# Makromolekulák 10.

Simon István

# A béta-glikozidos kötés konfigurációja

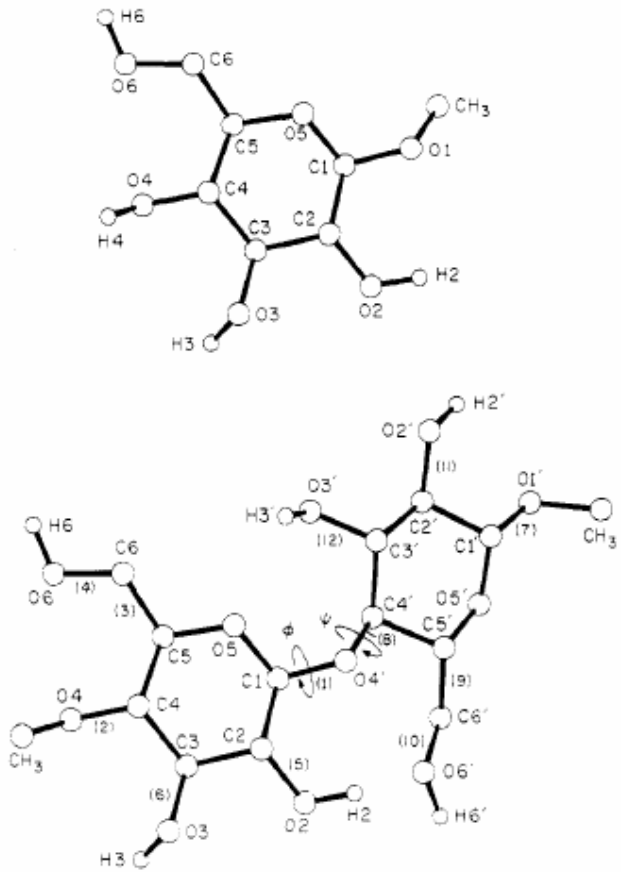



**Figure 1.** Nomenclature used for the atoms and dihedral angles in the mono- and disaccharide: top, methyl β-D-glucopyranoside (for glucose, the terminal $CH_3$ group is replaced by an H atom designated as H1); bottom, dimethyl β-D-diglucopyranoside (for cellobiose, the two terminal $CH_3$ groups are replaced by H atoms, designated as H4 and H1′).

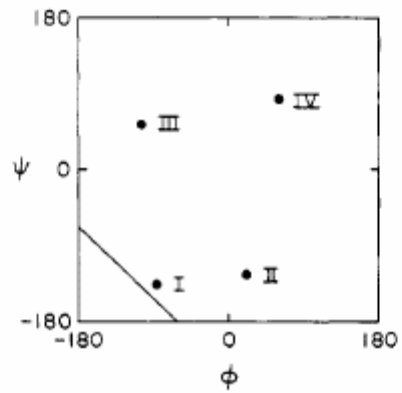



**Figure 2.** Location of the four energy minima and the line corresponding to the values of $\phi$ and $\psi$ for a two-fold screw axis (a second portion of this line, near minimum IV, has been omitted). Relative energies in kcal/mol: I, 0.0; II, 18; III, 33; IV, 224.

# A CVFF forcefield

$$E_{pot} = \underset{(1)}{\sum_b D_b\left[1 - e^{-\alpha(b-b_0)^2}\right]} + \underset{(2)}{\frac{1}{2}\sum_\theta H_\theta(\theta-\theta_0)^2} + \underset{(3)}{\frac{1}{2}\sum_\phi H_\phi[1 + s\cos(n\phi)]} +$$

$$+ \underset{(4)}{\frac{1}{2}\sum_\chi H_\chi \chi^2} + \underset{(5)}{\sum_b \sum_{b'} F_{bb'}(b-b_0)(b'-b_0')} + \underset{(6)}{\sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta_0')} +$$

$$+ \underset{(7)}{\sum_b \sum_\theta F_{b\theta}(b-b_0)(\theta-\theta_0)} + \underset{(8)}{\sum_\phi F_{\phi\theta\theta'}\cos\phi(\theta-\theta_0)(\theta'-\theta_0)} + \underset{(9)}{\sum_\chi \sum_{\chi'} F_{\chi\chi'}\chi\chi}$$

$$+ \underset{(10)}{\sum \varepsilon\left[\left(\frac{r^*}{r}\right)^{12} - 2\left(\frac{r^*}{r}\right)^6\right]} + \underset{(11)}{\sum \frac{q_i q_j}{\varepsilon r_{ij}}}$$

# Az ECEPP forcefield

Coulomb term:

$$U_e = \frac{332\, q_i\, q_j}{D\, r_{ij}}$$

Lennard-Jones 6-12 potencial:

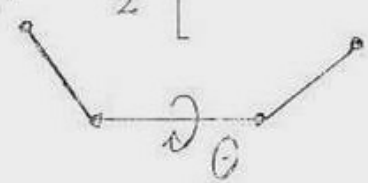
$$U_{6\text{-}12} = \varepsilon_{ij}\left[F\left(\frac{r_{ij}^{o}}{r_{ij}}\right)^{12} - 2\left(\frac{r_{ij}^{o}}{r_{ij}}\right)^{6}\right]$$

Hydrogen-bonding potencial:

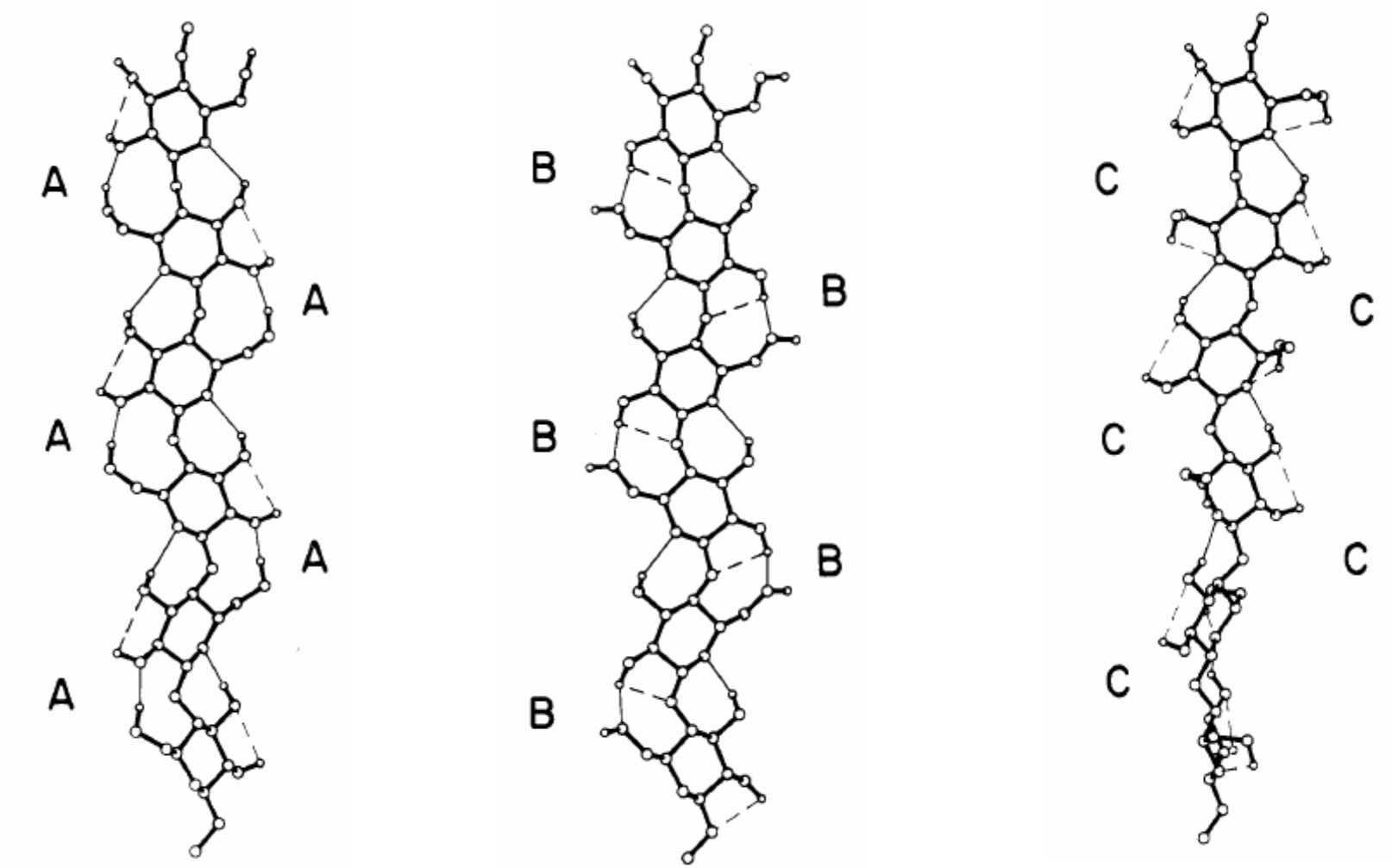
$$U_{HB} = \varepsilon_{ij}\left[\left(\frac{r_{ij}^{o}}{r_{ij}}\right)^{12} - 2\left(\frac{r_{ij}^{o}}{r_{ij}}\right)^{10}\right]$$

Intrinsic torsional potencial:

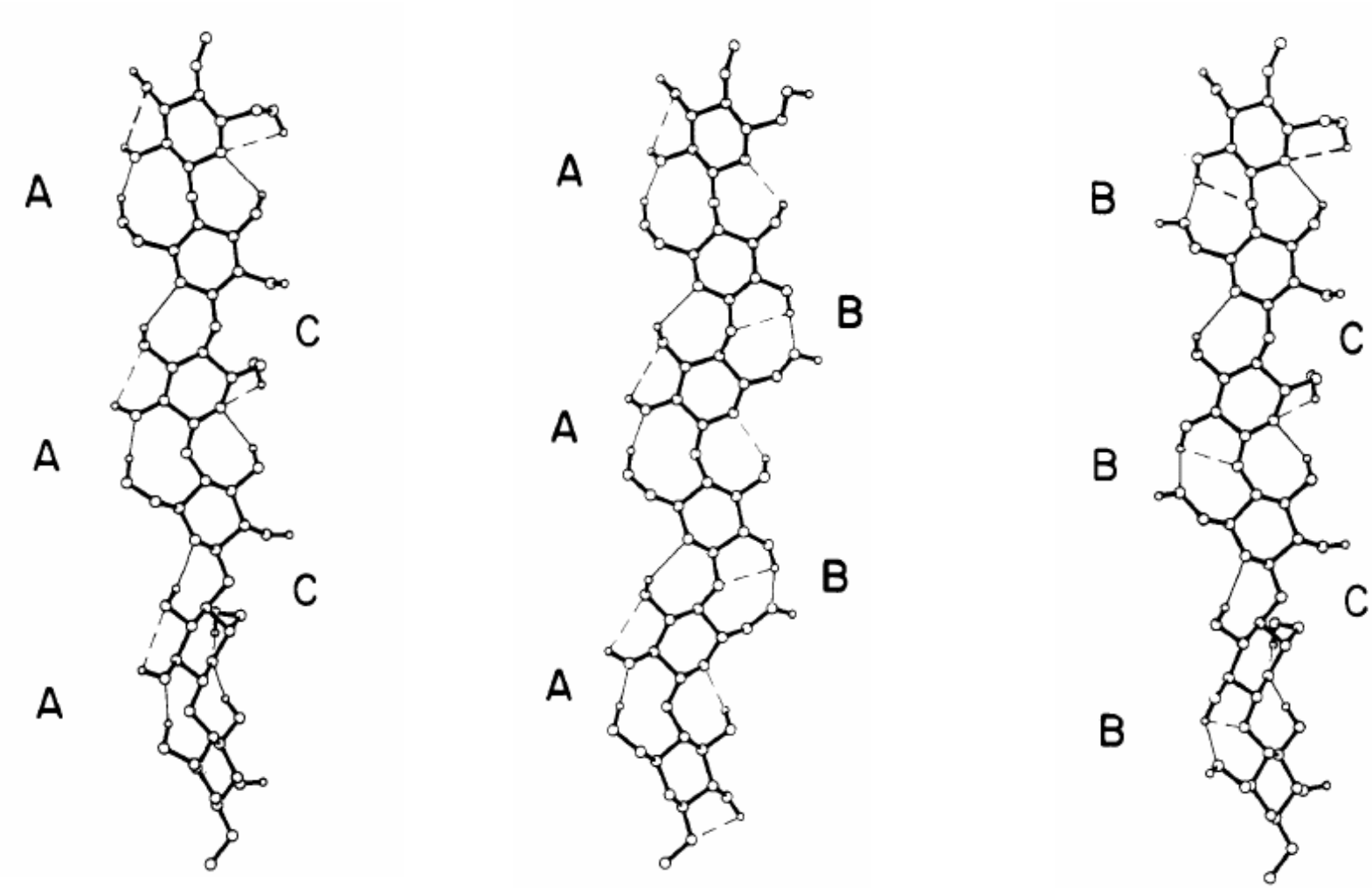
$$U_t = \frac{U_o}{2}\left[1 + k\cos(n\theta)\right]$$



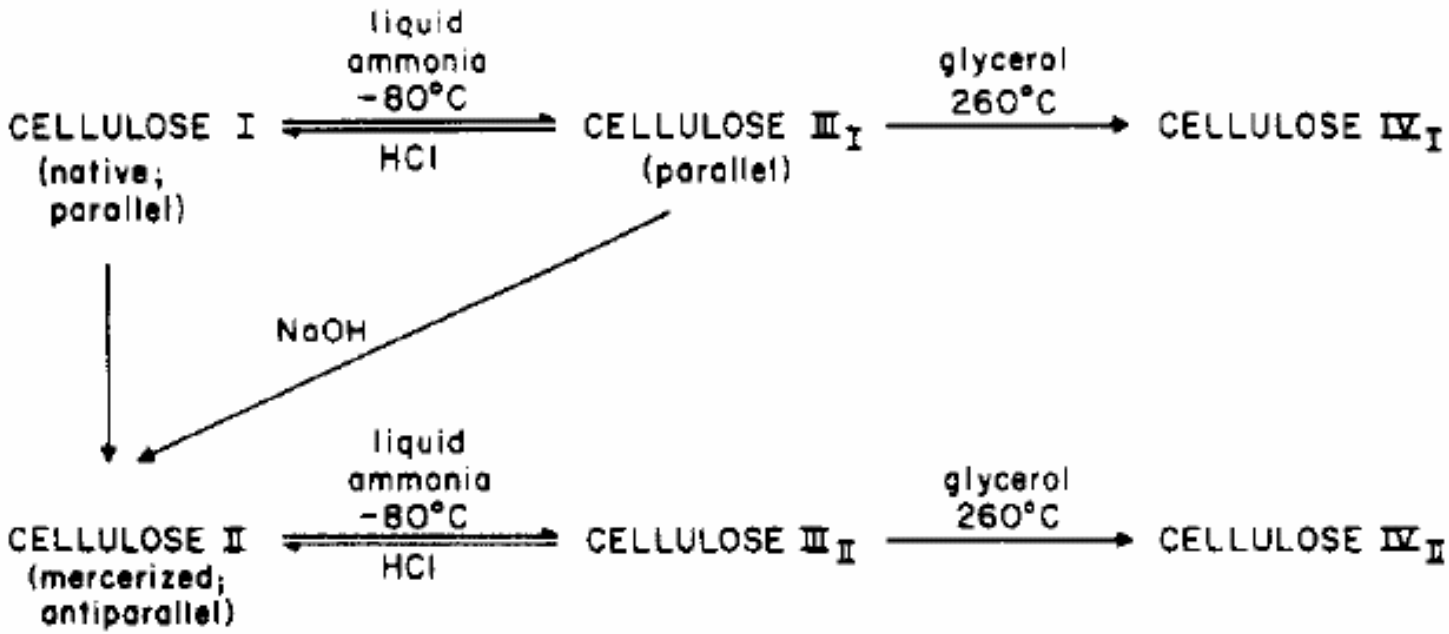
# Azonos diszaccharidokból felépülő hexaszaccharid



# Váltakozó szerkezetű diszaccharidokból felépülő hexaszaccharid



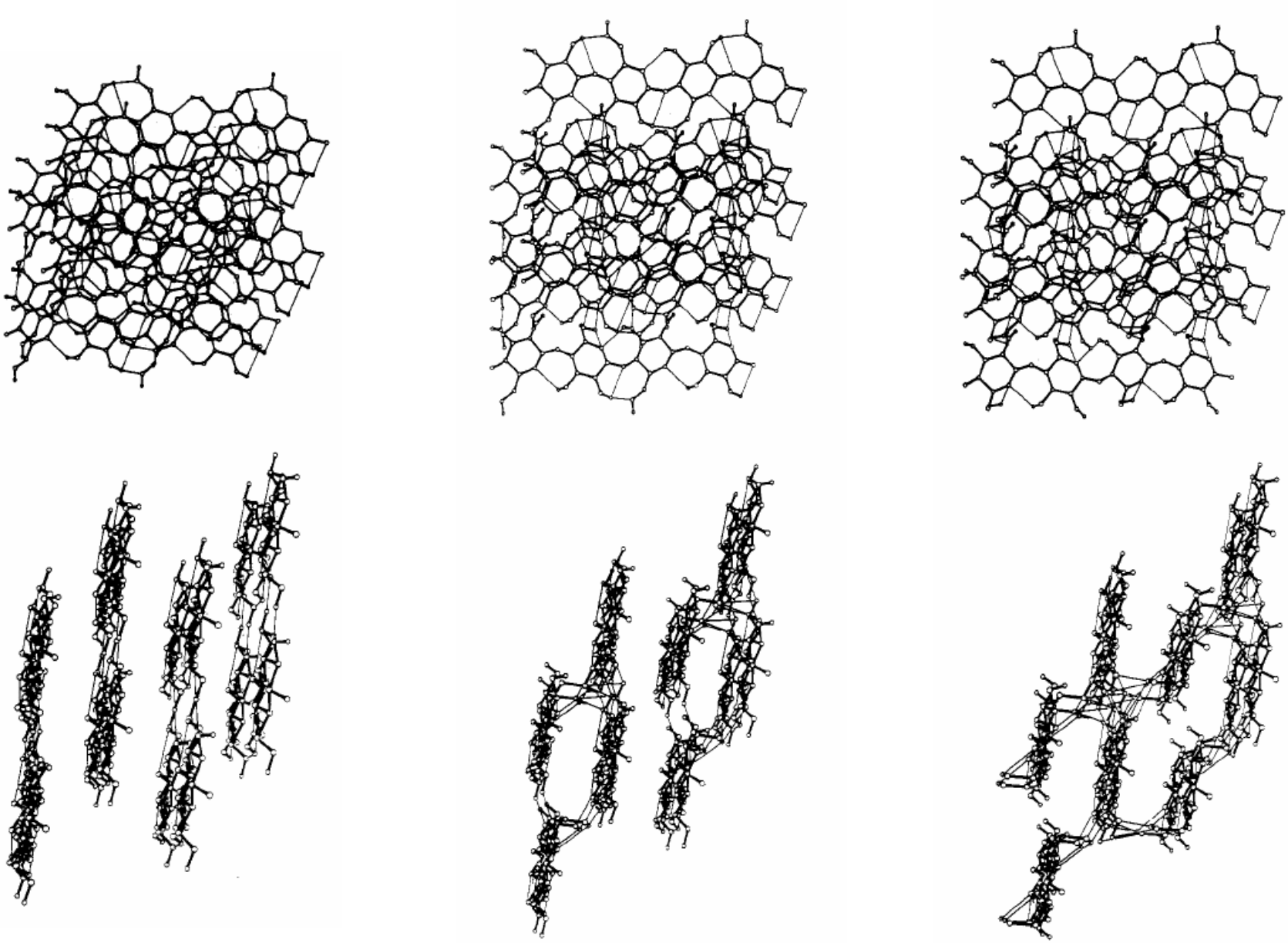
# A cellulóz különböző módosulatai



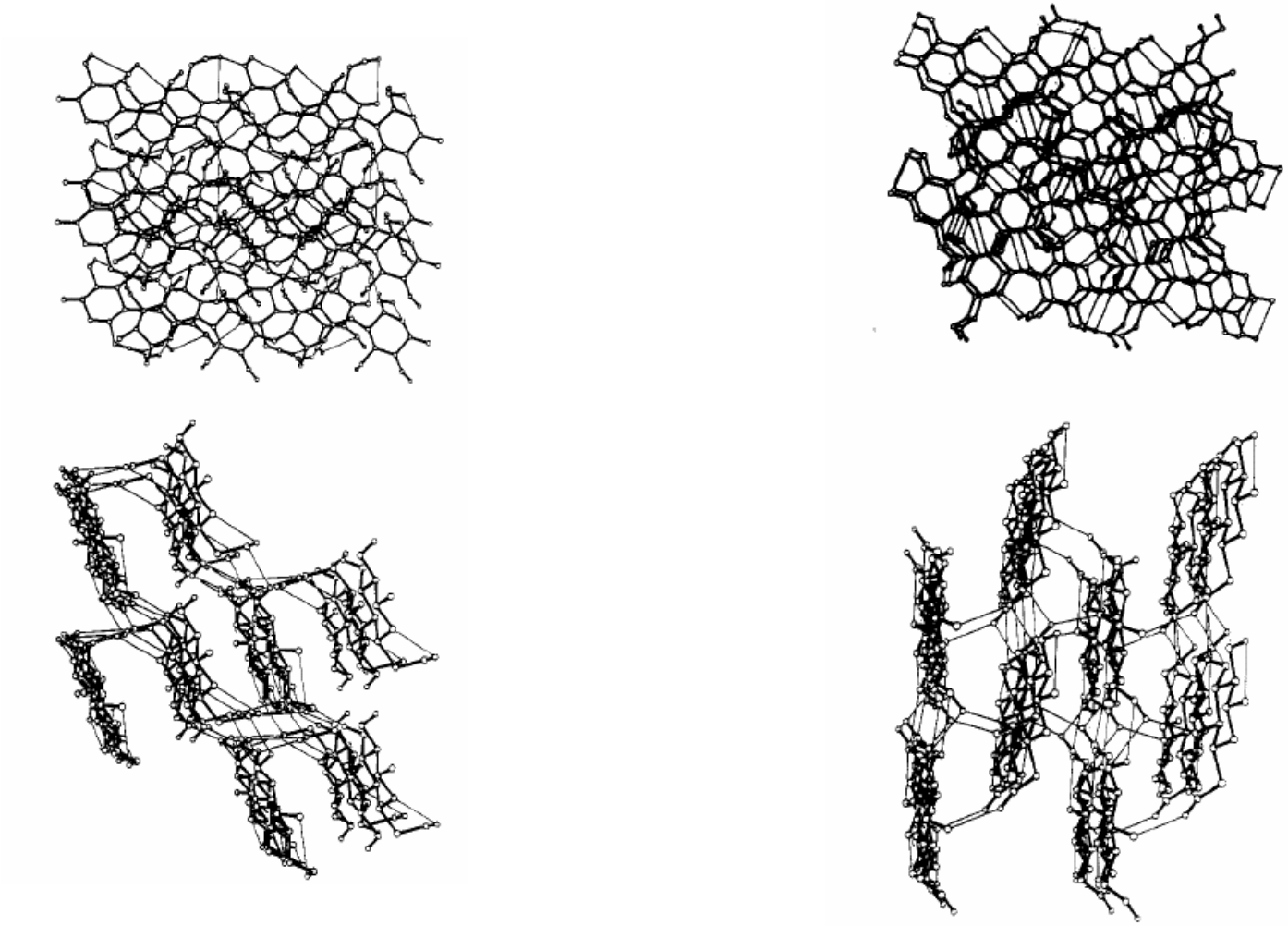
# Alacsony energiájú parallel és antiparallel elrendezésű cellulóz elemi cellák

| | corner/center | $\Delta E$ | $a$ | $b$ | $c$ | $\alpha$ | $\beta$ | $\gamma$ | $x_0$ | $y_0$ | $z_0$ | $D$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Parallel | | | | | | | |
| | cellulose I (X-ray)[1] | | 10.3 | 8.35 | 7.90 | 84° | 90° | 90° | | | | |
| 1 | $(BB)_n/(BB)_n$ | 0.00 | (10.23)[c] | 8.28 | 8.22 | 76.15° | 90.74° | 89.85° | 0.241 | 0.487 | 0.505 | 2.57° |
| 2[b] | $(CB)_n/(BB)_n$ | 0.49 | (10.23) | 8.13 | 9.66 | 58.70° | 91.43° | 89.33° | 0.228 | 0.491 | 0.505 | −9.90° |
| 3 | $(CC)_n/(BB)_n$ | 1.34 | (10.23) | 8.07 | 9.62 | 58.68° | 91.00° | 89.83° | 0.228 | 0.491 | 0.503 | 11.57° |
| | | | | | Antiparallel | | | | | | | |
| | cellulose II (X-ray)[3] | | 10.36 | 8.01 | 9.04 | 117.1° | 90° | 90° | | | | |
| 4 | $(AA)_n/(CC)_n$ | −5.95 | (10.23) | 7.74 | 9.75 | 122.46° | 90.09° | 89.66° | 0.620 | 0.613 | 0.457 | 12.15° |
| 5 | $(BB)_n/(BB)_n$ | −2.07 | (10.23) | 8.24 | 7.71 | 90.18° | 89.99° | 90.32° | 0.623 | 0.664 | 0.500 | 0.89° |

# Parallel elrendezésű elemi cellák



# Antiparallel elrendezésű elemi cellák

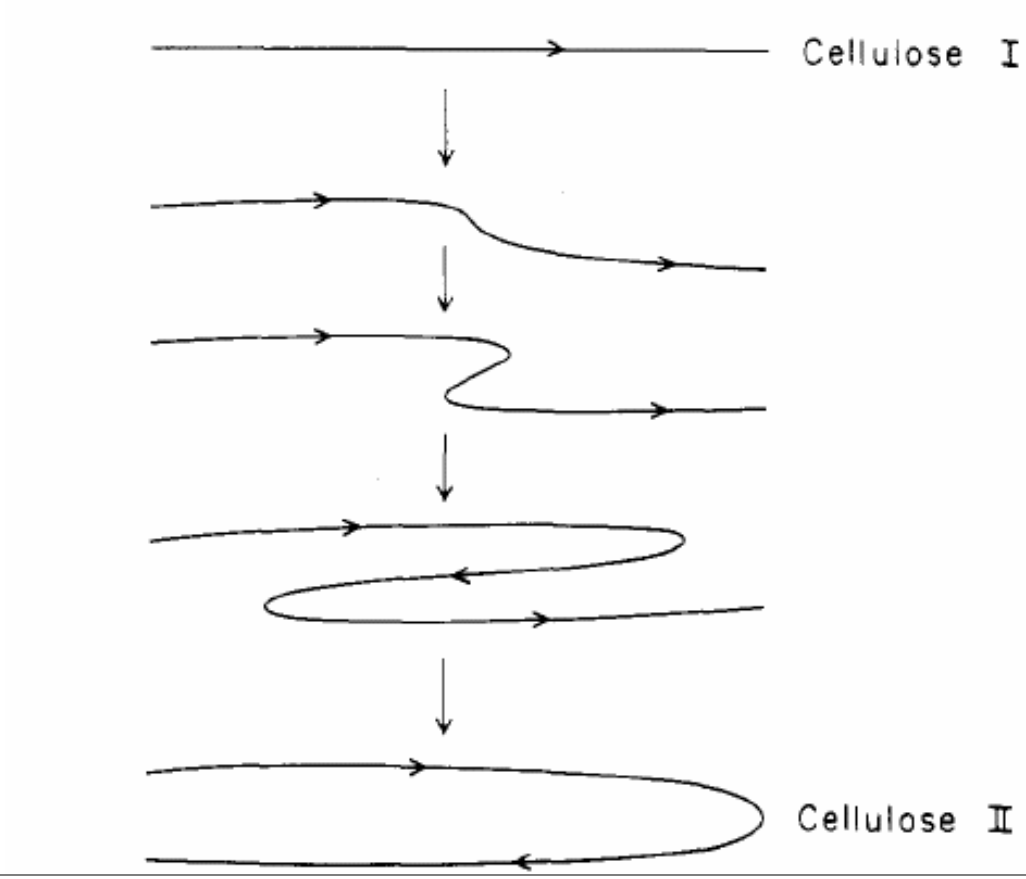
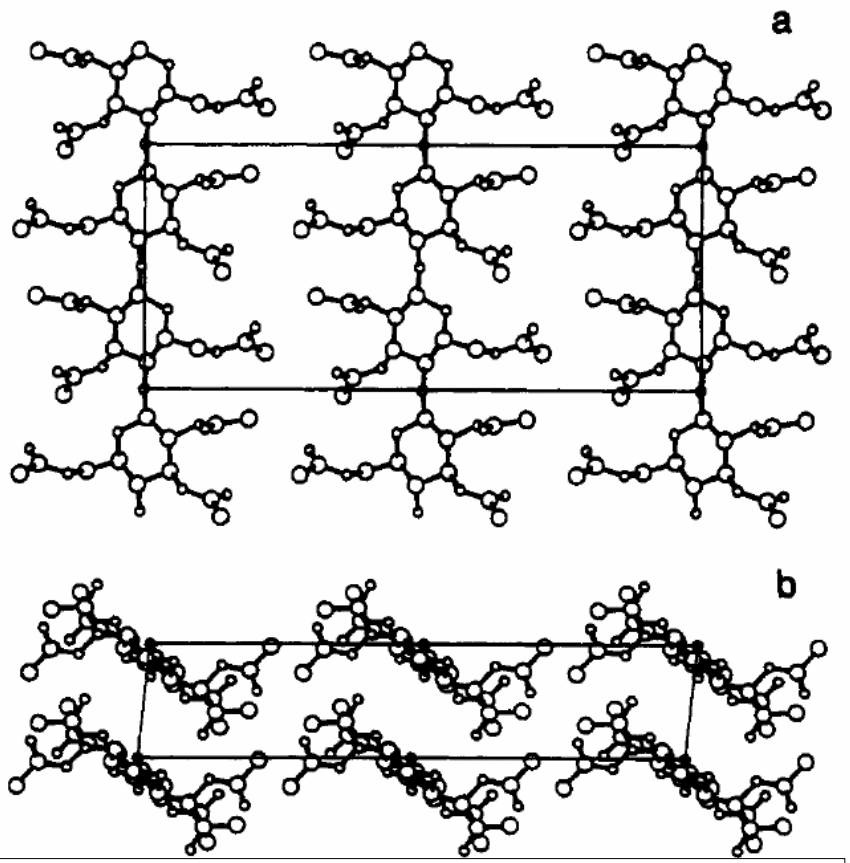
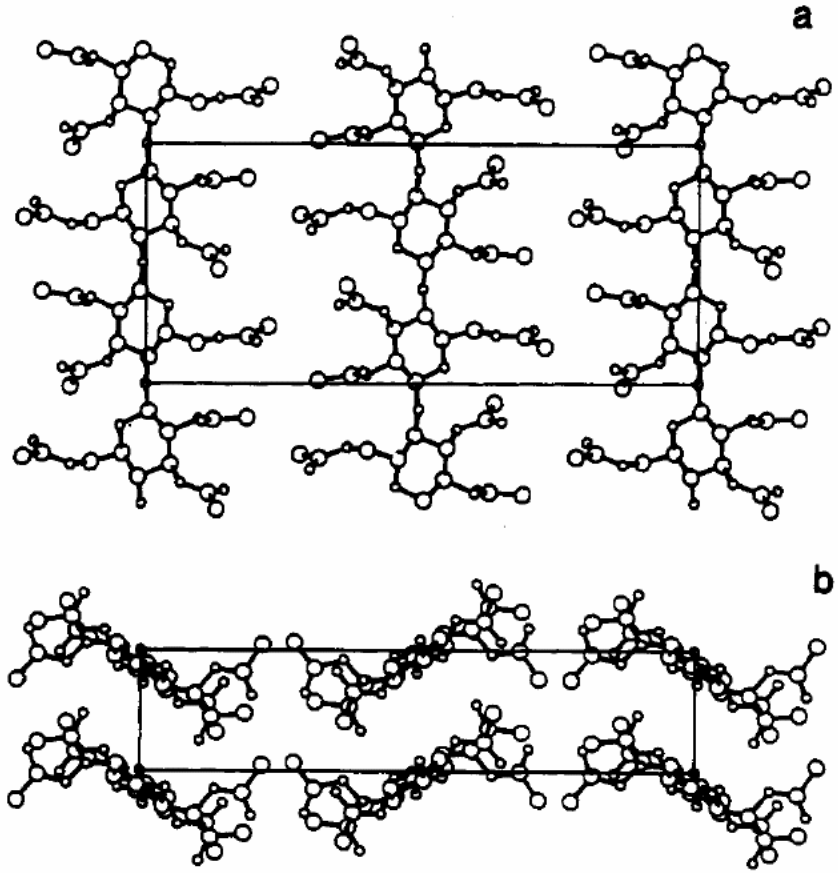


# Cellulóz szerkezetek azonosítása

**Lengths (Å) of Hydrogen Bonds[a] Stabilizing Cellulose Structures**

| struct[b] | intrachain[c] | intrasheet[d] | intersheet[d] |
|---|---|---|---|
| | Parallel (Cellulose I) | | |
| 1 | O4···H2 (2.62) | O3···H6 (1.79) | none |
| | O5···H3 (2.15) | | |
| | O6···H2 (1.76) | | |
| 2 | O4···H2 (2.62) | O3···H6 (1.76) | O3···H6 (2.61) |
| | O5···H3 (2.27) | | O6···H2 (1.87) |
| | O5···H6 (2.44) | | O6···H3 (2.23) |
| | O6···H2 (1.75) | | O6···H6 (1.84) |
| 3 | O4···H2 (2.71) | O3···H6 (1.77) | O3···H6 (2.61) |
| | O5···H3 (2.30) | | O6···H2 (1.87) |
| | O5···H6 (2.40) | | O6···H3 (2.23) |
| | O6···H2 (1.85) | | O6···H6 (1.84) |
| | Antiparallel (Cellulose II) | | |
| 4 | O2···H6 (1.73) | none | O2···H2 (1.80) |
| | O3···H2 (2.69) | | O2···H6 (2.33) |
| | O4···H2 (2.80) | | O6···H3 (1.73) |
| | O4···H6 (2.80) | | O6···H6 (2.74) |
| | O5···H3 (2.56) | | |
| | O5···H6 (2.58) | | |
| 5 | O4···H2 (2.59) | O3···H6 (2.67) | O4···H6 (2.18) |
| | O5···H3 (2.35) | O6···H3 (2.66) | |
| | O6···H2 (1.74) | | |

# Antiparallel cellulóz szerkezet kialakulása



# Parallel és antiparallel cellulóz-triacetát