G. W. Allman, P. B. Savage, *J. Am. Chem. Soc.* **1999**, *121*, 931 – 940.
[20] C. Li, M. R. Lewis, A. B. Gilbert, M. D. Noel, D. H. Scoville, G. W. Allman, P. B. Savage, *Antimicrob. Agents Chemother.* **1999**, *43*, 1347 – 1349.
[21] W. G. Pitt, M. O. McBride, J. K. Lunceford, R. J. Roper, R. D. Sagers, *Antimicrob. Agents Chemother.* **1994**, *38*, 2577 – 2582.

Polymorphism in the Crystal Structure of the Cellulose Fragment Analogue Methyl 4-*O*-Methyl-β-D-Glucopyranosyl-(1-4)-β-D-Glucopyranoside**

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Cellulose, the most abundant polymer on earth, usually consists of a mixture of highly crystalline and amorphous regions. The crystalline parts display one chain conformation, made up of a twofold ribbon, but many possible packing arrangements, with either parallel chains (cellulose I, III_I, and IV_I) or antiparallel chains (cellulose II, III_{II}, and IV_{II}) (for a review see ref. [1]). The three-dimensional structure of native cellulose is highly complex and not yet completely resolved because two distinct crystalline forms, cellulose Iα and Iβ[2] showing triclinic and monoclinic symmetry, respectively, coexist. The crystalline phases Iα and Iβ occur in variable proportions according to the source of the cellulose; that of primitive organisms (bacteria, alga, etc.) is enriched in the Iα phase whereas that of higher plants (woody tissues, cotton, ramie, etc.) consists mainly of the Iβ phase,[3] and cellulose of the outer membrane of marine animals is uniquely composed of the Iβ phase.[4] Modeling studies have established that the two crystalline arrangements correspond to two low-energy structures arising from parallel associations of cellulose chains.[5]

Cellobiose has been crystallized in its native form and in the form of derivatives and salts.[6] In all crystals, the packing arrangement corresponds to a low-energy arrangement of small molecules and does not provide any clues to the polymorphism of the polysaccharide. Only in crystals of methyl β-cellotrioside[7] and β-cellotetraose[8,9] chain-like arrangements were found. In these two cases, the molecules are arranged in an antiparallel way, which represents the packing of lowest energy, and the resulting structures are similar to that of cellulose II. We describe here the crystal structure analysis of a cellulose fragment that displays a parallel arrangement of molecules and that can therefore be directly compared with the two polymorphs of natural cellulose I.

Crystals of methyl 4-*O*-methyl-β-D-glucopyranosyl-(1-4)-β-D-glucopyranoside were obtained in the triclinic space group *P*1 (form **I**) using conditions which decreased the crystallization rate as compared to the crystallization of the monoclinic polymorph (group $P2_1$, form **II**).[10] The crystal structure of form **II** has been described recently from data collected at low temperature (220 K).[11] We redetermined the structure at room temperature[12] and found the differences in cell dimensions, cell volumes, and geometrical details to be less than 0.8%. Therefore, the structure is not shown here, but its data will be used in the tables to allow direct comparison between form **I** and form **II** geometries.

The molecular structure of form **I** is shown in Figure 1. Geometry calculations and ORTEP illustrations of the crystal structure were obtained with PLATON.[13] Both glucose rings have the usual $^4C_1$ shape. Intra-ring bond lengths and valence angles are in the range of standard values (Table 1). The short C1′–O4 bond at the glycosidic linkage is in agreement with the anomeric effect.[14] The C5–C6 and C6–O6 linkages of the

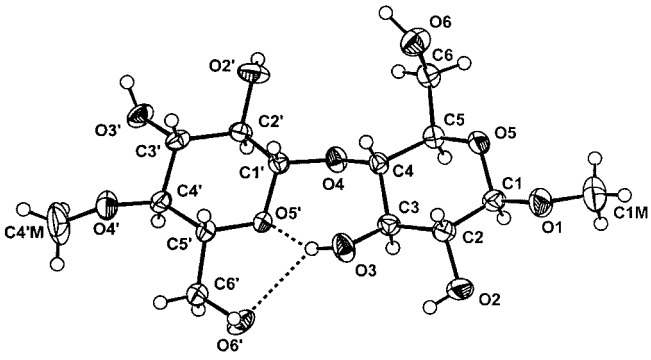

Figure 1. ORTEP representation of the molecular structure of form **I**. Thermal ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are represented as dashed lines.

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Table 1. Comparison of geometrical characteristics of form **I** and form **II** cellobioside.

	Form **I**	Form **II**
glycosidic bond lengths [Å]		
C1′-O4	1.395(2)	1.386(2)
C4-O4	1.445(2)	1.437(2)
hydroxymethyl groups bond lengths [Å]		
C5-C6	1.489(2)	1.511(2)
C6-O6	1.396(2)	1.406(2)
C5′-C6′	1.502(2)	1.510(3)
C6′-O6′	1.431(2)	1.414(2)
C1M-O1	1.414(3)	1.423(3)
glycosidic valence angle [°]		
C1′-O4-C4	116.7(1)	117.3(1)
glycosidic torsion angles [°]		
O5′-C1′-O4-C4	−90.0(2)	−88.8(1)
C1′-O4-C4-C5	−159.2(1)	−151.3(1)
exocyclic torsion angles [°]		
O5-C5-C6-O6	−59.4(2)	−54.5(2)
O5-C1-O1-C1M	−83.0(2)	−67.7(2)
O5′-C5′-C6′-O6′	57.8(2)	59.0(1)
C3′-C4′-O4′-C4′M	107.5(2)	96.9(2)

hydroxymethyl group of the reducing unit are significantly shorter than standard bonds and also shorter than the bonds of the equivalent group in polymorph **II** (Table 1). In both forms, the orientations of the hydroxymethyl groups at O6 and O6′ are *gg* and *gt*, respectively, as found in most crystal structures of cellodextrins.[15]

The conformation at the glycosidic linkage of form **I** is characterized by interglycosidic torsion angles Φ(O5′-C1′-O4-C4) = −90.0° and Ψ(C1′-O4-C4-C5) = −159.2°, almost identical to those observed in methyl cellobioside crystallized as solvate complex with methanol (Φ = −88.9°, Ψ = −160.7°).[16] Form **II** has a similar conformation, with only 8° difference in Ψ (Φ = −88.8°, Ψ = −151.3°). Both forms are therefore similar in shape and can be compared with the longer cellodextrins such as methyl cellotrioside (average value of Φ = −94.4° and Ψ = −146.4°)[7] and cellotetraose (average value of Φ = −94.4° and Ψ = −146.8°).[8,9] As reported recently,[15] the structures cited above cluster in one group of cellobiose glycosidic linkage conformations that are characterized by a pseudo-2_1 axis of rotation around the long axis of the molecule: propagating such conformations leads to a flat ribbon-like molecule, similar to the conformation observed in all crystalline cellulose. This family of conformations is significantly different from the conformation of lowest energy found in the crystal structure of β-cellobiose having a more folded shape (Φ = −75° and Ψ = −130°).[17]

The "flat" disaccharide conformation observed in cellodextrins and in the two polymorphs of methyl 4′-*O*-methyl-β-cellobioside described here is also characterized by the

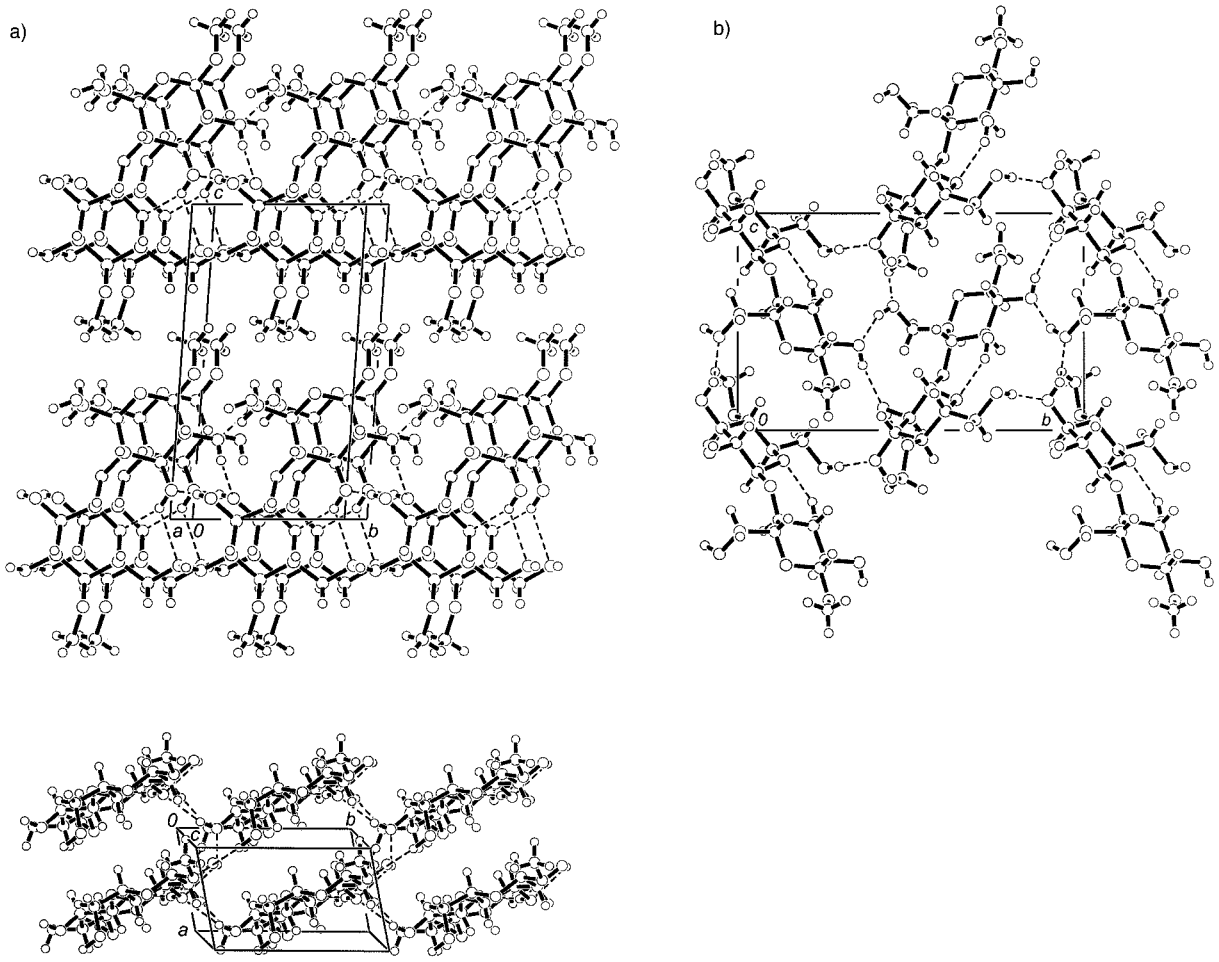

Figure 2. a) Two different views of the packing arrangement of form **I** cellobioside. b) Packing arrangement of form **II** cellobioside. Hydrogen bonds are represented as dashed lines.

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occurrence of two hydrogen bonds between the two rings involving O3 as donor and O5′ and O6′ as acceptors. In this three-centered hydrogen bond O3–H···O5′ is the stronger (d(O···O) > 2.8 Å) and O3–H···O6′ the weaker part (d(O···O) > 3.0 Å) (for details see the Supporting Information). This is also observed in crystals of longer cellodextrins and in cellulose chains studied by neutron diffraction.[18]

Whereas the molecular structures of the two polymorphs are very similar (rms calculated on all heavy atoms: 0.206 Å), their packing arrangements are completely different. In the triclinic form **I** (Figure 2a), the disaccharides are arranged as parallel molecules, connected by a complex network of intermolecular hydrogen bonds. Each molecule establishes ten intermolecular O–H···O hydrogen bonds (Figure 3a and Supporting Information), four with its two neighbors on each side, resulting from a single translation along the b axis, and six with the neighbors in the sheets above and below (translation along a). In addition, four intermolecular C–H···O hydrogen bonds are also observed (not shown). The translation along a is the shortest cell parameter (a = 4.6726(2) Å). It corresponds to the stacking of a cellobiose molecule with the ones above, in which numerous van der Waals contacts and hydrogen bonds are involved. Van der Waals interactions are established by the methyl groups on both sides of the disaccharide. As can be seen from Figure 2a, a hydrophobic layer of methyl groups at O1 interacts with an equivalent layer of methyl groups at O4′. The contact along the c axis is therefore mediated only by hydrophobic interactions.

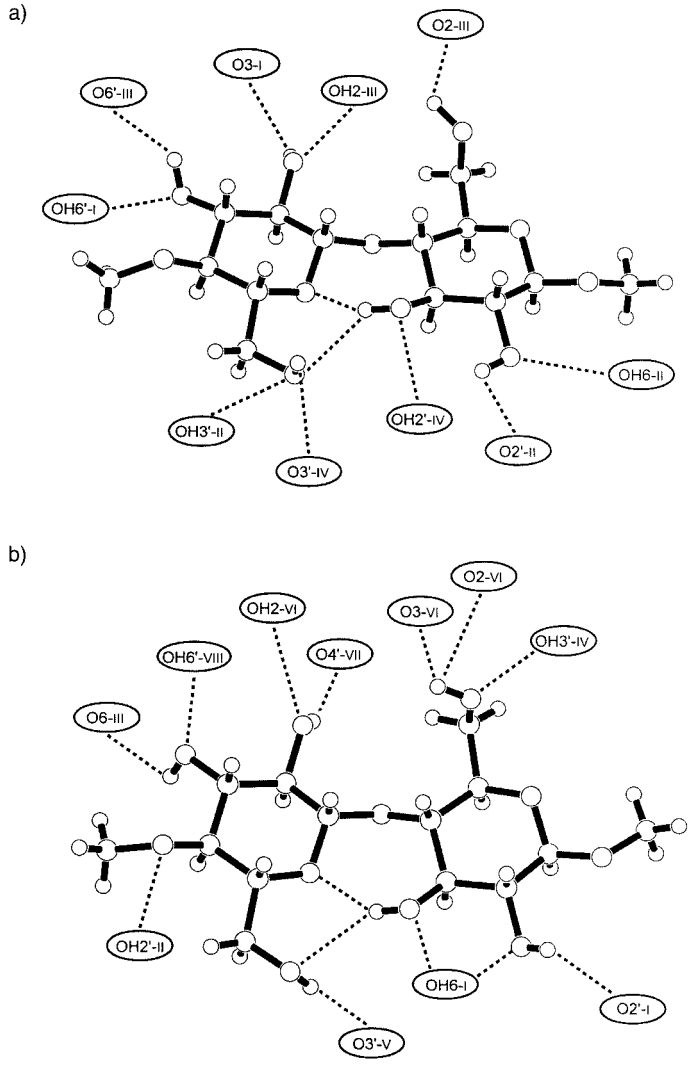

Figure 3. Network of hydrogen bonds O–H···O in the crystal structures of form **I** cellobioside (a) and form **II** cellobioside (b). The neighboring atoms have been given a code to indicate the symmetry involved (**I/II**): (I) $x, y-1, z/-x, y+1/2, -z+1$; (II) $x-1, y+1, z/x-1, y, z$; (III) $x+1, y-1, z/x, y, z+1$; (IV) $x, y+1, z/x, y, z-1$; (V) $/-x, y+1/2, -z+2$; (VI) $/-x, y-1/2, -z+1$; (VII) $/-x+1, y+1/2, -z$; (VIII) $/-x, y-1/2, -z+2$.

The packing arrangement of the monoclinic form **II** is completely different (Figure 2b). As described previously from the low-temperature data,[11] the disaccharides adopt an almost perpendicular orientation. Each molecule establishes twelve O–H···O and six C–H···O intermolecular hydrogen bonds with its neighbors (Figure 3b and Supporting Information).

We report here the first detection of crystalline polymorphism in an anhydrous oligosaccharide. A comparison of the two crystal structures may allow for rationalization of observed physicochemical data such as differences in melting points and in solid-state NMR spectra. The melting point of form **II** is 22 K higher than that of form **I** (493 K versus 471 K), suggesting that the monoclinic polymorph is thermodynamically preferred. Also, crystals of form **I** are more difficult to obtain; they have to be grown slowly. The crystal stability can be estimated by counting the number of contacts that a single molecule establishes with its neighbors and by evaluating the resulting energy of interaction or lattice energy. The mode of molecular packing was analyzed by applying the atom-pair procedure of Kitaigorodsky.[19] In this procedure, all contacts of a reference molecule with the surrounding molecules are explored. The energy of interaction was evaluated by molecular mechanics, comparing the energy of a minicrystal (11 and 15 molecules for forms **I** and **II**, respectively) with the energy of the same ensemble but with the reference molecule placed 100 Å away from the minicrystal.[20] In form **II**, each molecule makes contacts with 14 neighbors, compared to only 10 in form **I**. Both the number of contacts and the energy of interaction (Table 2) indicate that the monoclinic form **II** is thermodynamically favoured over form **I**.

In the solid-state NMR spectra of both polymorphs (Figure 4), there are clear differences, especially for the resonances of carbons C1, C1′, and C4, C4′ and in the region of

Table 2. Evaluation of the interaction between one molecule and its neighbors in both crystal forms.

	Form **I**	Form **II**
number of neighboring molecules[a]	10	14
number of intermolecular contacts[a]	84	106
number of intermolecular hydrogen bonds[b]		
O–H···O	5	6
C–H···O	2	3
energy of interaction in the minicrystal		
van der Waals contribution	−55.1 kcal mol^{-1}	−61.2 kcal mol^{-1}
electrostatic contribution	−6.9 kcal mol^{-1}	−7.1 kcal mol^{-1}
total interaction energy	−62.0 kcal mol^{-1}	−68.3 kcal mol^{-1}

[a] Evaluated as proposed by Kitaigorodski.[19] [b] Evaluated according to the criteria described by Jeffrey.[26]

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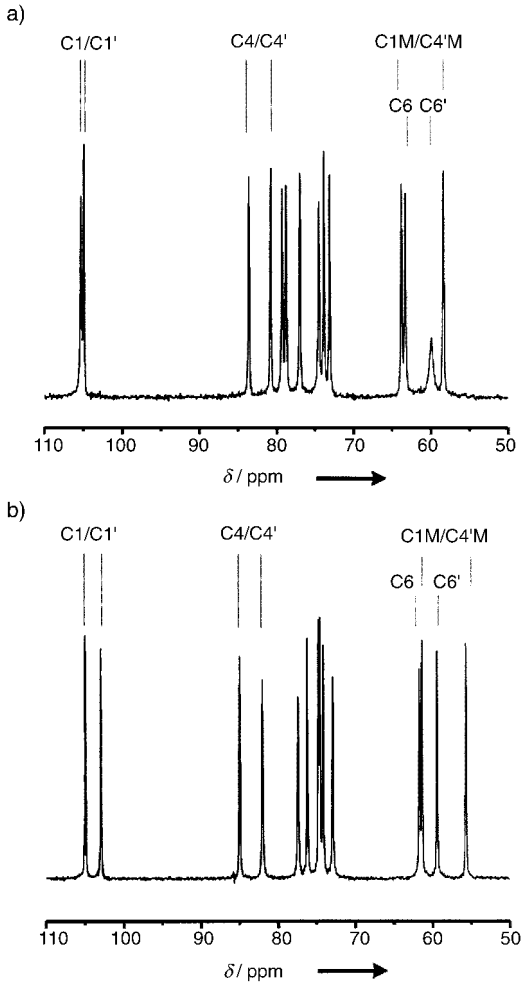

Figure 4. CP-MAS ^{13}C NMR spectra of form **I** (a) and form **II** (b) cellobioside.

carbons C6 and C6′. Since both forms have nearly identical shapes in the crystal the differences in chemical shifts cannot be attributed to differences in the conformation but suggest that the packing has a strong effect on the chemical shifts in the solid state. Another intriguing feature is the broadening of the C6 peak in the spectrum of form **I**. The assignment of C6 and C6′ to $\delta = 59.9$ and 63.3 ppm, respectively, is based on previous studies by Horii et al.,[21] and is in agreement with the *gg* and *gt* orientations of their hydroxymethyl groups. Broadening of only the peak for C6 in form **I** cannot be attributed to an increased mobility of this group since thermal parameters do not indicate any additional mobility and no disorder is observed. The only special features at this group are that O6 is involved in a C–H···O hydrogen bond with C5 of a neighboring molecule and that both C5–C6 and C6–O6 bonds are shorter than usual values (see Table 1).

The parallel arrangement of molecules in the triclinic form **I** and the proposed models for native cellulose Iα and Iβ[5] are compared in Figure 5. In the latter, the molecules have the shape of a flat ribbon with 2_1 symmetry, whereas in form **I** cellobioside, the symmetry is less perfect. The three stacking modes differ in the orientation of each ribbon compared to the sheet plane and in the translation between different planes. The main difference between the present crystal

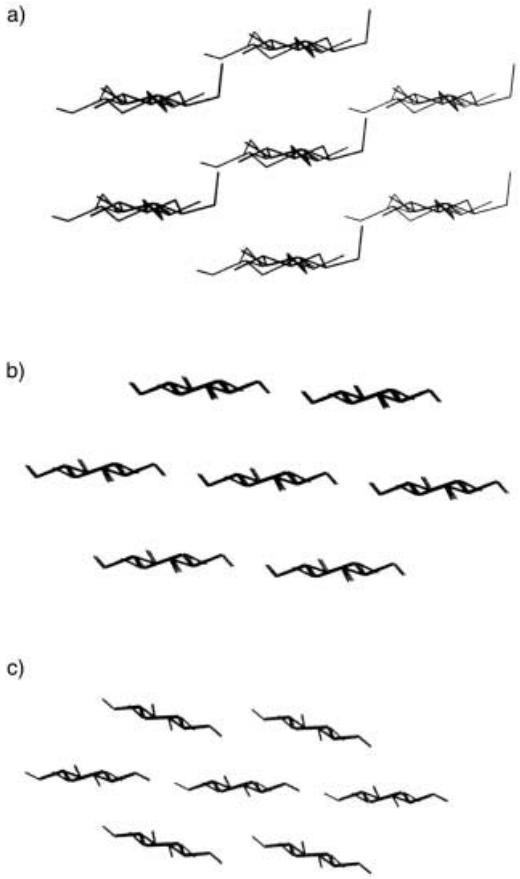

Figure 5. Parallel arrangement of molecules in triclinic form **I** cellobioside (a) compared to models for native cellulose Iα (b) and Iβ (c).

structure and the two polymer models is that the dimer does not form flat sheets. This opens up new perspectives about the occurrence of structures of parallel cellulose.

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[1] A. C. Sullivan, *Cellulose* **1997**, *4*, 173.
[2] R. H. Atalla, D. L. VanderHart, *Science* **1984**, *223*, 283.
[3] J. Sugiyama, T. Okana, H. Yamamoto, F. Horii, *Macromolecules* **1990**, *23*, 3198.
[4] P. S. Belton, S. F. Tanner, N. Cartier, H. Chanzy, *Macromolecules* **1989**, *22*, 1615.
[5] R. J. Vietor, K. Mazeau, M. Lakin, S. Pérez, *Biopolymers* **2000**, *54*, 342.
[6] S. Pérez, C. Gautier, A. Imberty in *Oligosaccharides in Chemistry and Biology: A Comprehensive Handbook* (Eds.: B. Ernst, G. Hart, P. Sinay), Wiley-VCH, Weinheim, **2000**.
[7] S. Raymond, B. Henrissat, D. T. Qui, A. Kvick, H. Chanzy, *Carbohydr. Res.* **1995**, *277*, 209.
[8] K. Gessler, N. Krauss, T. Steiner, C. Betzel, A. Sarko, W. Saenger, *J. Am. Chem. Soc.* **1995**, *117*, 11397.
[9] S. Raymond, A. Heyraud, D. Tran Qui, A. Kvick, H. Chanzy, *Macromolecules* **1995**, *28*, 2096.
[10] Conditions for crystal growing: Form **I** crystals were obtained by the hanging-drop method using 9:1 PEG 400/water as precipitant. The stock solution had a concentration of 60 mg mL^{-1} water which was diluted to give a 3:2 ratio of stock solution and PEG. The drop volume was 20 μL. Crystals were isolated after 3 days.
[11] I. D. Mackie, J. Röhrling, R. O. Gould, J. Pauli, C. Jäger, M. Walkinshaw, A. Potthast, T. Rosenau, P. Kosma, *Carbohydr. Res.* **2002**, *337*, 161.

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[12] X-ray analyses: Cellobioside crystals **I** and **II** were mounted on glass fibres. Diffraction data were collected on a κ-CCD (ENRAF-NONIUS) diffractometer, $T = 298$ K, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å (graphite monochromator). The structures were solved by direct methods (SIR-92).[22] Lorentz and polarization corrections were applied, but no correction was made for absorption, given the small crystal dimensions and the wavelength used. Refinement was performed using full-matrix least-squares on F^2 (TeXsan program[23]). Crystal data for form **I**: triclinic, $P1$; $a = 4.6726(2)$, $b = 7.5120(7)$, $c = 12.427(1)$ Å, $\alpha = 84.7(5)$, $\beta = 86.0(3)$, $\gamma = 79.7(4)°$, $V = 426.7(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.44$ g cm^{-3}, $\mu = 1.25$, 10936 reflections measured, 8271 crystallographically independent ($R_{int} = 0.0345$), and 6419 with $I > 2\sigma(I)$, $2\theta_{max} = 64°$, $R = 0.055$, $Rw = 0.065$, 223 parameters, H atoms isotropic. Crystal data for form **II**: monoclinic, $P2_1$; $a = 6.617(7)$, $b = 14.117(6)$, $c = 9.344(6)$ Å, $\beta = 108.81(9)°$; $V = 826(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.49$ g cm^{-3}, $\mu = 1.25$, 2631 reflections measured, 2500 crystallographically independent ($R_{int} = 0.0218$), and 2053 with $I > 2\sigma(I)$, $2\theta_{max} = 60°$, 226 parameters: $R = 0.0387$, $Rw = 0.0367$. CCDC-184139 (form **I**) and CCDC-184140 (form **II**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
[13] A. L. Spek, *J. Appl. Crystallogr.* **1988**, *21*, 578.
[14] I. Tvaroska, T. Bleha, *Adv. Carbohydr. Chem. Biochem.* **1989**, *47*, 45.
[15] Z. Peralta-Inga, G. P. Johnson, M. K. Dowd, J. A. Rendleman, E. D. Stevens, A. D. French, *Carbohydr. Res.* **2002**, *337*, 851.
[16] J. T. Ham, D. G. Williams, *Acta Crystallogr. Sect. B* **1970**, *26*, 1373.
[17] S. S. C. Chu, G. A. Jeffrey, *Acta Crystallogr. Sect. B* **1968**, *24*, 830.
[18] P. Langan, Y. Nishiyama, H. Chanzy, *J. Am. Chem. Soc.* **1999**, *121*, 9940.
[19] A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, **1973**.
[20] To evaluate the difference in the energy of interaction in forms **I** and **II**, energy calculations were performed using the Tripos force field[24] present in Sybyl software.[25] Gasteiger–Marsili charges were assigned to the molecules, and the lengths of C–H···O and O–H···O hydrogen bonds were corrected to the theoretical lengths (1.050 and 0.950 Å, respectively). The interaction energy was defined as the difference between the energy of a minicrystal composed of a reference molecule surrounded by the nearest neighbors (i.e., by 11 molecules for form **I** and by 15 molecules for form **II**) and the energy of the same minicrystal but with the reference molecule pulled 100 Å away from its central position (i.e., noninteracting).
[21] F. Horii, A. Hirai, R. Kitamura, *Polymer Bull.* **1983**, *10*, 357.
[22] A. Altomare, M. C. Burla, G. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1984**, *27*, 435.
[23] TeXsan, MSC, The Woodlands, TX.
[24] M. Clark, R. D. I. Cramer, N. van den Opdenbosch, *J. Comput. Chem.* **1989**, *8*, 982.
[25] SYBYL, 1699 S. Hanley Road, Suite 303, St Louis, MO, USA.
[26] G. A. Jeffrey, *J. Mol. Struct.* **1999**, *485*–486, 293.

The Role of Nucleation Inhibition in Optical Resolutions with Families of Resolving Agents**

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The separation of enantiomers by diastereomeric salt formation, essentially unchanged in technique since the original description by Pasteur,[1] remains the most widely used method in industry for obtainment of enantiomerically pure organic compounds.[2] In 1998 a significant modification of this classic technique was reported by some of us.[3] Upon simultaneous addition of structurally related resolving agents, high diastereomeric excesses (*de* values) of the first salts were obtained in a large number of resolutions. The success rate was 90–95 % compared to the usual 20–30 % estimated in one of the few studies published.[4] Structurally related resolving agents were denoted as family members and the method itself has become known as "Dutch Resolution".

In practice, three structurally related resolving agents are used in a 1:1:1 ratio. A mixture of these resolving agents was usually found in the first salt, but in nonstoichiometric ratios. In general, the families of resolving agents show solid-solution behavior. However, in the 46 examples of resolutions of single racemates reported in ref. [3], in ten cases no detectable amount of one (or more) of the three resolving agents was present in the salt. In three other cases, one of the resolving agents was present in < 10 mol %. The resolving agents that are regularly not incorporated, or which are incorporated only to a small extent, in the salt are shown in italics in Scheme 1 for the families used in the current work.[5]

Although direct comparisons are difficult owing to differences in solubilities and the almost certain involvement of

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