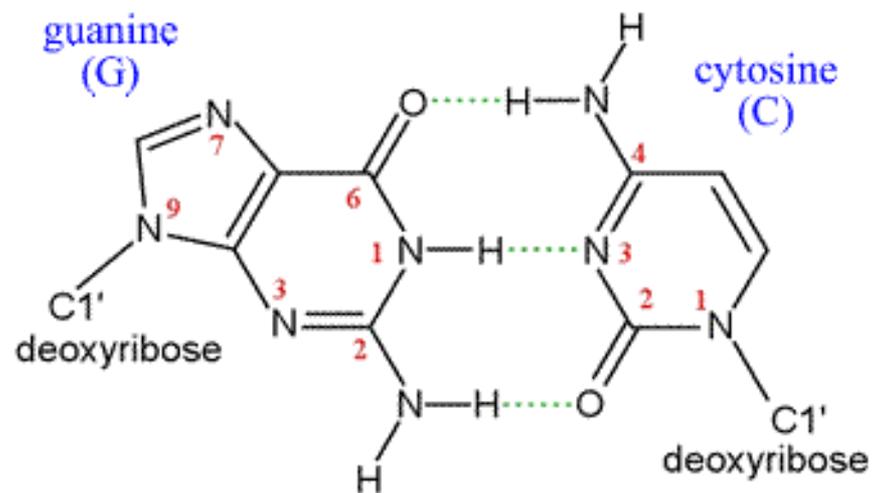
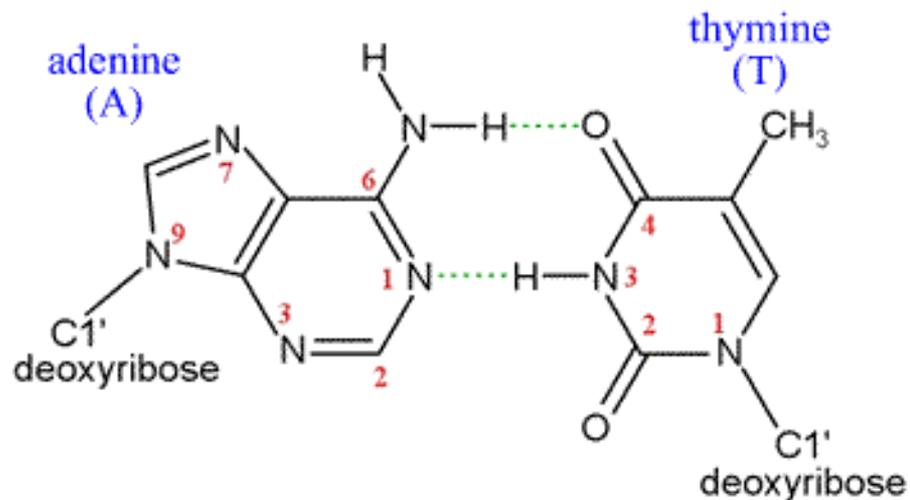


分子集合体化学

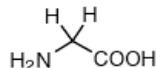
2024年6月24日

核酸塩基

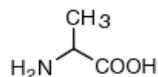


アミノ酸

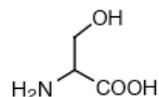
Small



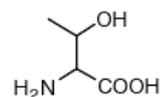
Glycine (Gly, G)
MW: 57.05



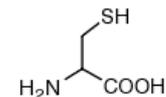
Alanine (Ala, A)
MW: 71.09



Serine (Ser, S)
MW: 87.08, pK_a ~ 16

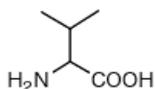


Threonine (Thr, T)
MW: 101.11, pK_a ~ 16

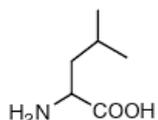


Cysteine (Cys, C)
MW: 103.15, pK_a = 8.35

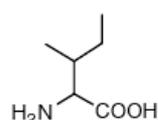
Hydrophobic



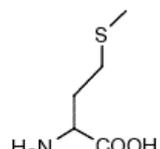
Valine (Val, V)
MW: 99.14



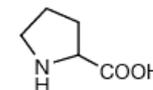
Leucine (Leu, L)
MW: 113.16



Isoleucine (Ile, I)
MW: 113.16

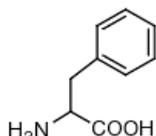


Methionine (Met, M)
MW: 131.19

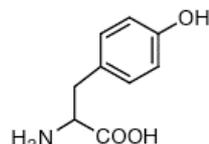


Proline (Pro, P)
MW: 97.12

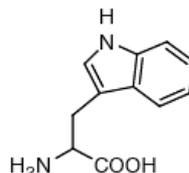
Aromatic



Phenylalanine (Phe, F)
MW: 147.18

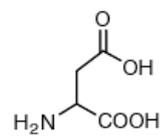


Tyrosine (Tyr, Y)
MW: 163.18

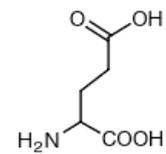


Tryptophan (Trp, W)
MW: 186.21

Acidic

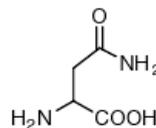


Aspartic Acid (Asp, D)
MW: 115.09, pK_a = 3.9

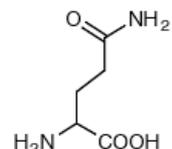


Glutamic Acid (Glu, E)
MW: 129.12, pK_a = 4.07

Amide

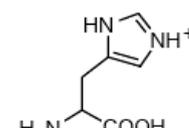


Asparagine (Asn, N)
MW: 114.11

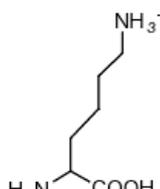


Glutamine (Gln, Q)
MW: 128.14

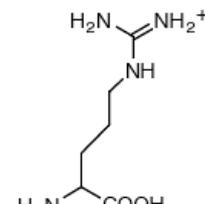
Basic



Histidine (His, H)
MW: 137.14, pK_a = 6.04



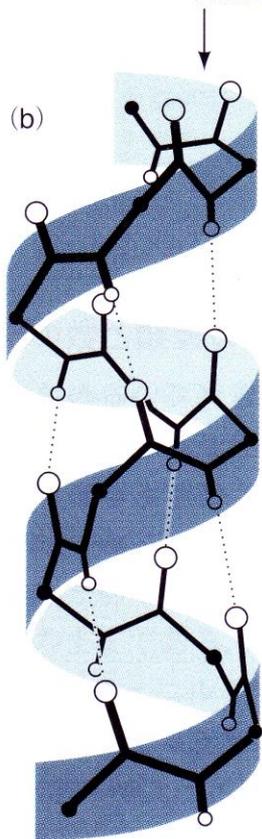
Lysine (Lys, K)
MW: 128.17, pK_a = 10.79



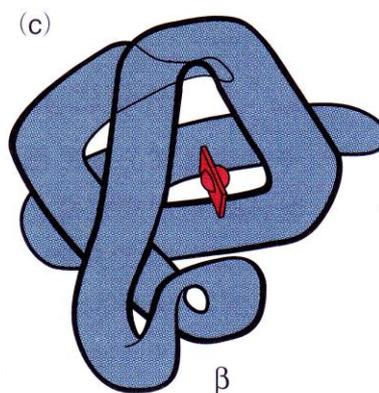
Arginine (Arg, R)
MW: 156.19, pK_a = 12.48

タンパク質の階層構造

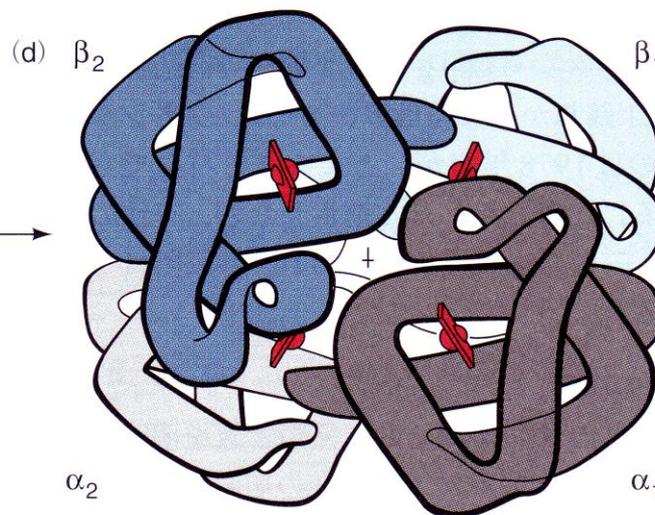
(a) - Lys - Ala - His - Gly - Lys - Lys - Val - Leu - Gly - Ala -
一次構造(ポリペプチド鎖のアミノ酸配列)



二次構造(ヘリックス)



三次構造:
タンパク質の一本鎖の構造
(ヘモグロビンのβ鎖)



四次構造:
4本の鎖が集まって
オリゴマータンパク,
ヘモグロビンを形成

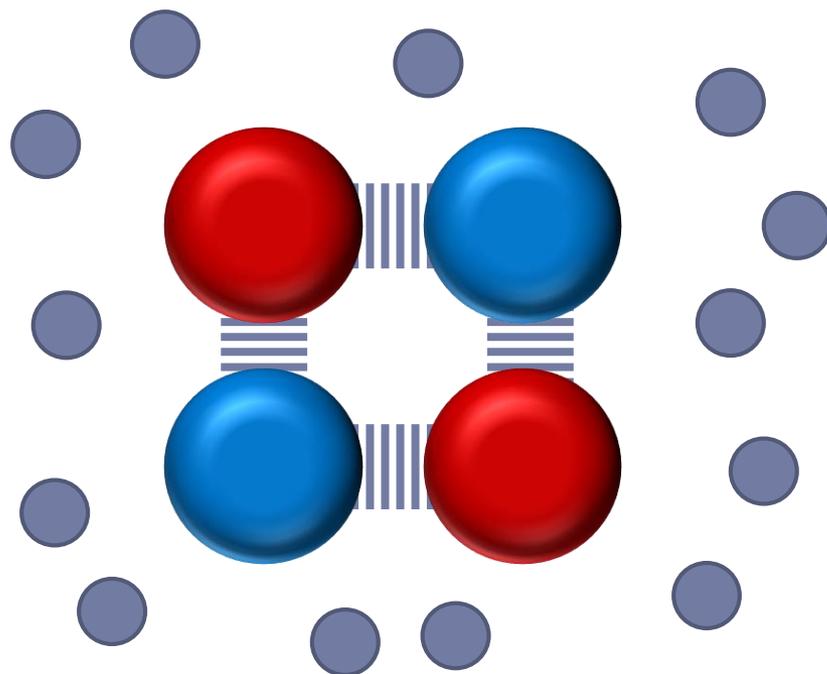
©
IRVING
GEIS

分子集合体における結合・相互作用

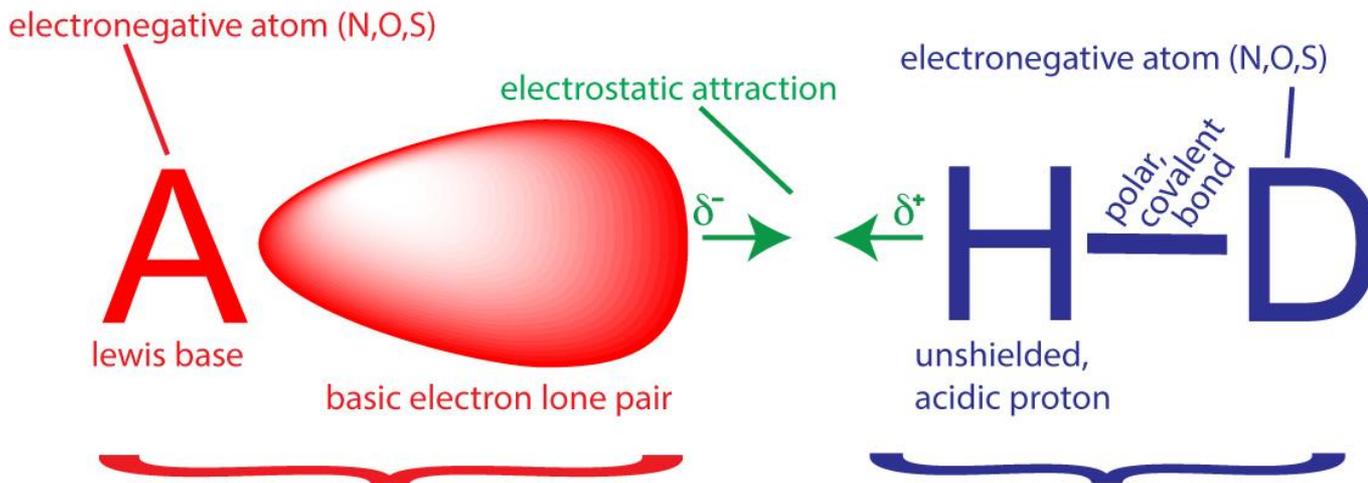
分子・官能基を結び付ける手段

可逆的

周辺微視的環境との相互作用よりは強い



水素結合



水素結合： 受容体 (acceptor)

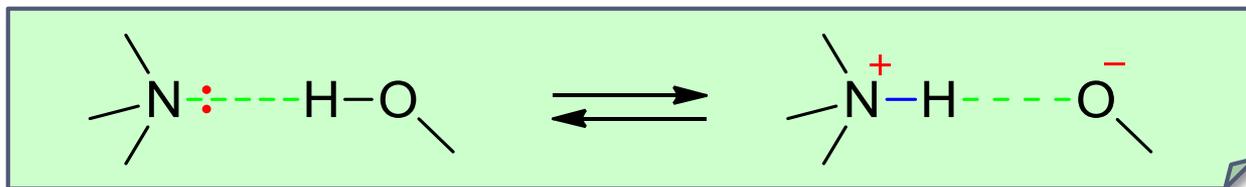
プロトン： 受容体 (acceptor)

電子： 供与体 (donor)

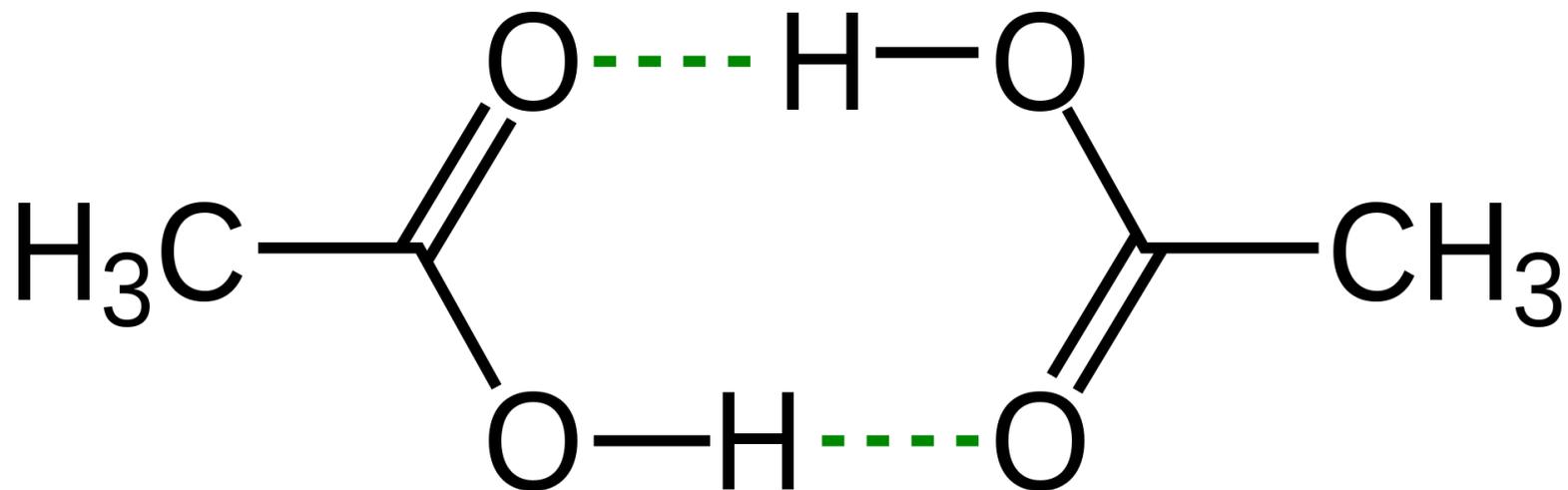
供与体 (donor)

供与体 (donor)

受容体 (acceptor)



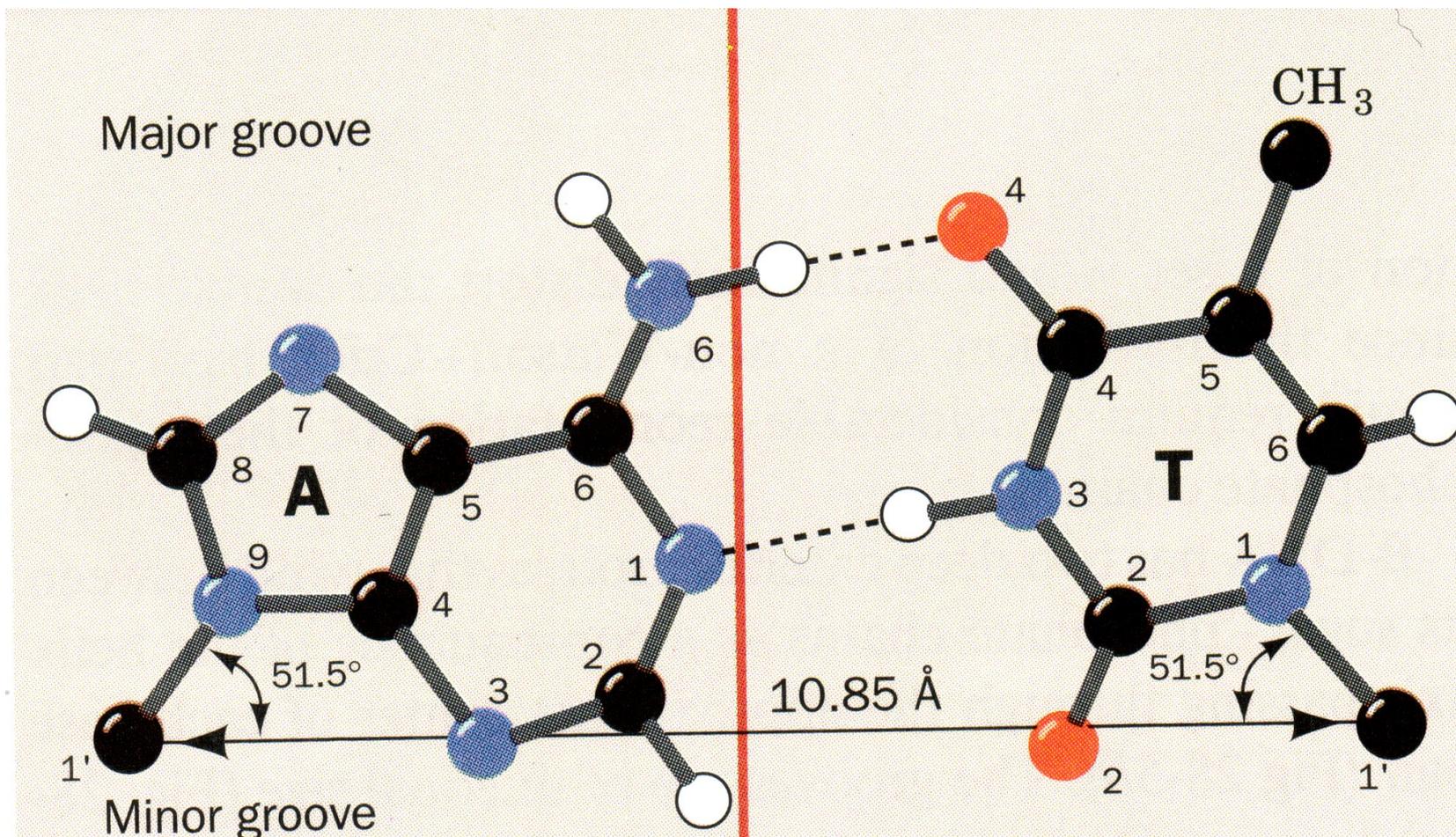
水素結合



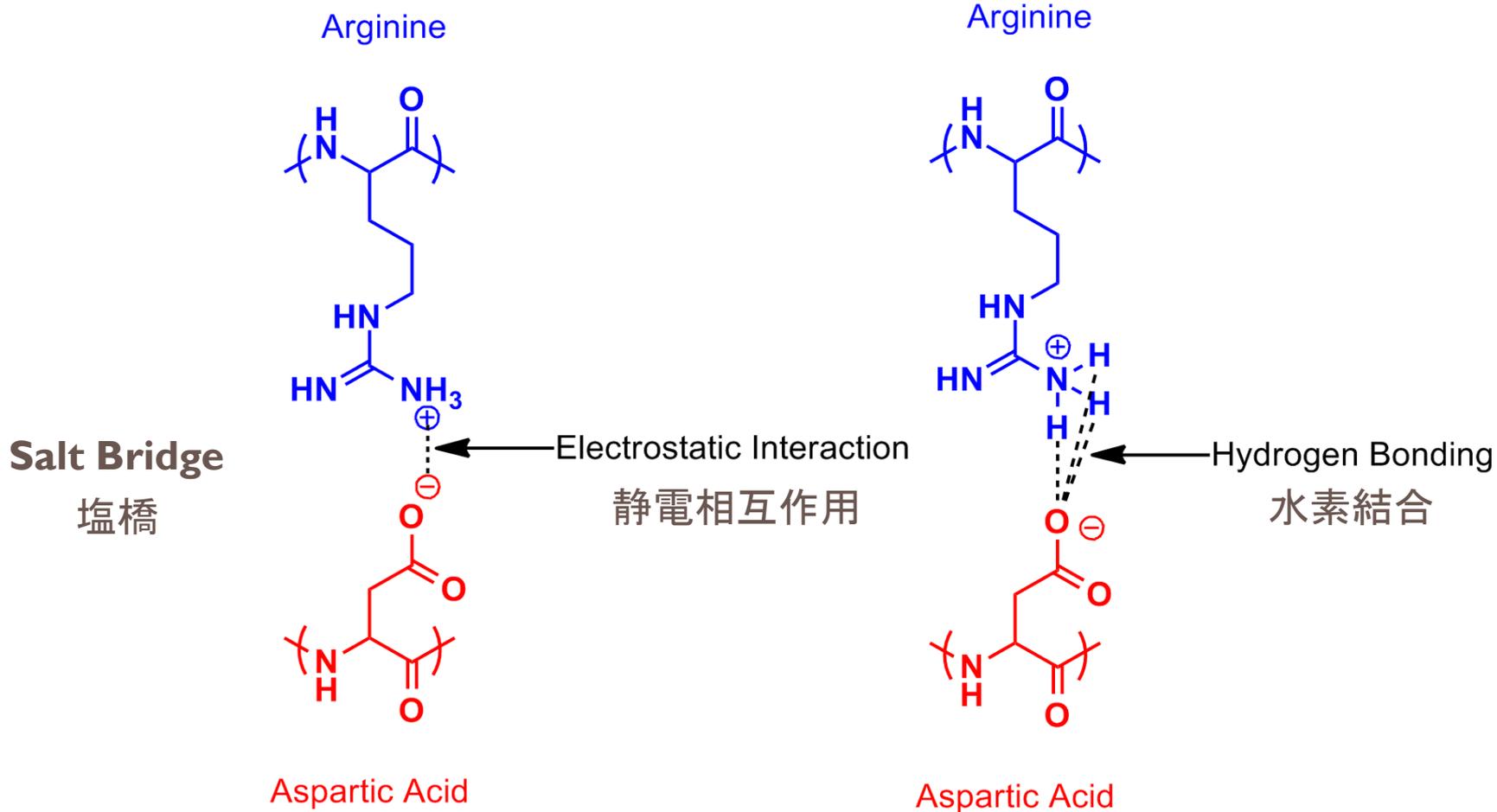
水素結合

水素結合	kJ/mol	kcal/mol
F-H...:F ⁻	155	38.6
O-H...:N	29	6.9
O-H...:O	21	5.0
N-H...:N	13	3.1
N-H...:O	8	1.9
OH ₃ ⁺ ...:OH ₂	18	4.3

水素結合



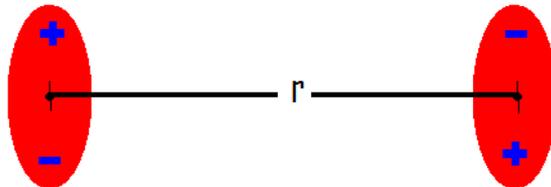
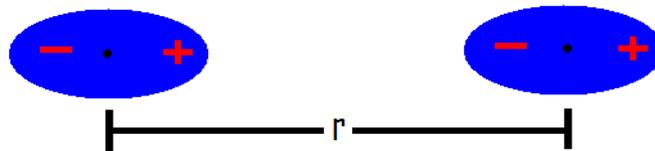
イオン結合



双極子相互作用

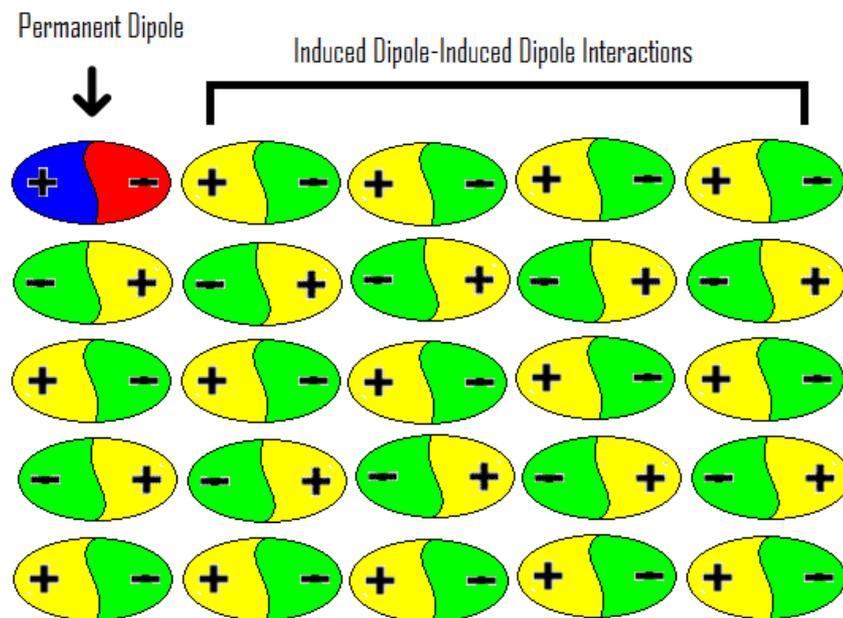
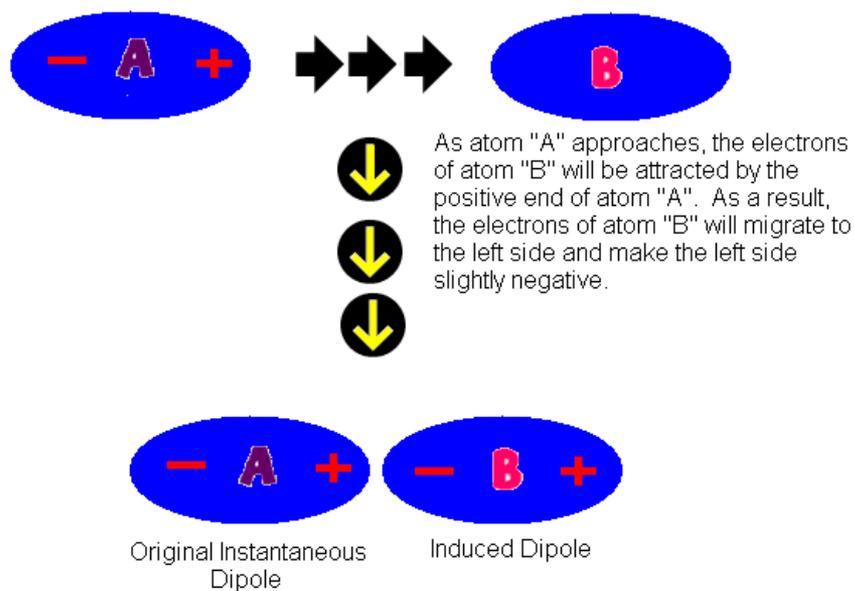
静電相互作用に分類

クーロン力(古典的な静電力)を与える部分電荷($\delta+$ や $\delta-$)

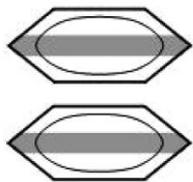


双極子相互作用

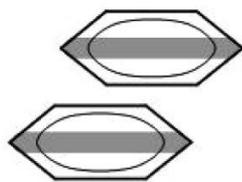
ある分子の電荷分離が近傍の分子の双極子を誘起して、その結果、双極子が整列した分子集団が形成される



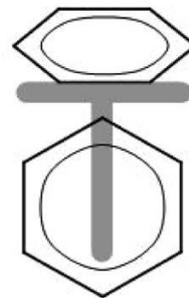
π相互作用



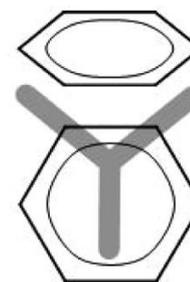
Sandwich
(S)



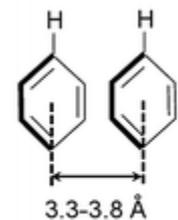
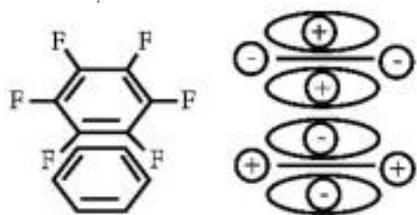
Parallel Displaced
(PD)



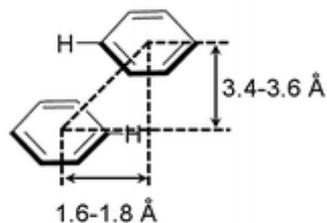
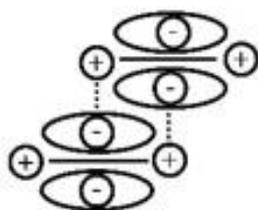
T-shaped
(T)



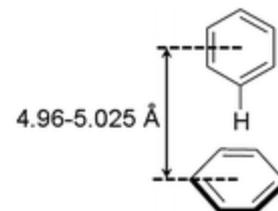
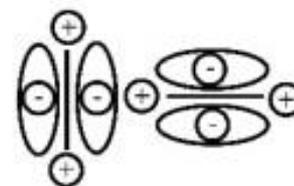
Y-shaped
(Y)



-1.48 Kcal/mol

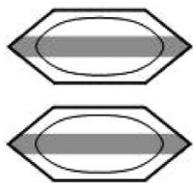


-2.48 Kcal/mol

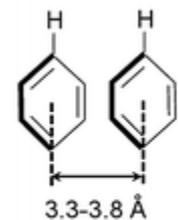
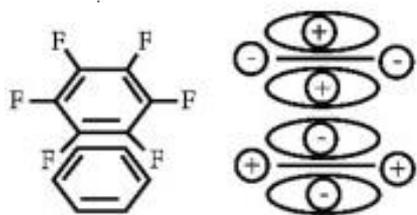


-2.46 Kcal/mol

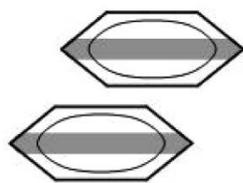
π相互作用



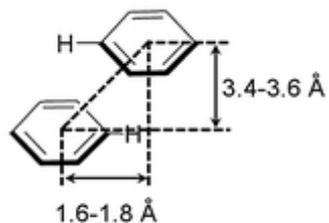
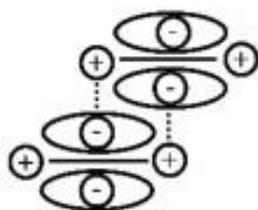
Sandwich
(S)



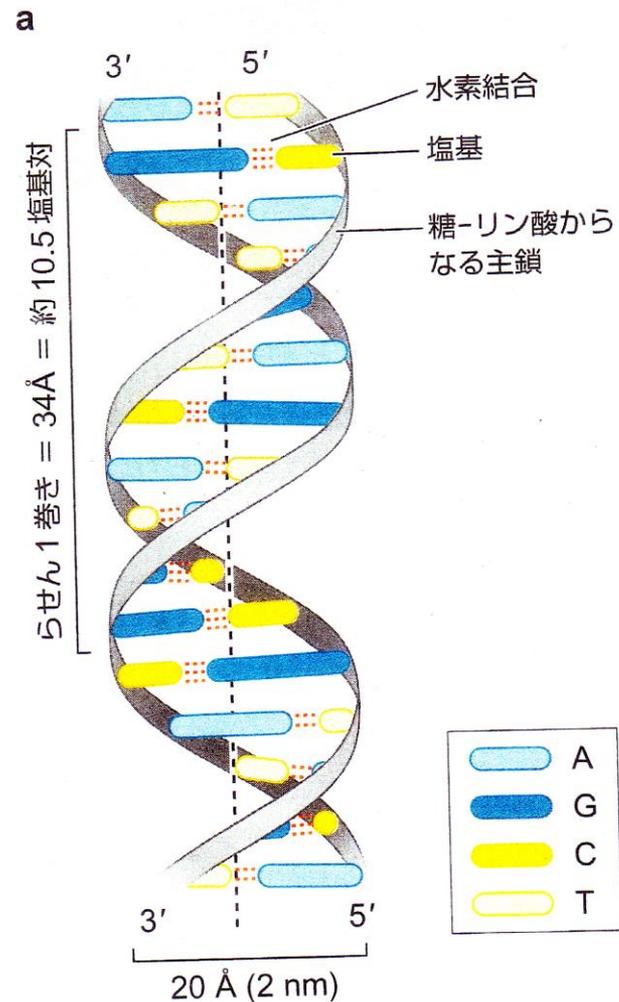
-1.48 Kcal/mol



Parallel Displaced
(PD)

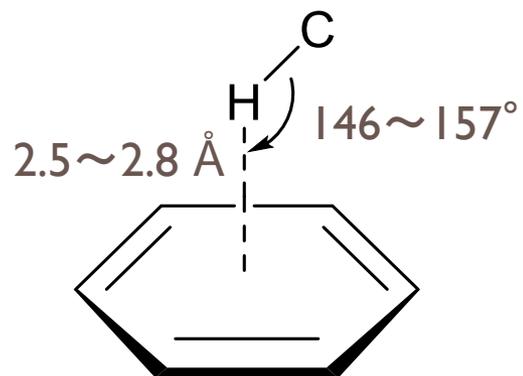


-2.48 Kcal/mol



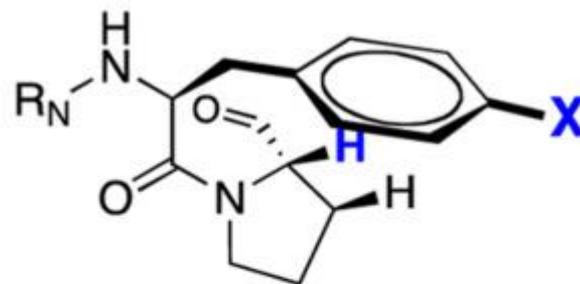
π相互作用

CH-π interaction



Nishio, *Phys. Chem. Chem. Phys.*, **2011**, 13, 13873-13900

(a)



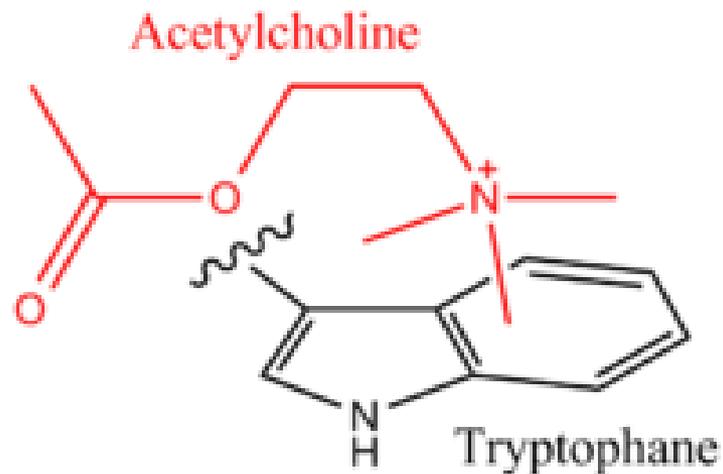
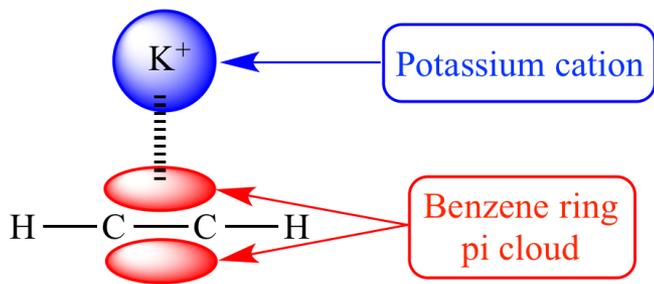
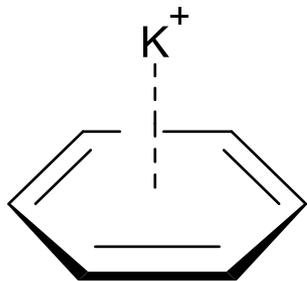
(b)



<https://doi.org/10.1002/pro.2814>

π 相互作用

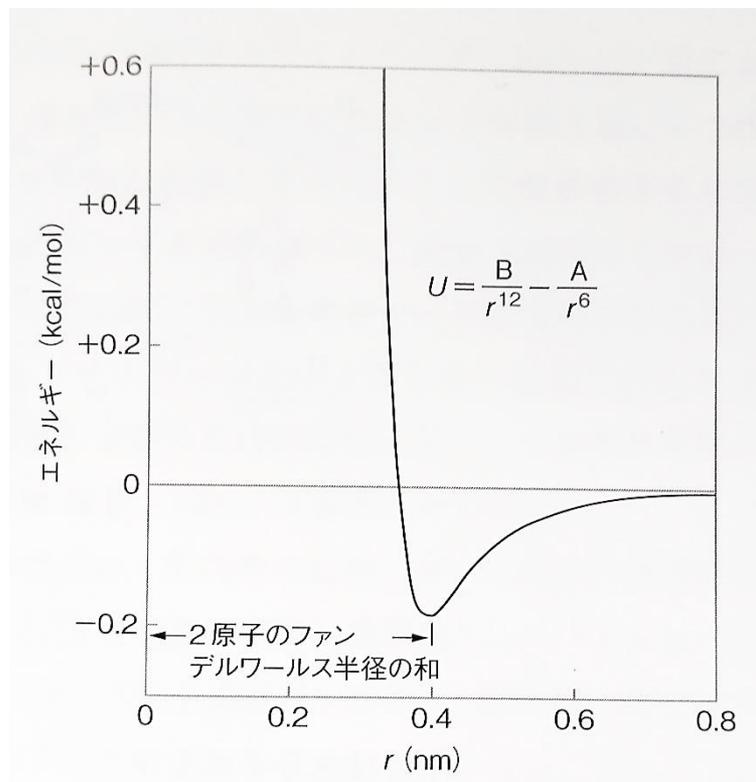
Cation- π interaction



ファンデルワールス力

弱い非共有結合の力

原子核の周りに滞在する電子は、量子力学的効果によって揺らいでおり、ほかの原子と接近するとその揺らぎに変化が生じ、その変化がわずかな安定化をもたらす。この相互作用(ロンドン分散力ともいう)は、原子間距離の6乗に反比例する引力である。おおよそ0.2 kcal/molの弱い力だが、すべての原子に働くため、タンパク質全体の総和では大きな寄与がある。

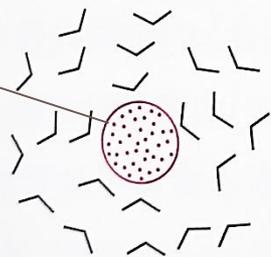


Lennard-Jones potential

「疎水性相互作用」

疎水性が高い構造が水溶媒中で集合する効果
室温付近ではエントロピー駆動型である

シクロヘキサン



$$T = 20^{\circ}\text{C}$$

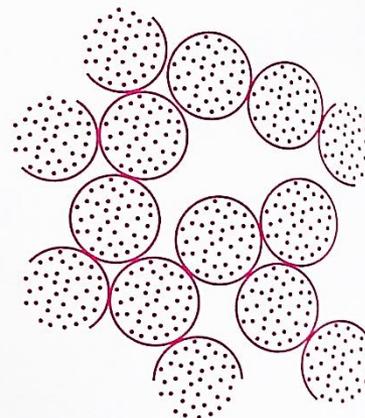
$$\Delta H = 0 \text{ kJ/mol}$$
$$T\Delta S = +25 \text{ kJ/mol}$$

$$\Delta G = -25 \text{ kJ/mol}$$
$$\Delta C_p = -450 \text{ J/K}\cdot\text{mol}$$

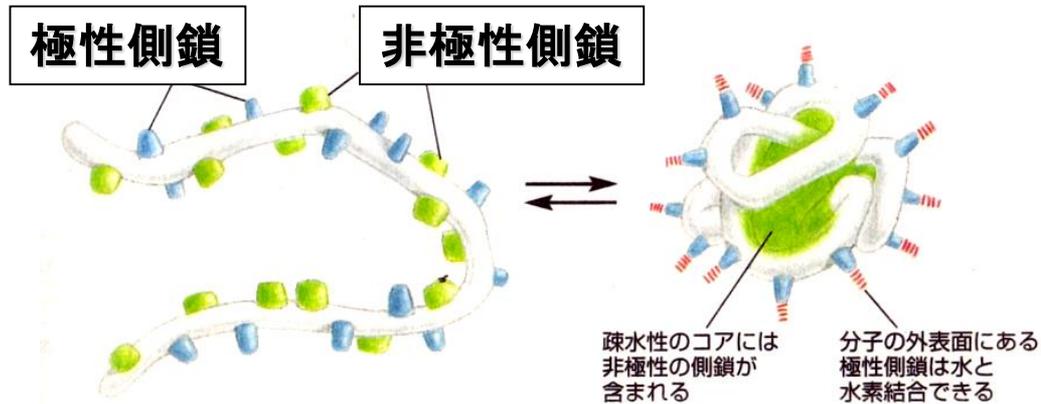
$$T = 140^{\circ}\text{C}$$

$$\Delta H = -30 \text{ kJ/mol}$$
$$T\Delta S = 0 \text{ kJ/mol}$$

$$\Delta G = -30 \text{ kJ/mol}$$
$$\Delta C_p = -200 \text{ J/K}\cdot\text{mol}$$



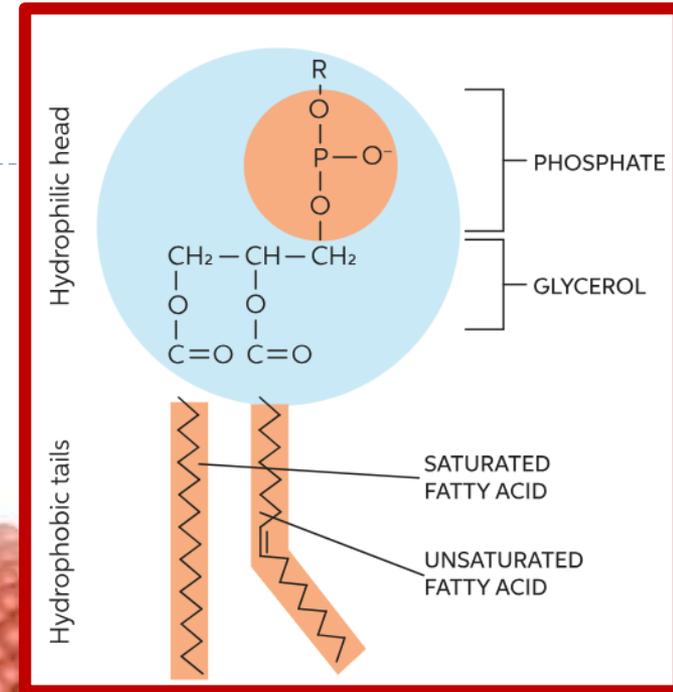
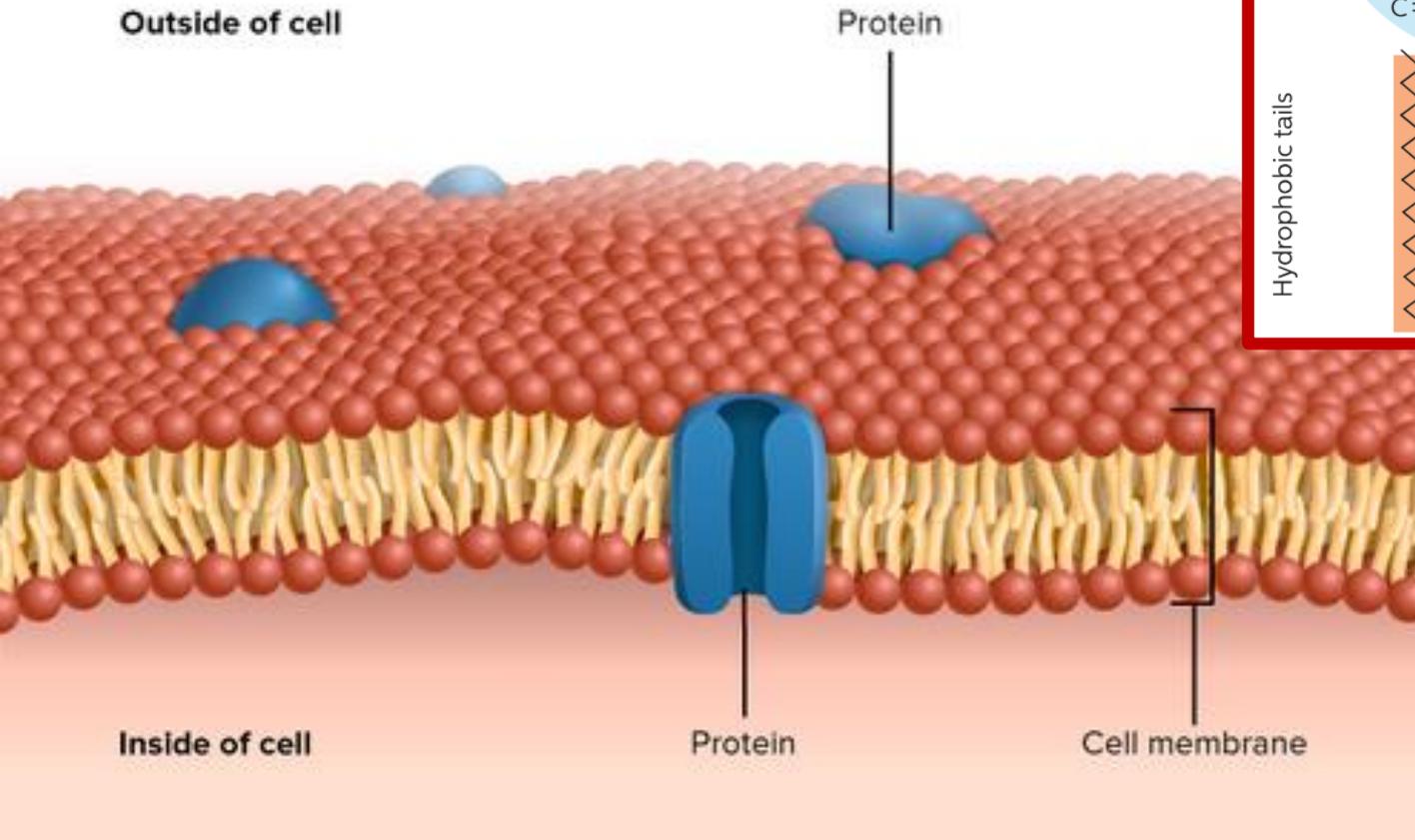
「疎水性相互作用」



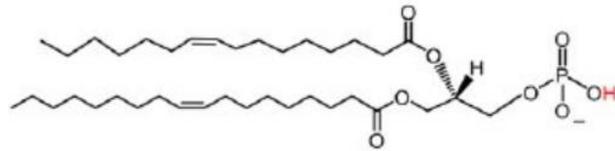
ハイドロパシー指標

アミノ酸	指標	アミノ酸	指標
Ile	4.5	Ser	- 0.8
Val	4.2	Tyr	- 1.3
Leu	3.8	Pro	- 1.6
Phe	2.8	His	- 3.2
Cys	2.5	Glu	- 3.5
Met	1.9	Gln	- 3.5
Ala	1.8	Asp	- 3.5
Gly	- 0.4	Asn	- 3.5
Thr	- 0.7	Lys	- 3.9
Trp	- 0.9	Arg	- 4.5

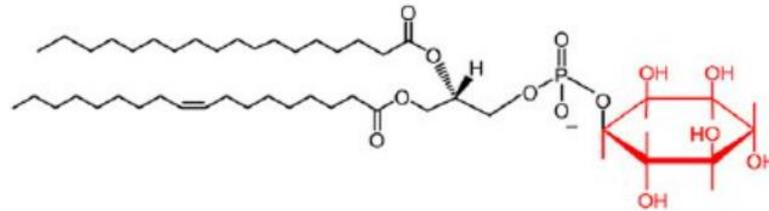
脂質二重層



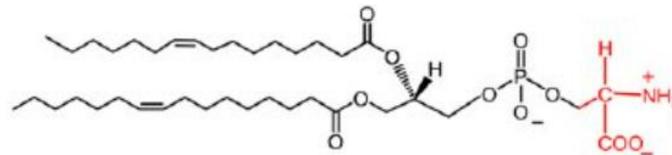
脂質二重層



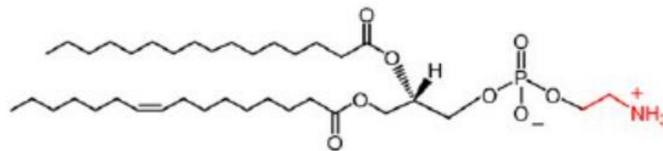
PA (ホスファチジン酸)



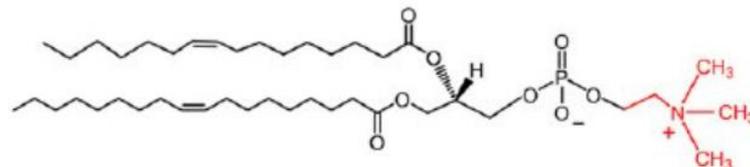
PI



PS

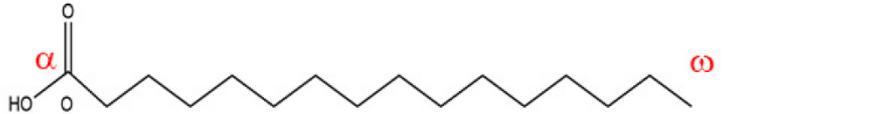
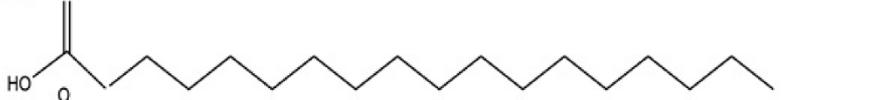
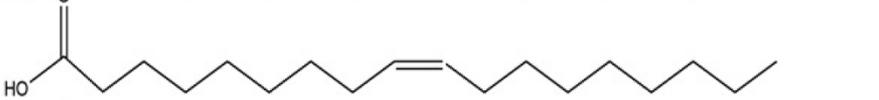
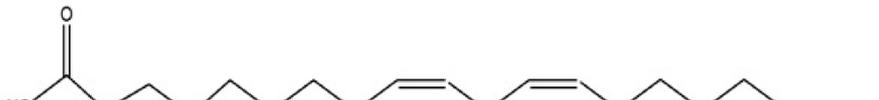
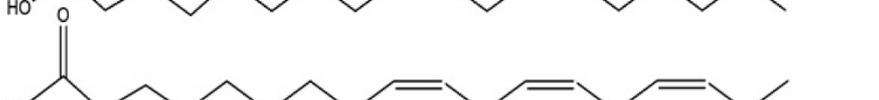
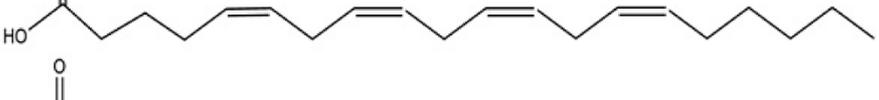
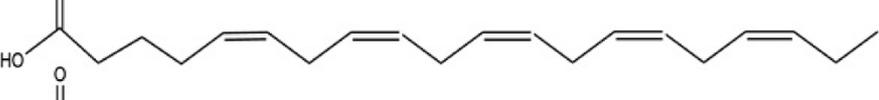


PE

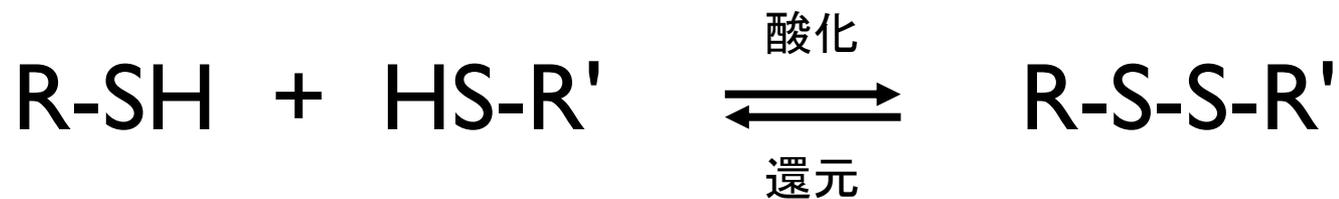


PC

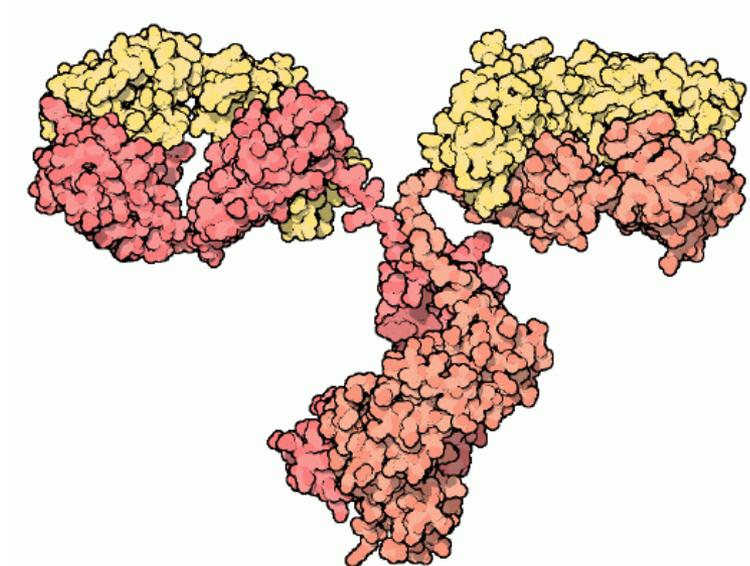
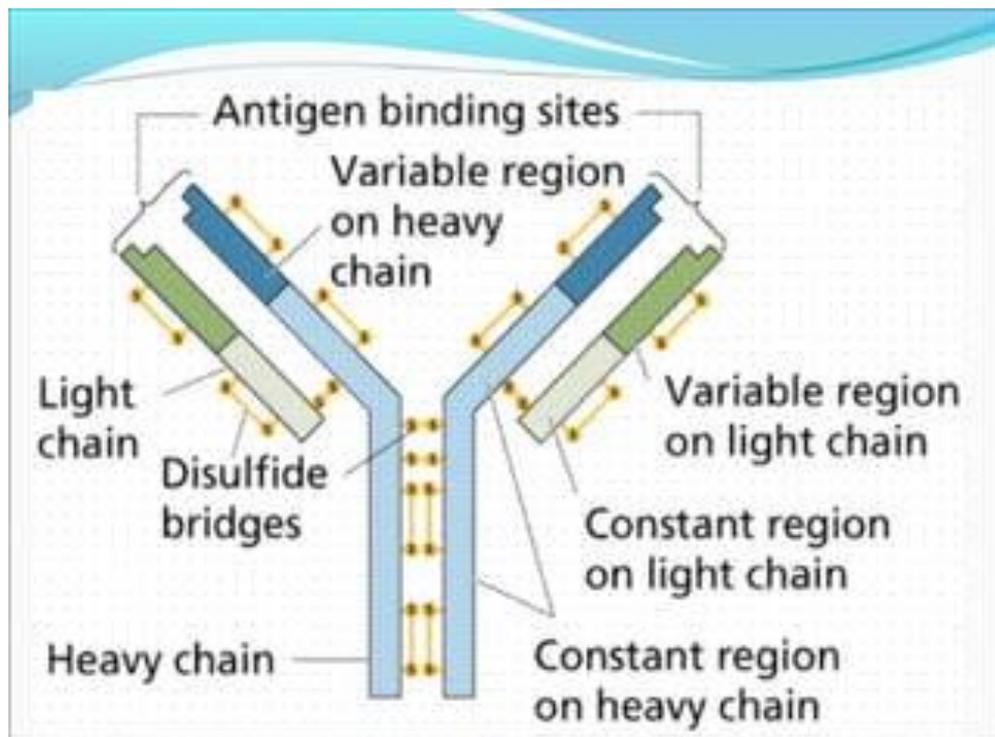
脂質二重層

	Common name	Standard nomenclature	Alternative nomenclature
	Palmitic acid (PA)	16:0	-
	Stearic acid (SA)	18:0	-
	Oleic acid (OA)	18:1 Δ^9	ω -9
	Linoleic acid (LA)	18:2 $\Delta^{9,12}$	ω -6
	α -Linolenic acid (ALA)	18:3 $\Delta^{9,12,15}$	ω -3
	Arachidonic acid (AA)	20:4 $\Delta^{5,8,11,14}$	ω -6
	Eicosapentaenoic (EPA)	20:5 $\Delta^{5,8,11,14,17}$	ω -3
	Docosahexaenoic (DHA)	22:6 $\Delta^{4,7,10,13,16,19}$	ω -3

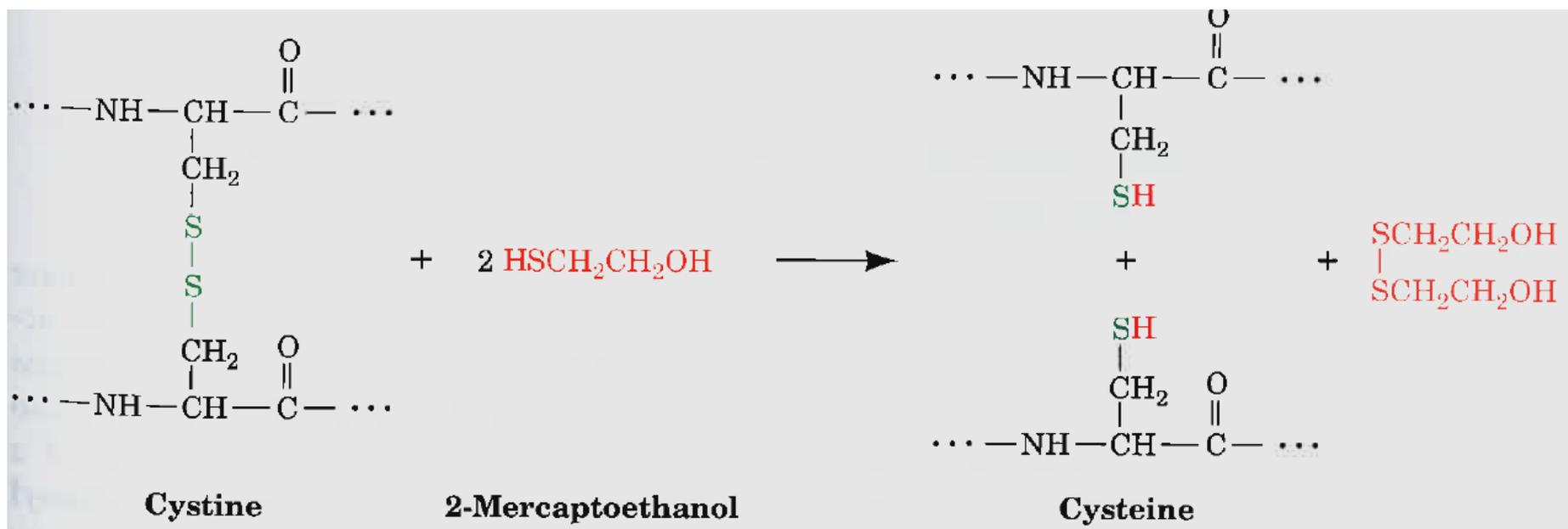
可逆的な共有結合



可逆的な共有結合

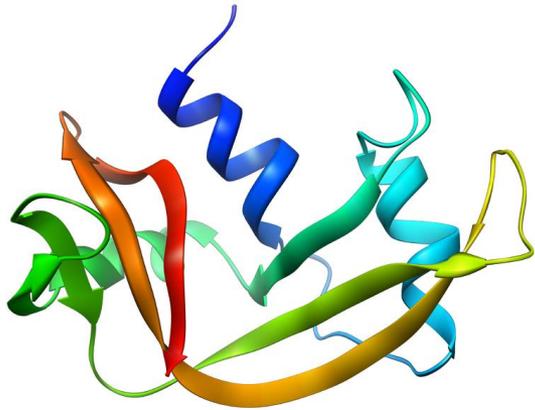


可逆的な共有結合



リボヌクレアーゼAの再生実験

リボヌクレアーゼA
(124アミノ酸)

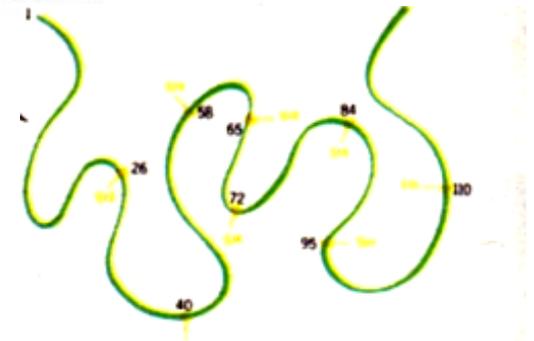


天然型



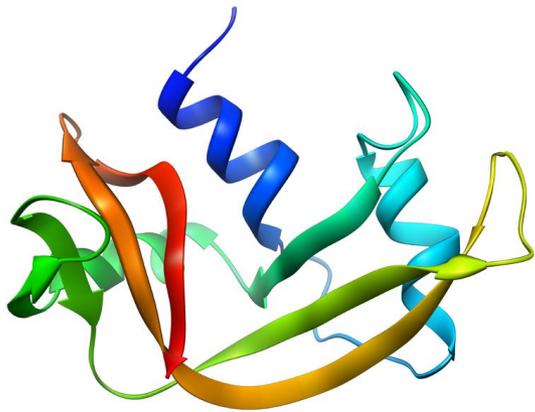
$\text{H}_2\text{N}(\text{CO})\text{NH}_2$ で処理
 $\text{HOCH}_2\text{CH}_2\text{SH}$ で還元
(変性条件)

変性後
(不活性)

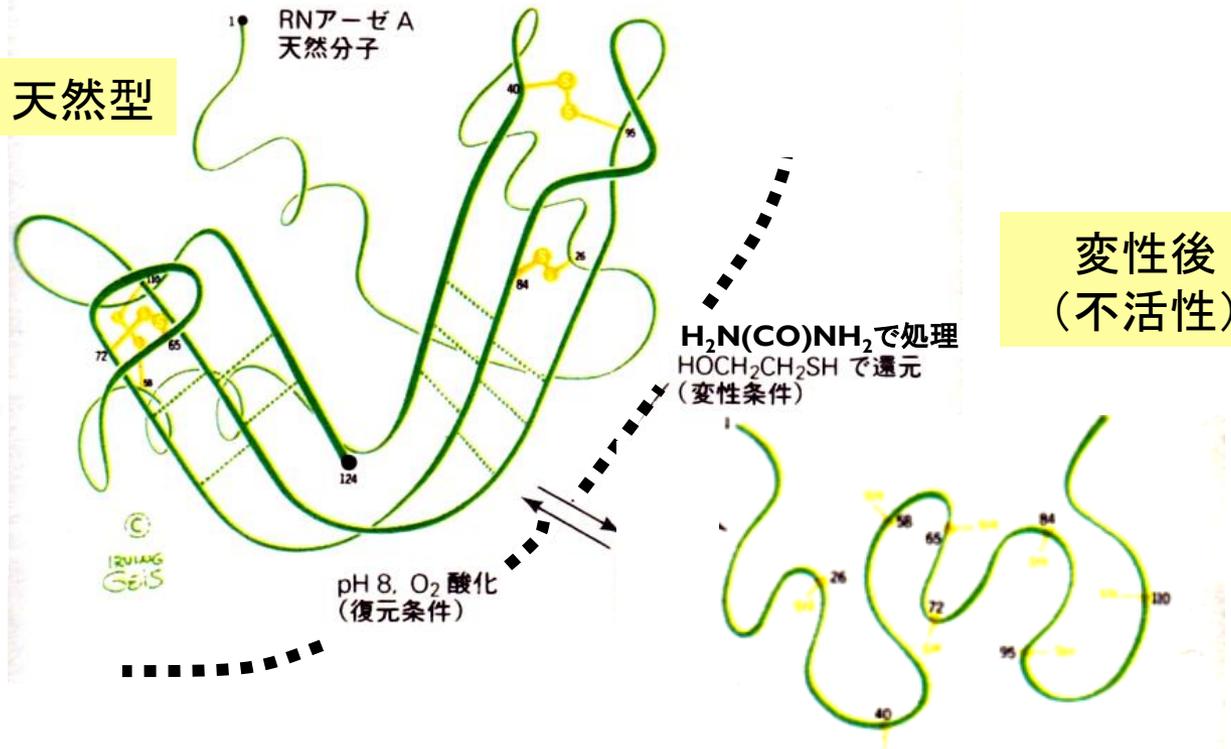


リボヌクレアーゼAの再生実験

リボヌクレアーゼA
(124アミノ酸)



天然型

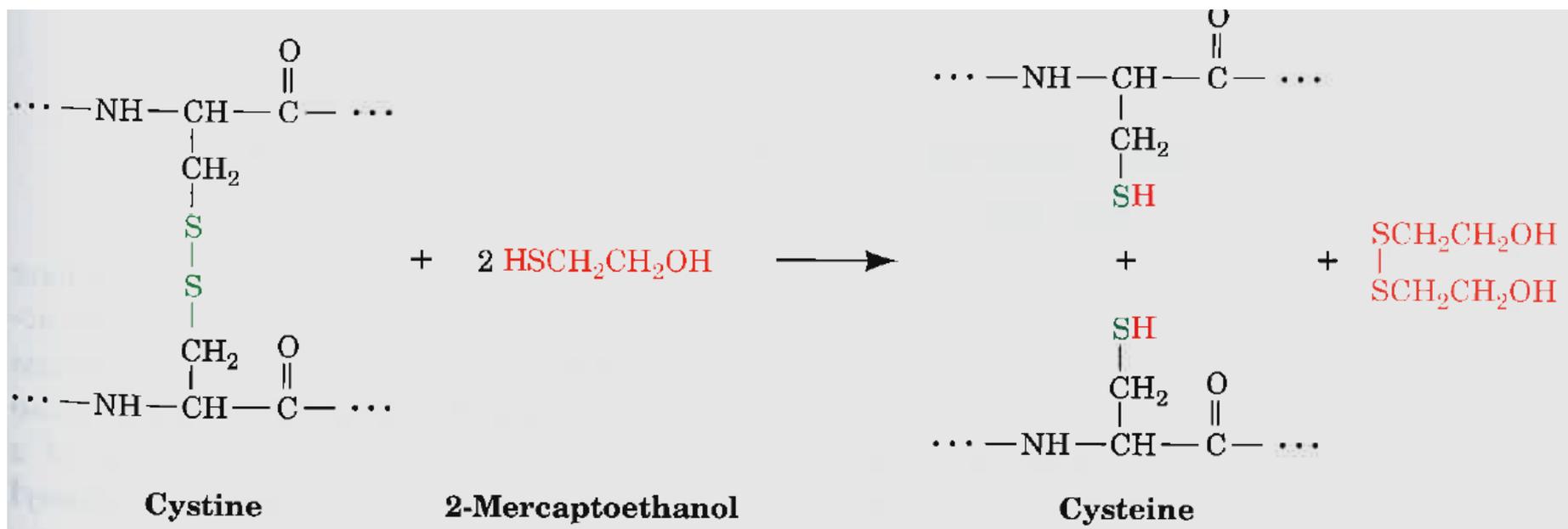


尿素（水素結合破壊）とメルカプトエタノール（S-S結合を還元開裂）で処理

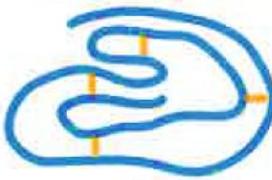
→ 変性タンパク（酵素活性なし）

→ 尿素を除去し、空気で酸化すると酵素活性が完全に回復

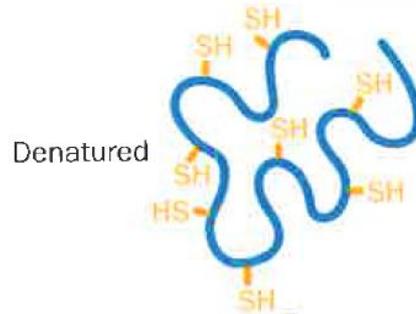
メルカプトエタノールによるジスルフィド結合の還元的開裂



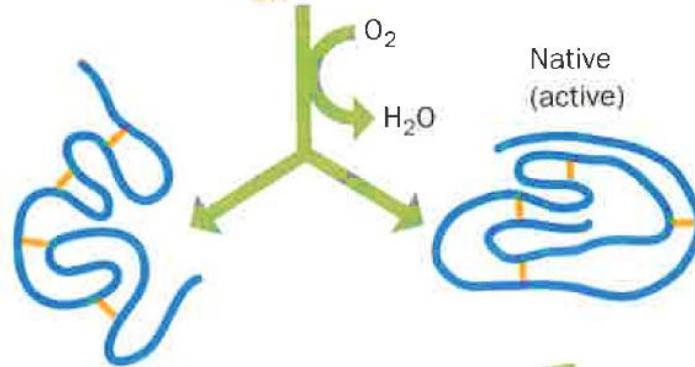
RNase A Native (active)



1) 8 M urea denatures the protein, and mercaptoethanol cleaves its disulfide bonds.

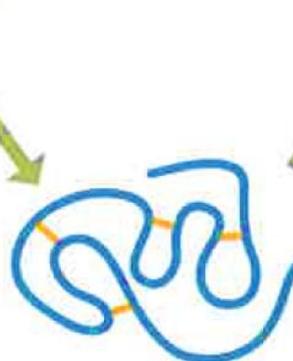


3) Removal of only the mercaptoethanol allows the disulfide bonds to reform in the denatured protein.



2) Removal of the denaturant (urea) and reductant (mercaptoethanol) allows the protein to renature and re-form disulfide bonds in the presence of oxygen.

4) Subsequent removal of the urea generates an enzymatically inactive protein in which the disulfide bonds have formed at random.



5) Adding a small amount of mercaptoethanol to the scrambled protein in the absence of O₂ catalyzes its conversion to the active enzyme through disulfide interchange reactions that allow the native disulfide bonds to form.

Scrambled (inactive)

相互作用による安定化

相互作用	kJ / mol	nm
van der Waars	0.4-4.0	0.3-0.6
Hydrogen bonds	12-30	0.3
Ionic Interactions	20	0.25
Hydrophobic Interactions	<40	varies

Protein Data Bank

RCSB PDB Deposit Search Visualize Analyze Download Learn About Documentation Careers COVID-19 MyPDB Contact us

RCSB PDB PROTEIN DATA BANK

206,239 Structures from the PDB

1,068,577 Computed Structure Models (CSM)

3D Structures ? Enter search term(s), Entry ID(s), or sequence Include CSM ?

Advanced Search | Browse Annotations Help

PDB-101 PDB EMDataResource NDB NUCLEIC ACID DATABASE wwPDB Foundation PDB-Dev

New: More Computed Structure Models (CSM) available [Learn more](#)

Welcome

Deposit

Search

Visualize

Analyze

Download

Learn

RCSB Protein Data Bank (RCSB PDB) enables breakthroughs in science and education by providing access and tools for exploration, visualization, and analysis of:

- Experimentally-determined 3D structures from the **Protein Data Bank (PDB)** archive
- Computed Structure Models (CSM)** from AlphaFold DB and ModelArchive

These data can be explored in context of external annotations providing a structural view of biology.

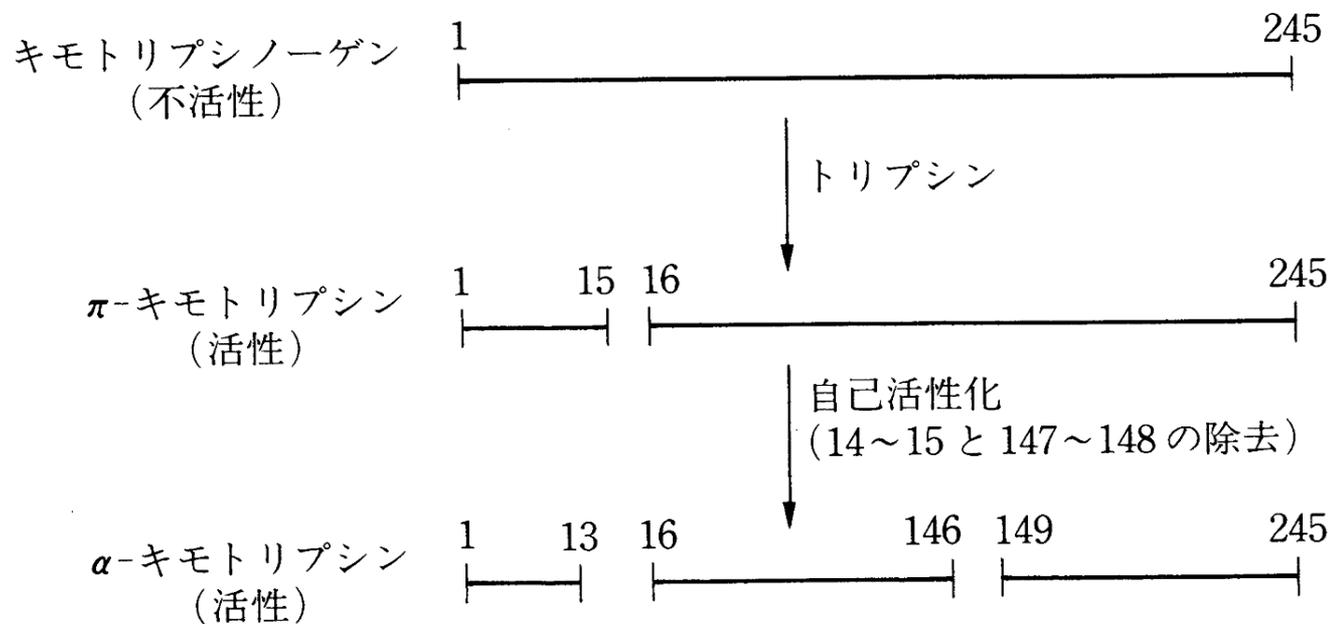
Explore NEW Features

PDB-101 Training Resources

June Molecule of the Month

Odorant Receptors

Biosynthesis of chymotrypsin

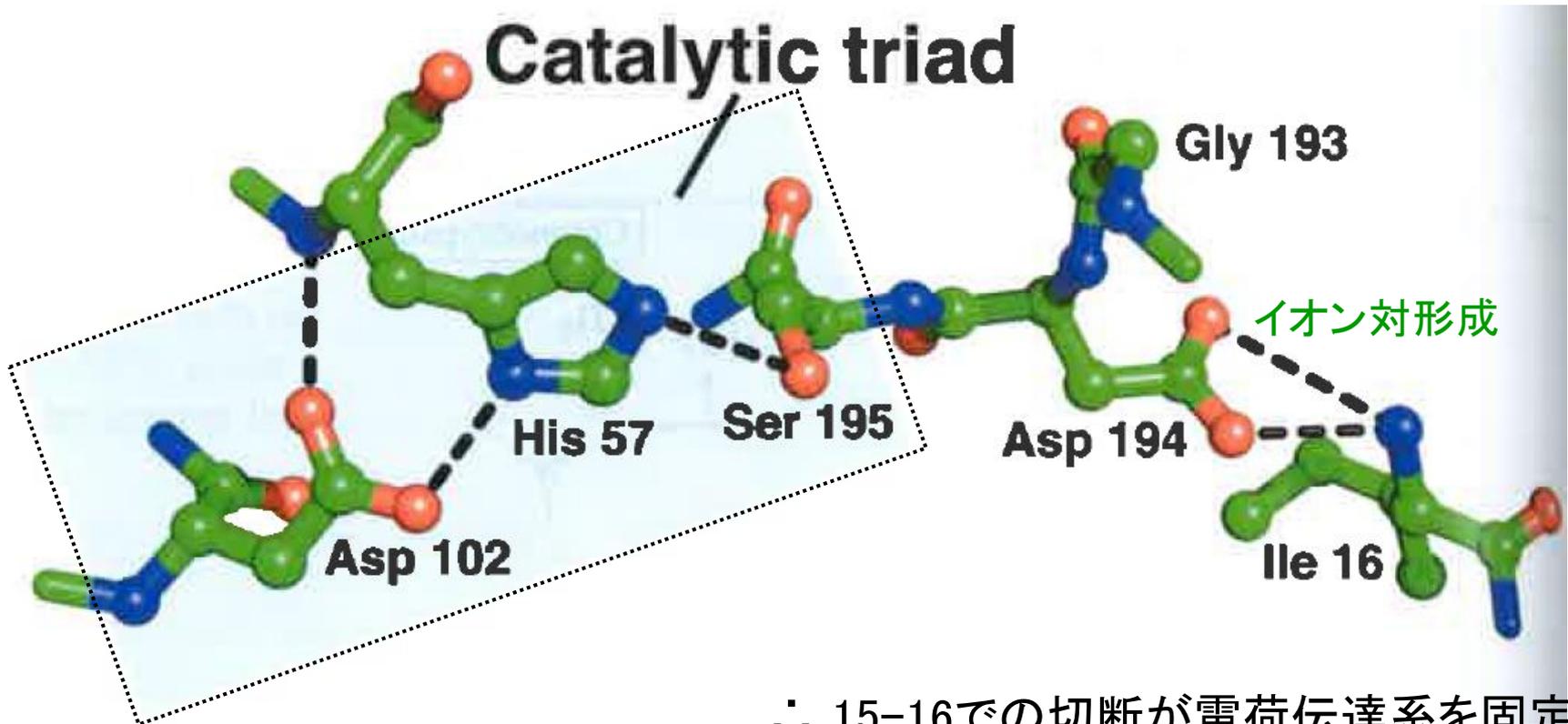


Active site residues of chymotrypsin

16位の切断と酵素機能の発現

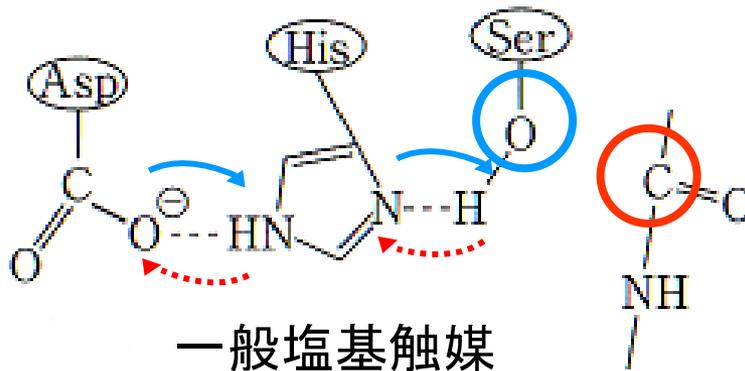
触媒三残基による電荷伝達系

Catalytic triad

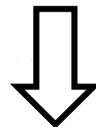


∴ 15-16での切断が電荷伝達系を固定し
酵素活性発現に必須

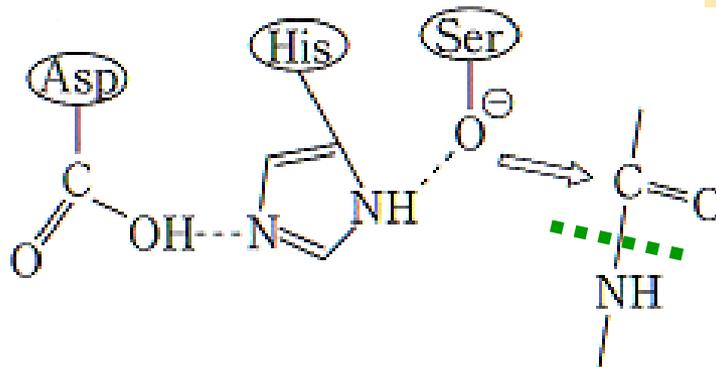
Peptide hydrolysis



電子移動
プロトン移動

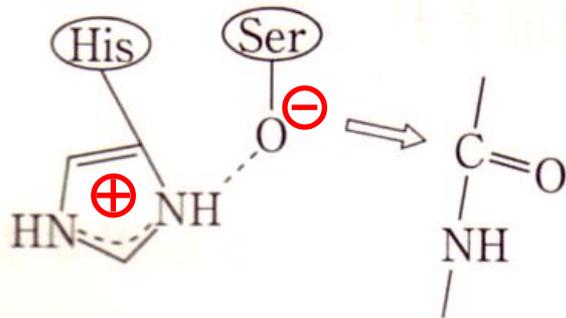
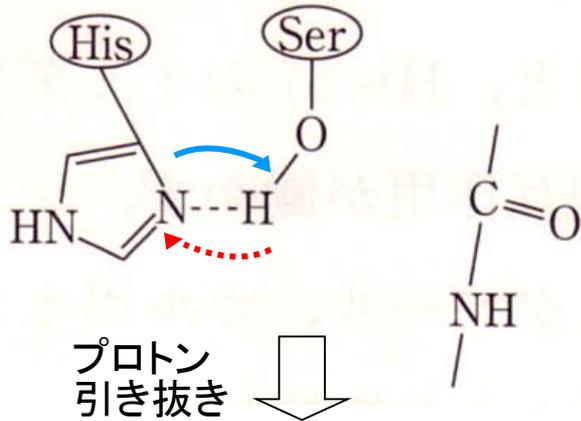


Ser→Hisのプロトン移動に伴って
His→Aspにプロトンを移動
(電子は逆に移動する)

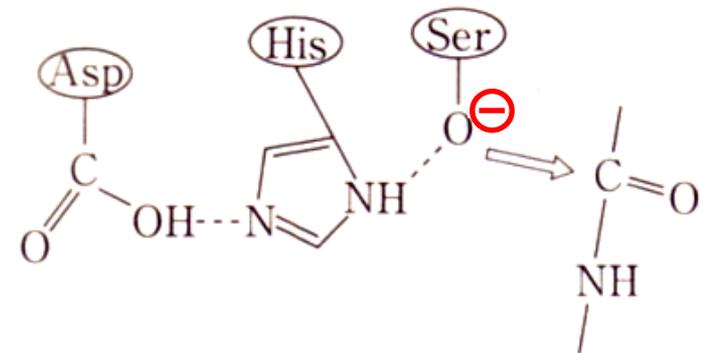
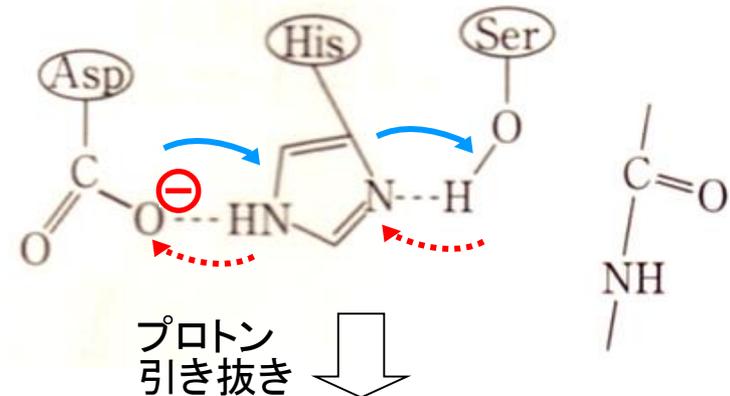


Role of the triad?

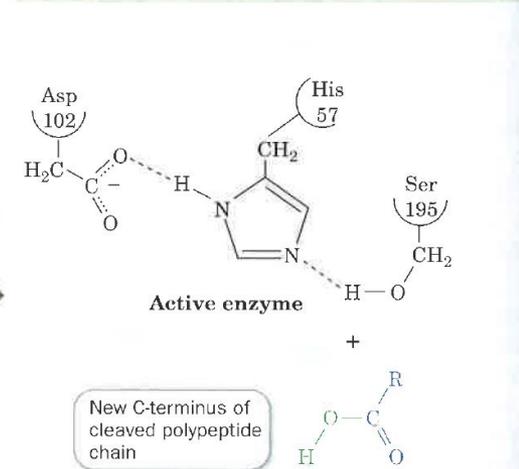
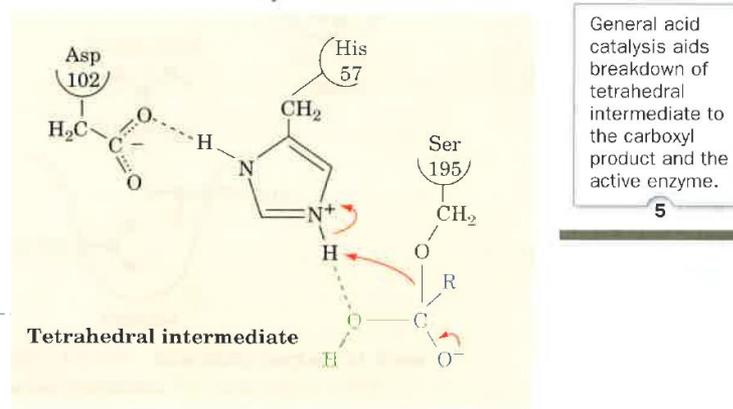
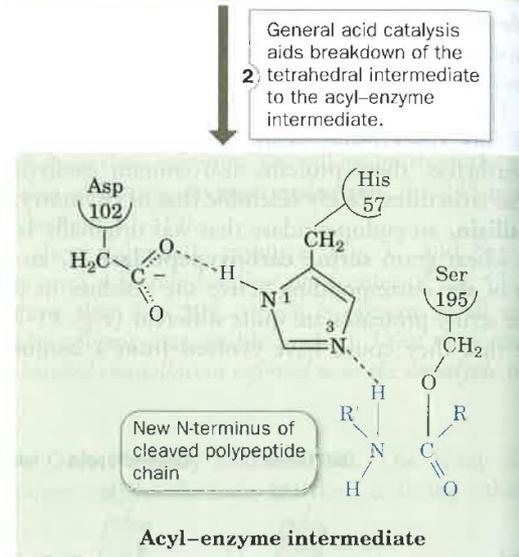
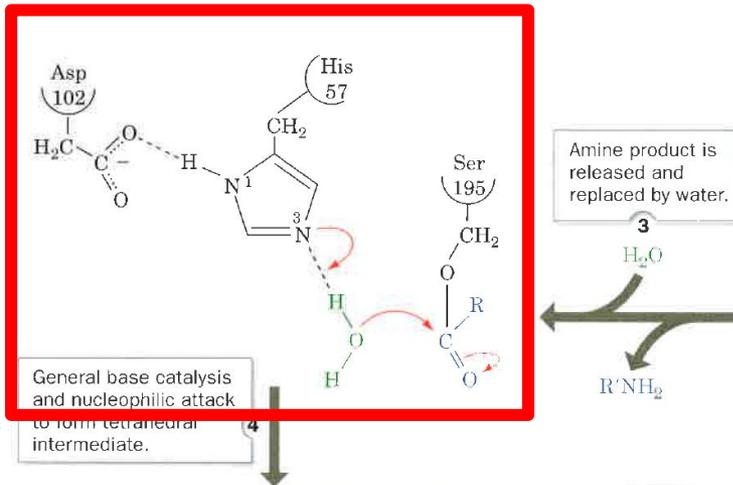
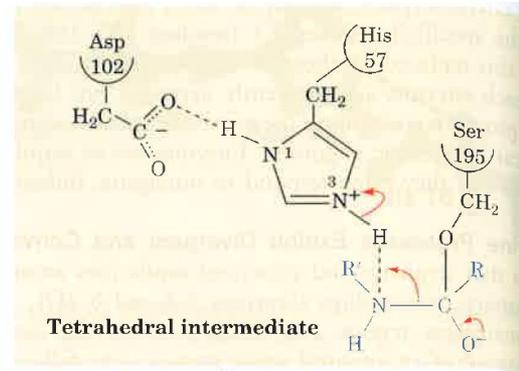
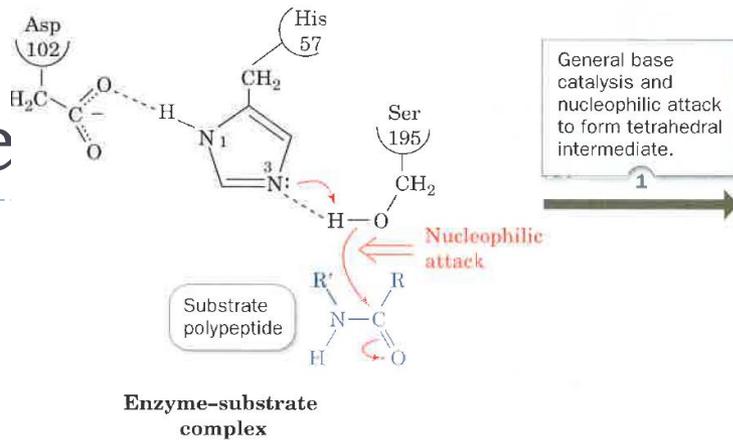
電荷伝達系なし



電荷伝達系あり

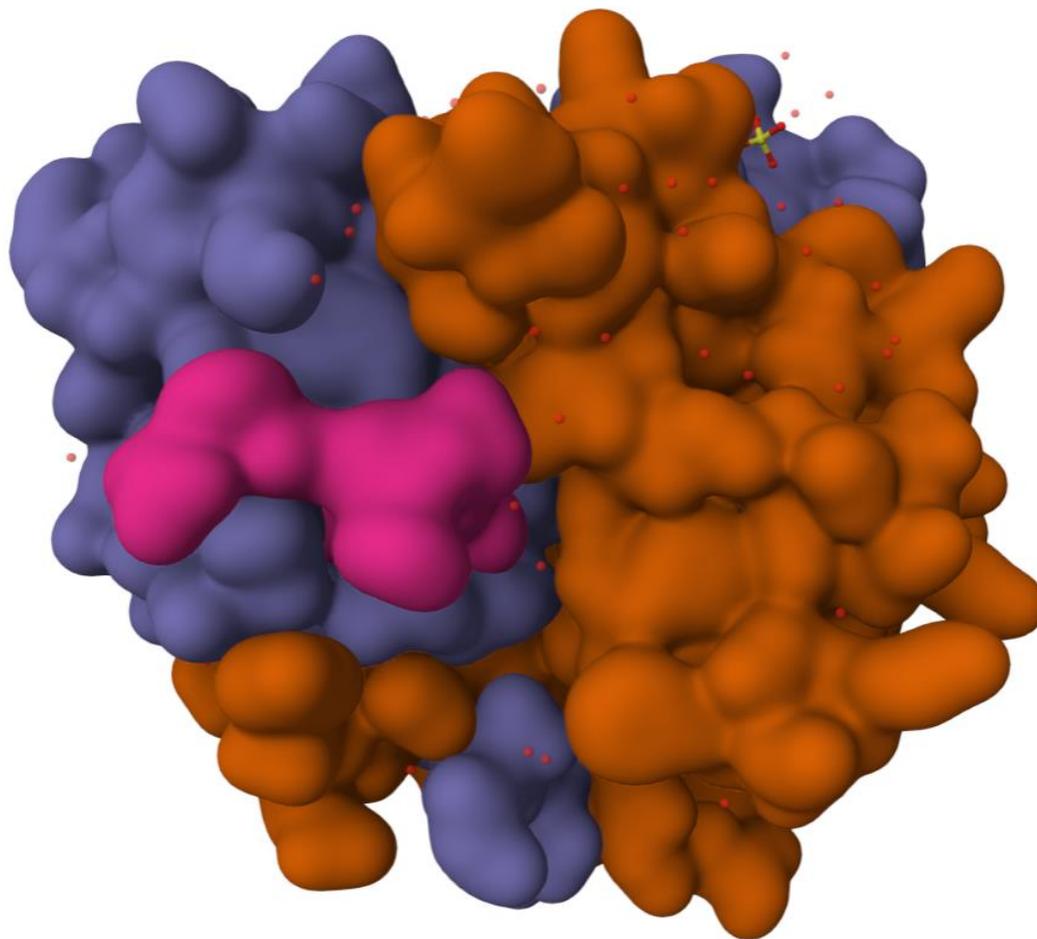


Prote



Protein Data Bank

Gaussian Surface: ON



Protein Data Bank

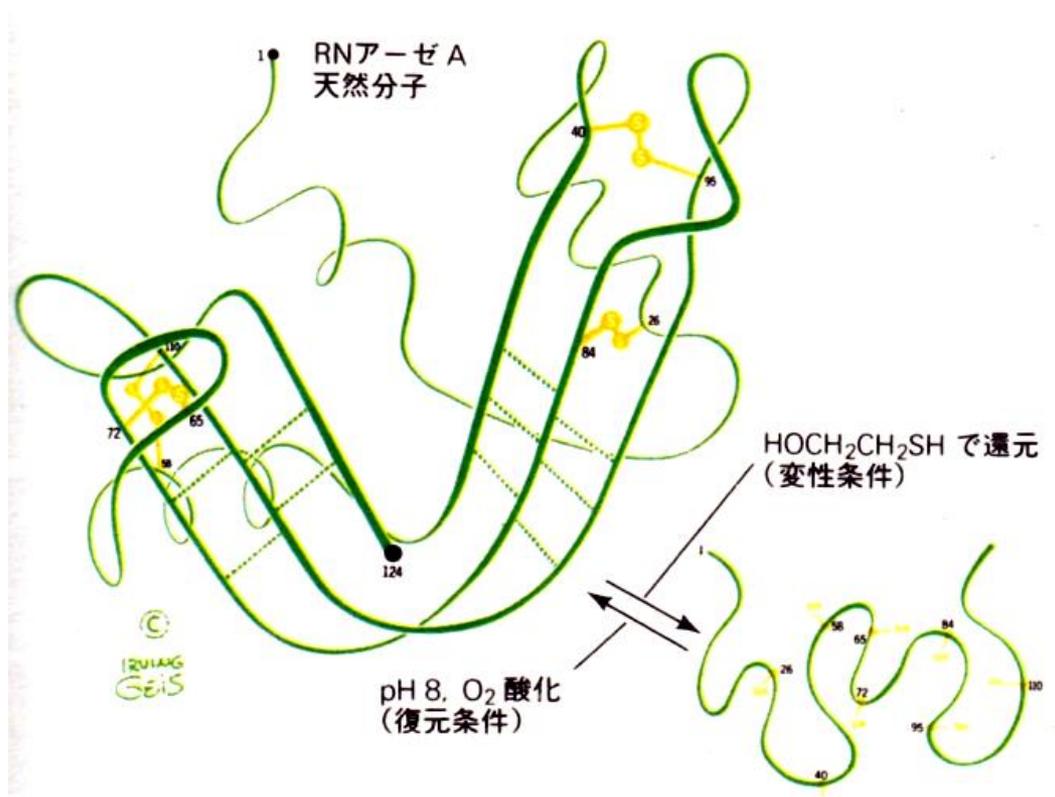
リボヌクレアーゼA

PDB ID:

2AAS

1JVU

(with Cytidine-2'-monophosphate)



Protein Data Bank

ジスルフィド

26-84

40-95

58-110

65-72

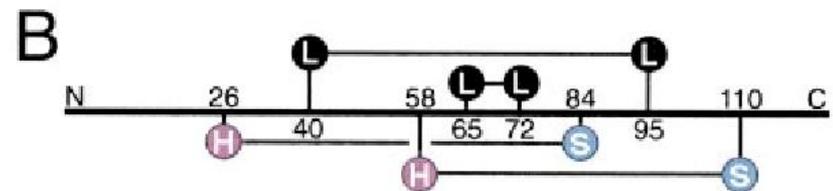
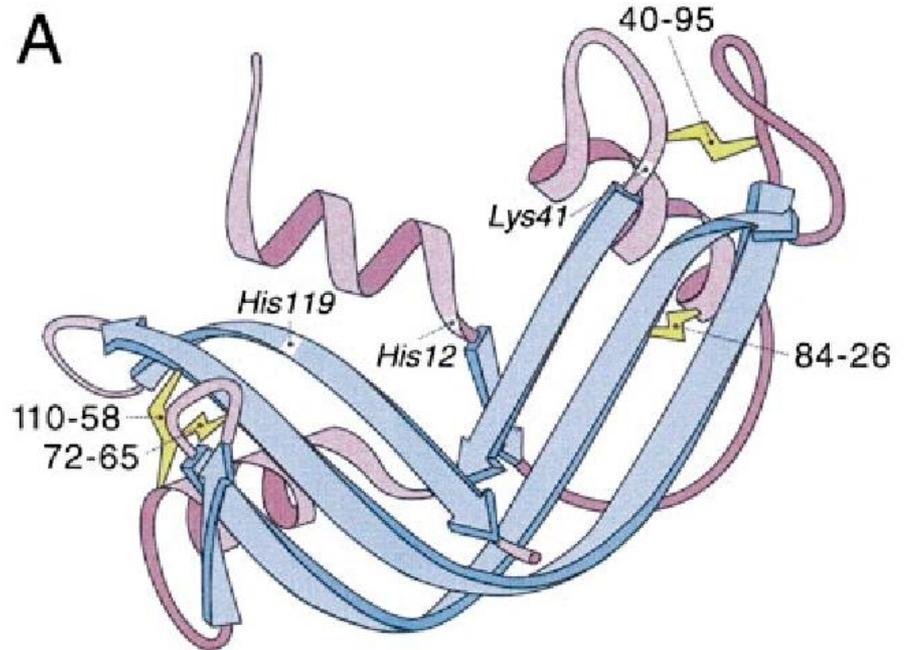


Fig. 1 Structural representations of ribonuclease A (A) Ribbon diagram

Protein Data Bank

反应点

