

Supporting Information

Table S2. Values of Glycosidic ϕ - ψ and Hydroxymethyl Group ω Orientations of the CAM-B3LYP DFT-optimized 4×Cello-Octamer Chain Sheet Models

Cellulose I α chain sheet model

Positions ^a		ϕ (degrees)	ψ (degrees)	ω (degrees)
Chain	Residue			
	Obsd.	-98.3	-139.0	166.8
<i>a</i>	+4	-91.1	-142.2	158.6
	+3	-94.5	-142.4	163.8
	+2	-92.0	-142.3	159.9
	+1	-94.9	-142.0	163.8
	-1	-92.3	-143.1	160.5
	-2	-95.5	-142.1	163.3
	-3	-92.1	-145.4	163.0
	-4	-	-	178.9
<i>b</i>	+4	-93.2	-141.6	162.9
	+3	-93.9	-142.8	164.2
	+2	-93.7	-142.3	163.7
	+1	-94.1	-142.6	164.3
	-1	-93.8	-142.9	164.3
	-2	-94.3	-142.2	163.6
	-3	-94.1	-144.1	165.3
	-4	-	-	-178.7
<i>c</i>	+4	-93.3	-142.4	164.0
	+3	-93.6	-142.2	163.9
	+2	-93.6	-142.3	163.9
	+1	-93.9	-142.6	164.2
	-1	-93.6	-142.5	163.9
	-2	-94.8	-143.1	165.0
	-3	-94.1	-143.3	164.1
	-4	-	-	-176.3
<i>d</i>	+4	-94.5	-140.9	163.3
	+3	-91.8	-142.4	160.4
	+2	-94.8	-141.4	163.7
	+1	-92.0	-142.6	160.8
	-1	-94.6	-140.9	162.9
	-2	-90.4	-143.5	161.7
	-3	-92.8	-137.9	160.5
	-4	-	-	-175.5

^a See Figure 1 for the definition of the position labeling. The chain labeling is arbitrary.

Cellulose I β chain sheet mode.

Positions ^a		ϕ (degrees)	ψ (degrees)	ω (degrees)
Chain	Residue			
	Obsd.	-98.4	-142.4	169.4
<i>a</i>	+4	-94.6	-140.8	163.3
	+3	-91.7	-142.4	160.3
	+2	-94.7	-141.3	163.6
	+1	-91.9	-142.7	160.7
	-1	-94.5	-140.8	162.8
	-2	-90.4	-143.5	161.7
	-3	-92.8	-138.0	160.8
	-4	-	-	-175.5
<i>b</i>	+4	-93.2	-142.4	164.0
	+3	-93.7	-142.3	163.9
	+2	-93.5	-142.2	163.7
	+1	-93.8	-142.6	164.2
	-1	-93.5	-142.2	163.6
	-2	-94.6	-143.3	164.9
	-3	-94.4	-143.3	164.3
	-4	-	-	-176.1
<i>c</i>	+4	-93.1	-141.7	162.9
	+3	-94.0	-142.8	164.3
	+2	-93.7	-142.3	163.6
	+1	-94.1	-142.7	164.4
	-1	-93.8	-142.8	164.1
	-2	-94.1	-142.1	163.4
	-3	-94.2	-143.3	164.2
	-4	-	-	-178.8
<i>d</i>	+4	-91.1	-142.2	158.5
	+3	-94.5	-142.5	163.9
	+2	-92.0	-142.4	159.9
	+1	-95.0	-142.0	163.8
	-1	-92.2	-142.9	160.3
	-2	-94.8	-141.5	163.0
	-3	-90.4	-142.6	161.4
	-4	-	-	155.6

^a See Figure 1 for the definition of the position labeling. The chain labeling is arbitrary.

Cellulose II (010) chain sheet model.

Positions ^a		ϕ (degrees)	ψ (degrees)	ω (degrees)
Chain	Residue			
	Obsd.	-96.8	-143.5	72.2
<i>a</i>	+4	-84.9	-144.8	68.2
	+3	-90.8	-152.8	55.9
	+2	-90.3	-155.7	57.8
	+1	-94.8	-147.9	60.3
	-1	-78.0	-135.5	57.2
	-2	-90.9	-144.8	58.3
	-3	-86.0	-140.1	56.3
	-4	-	-	74.1
<i>b</i>	+4	-88.7	-136.9	159.3
	+3	-86.6	-138.4	154.6
	+2	-84.7	-134.9	66.8
	+1	-86.2	-133.2	70.7
	-1	-89.3	-136.4	62.1
	-2	-86.9	-135.9	59.7
	-3	-101.4	-139.3	63.0
	-4	-	-	64.0
<i>c</i>	+4	-86.3	-137.4	77.7
	+3	-86.0	-149.1	64.9
	+2	-88.3	-130.3	57.8
	+1	-91.4	-137.5	62.6
	-1	-90.2	-136.5	62.5
	-2	-92.1	-138.0	63.5
	-3	-86.7	-135.1	59.5
	-4	-	-	60.2
<i>d</i>	+4	-86.4	-143.9	74.0
	+3	-87.4	-152.6	54.5
	+2	-96.5	-150.4	60.0
	+1	-79.8	-137.2	58.0
	-1	-94.5	-148.6	60.7
	-2	-78.0	-135.8	57.2
	-3	-90.5	-147.0	58.7
	-4	-	-	54.2

^a See Figure 1 for the definition of the position labeling. The chain labeling is arbitrary.

Cellulose II (020) chain sheet model.

Positions ^a		ϕ (degrees)	ψ (degrees)	ω (degrees)
Chain	Residue			
	Obsd.	-93.6	-150.8	58.1
<i>a</i>	+4	-87.3	-157.1	77.2
	+3	-86.1	-158.5	57.0
	+2	-86.4	-160.6	50.9
	+1	-86.7	-161.7	57.8
	-1	-86.5	-162.7	52.8
	-2	-87.7	-160.9	58.3
	-3	-87.6	-168.1	53.3
	-4	-	-	63.2
<i>b</i>	+4	-88.2	-161.4	79.5
	+3	-86.4	-165.7	55.2
	+2	-86.2	-163.3	54.0
	+1	-85.8	-164.8	52.9
	-1	-85.4	-164.8	53.9
	-2	-86.7	-164.3	52.9
	-3	-86.0	-166.4	53.5
	-4	-	-	55.5
<i>c</i>	+4	-88.7	-160.7	80.7
	+3	-86.2	-167.2	56.0
	+2	-86.2	-165.2	54.8
	+1	-85.8	-164.6	53.6
	-1	-86.0	-165.6	53.4
	-2	-86.2	-164.7	54.0
	-3	-85.9	-165.7	52.6
	-4	-	-	55.4
<i>d</i>	+4	-89.8	-163.9	71.1
	+3	-89.0	-166.7	57.2
	+2	-86.9	-164.6	60.4
	+1	-87.3	-162.1	53.6
	-1	-87.3	-163.1	58.2
	-2	-87.1	-162.7	54.2
	-3	-85.0	-169.2	56.7
	-4	-	-	56.8

^a See Figure 1 for the definition of the position labeling. The chain labeling is arbitrary.

Cellulose III₁ (1-10) chain sheet model

Positions ^a		ϕ (degrees)	ψ (degrees)	ω (degrees)
Chain	Residue			
	Obsd.	-92.0	-146.5	44.2
<i>a</i>	+4	-88.0	-157.1	51.9
	+3	-85.3	-152.0	62.2
	+2	-88.5	-154.7	59.7
	+1	-85.8	-151.0	61.6
	-1	-88.5	-155.4	60.0
	-2	-86.1	-150.3	61.5
	-3	-86.3	-162.8	56.9
	-4	-	-	61.0
<i>b</i>	+4	-87.1	-151.1	51.7
	+3	-88.0	-150.6	59.1
	+2	-86.9	-151.9	60.3
	+1	-88.5	-150.2	60.7
	-1	-86.2	-152.8	60.0
	-2	-89.4	-149.4	60.8
	-3	-82.5	-157.3	56.2
	-4	-	-	60.8
<i>c</i>	+4	-87.5	-151.1	52.2
	+3	-87.6	-150.8	58.9
	+2	-86.6	-152.3	61.2
	+1	-88.6	-149.8	60.2
	-1	-86.3	-153.3	60.2
	-2	-88.5	-149.2	60.3
	-3	-82.8	-157.3	55.9
	-4	-	-	61.7
<i>d</i>	+4	-84.5	-150.5	57.8
	+3	-89.8	-155.5	58.8
	+2	-83.7	-153.2	62.3
	+1	-90.1	-152.6	60.2
	-1	-83.9	-154.0	61.9
	-2	-90.4	-152.2	60.7
	-3	-84.6	-155.3	62.1
	-4	-	-	60.6

^a See Figure 1 for the definition of the position labeling. The chain labeling is arbitrary.