

Peptidna veza

- Podsetnik iz termodinamike
- Stabilnost peptidne veze u vodenoj sredini?
 - termodinamička stabilnost
 - kinetička inertnost
- Gradjenje peptidne veze u vodenoj sredini
 - aktiviranje karboksilne grupe *in vitro* i *in vivo*
- Strukturne karakteristike peptidne veze

Podsetnik iz termodinamike:

Entalpija

Entropija

Slobodna (Gibbsova) energija

B. Enthalpy and entropy

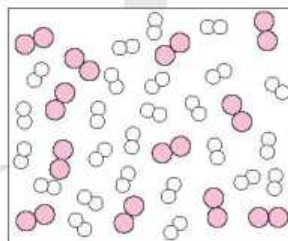
ΔH : change of enthalpy, heat exchange

$$\Delta G = \Delta H - T \cdot \Delta S$$

Gibbs-Helmholtz equation

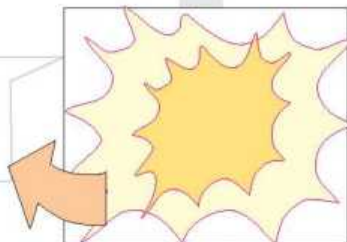
ΔS : change of entropy, i.e. degree of order

1 mol H_2
1/2 mol O_2

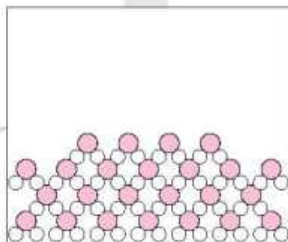


Low degree of order

System releases heat,
 $\Delta H < 0$
(exothermic)



1 mol H_2O
(liquid)

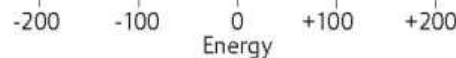


Higher degree of order,
 $\Delta S < 0$

$\Delta H = -287 \text{ kJ} \cdot \text{mol}^{-1}$

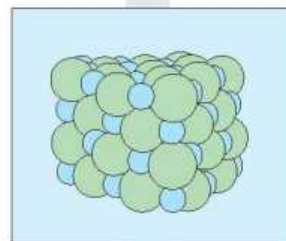
$-T \cdot \Delta S = +49 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta G = -238 \text{ kJ} \cdot \text{mol}^{-1}$



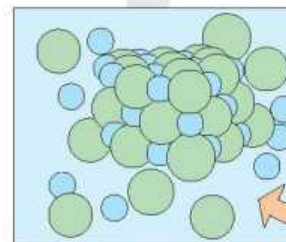
1. "Knall-gas" reaction

1 mol NaCl
(crystalline)

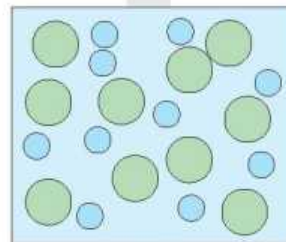


High degree of order

System absorbs heat,
 $\Delta H > 0$
(endothermic)



1 mol Na^+
1 mol Cl^-

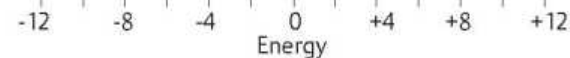


Lower degree of order
 $\Delta S > 0$

$\Delta H = +3.8 \text{ kJ} \cdot \text{mol}^{-1}$

$-T \cdot \Delta S = -12.8 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta G = -9.0 \text{ kJ} \cdot \text{mol}^{-1}$



2. Dissolution of NaCl in water

Nastajanje i stabilnost peptidne veze u vodenoj sredini:

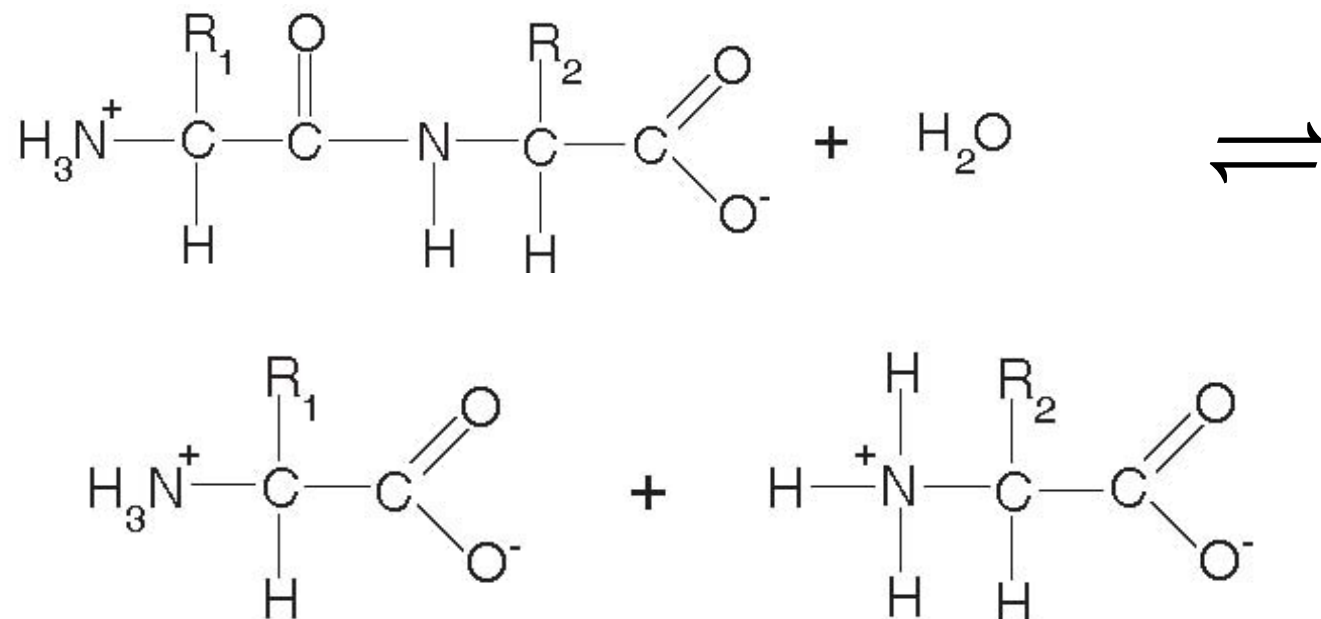
termodinamička stabilnost!
kinetička inertnost!

Reakcija hidrolize peptidne veze u vodi

Kako opstaje peptidna veza u vodi?
(termodinamički nestabilna, kinetički inertna)

Kako nastaje peptidna veza u vodenoj sredini?

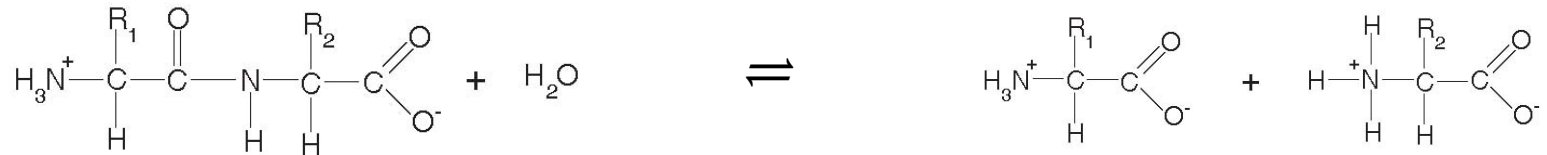
Reakcija hidrolize peptidne veze u vodi



Ravnoteža za ovu reakciju je "pomerena" u desno

$$K \sim 10^4$$

Zašto je reakcija hidrolize pomerenjena u desno???



$$\Delta G = -RT \ln K = -2.3RT \log K$$

$$\text{za } K \sim 10^4$$

$$\Delta G < 0 \quad \sim 20 \text{ kJ}$$

Zašto je $\Delta G < 0$?

$$\Delta G = \Delta H - \Delta S$$

Kako opstaje peptidna veza u vodi???

- Hidroliza peptidne (amidne) veze u vodi je **spora!** (konstanta BRZINE za ovu reakciju je mala!!!!)
- Peptidna veza je **TERMODINAMIČKI** nestabilna a **KINETIČKI** inertna!!!
- Reakcija hidrolize može da se **ubrza** (katalizuje):
kiseline, baze, enzimi !!!

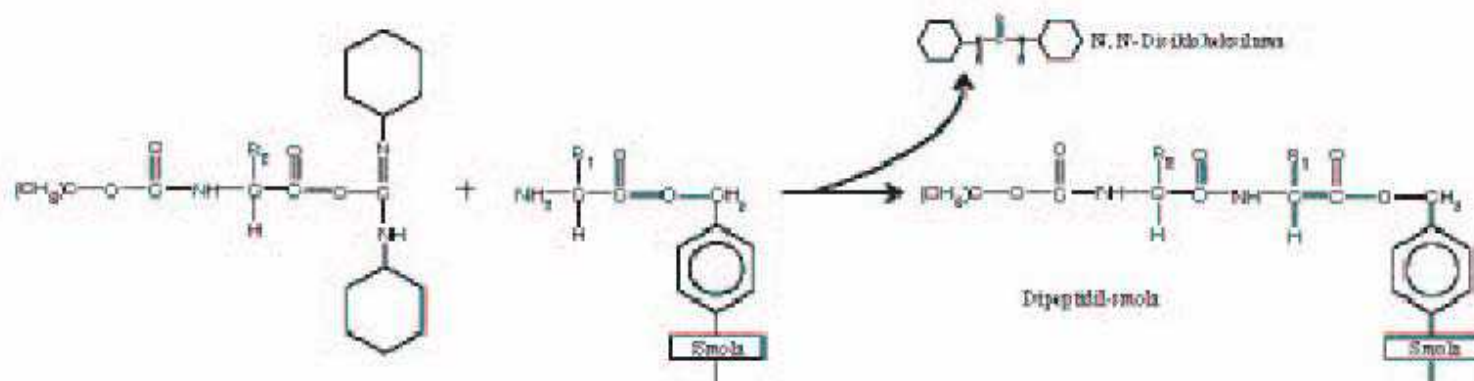
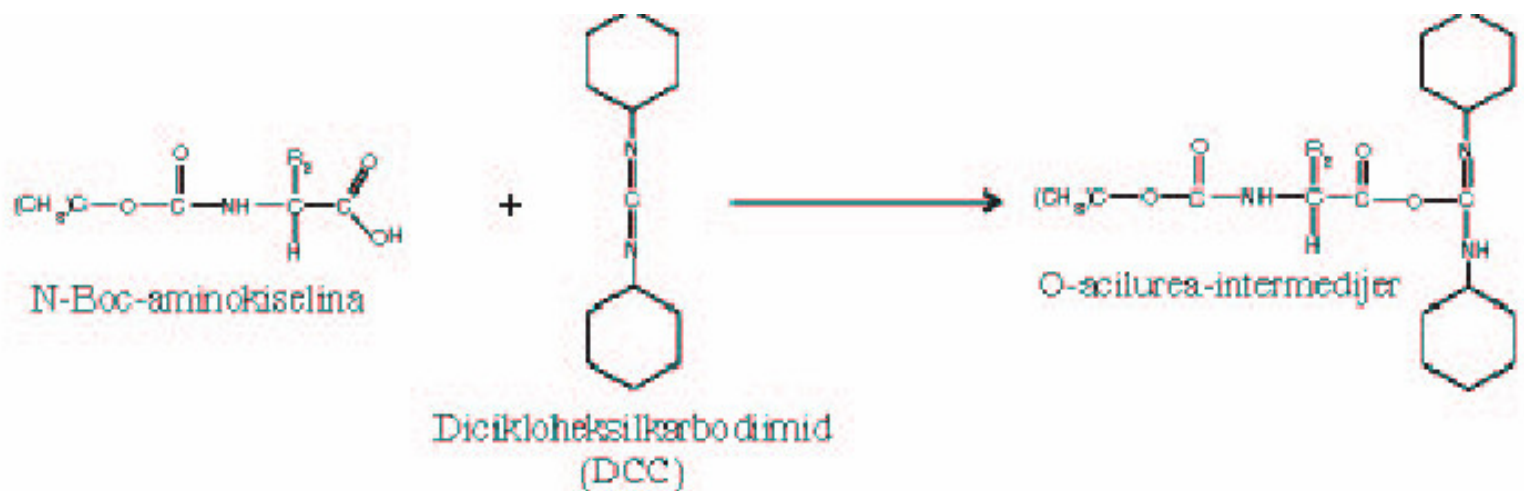
- Kako nastaje peptidna veza u vodenoj sredini?

- Za hidrolizu: $\Delta G < 0$

∴

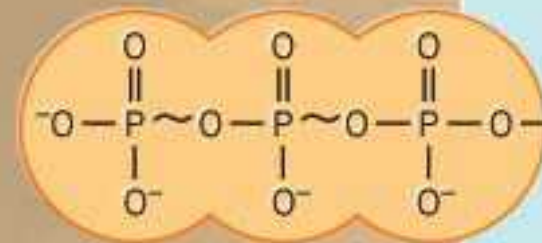
- Za sintezu: $\Delta G > 0$

Aktiviranje aminokiselina u hemijskoj sintezi

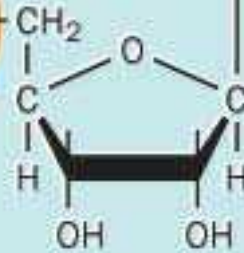
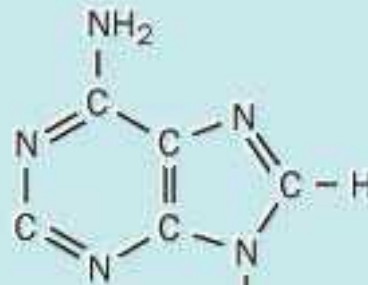




Phosphate groups



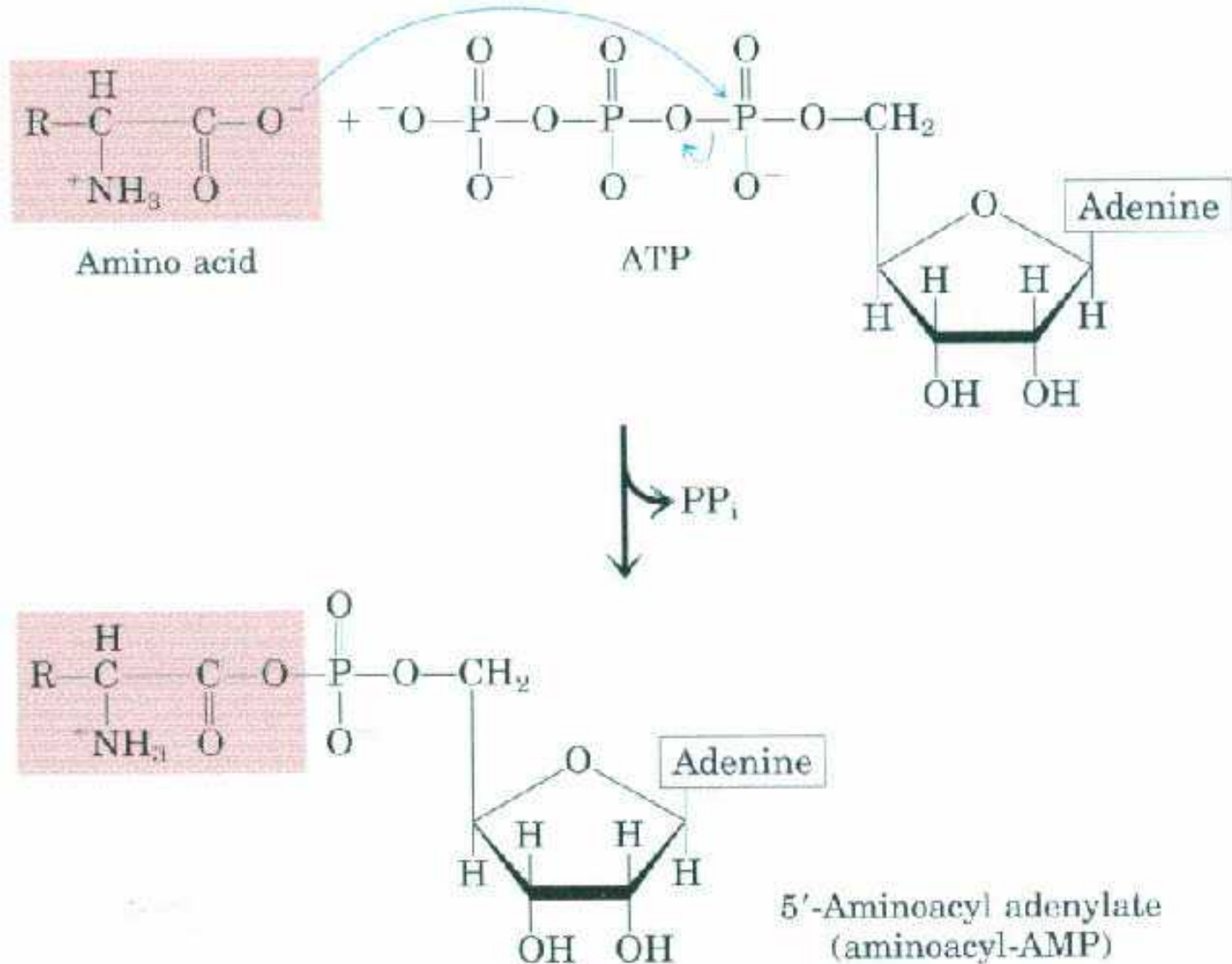
Adenine



Ribose

ATP

Aktiviranje aminokiselina sa ATP u biosintezi



Motion
Active transport
Biosyntheses
Signal amplification

ATP

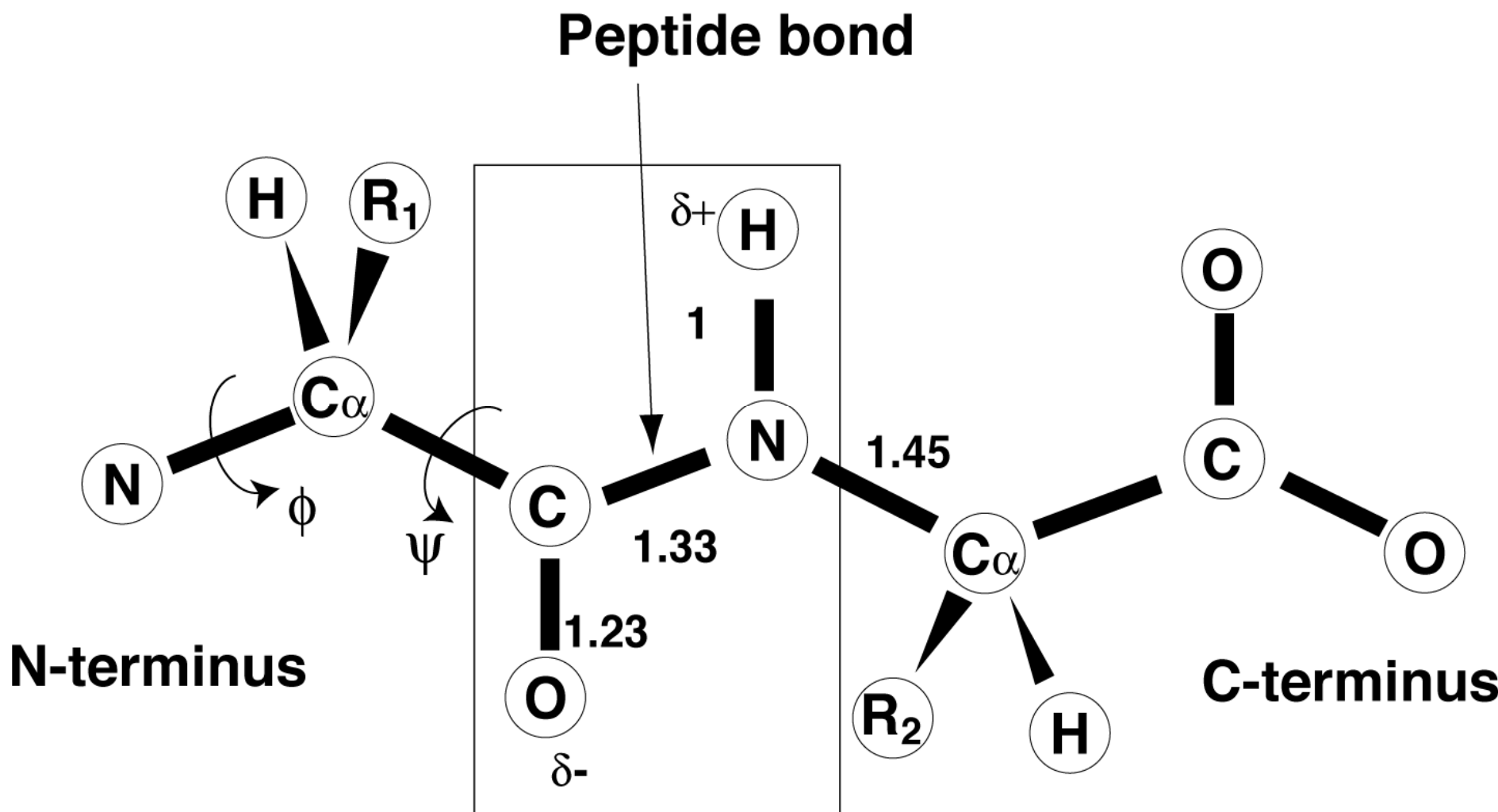
ADP

Oxidation of fuel
molecules
or
Photosynthesis



Strukturne karakteristike peptidne veze

- Parcijalni dvostruki karakter peptidne veze
- Dipolni karakter peptidne veze



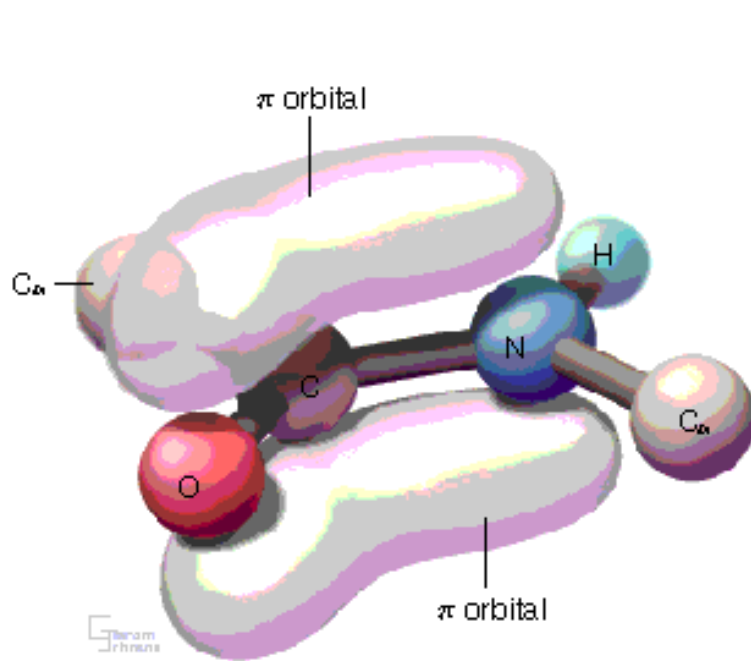
Dužina proste C-N veze je **1.49Å**

Dužina peptidne C-N veze je **1.33Å**

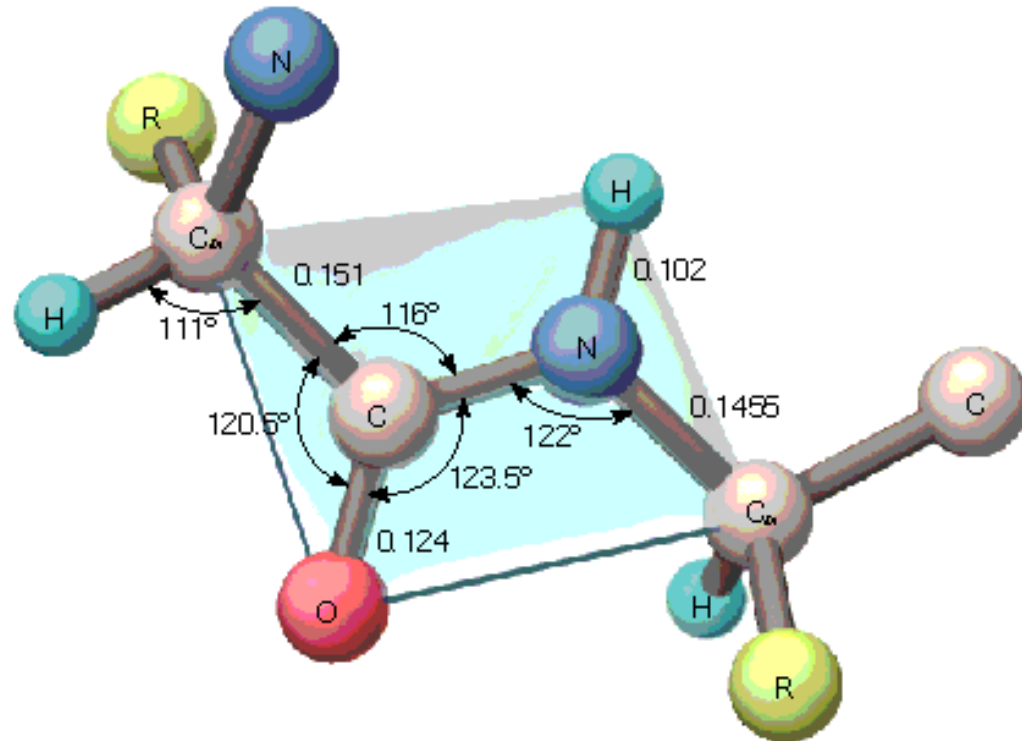
Dužina dvostruke C=O veze je **1.27 Å**

∴ Peptidna C-N veza ima **parcijalni dvostruki karakter**

Parcijalni dvostruki karakter peptidne veze



(a) Partial double-bond character of peptide bond

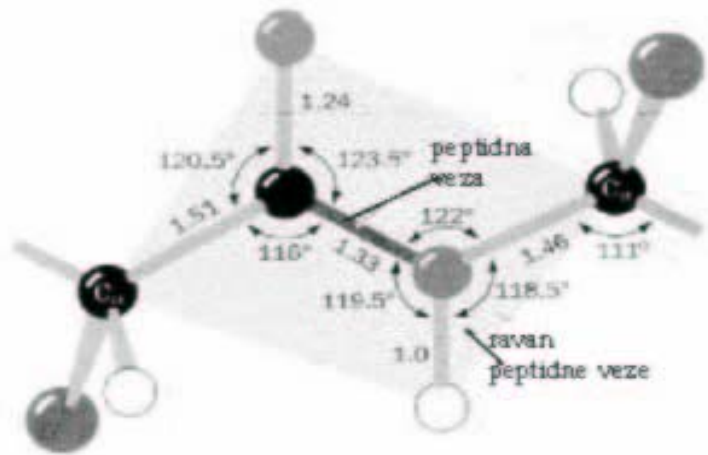


(b) Bond angles and lengths

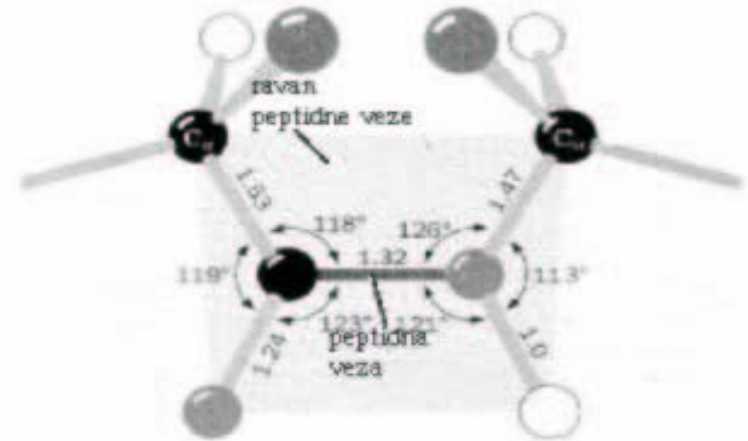
Peptidna veza ima parcijalni dvostruki karakter **zbog** delokalizacije π -elektrona nad O-C-N vezama.

Peptidna veza je **planarna**.

Trans i cis peptidna veza



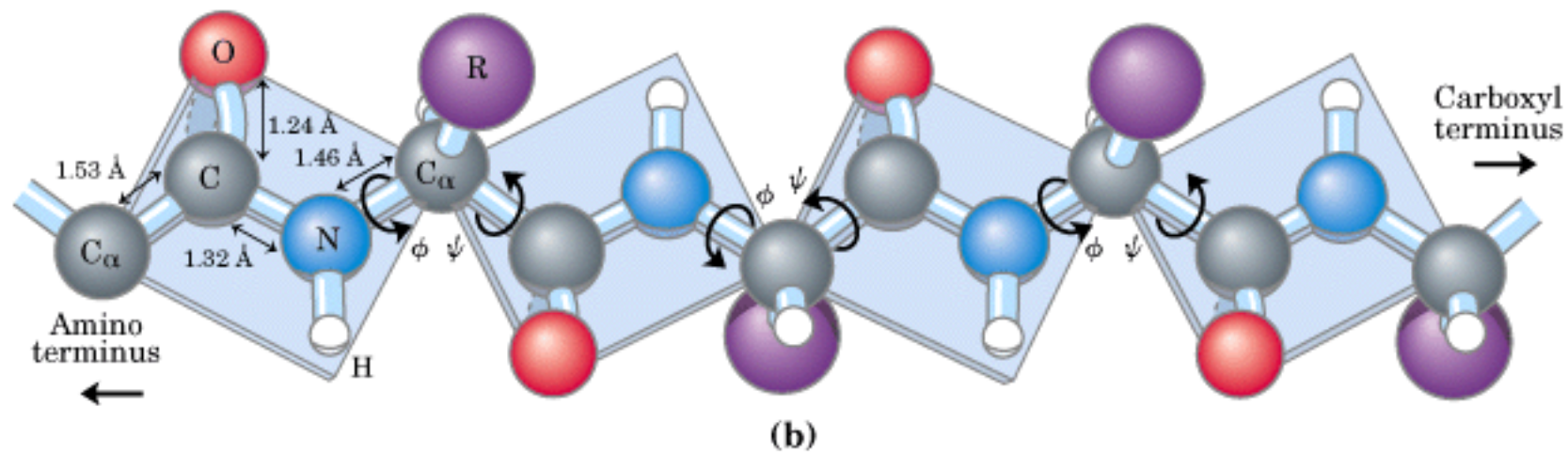
TRANS



CIS

Slika 3.1: Geometrija i dimenzije (u Å) u *trans* i *cis* peptidnoj grupi. [Prema: R.E. Marsh & J. Donohue, *Adv. Protein Chem.*, **22**, 249 (1967).]

Oko peptidne veze **nema** rotacije!



Dipolni karakter peptidne veze

