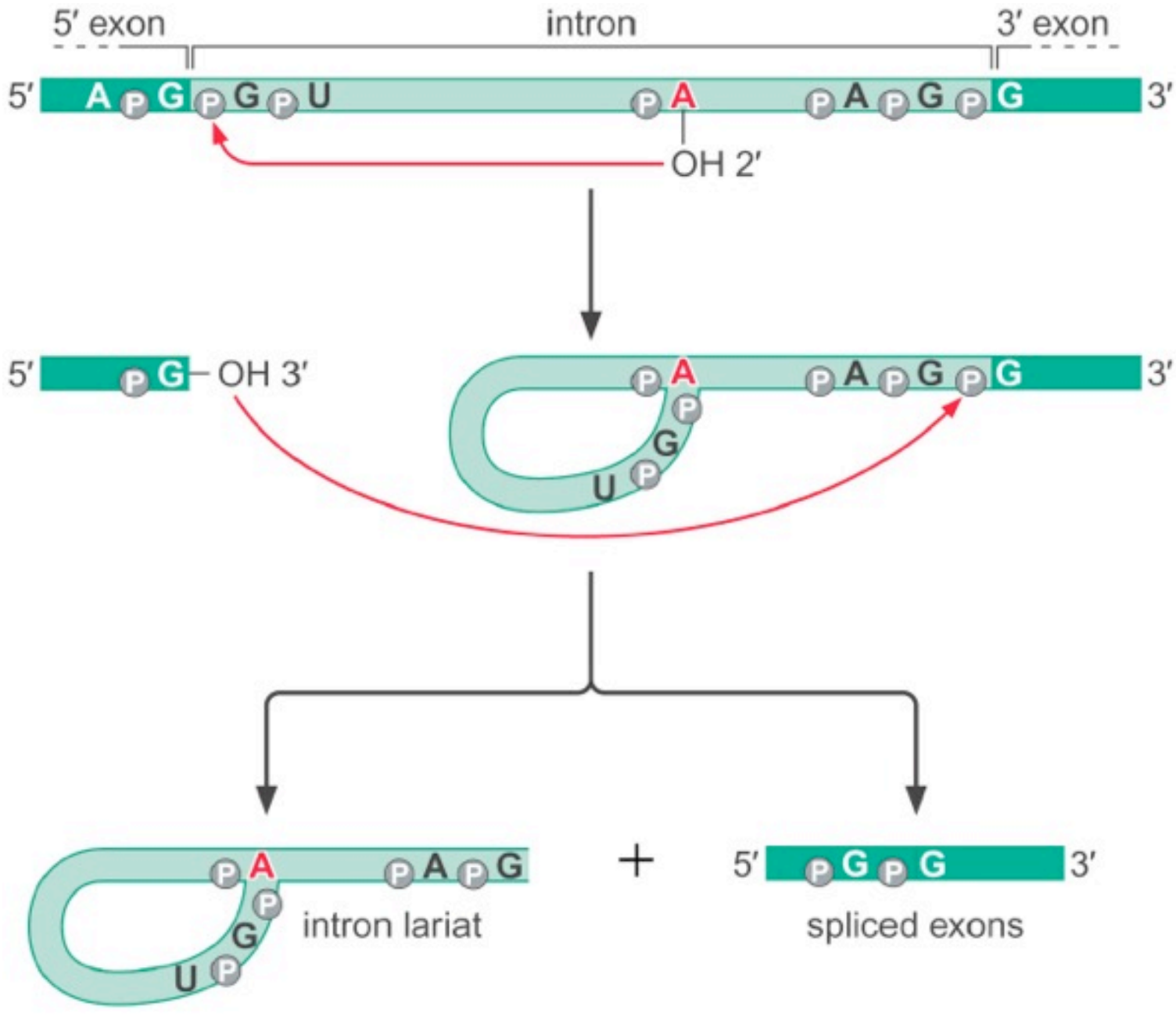
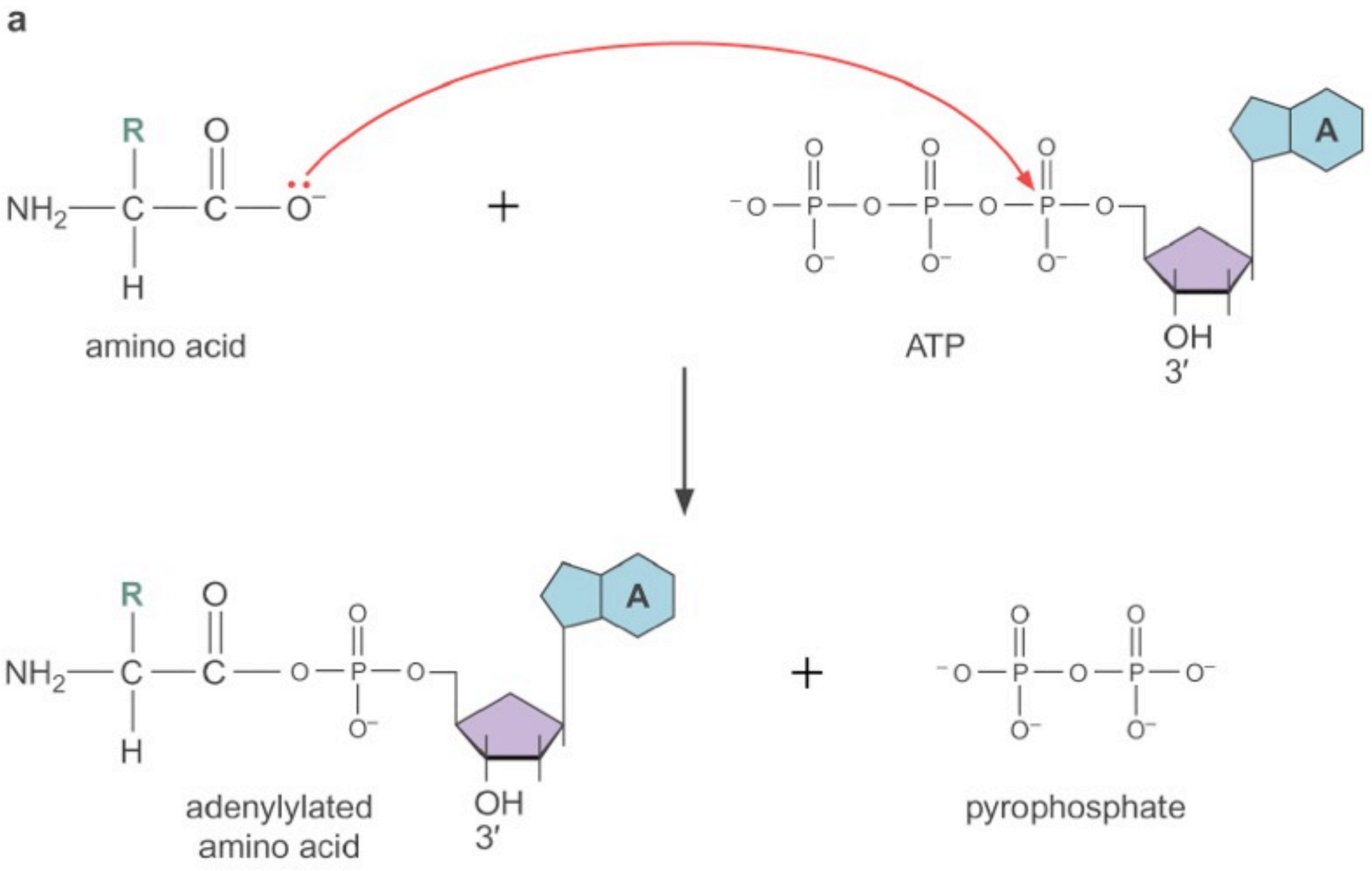
Nucleic Acid Structure

- Professor Craig Martin
- Dept of Chemistry
- http://people.chem.umass.edu/cmartin

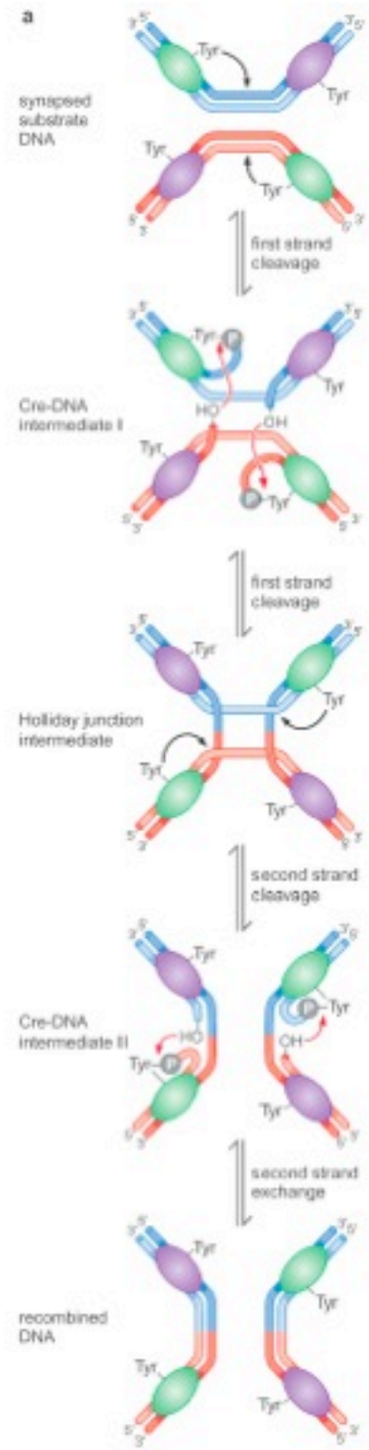
RNA Splicing



Translation



Recombination



DNA

DNA

A, C, G, and T - right?

Which is more stable?

(which has a higher melting temperature?)

ACCGCCACCGAAG

TGGCGGTGGCTTC

or

ACCGCCACCGAAG

TGGCGGTGGCTTA

Which is more stable?

(which has a higher melting temperature?)

ACCGCCACCGAAG
TGGCGGTGGCTTC

51.6° C

or

ACCGCCACCGAAG
TGGCGGTGGCTTA

Which is more stable?

(which has a higher melting temperature?)

ACCGCCACCGAAG
TGGCGGTGGCTTC

51.6° C

or

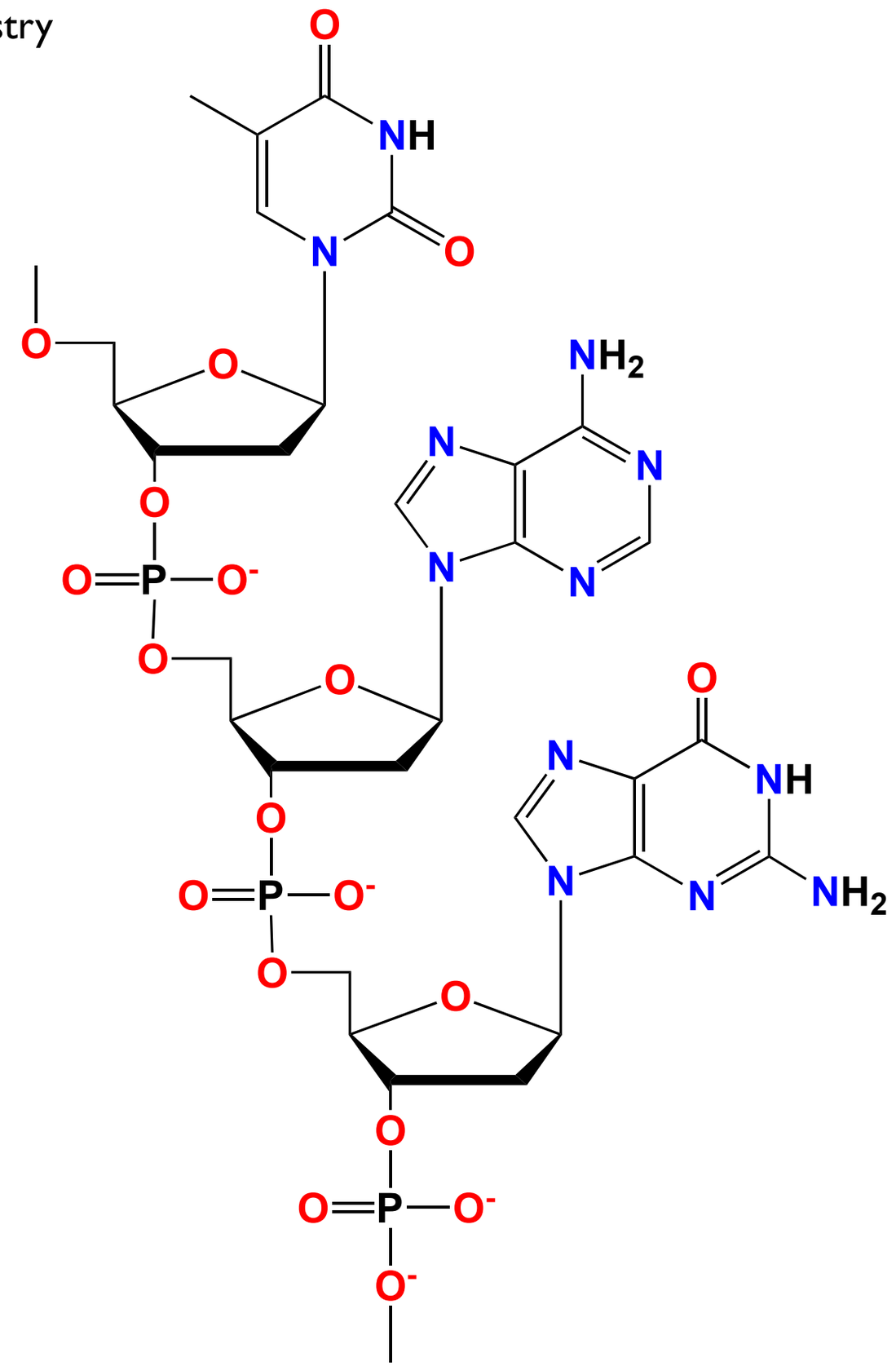
ACCGCCACCGAAG
TGGCGGTGGCTTA

52.5° C

Calculations from http://www.idtdna.com/analyzer/Applications/OligoAnalyzer/

DNA

A look at the Chemistry



DNA

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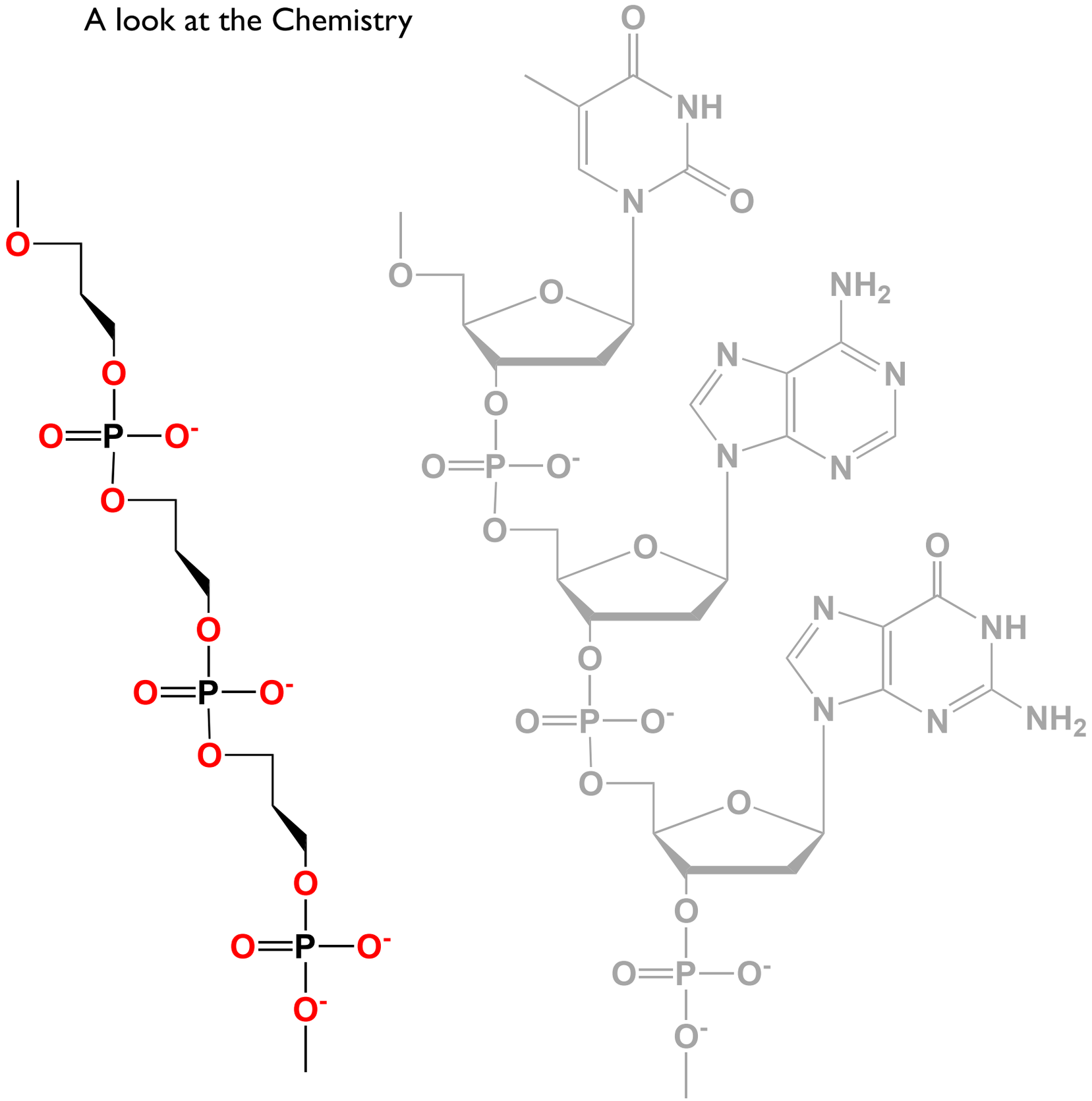

DNA

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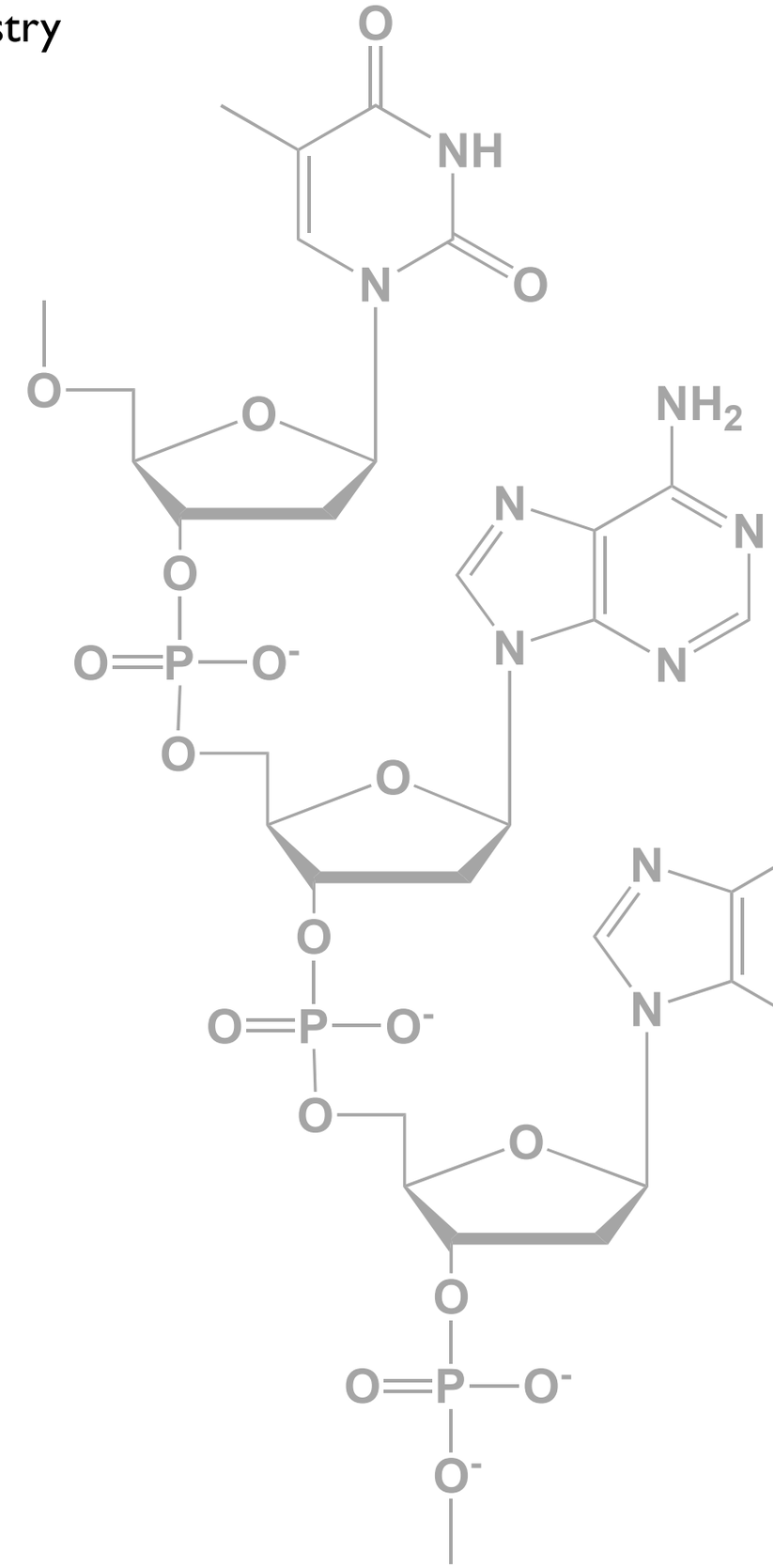

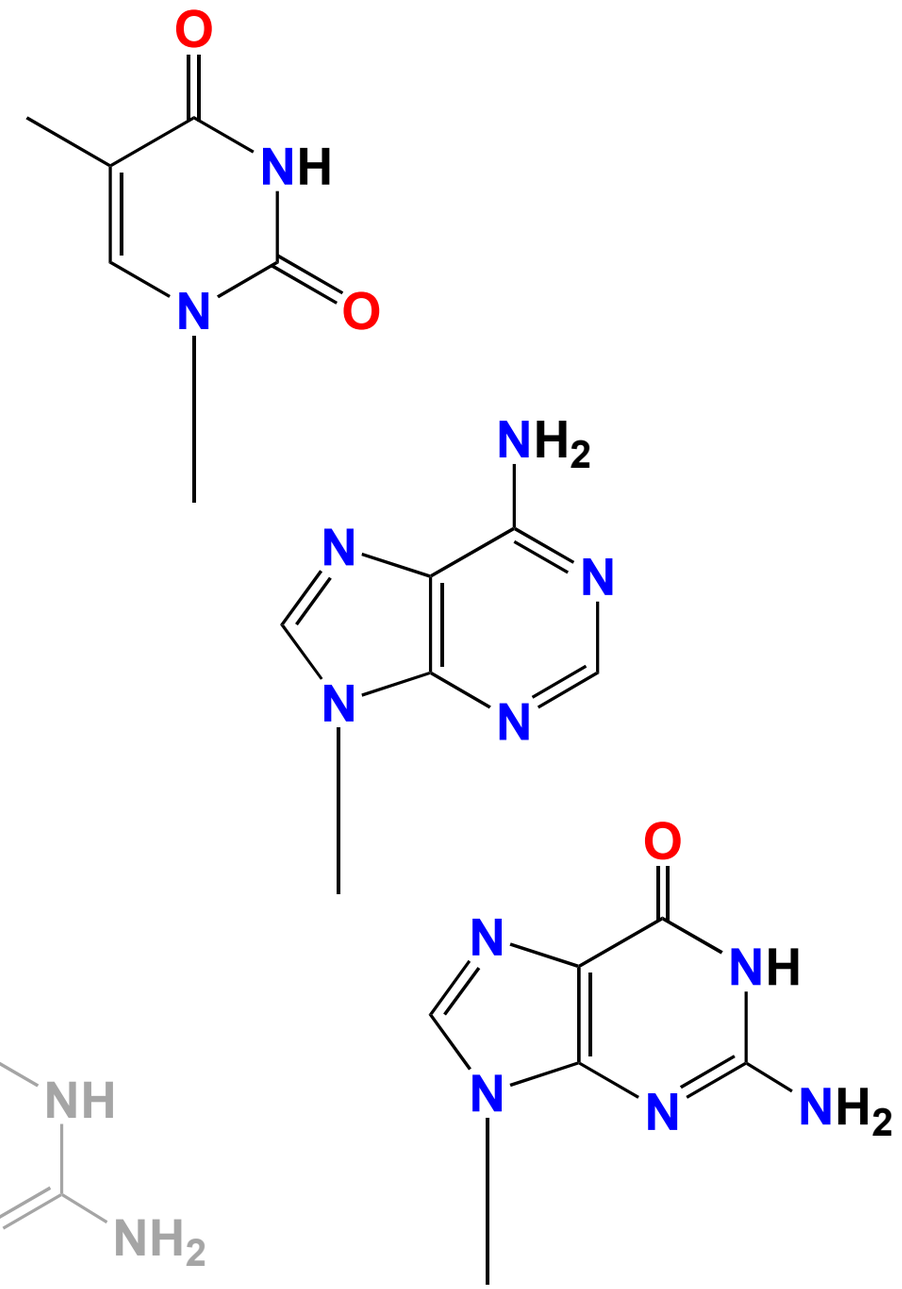

DNA

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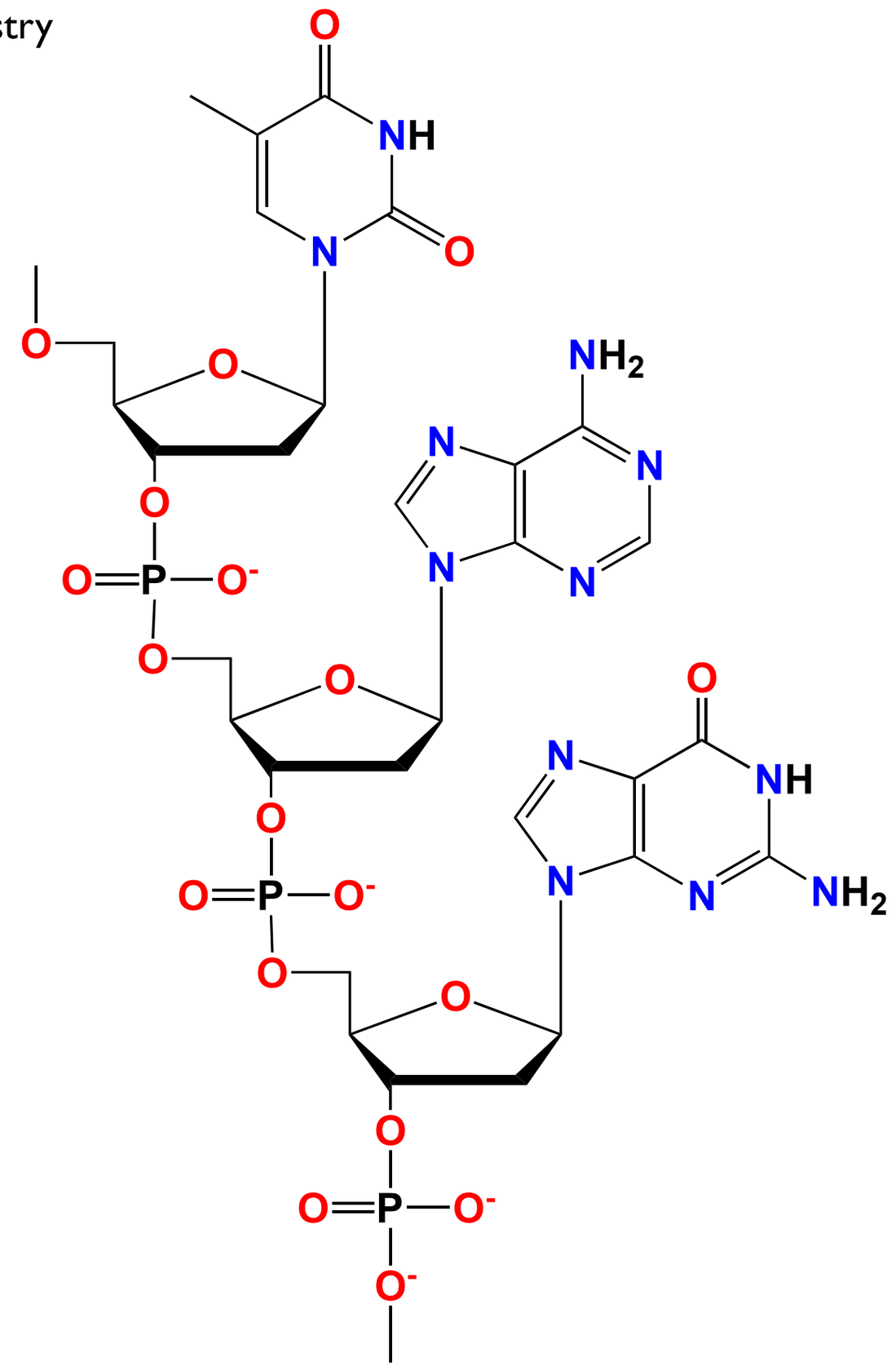

DNA

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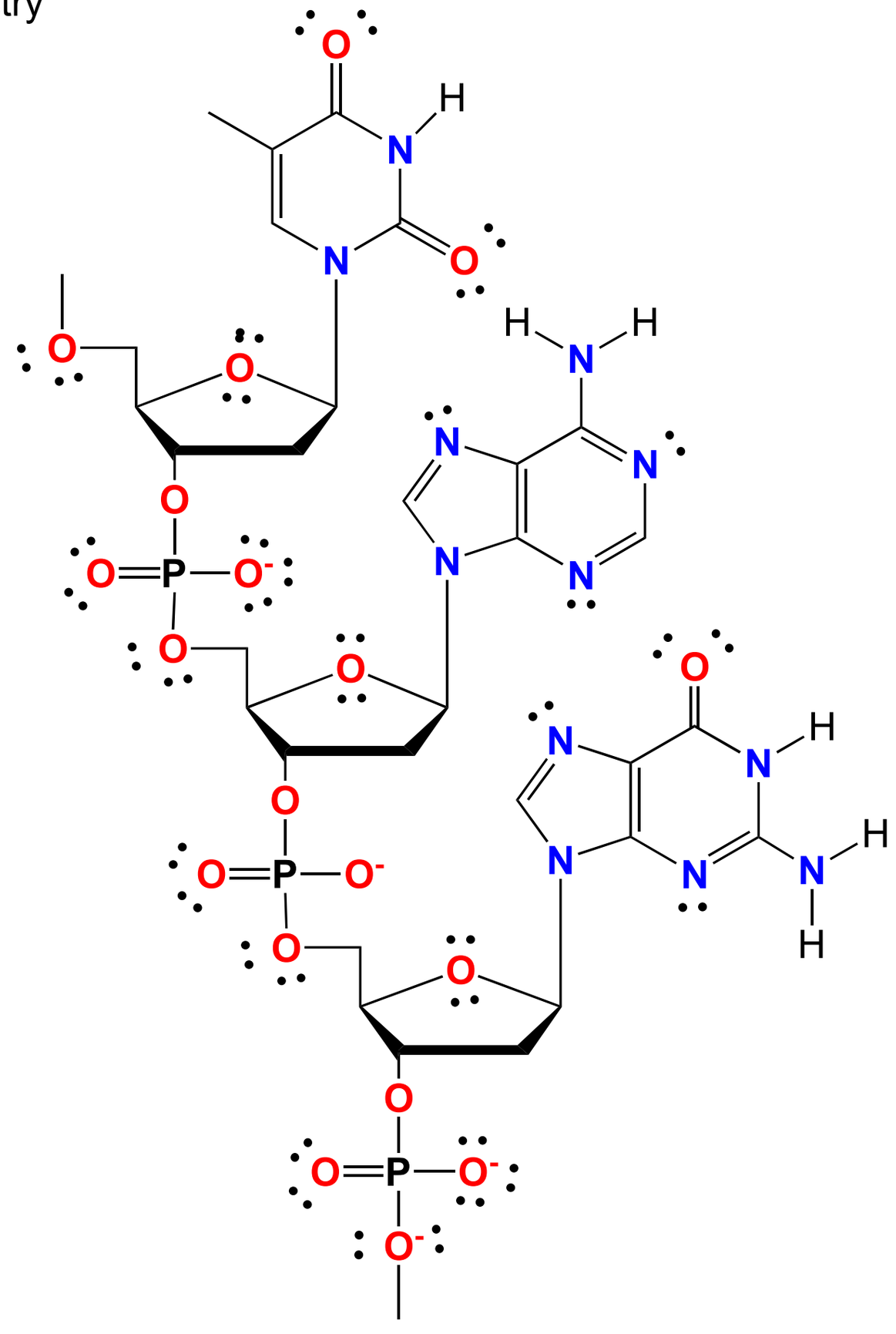

DNA

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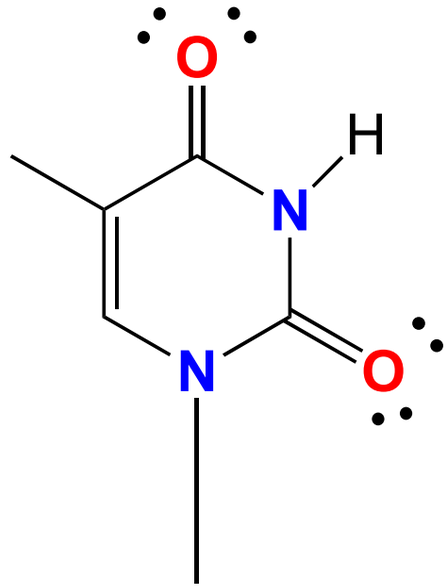

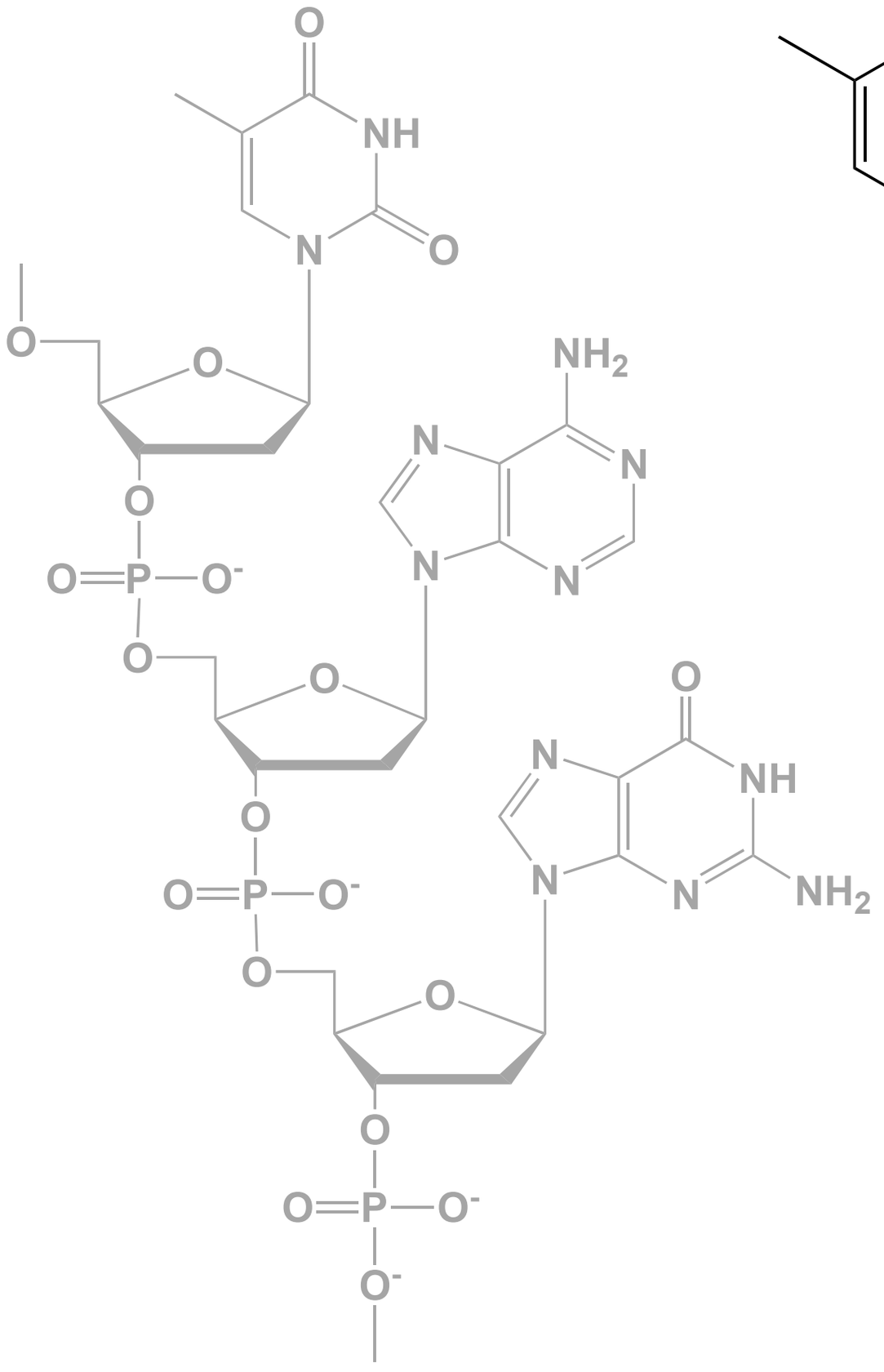

DNA

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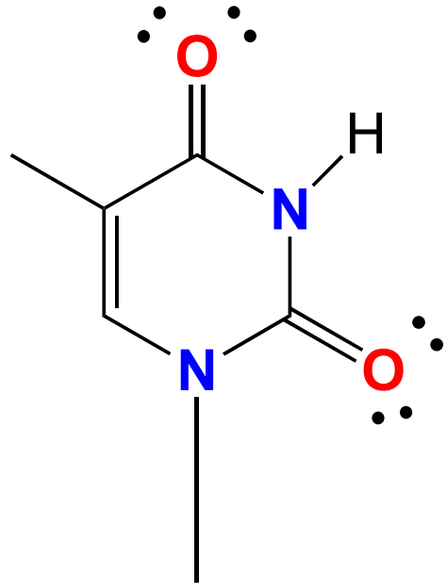

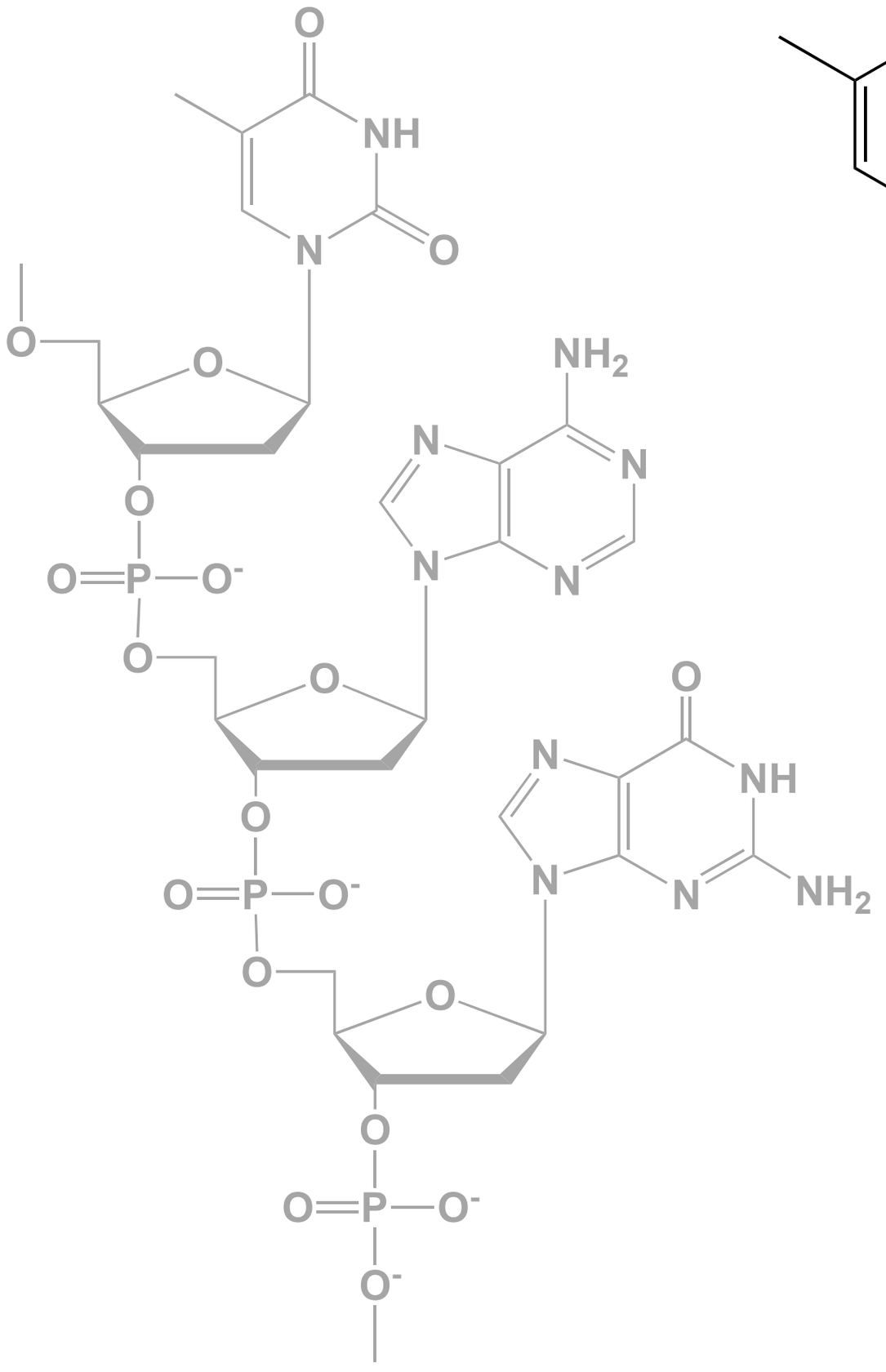

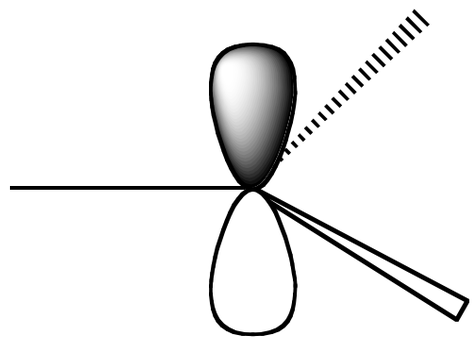

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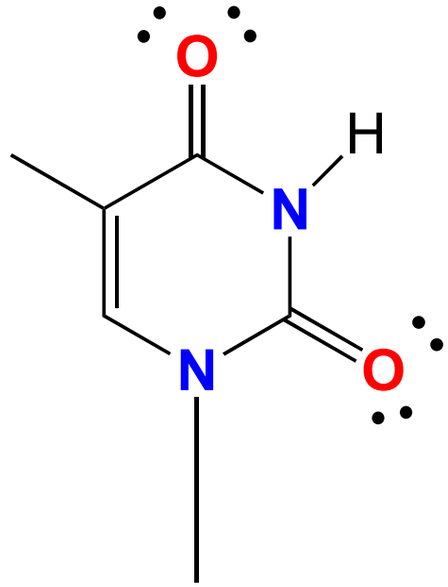

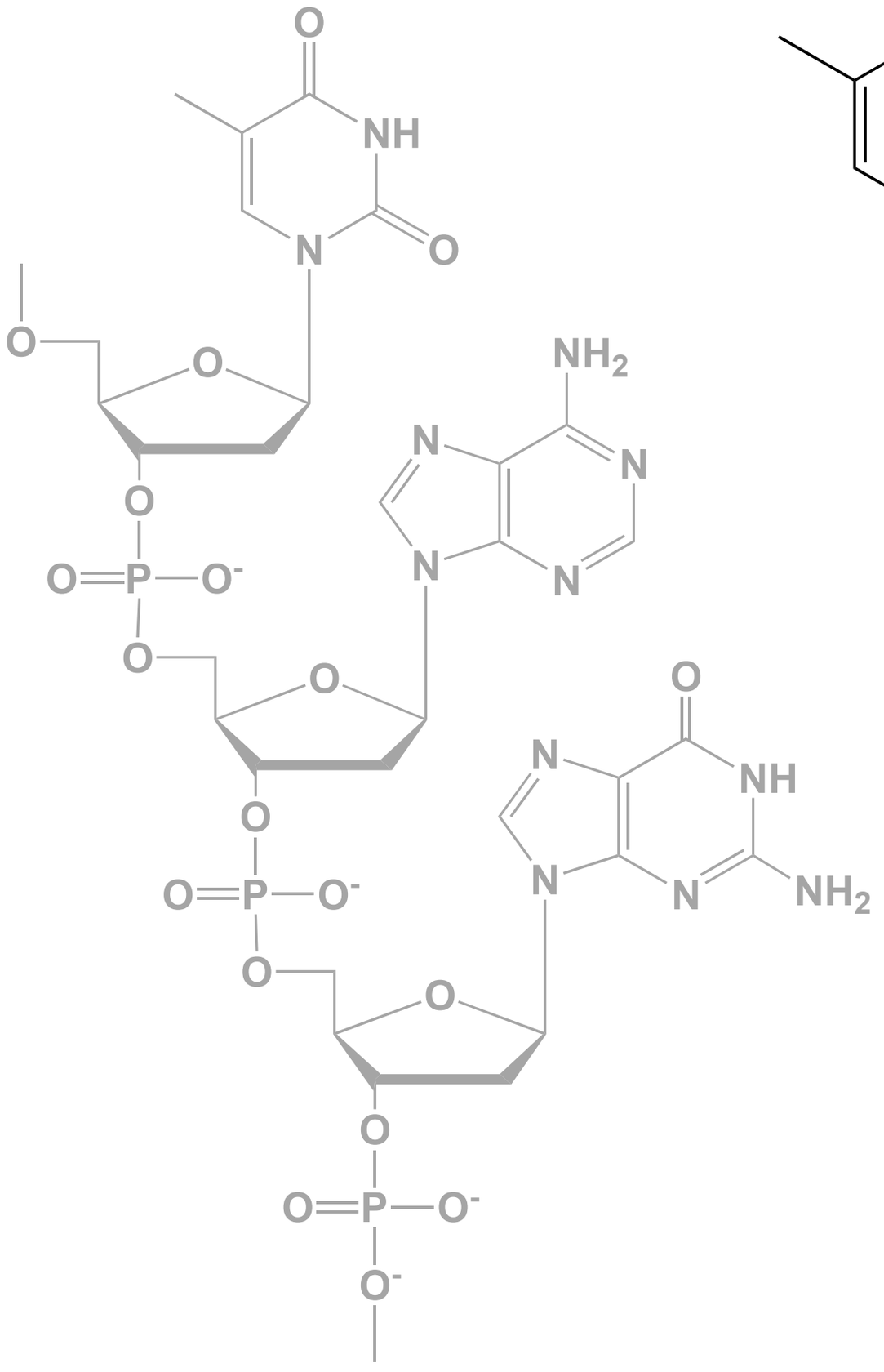

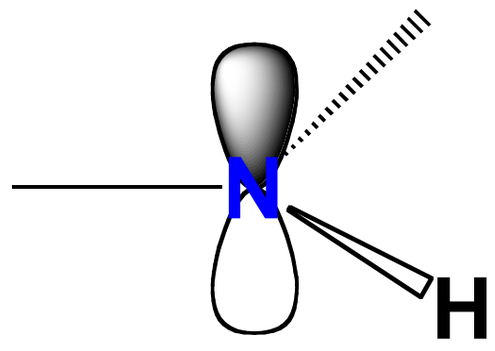

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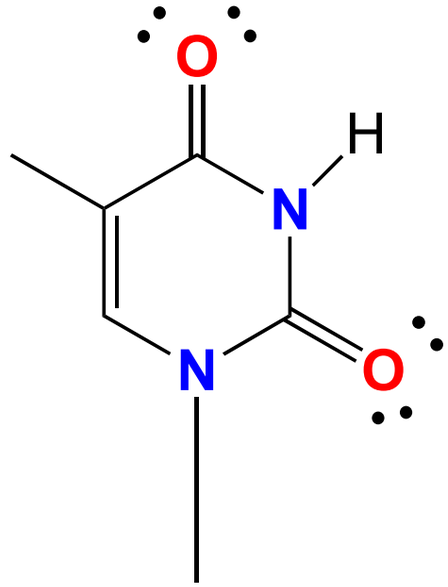

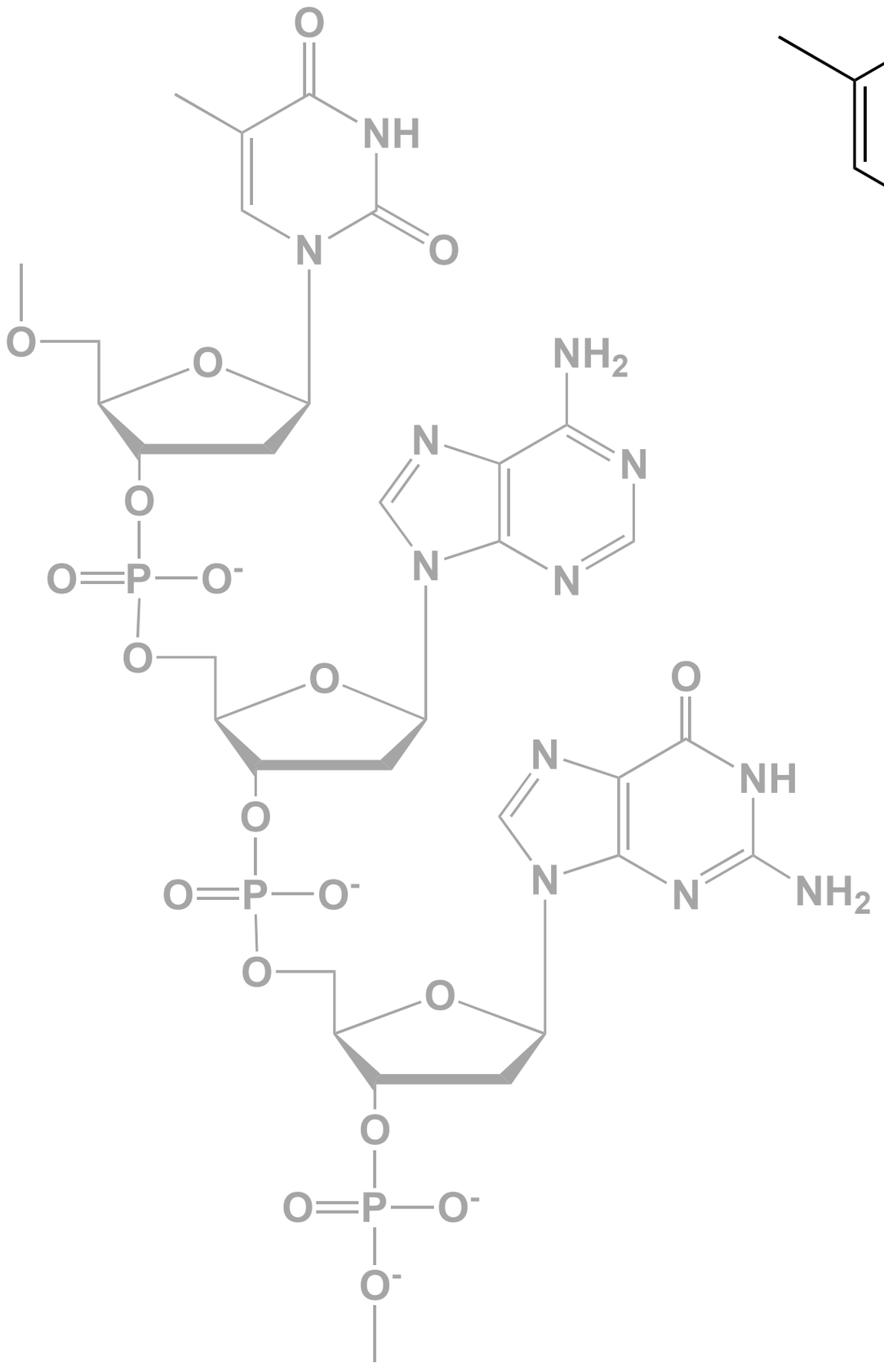

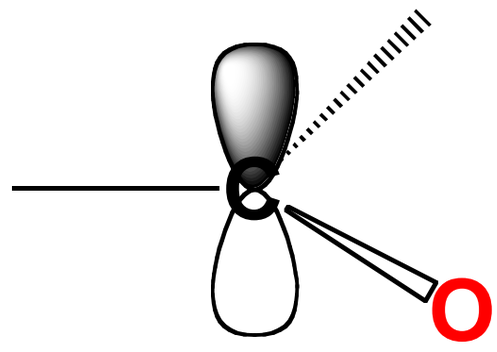

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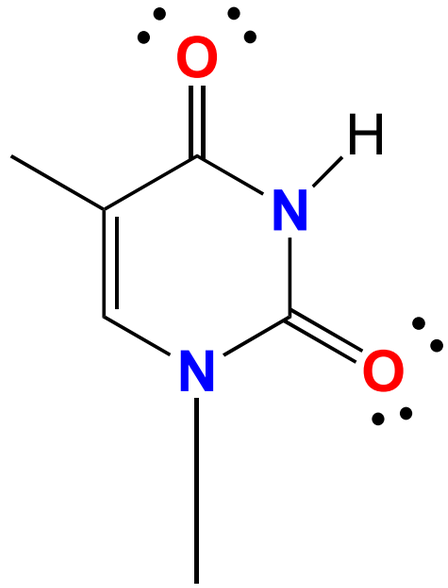

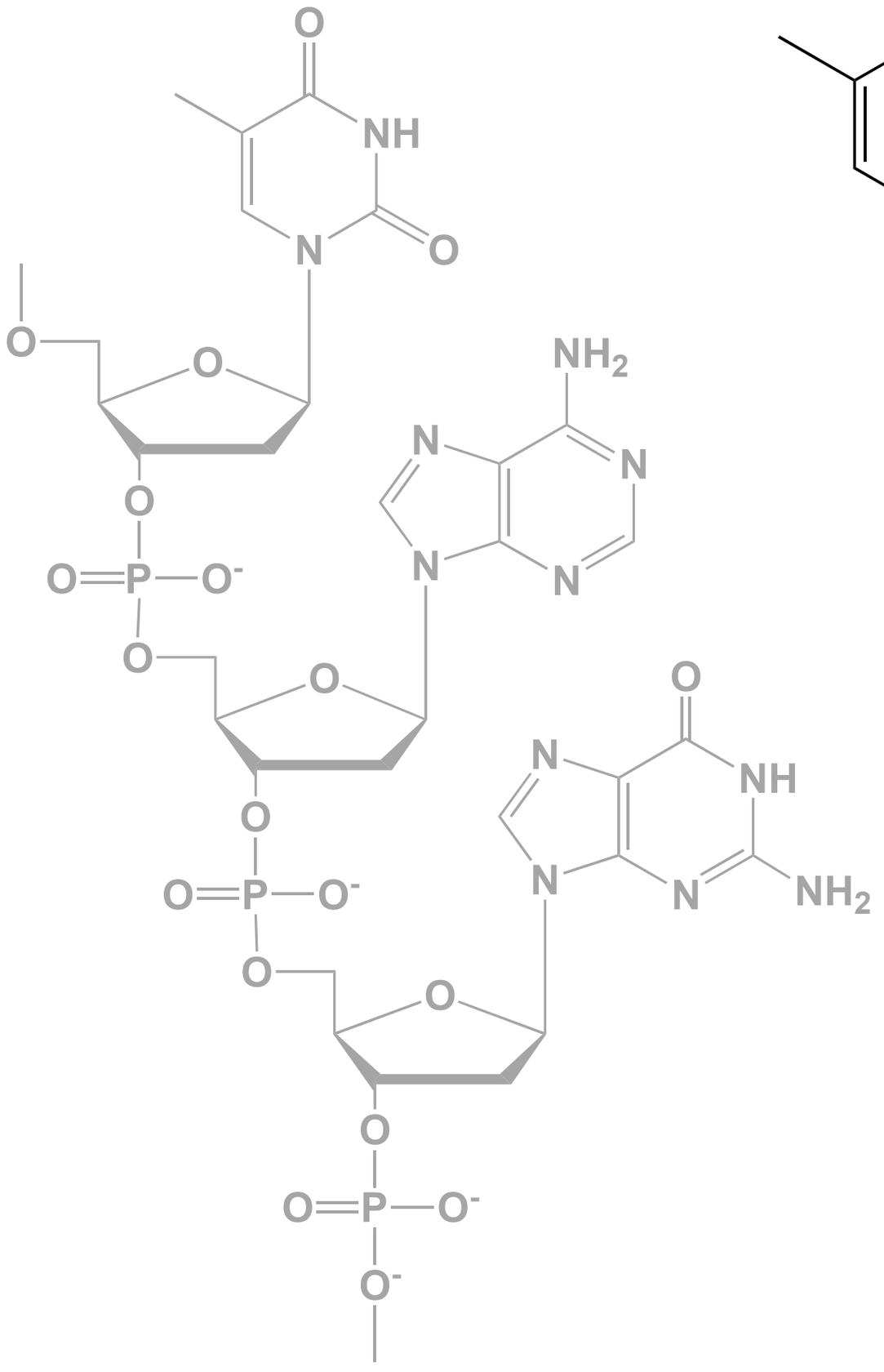

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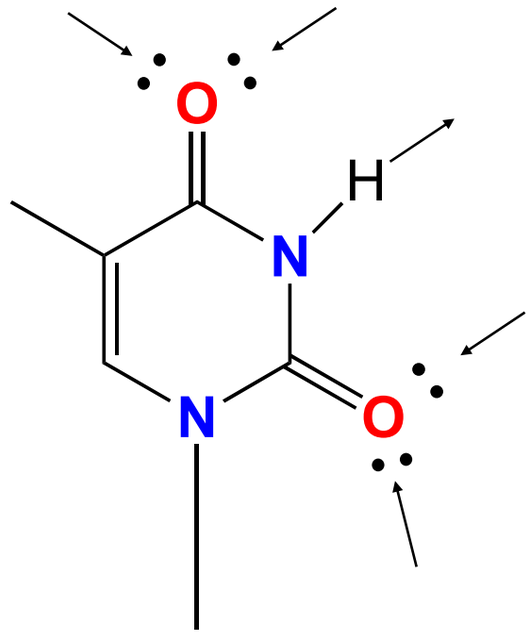

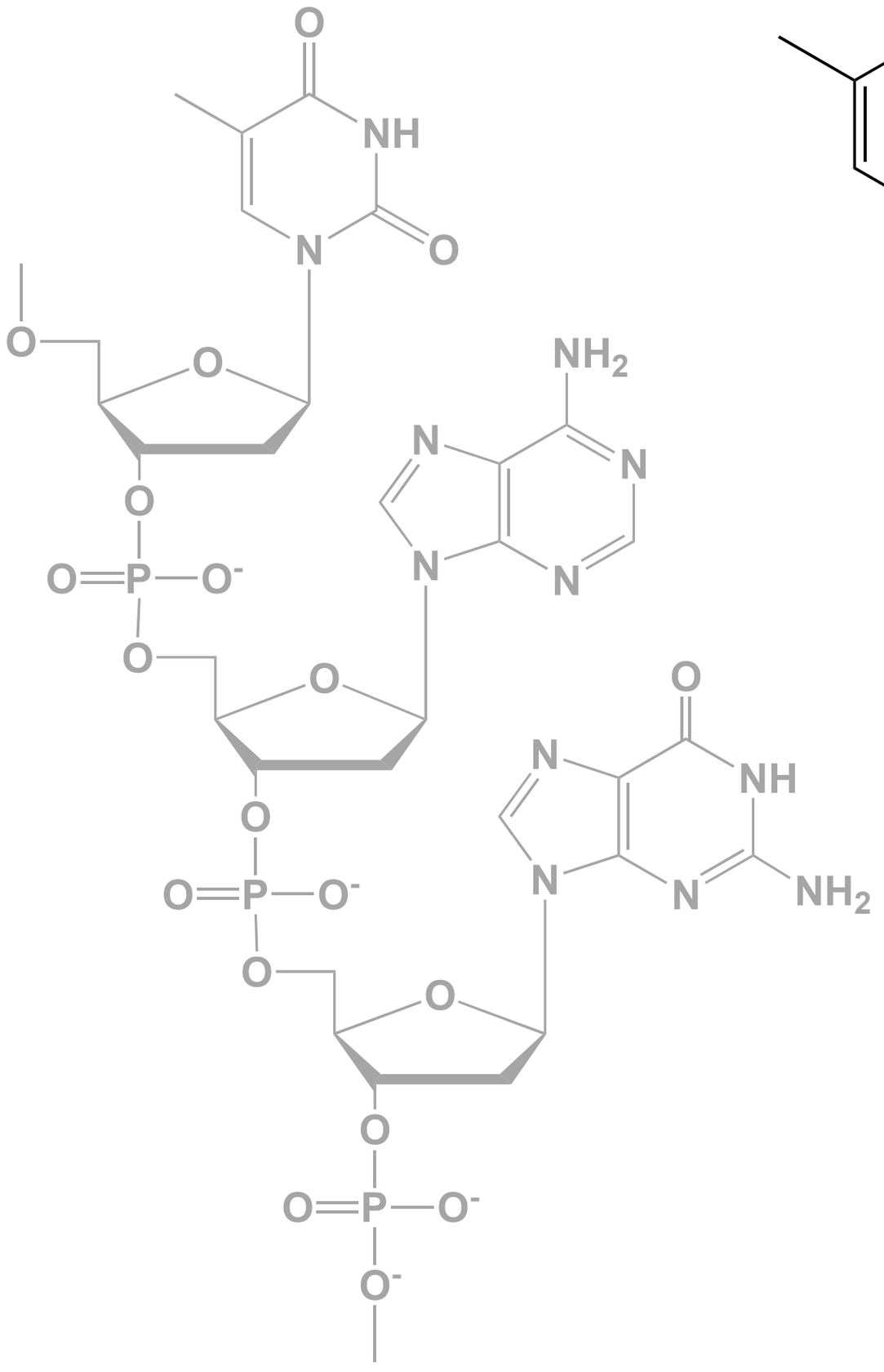

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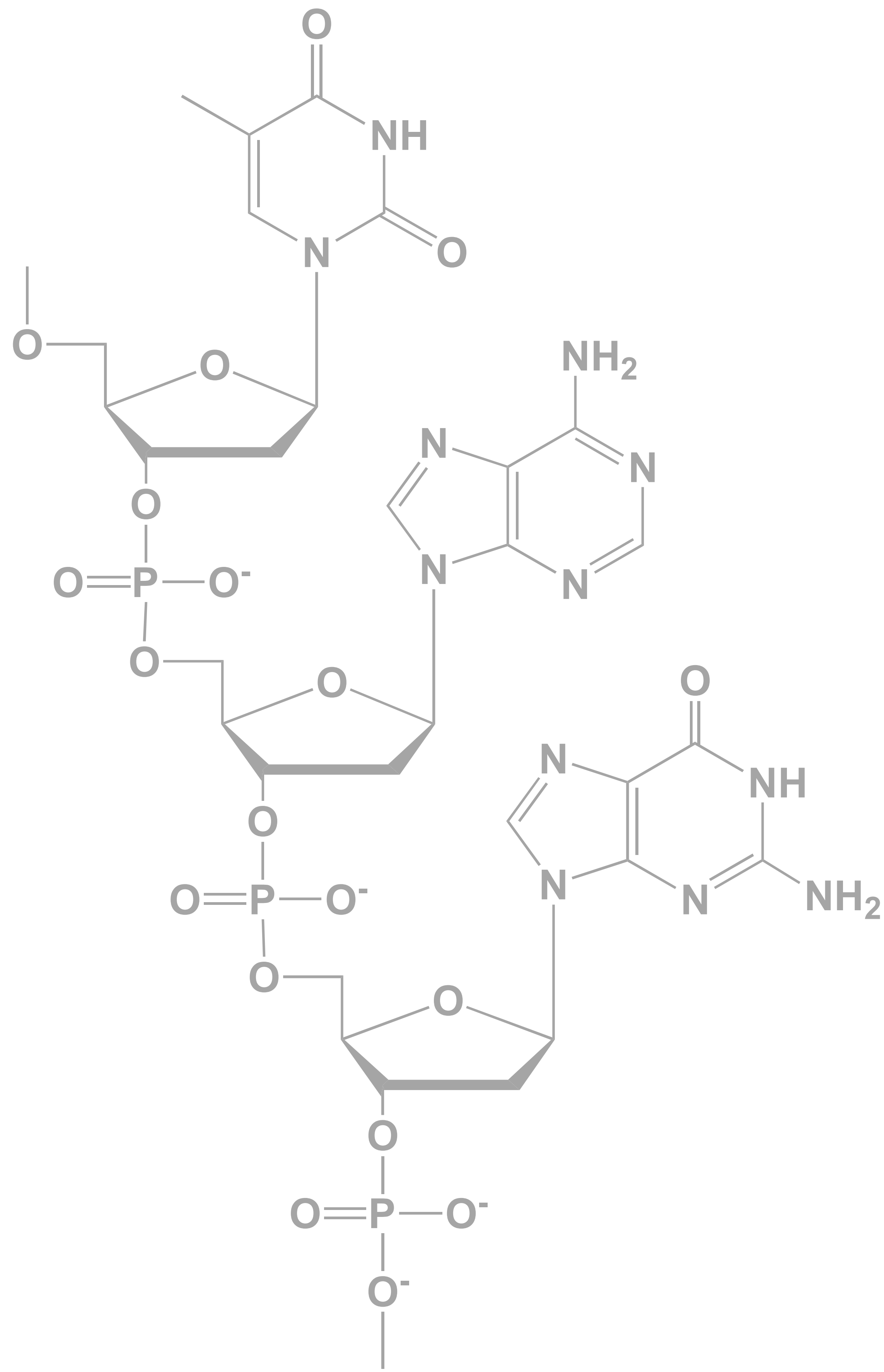

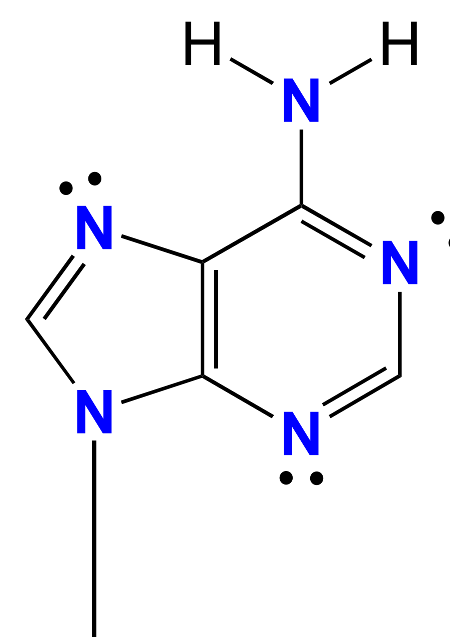

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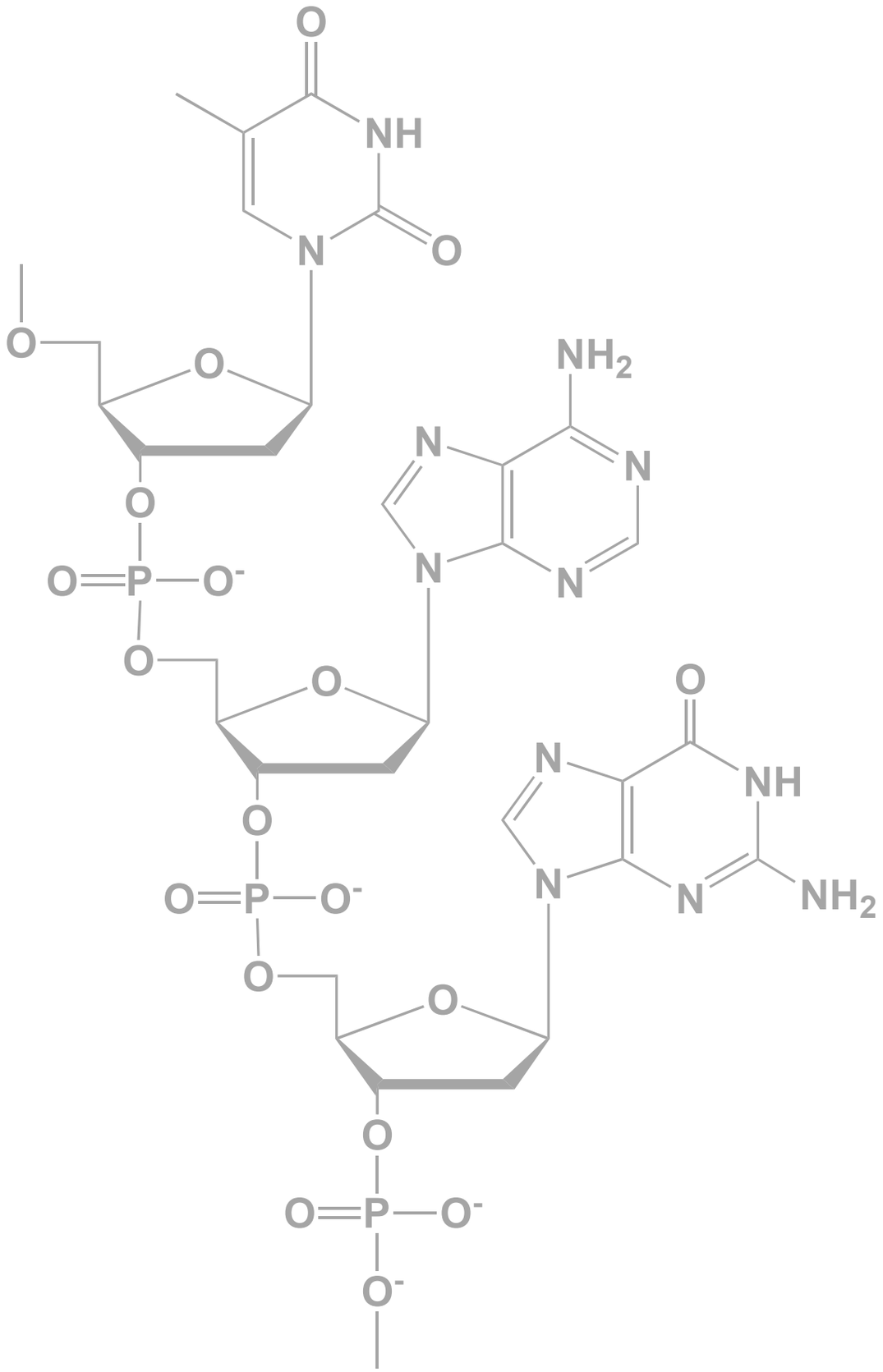

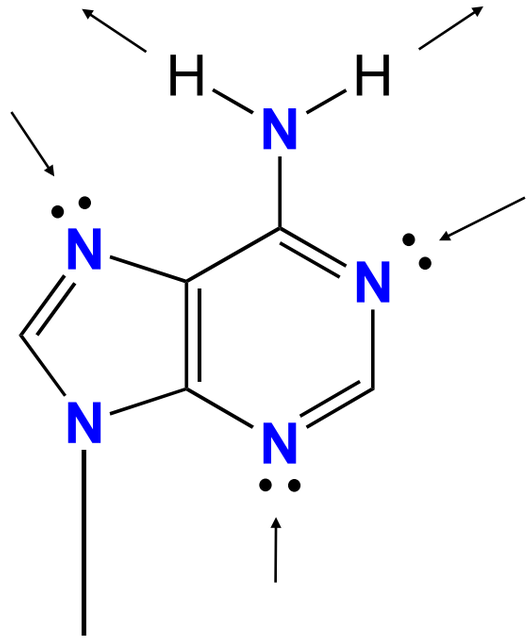

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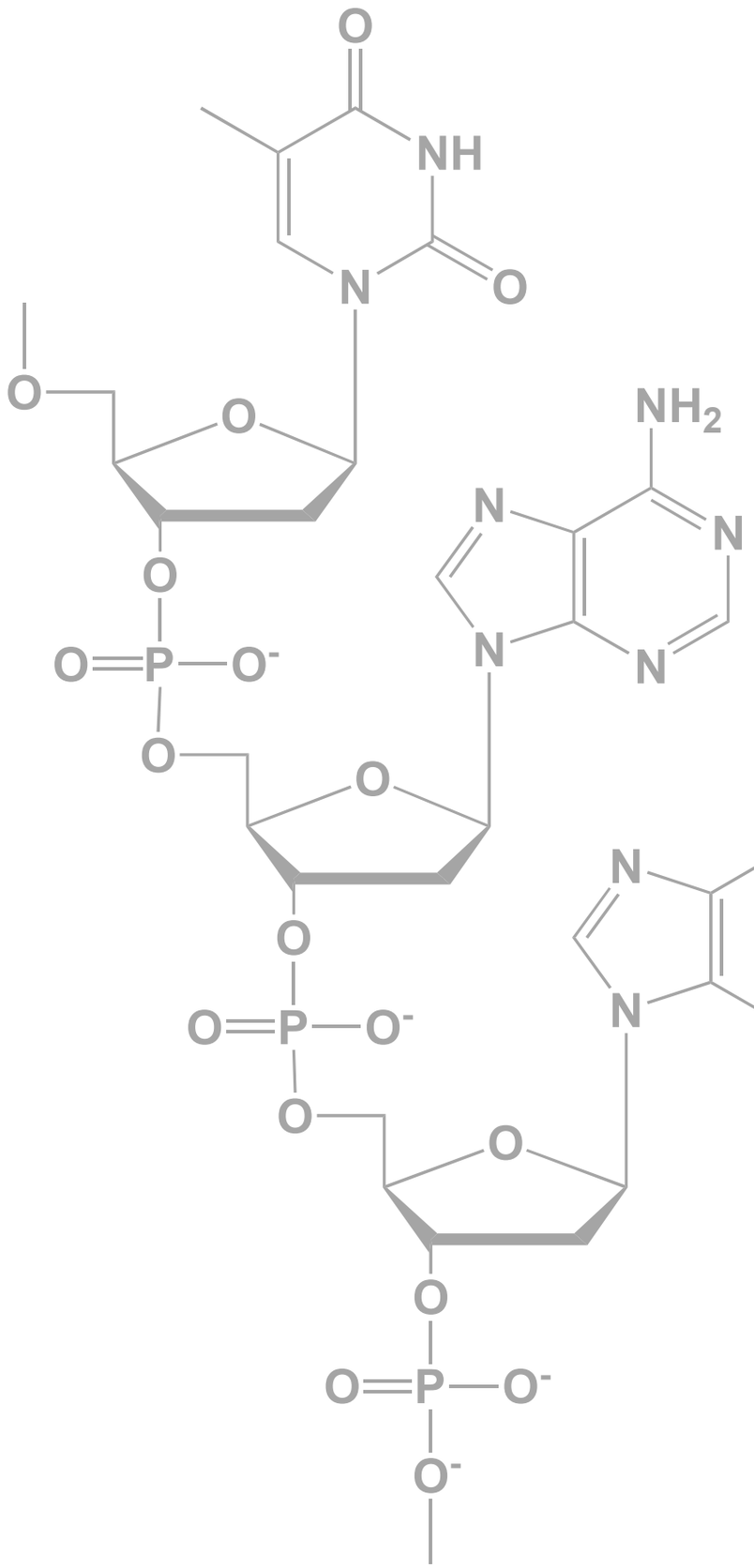
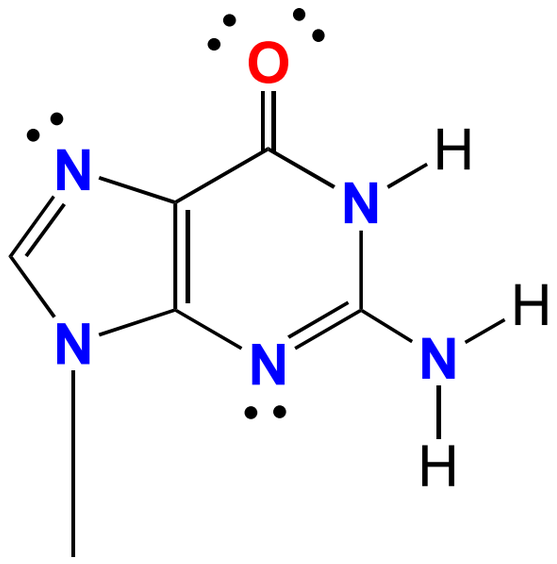
A look at the Chemistry





DNA

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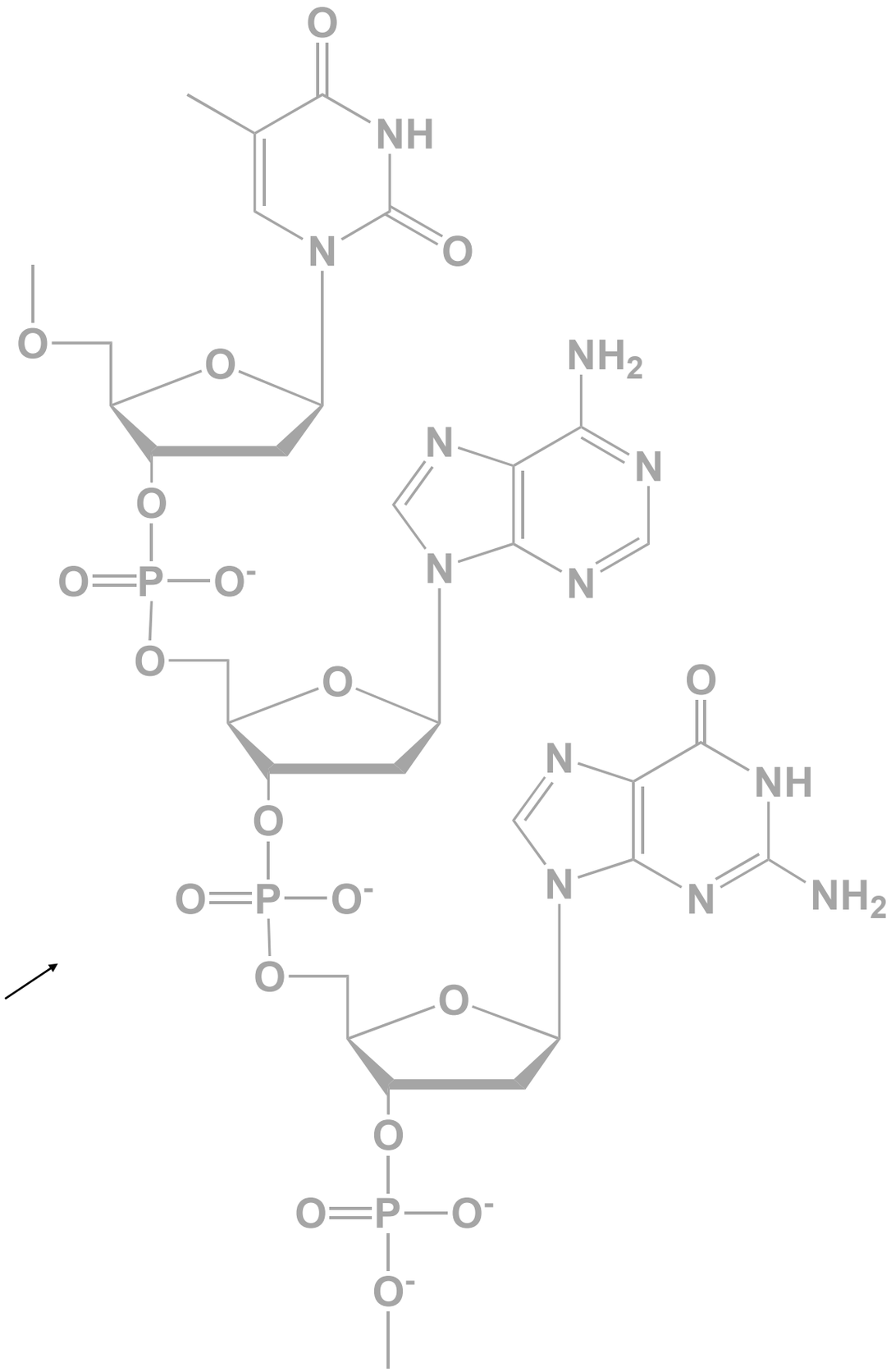
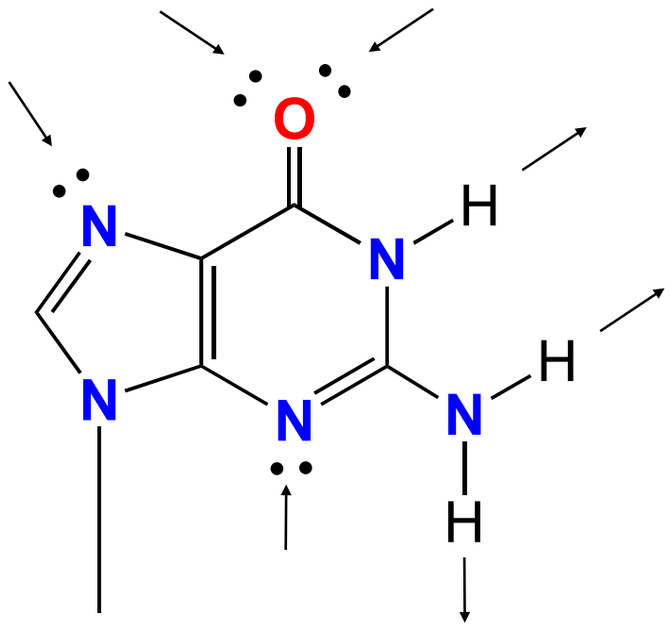
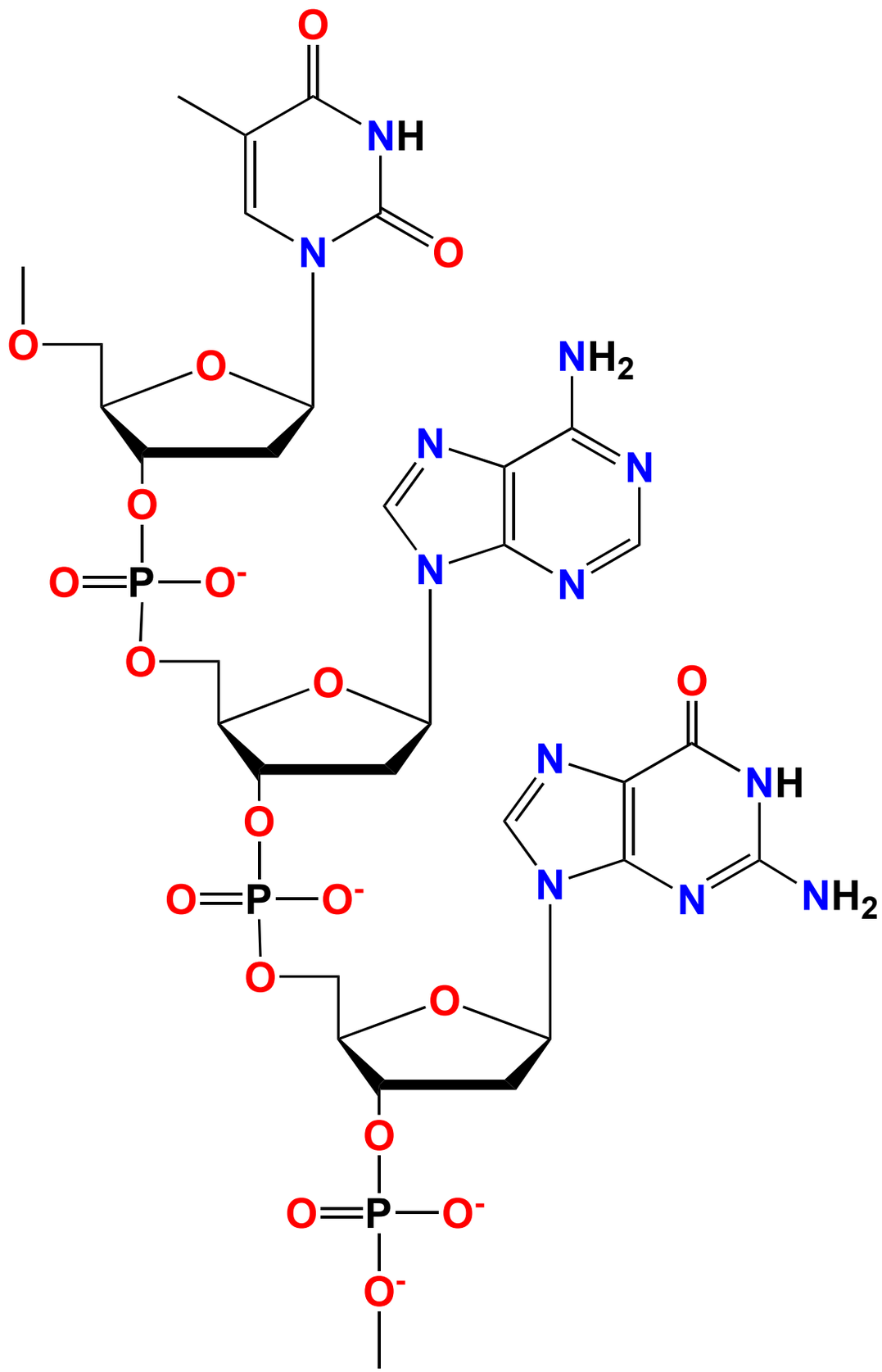


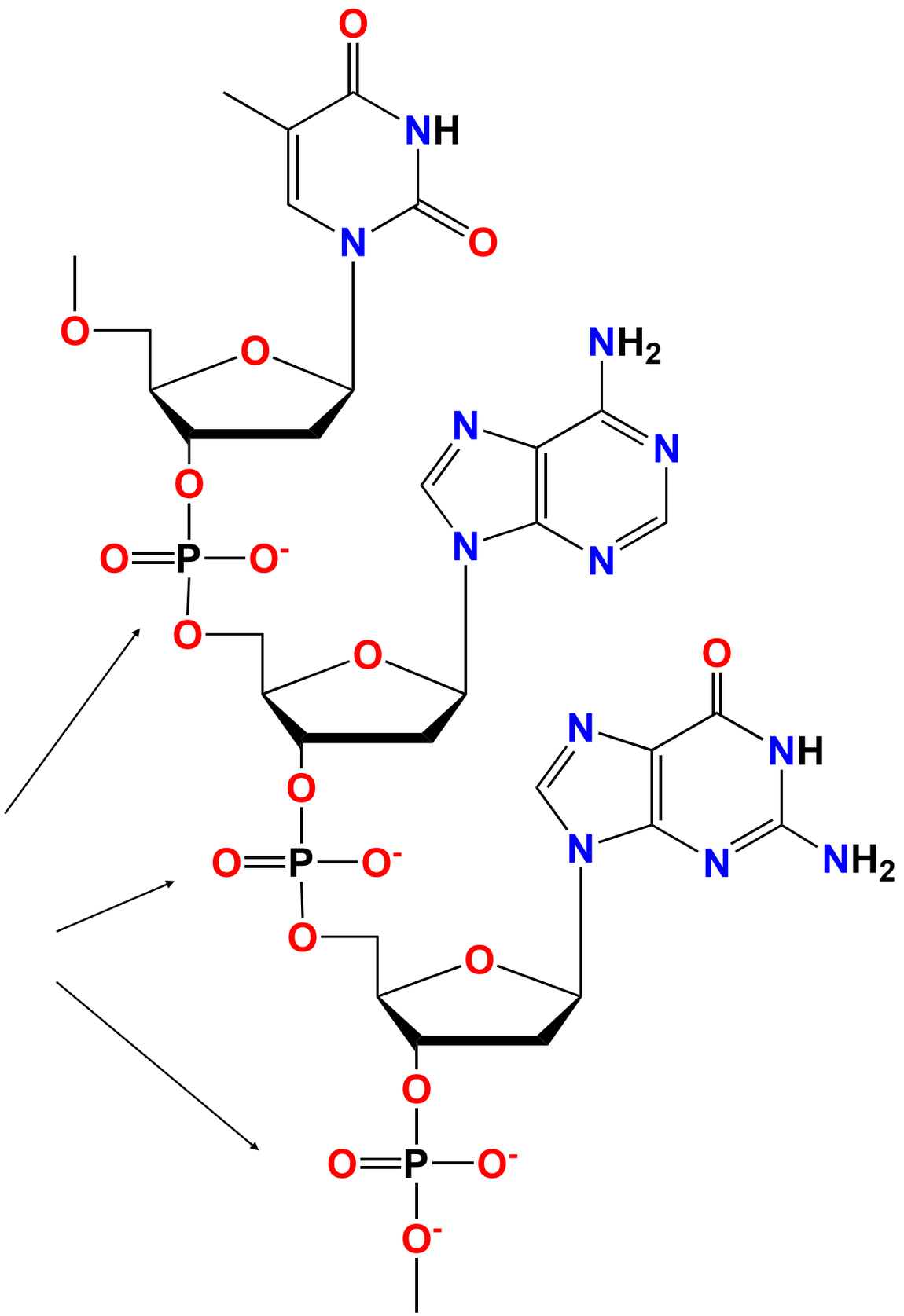


What forces are important?



What forces are important?

Electrostatics



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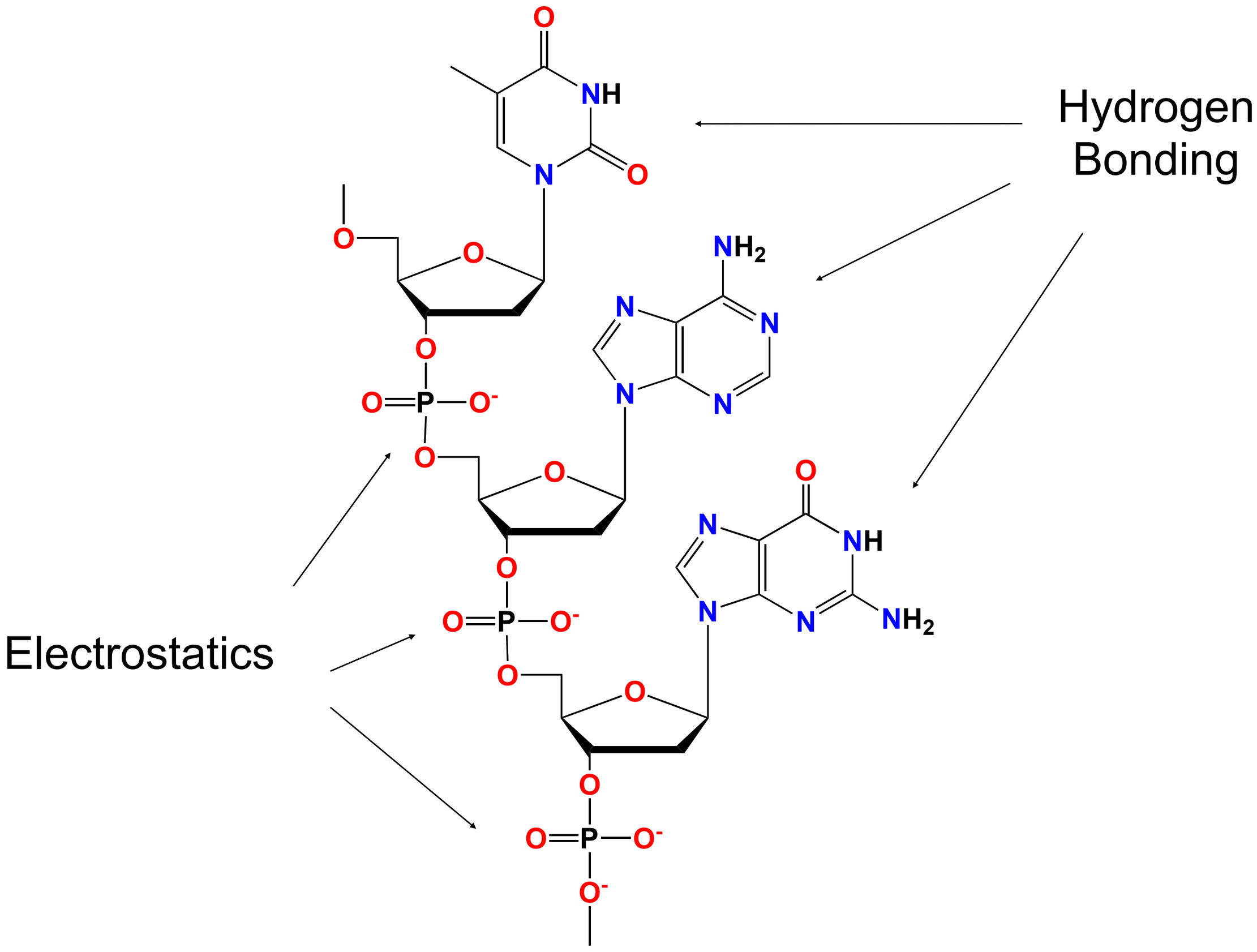

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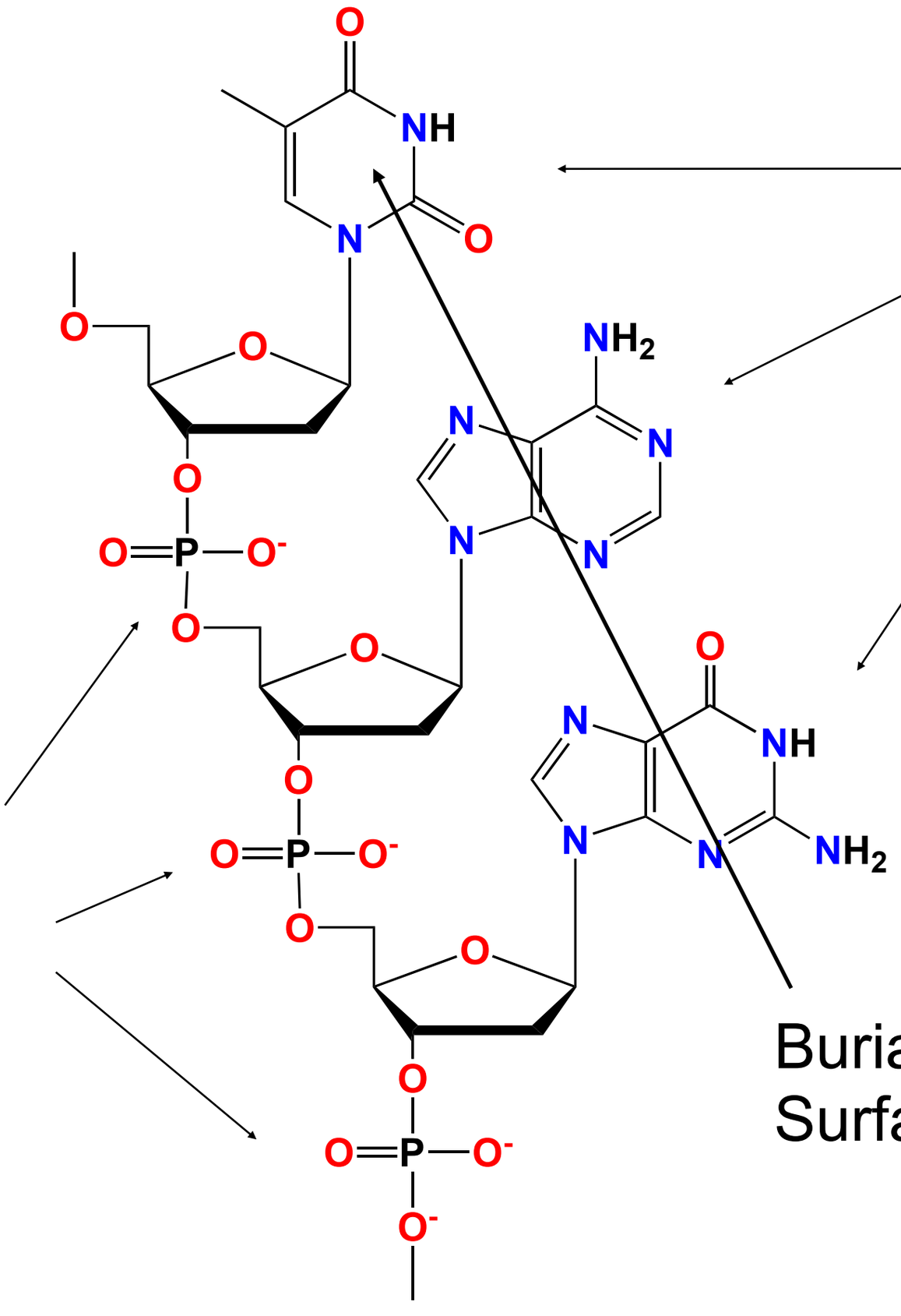
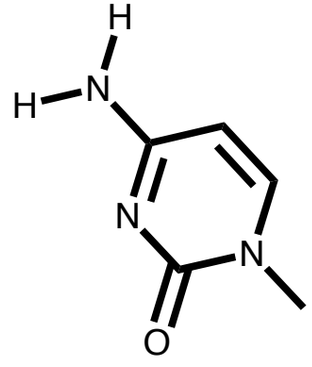


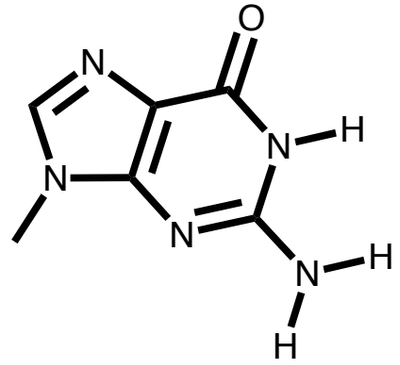
Hydrogen Bonding

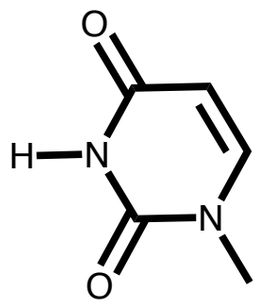
Electrostatics

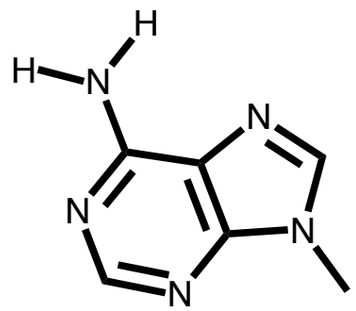
Burial of Hydrophobic Surface & Stacking

Base Pairs









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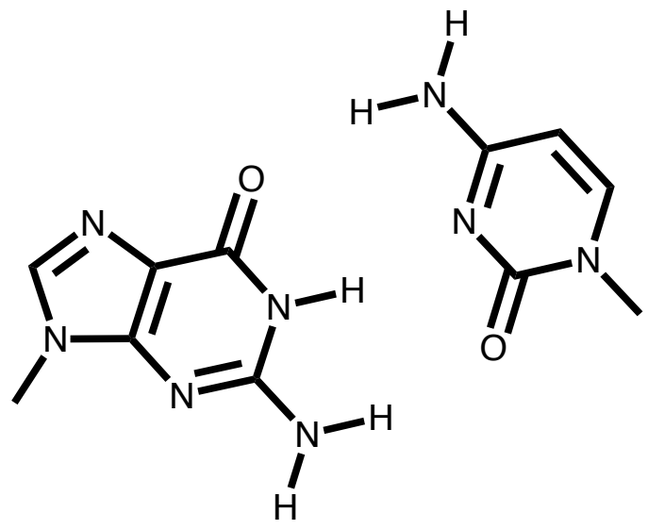

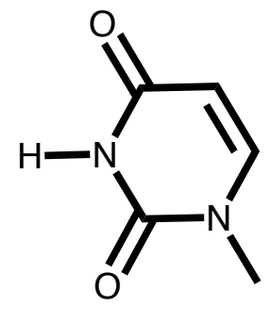

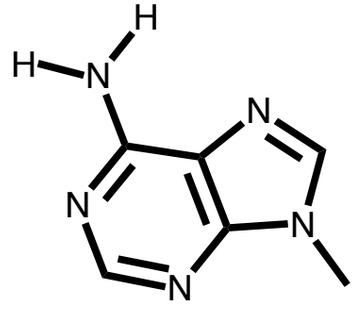

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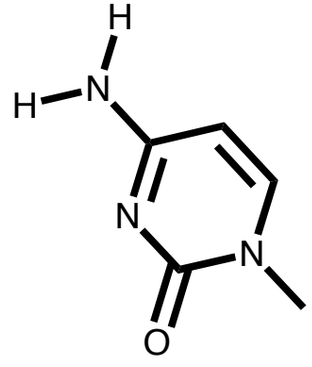

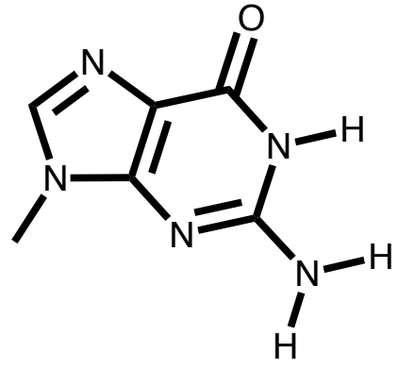

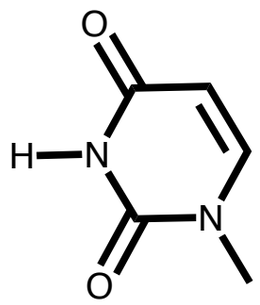

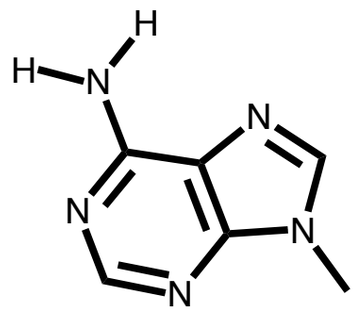

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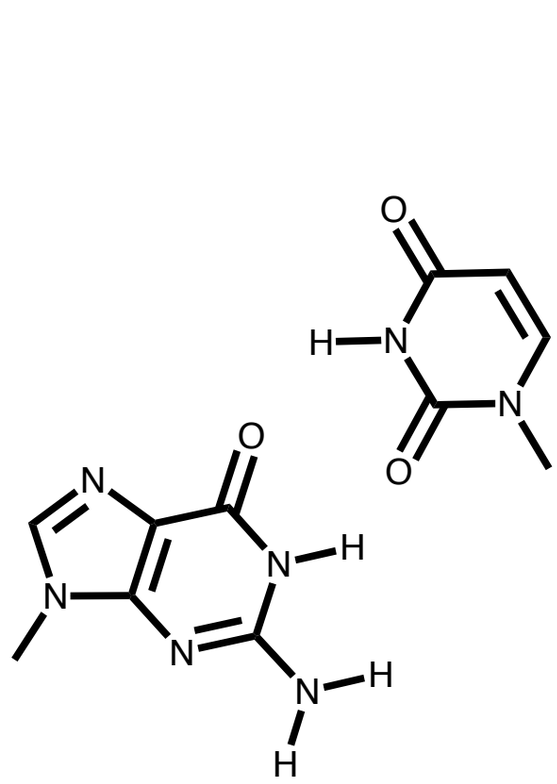

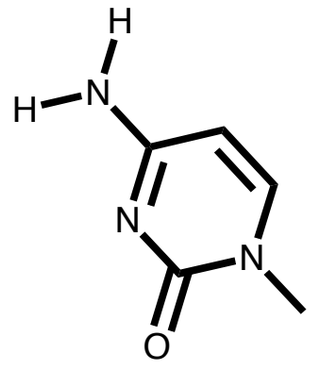

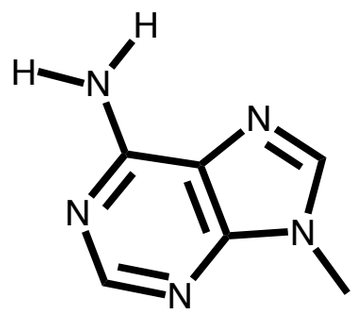

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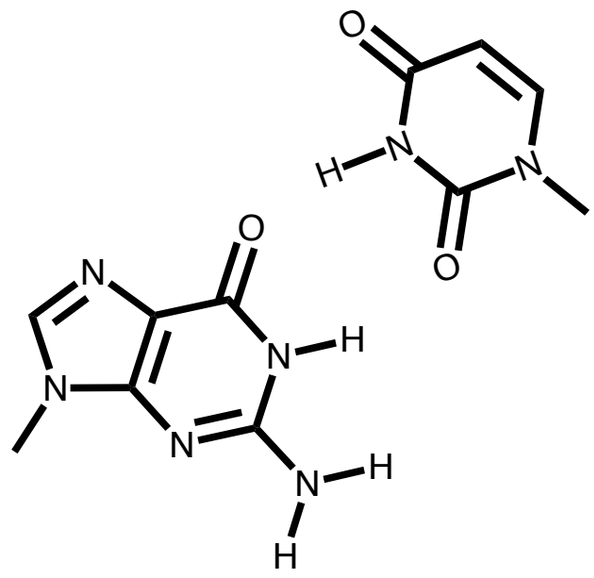

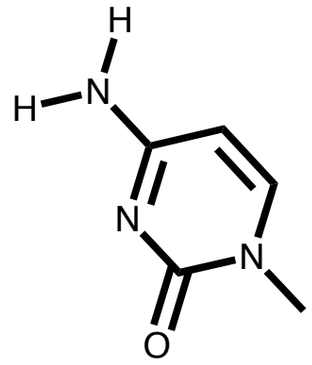

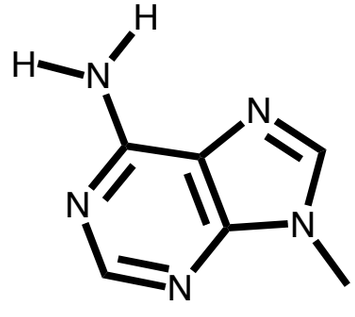

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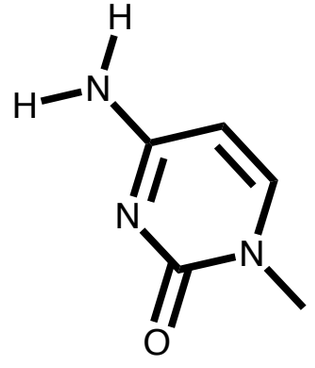
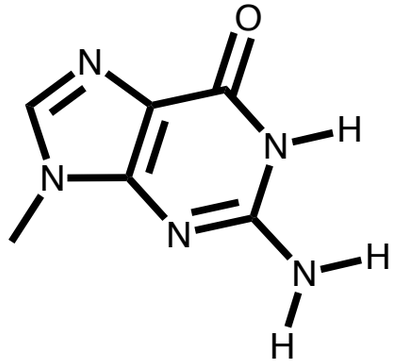
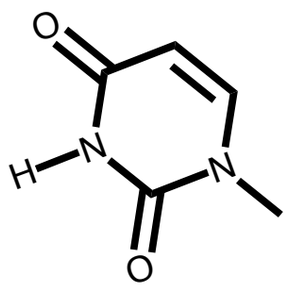
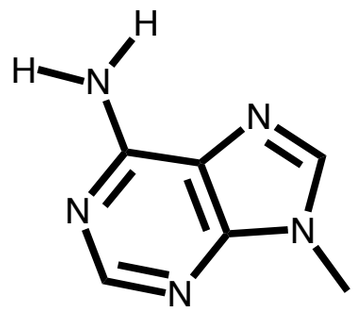
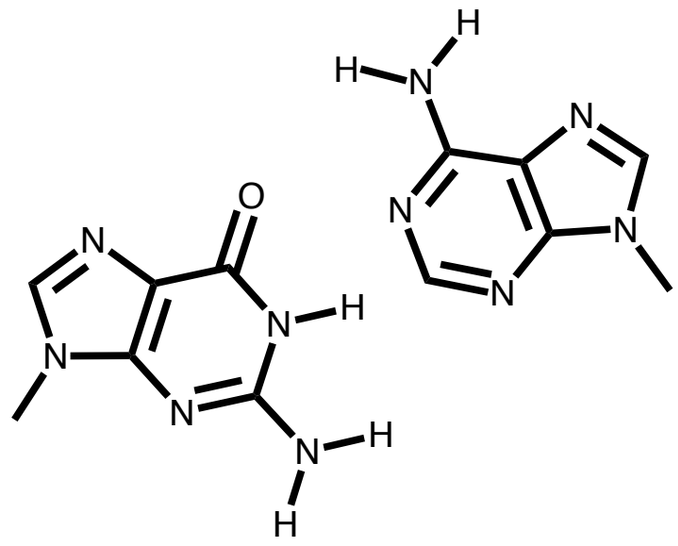


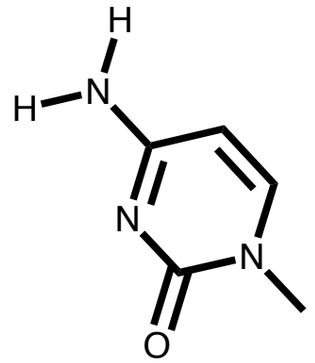


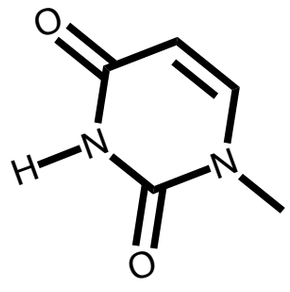




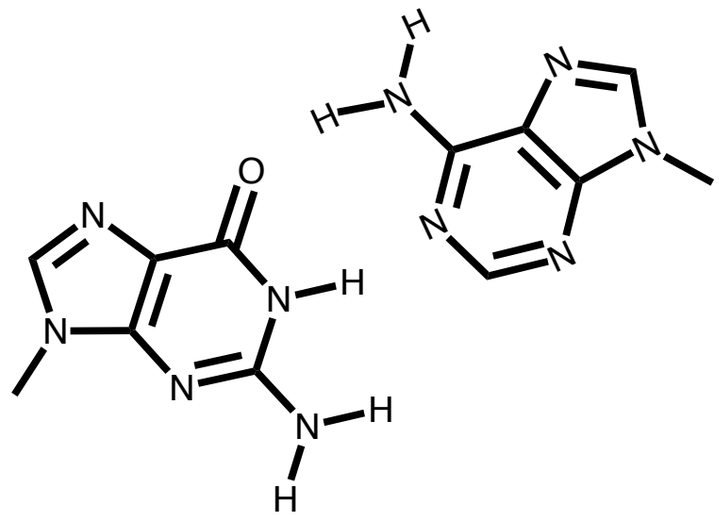
Base Pairs

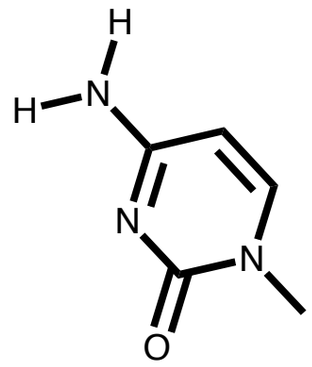


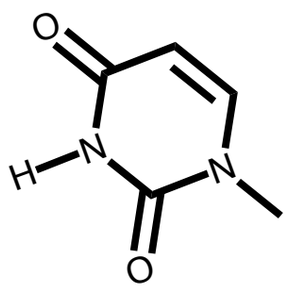




Base Pairs



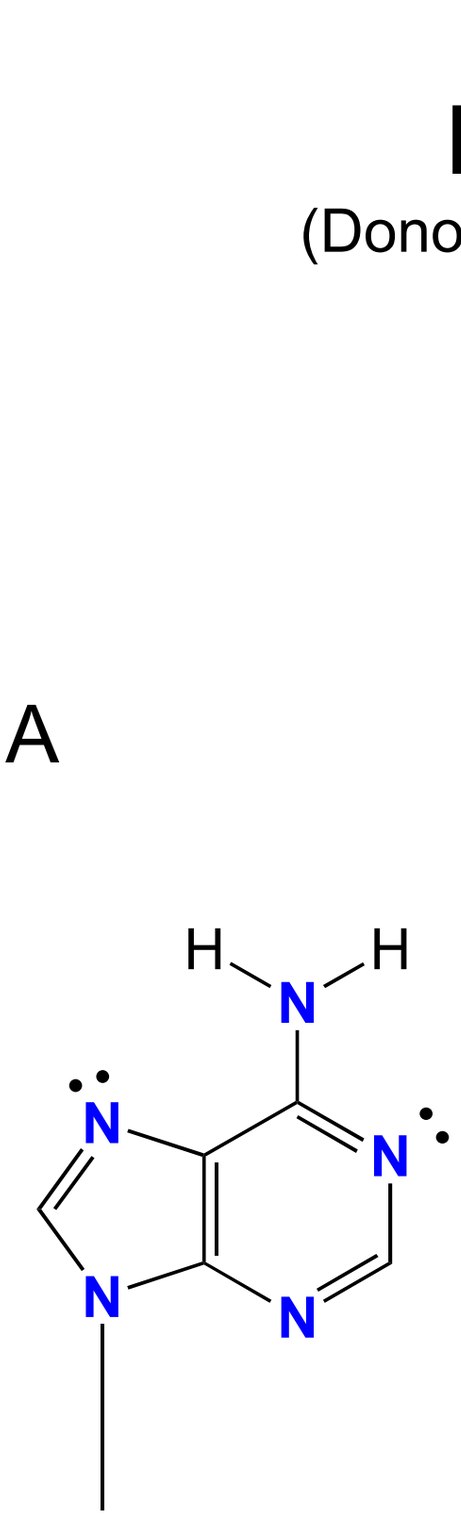


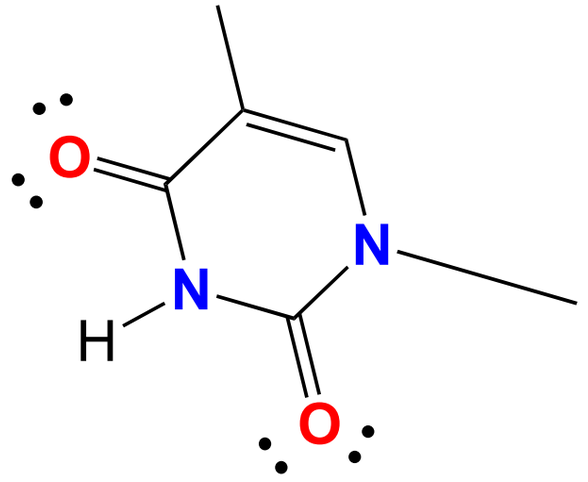


Base Pairing

(Donors matched to Acceptors)

A

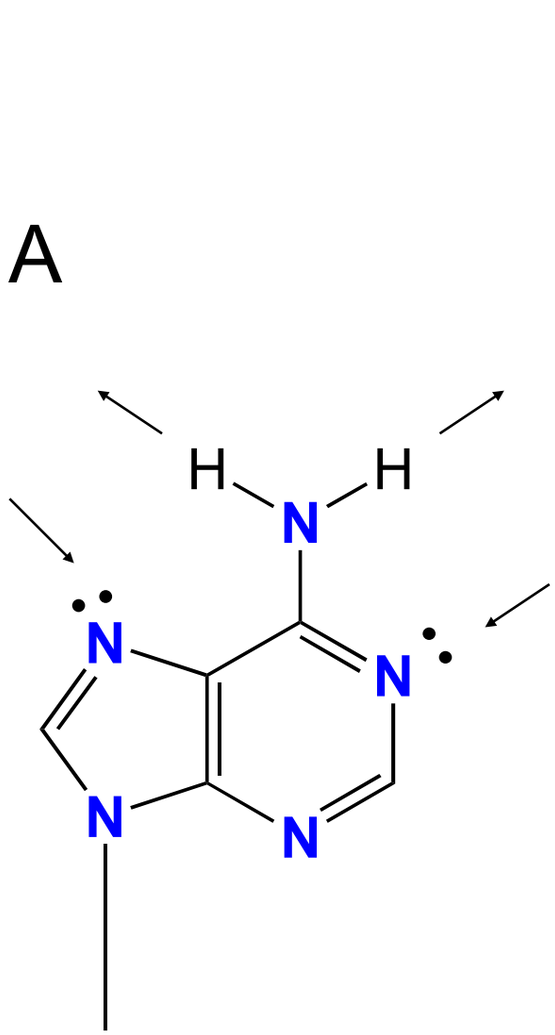


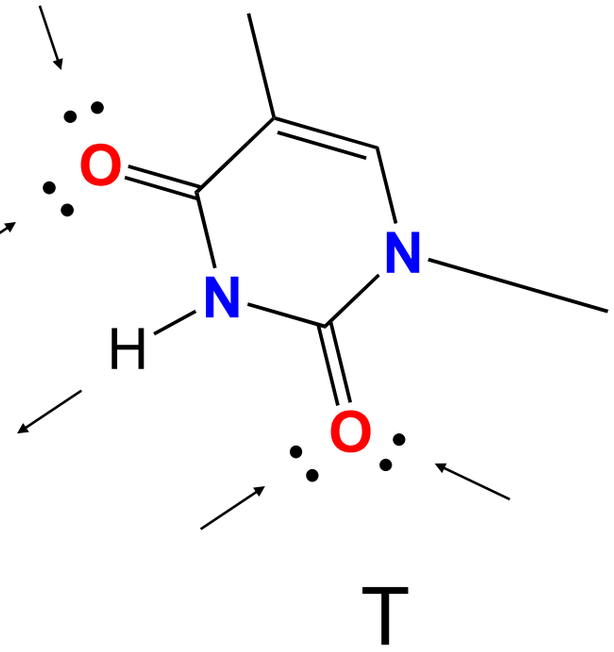


T

Base Pairing

(Donors matched to Acceptors)





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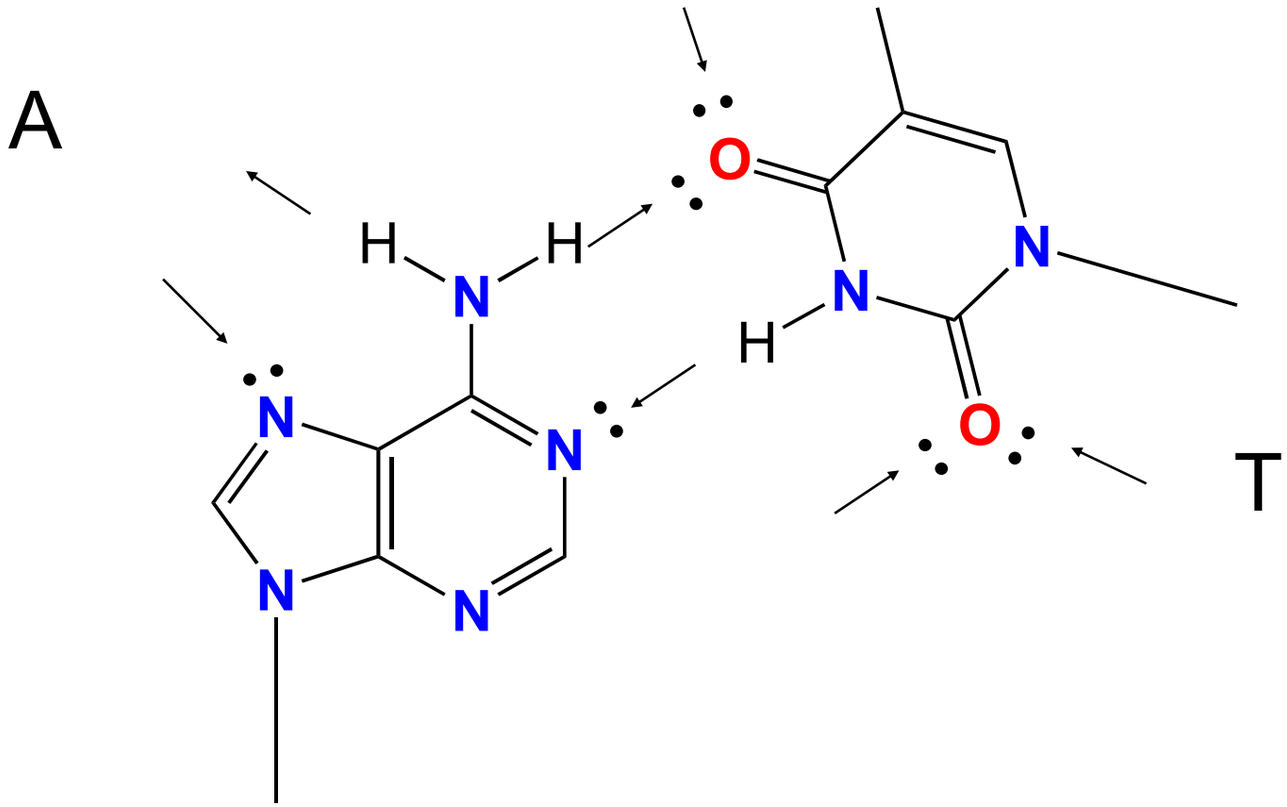
Base Pairing

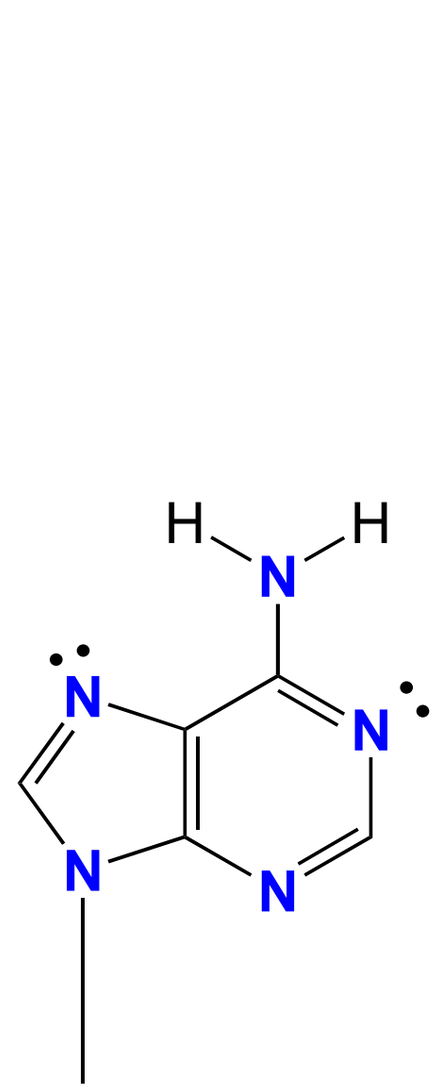
(Donors matched to Acceptors)

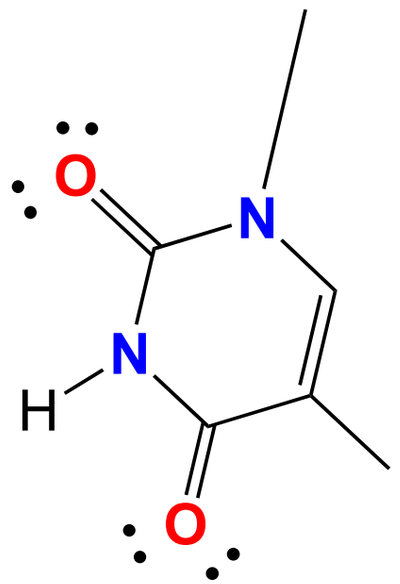


Base Pairing

(Donors matched to Acceptors)

A



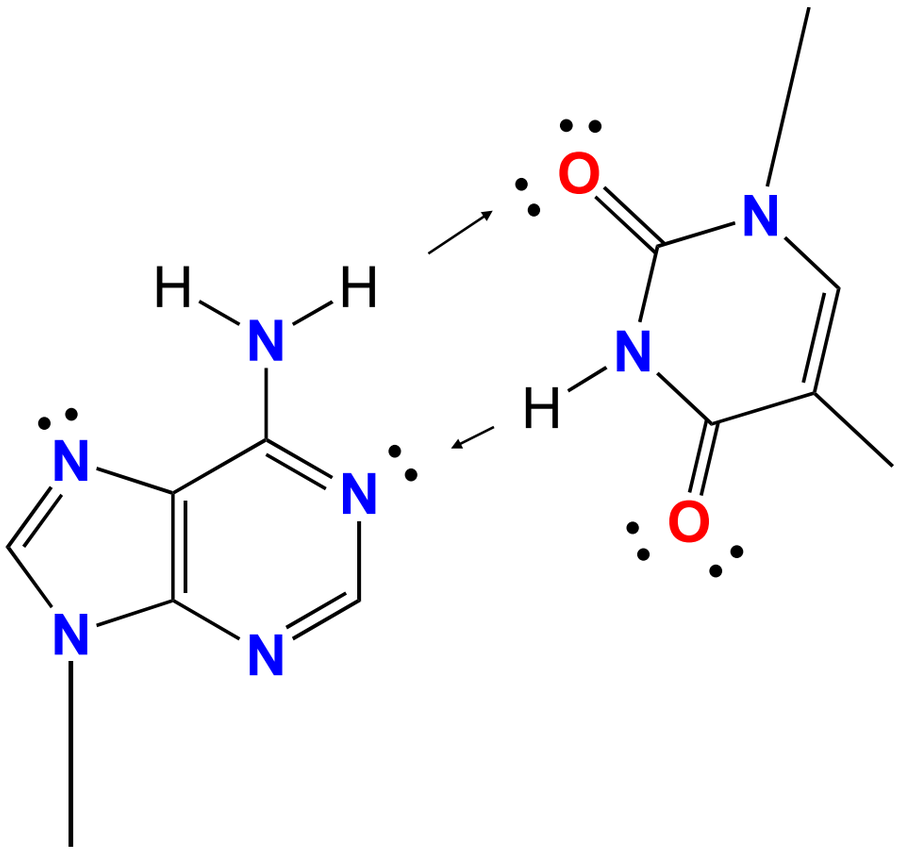


T

Base Pairing

(Donors matched to Acceptors)

A

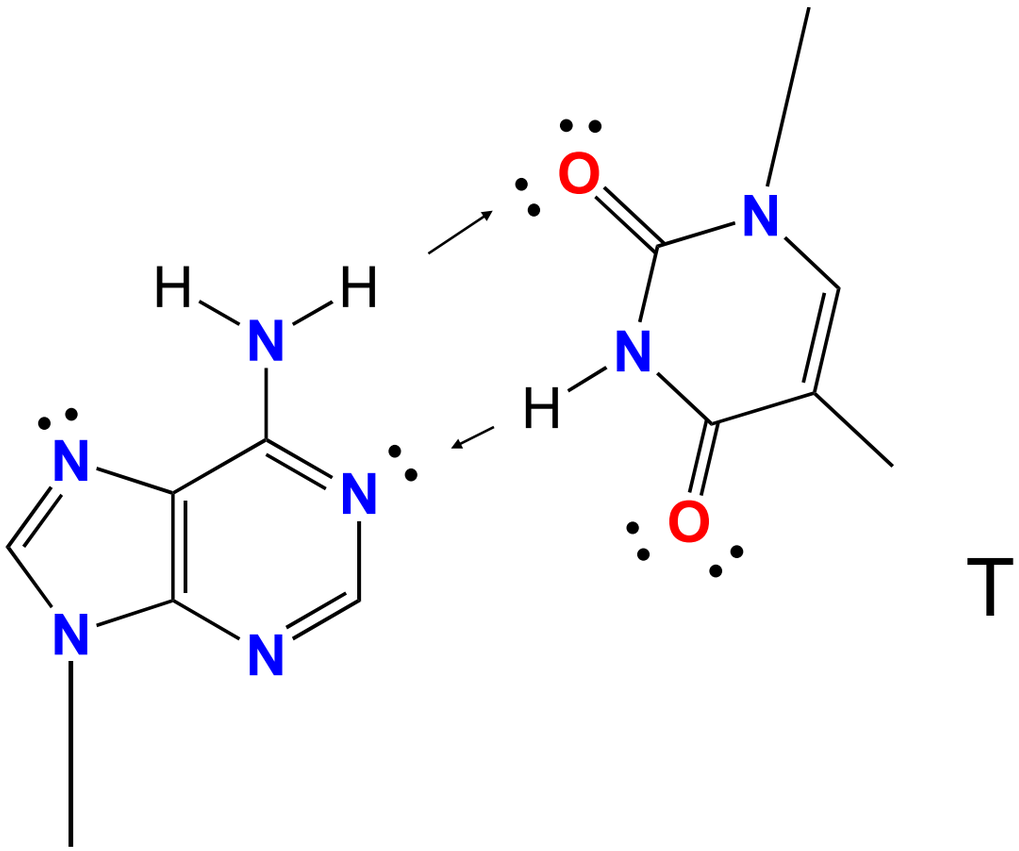


T

Base Pairing

(Donors matched to Acceptors)

A



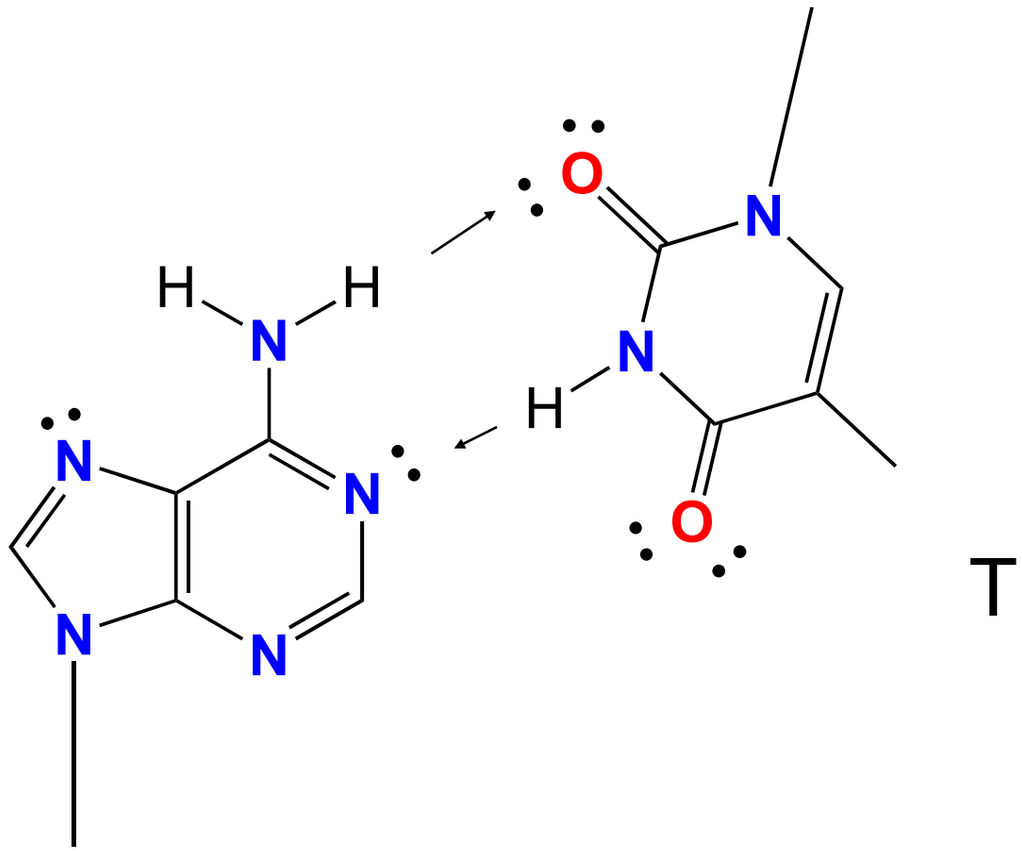
T

Good base pairing

Base Pairing

(Donors matched to Acceptors)

A



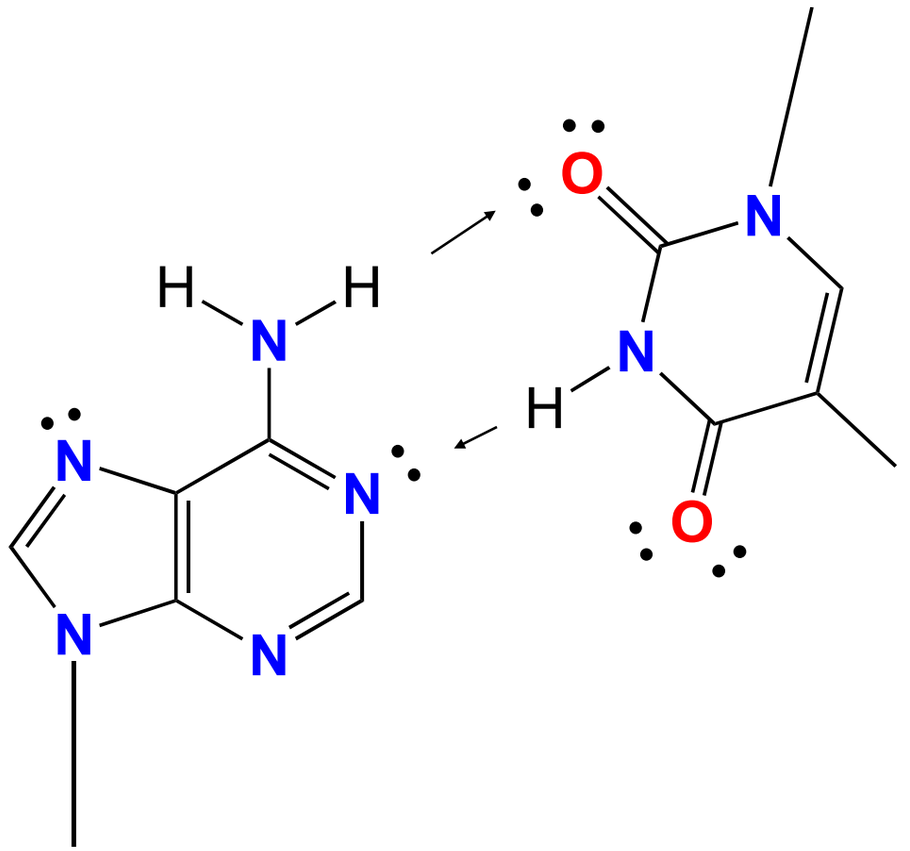
T

Good base pairing
Watson-Crick facing

Base Pairing

(Donors matched to Acceptors)

A



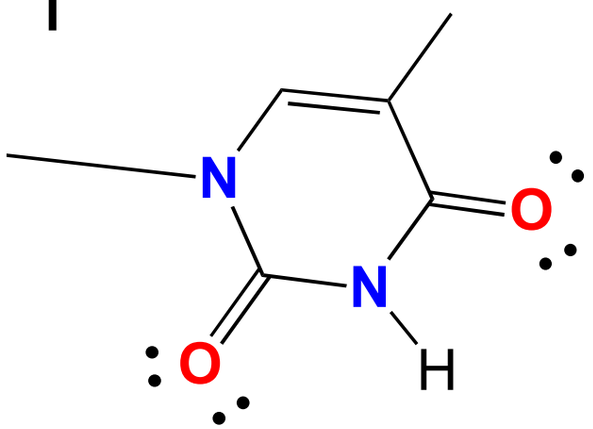
T

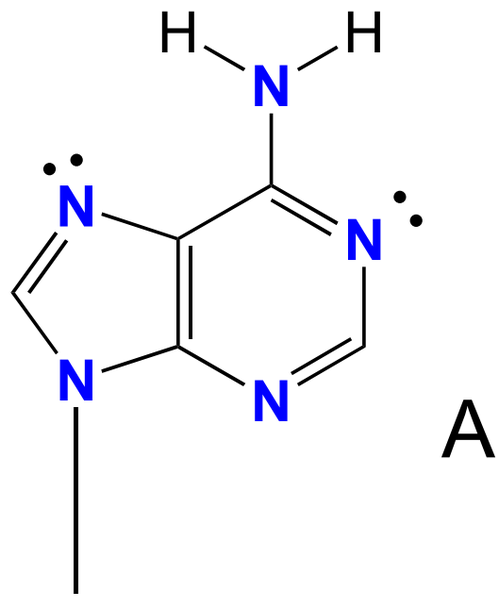
Good base pairing
Watson-Crick facing
but *Anti-Watson-Crick* orientation

Base Pairing

(Donors matched to Acceptors)

T



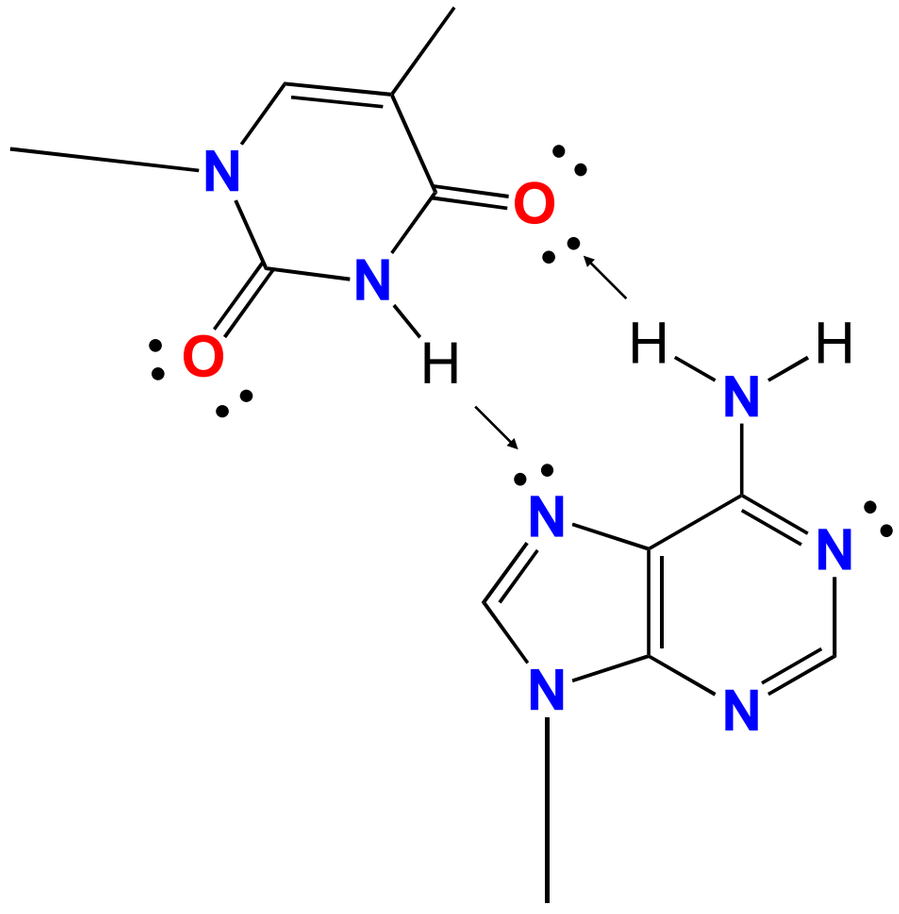


A

Base Pairing

(Donors matched to Acceptors)

T

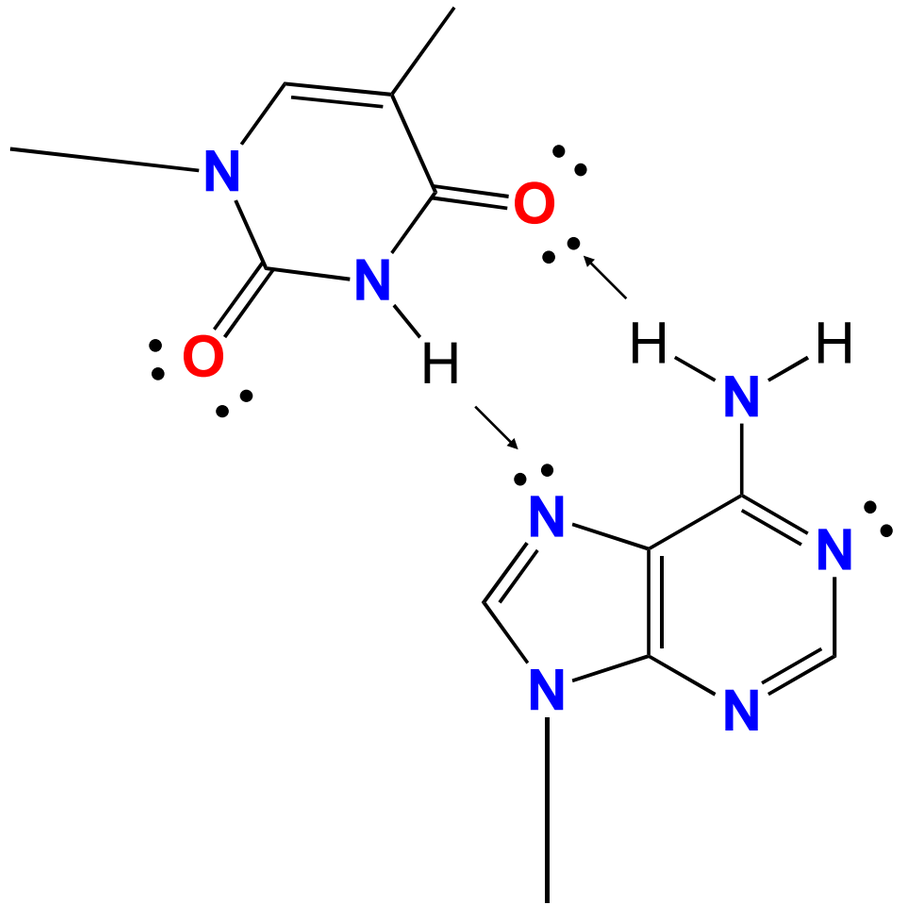


A

Base Pairing

(Donors matched to Acceptors)

T



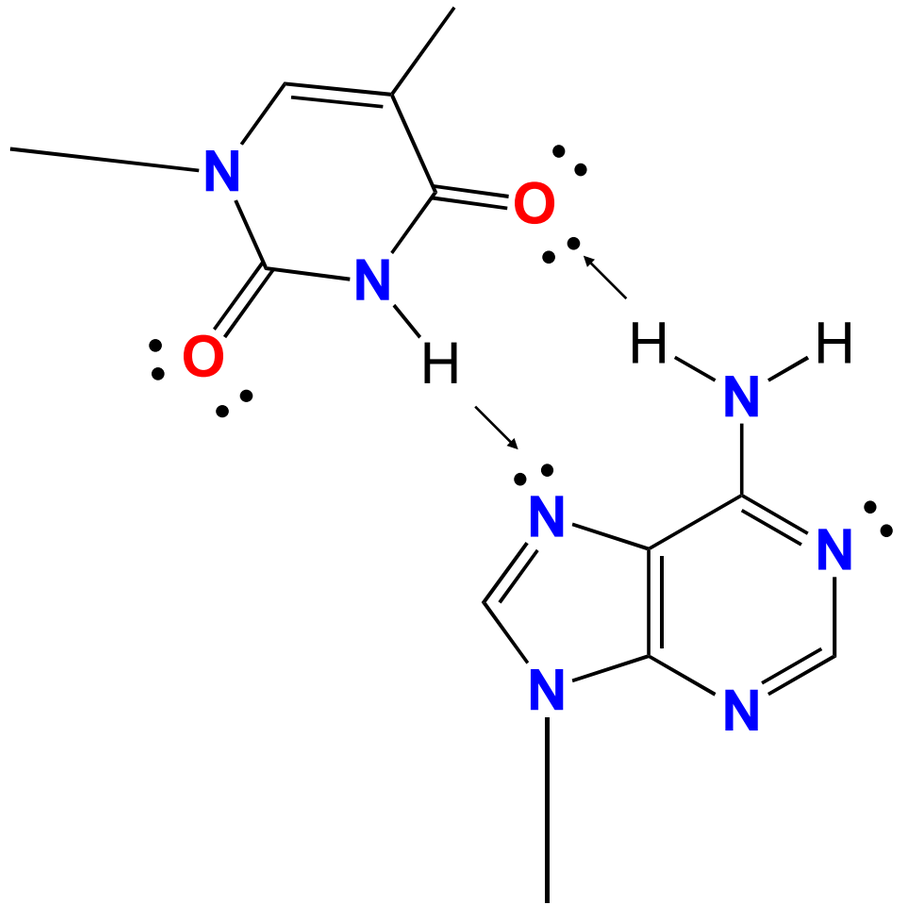
A

Good base pairing

Base Pairing

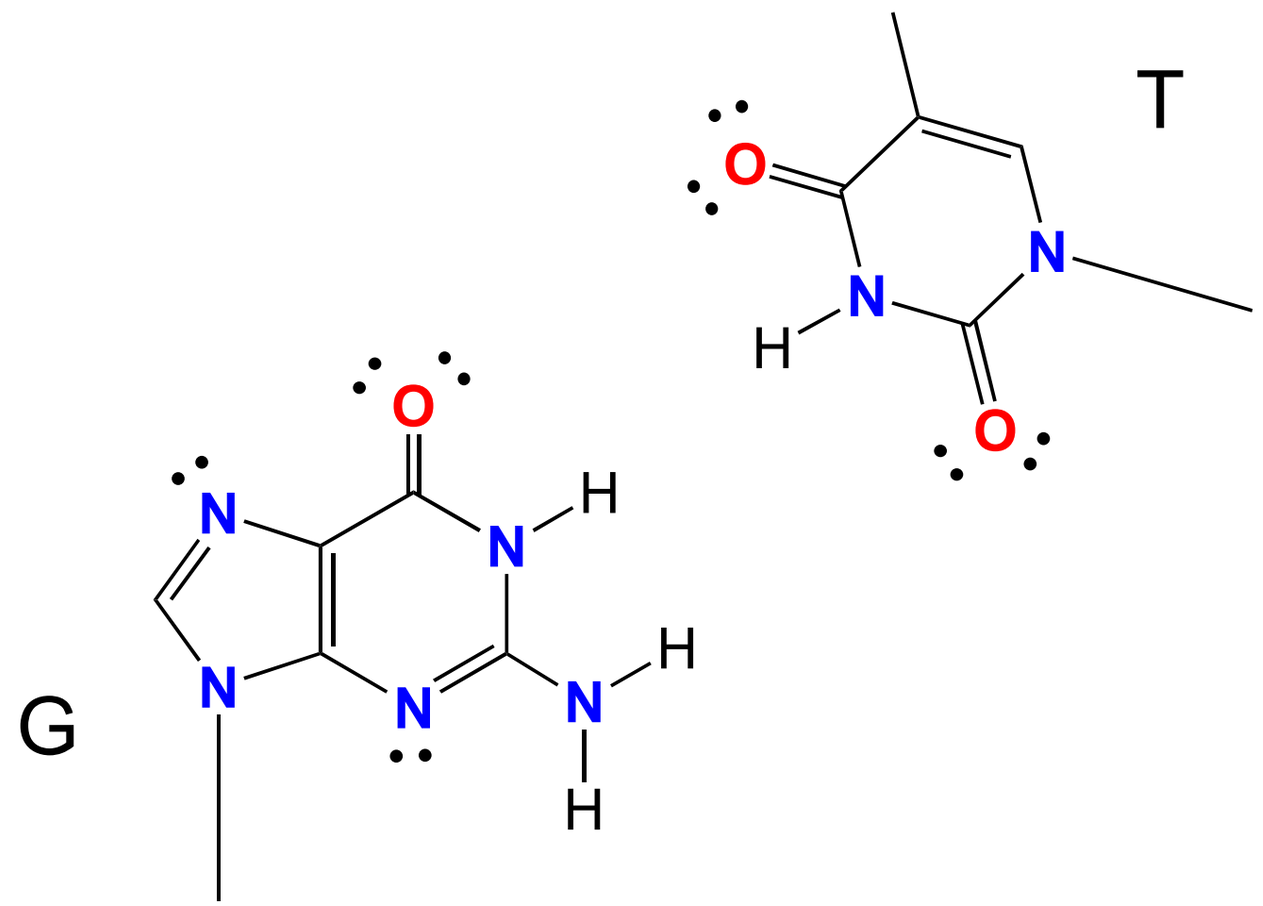
(Donors matched to Acceptors)

T



A

Good base pairing
WC-Hoogsteen facing


T
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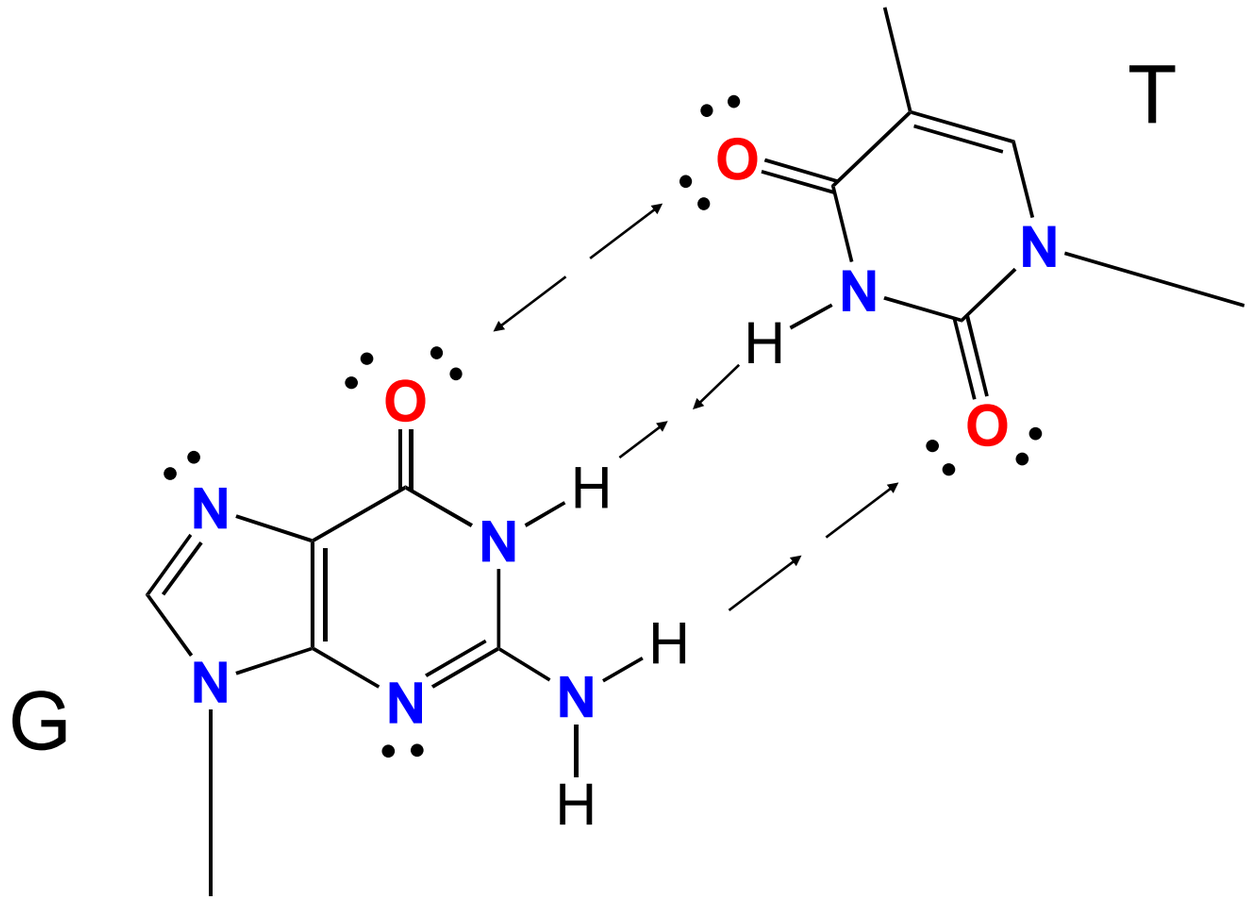
H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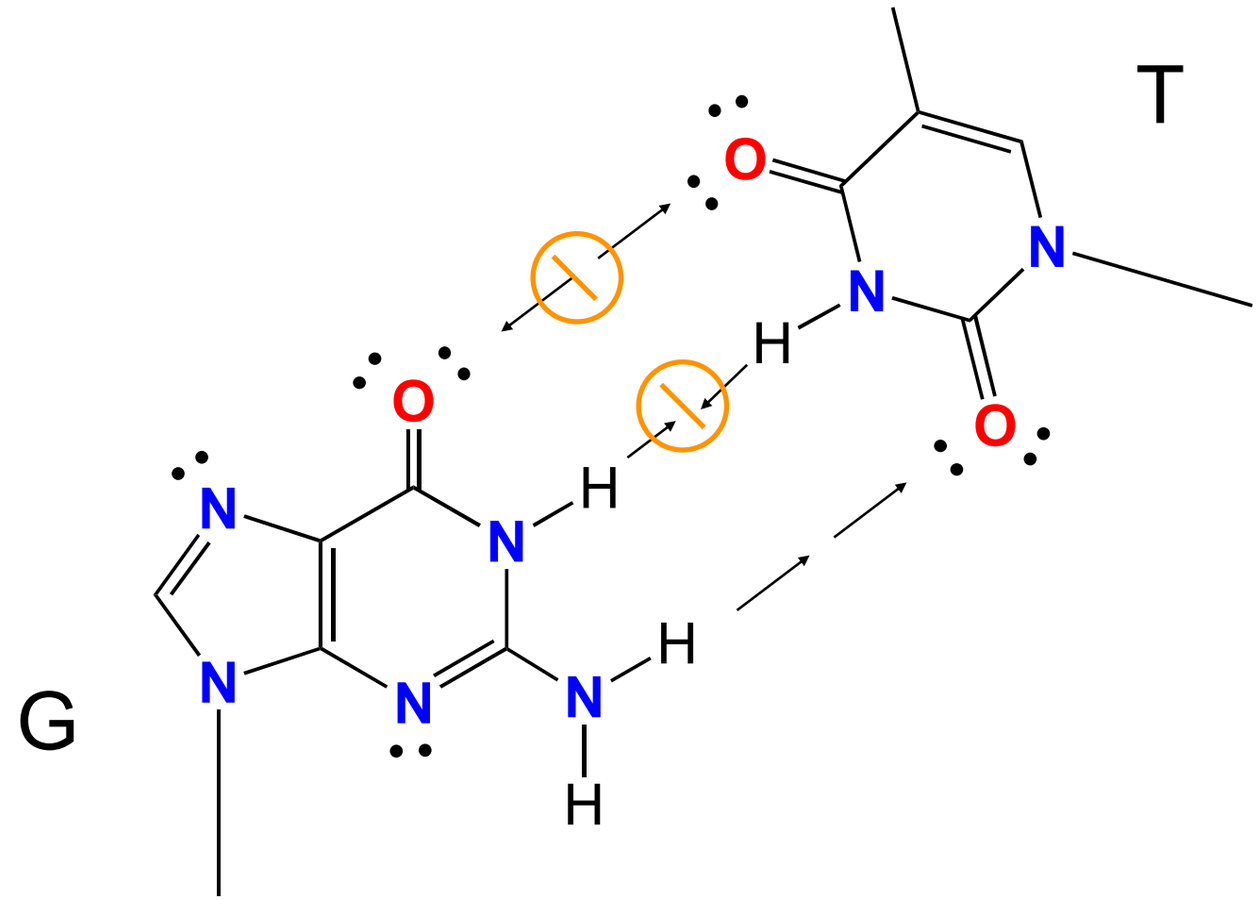
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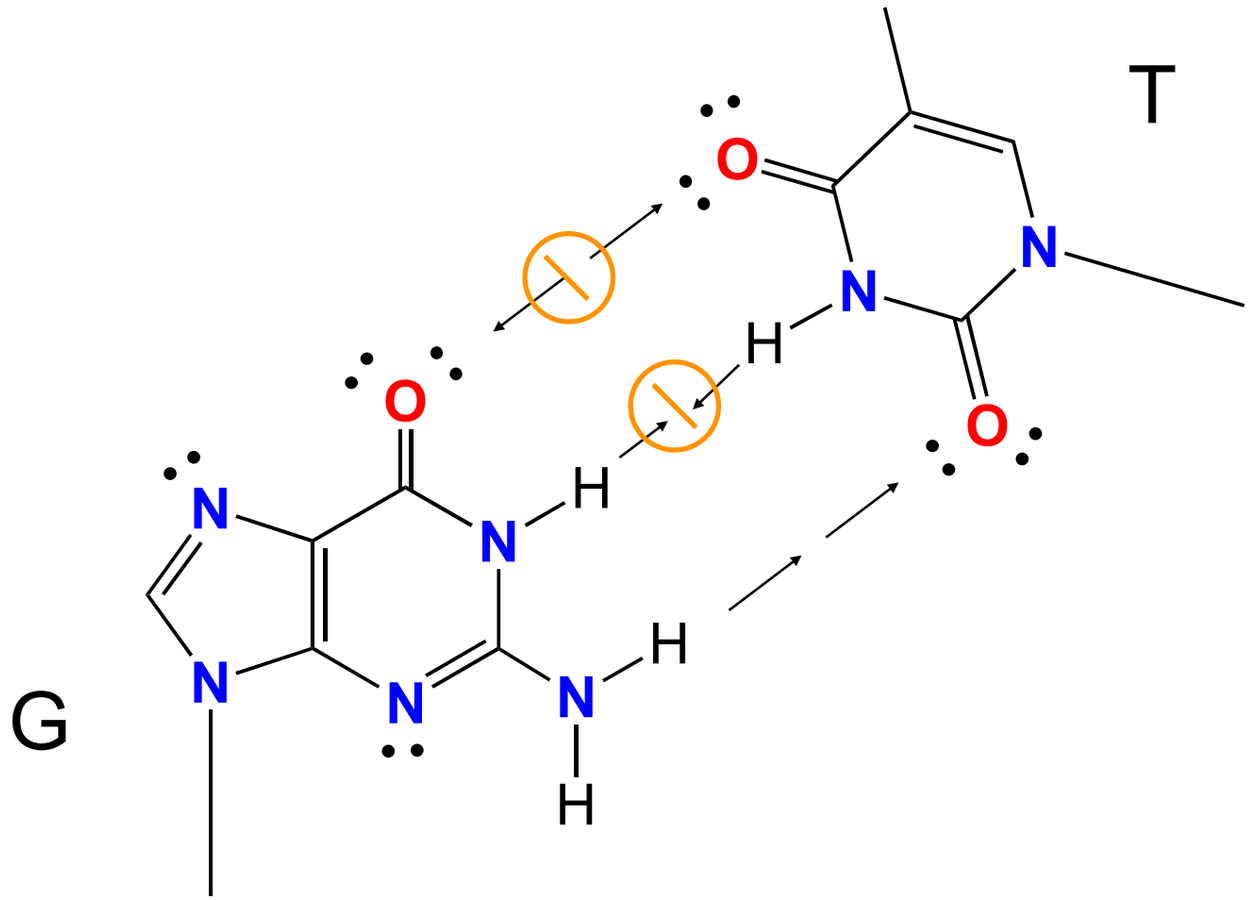
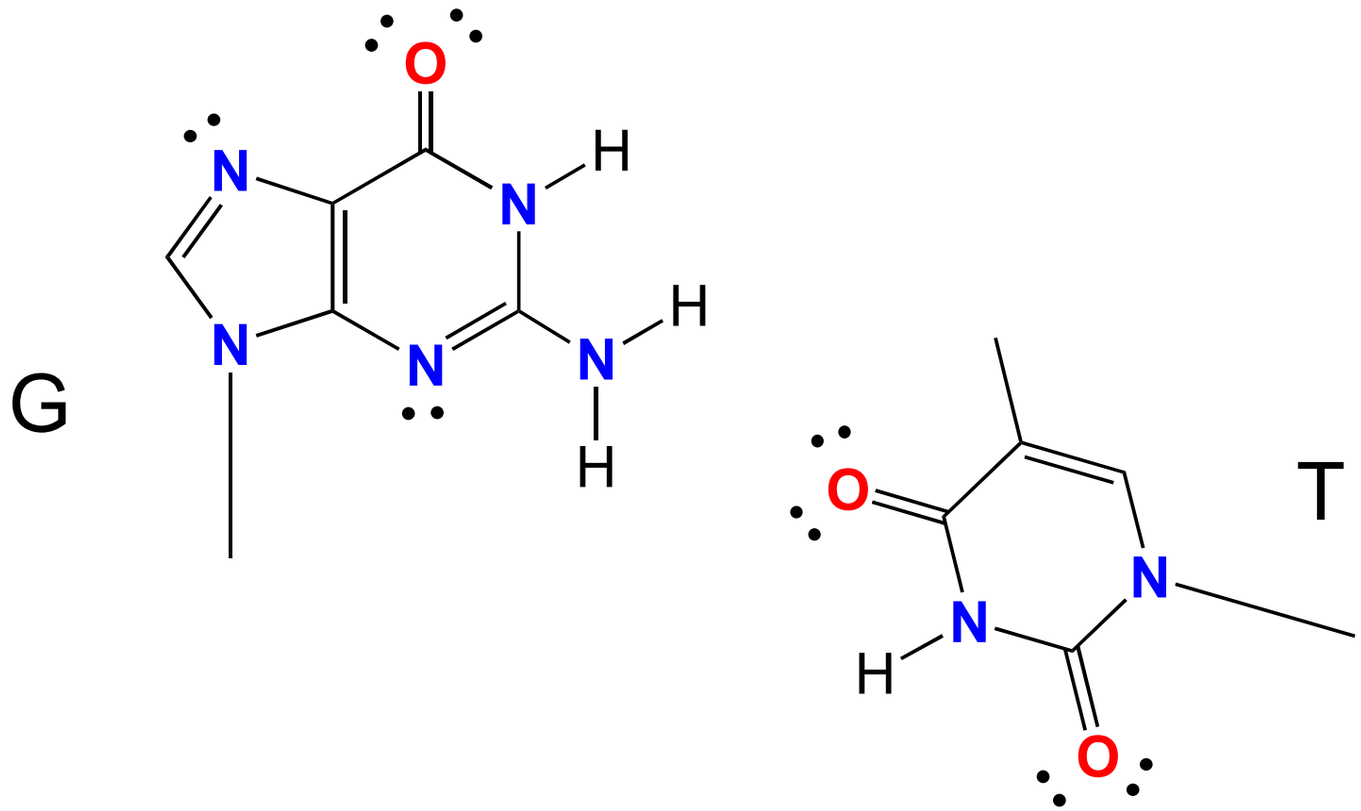
Bad Base Pairing

(Donors ***not*** matched to Acceptors)

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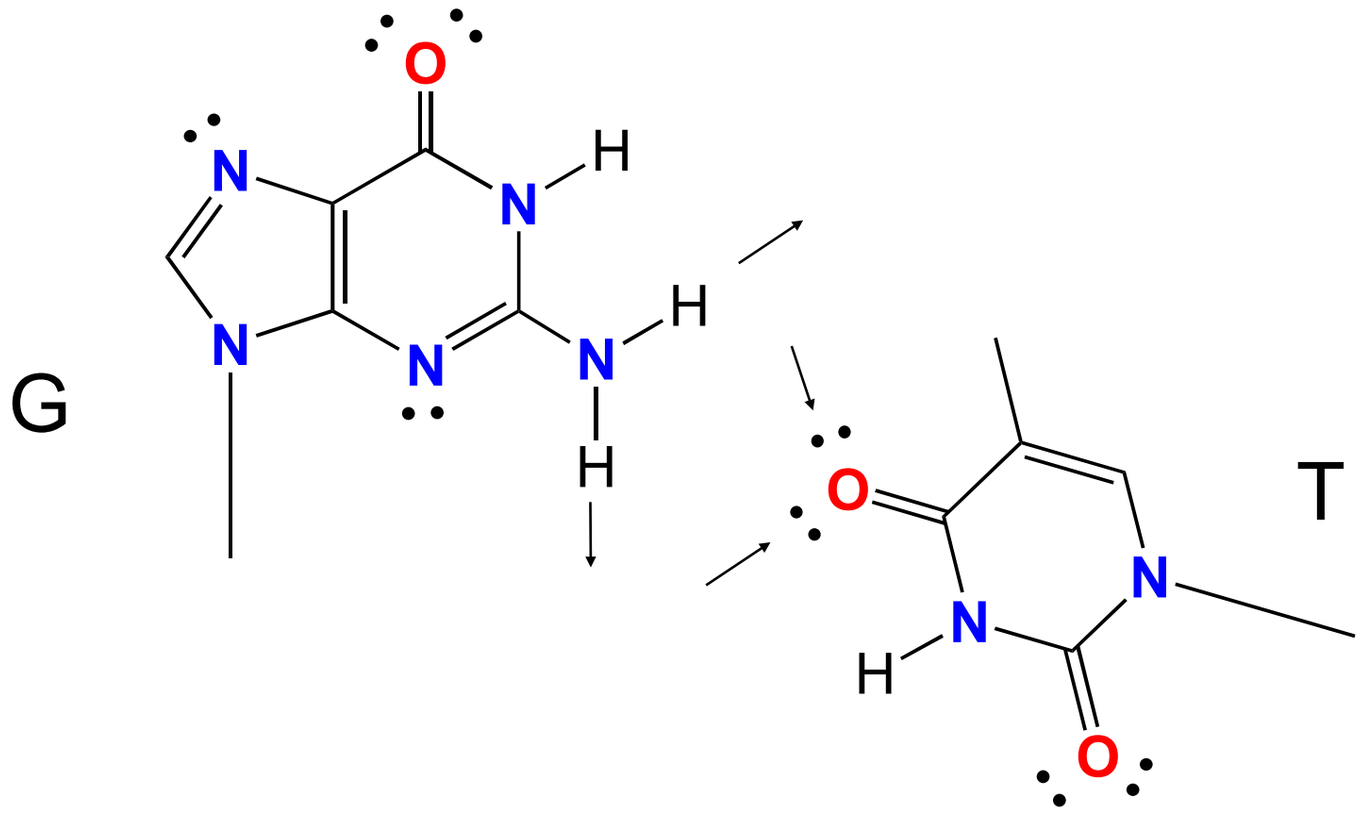
G
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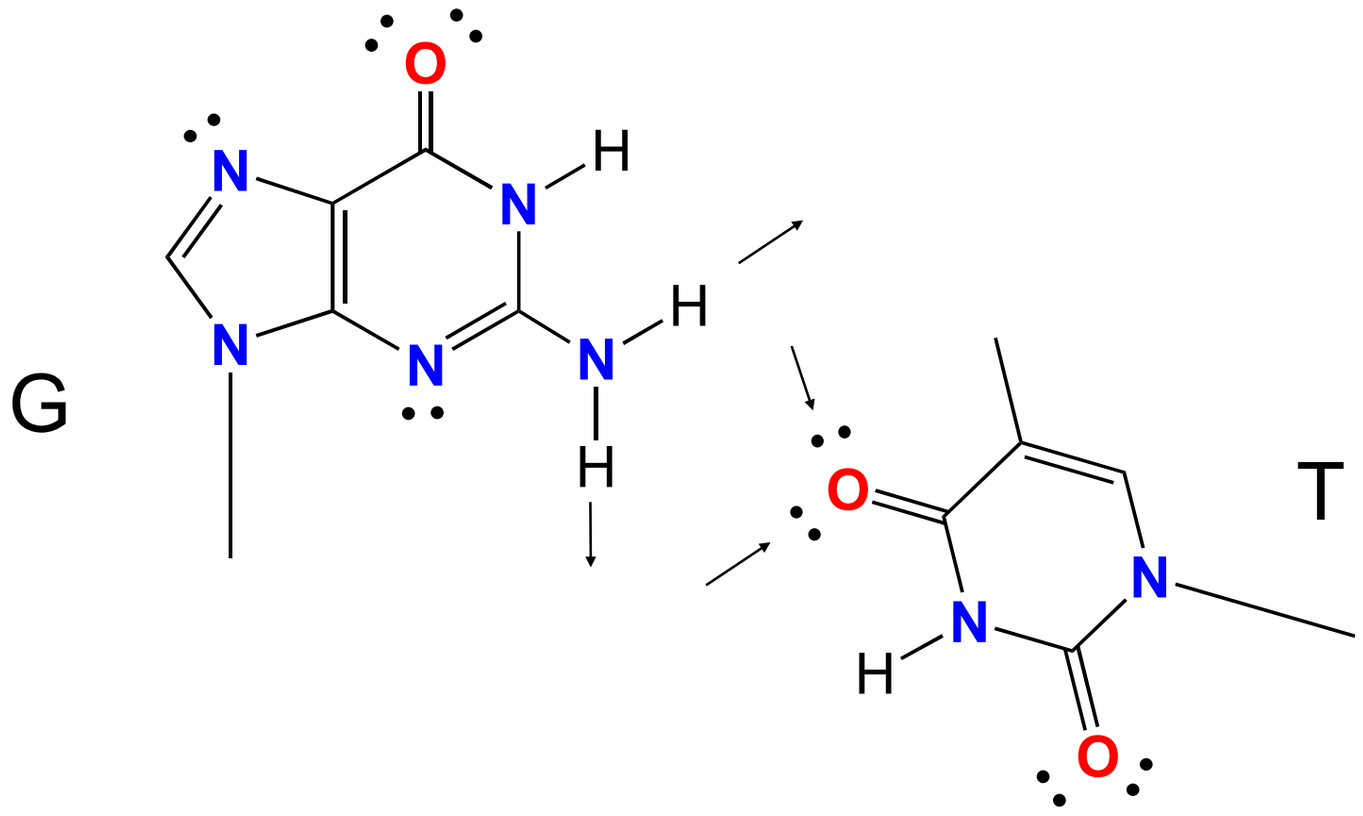
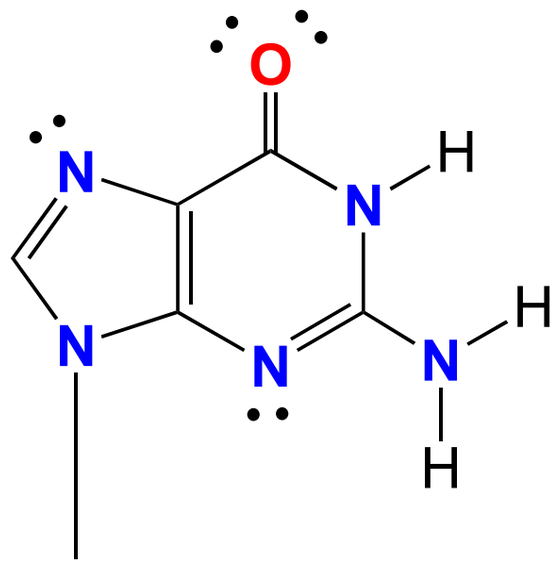
Bad Base Pairing

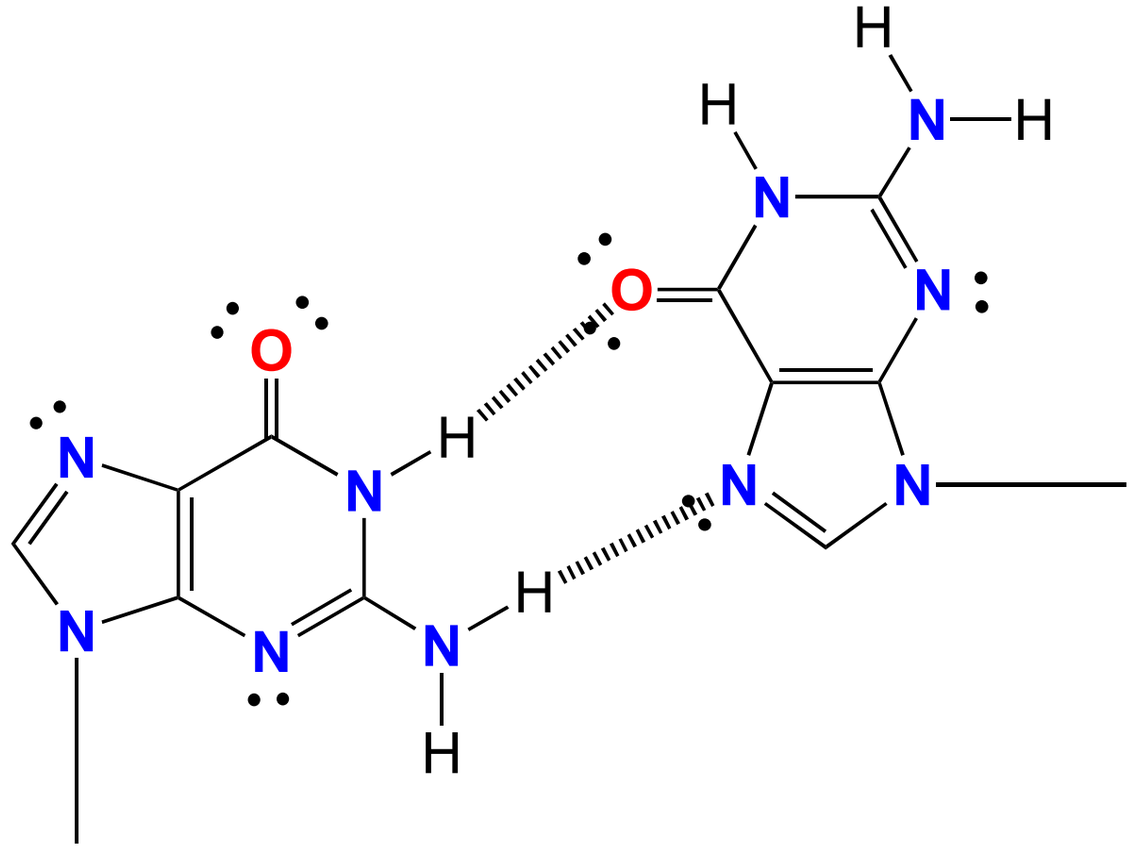
(Donors to Acceptors with ***terrible angles***)



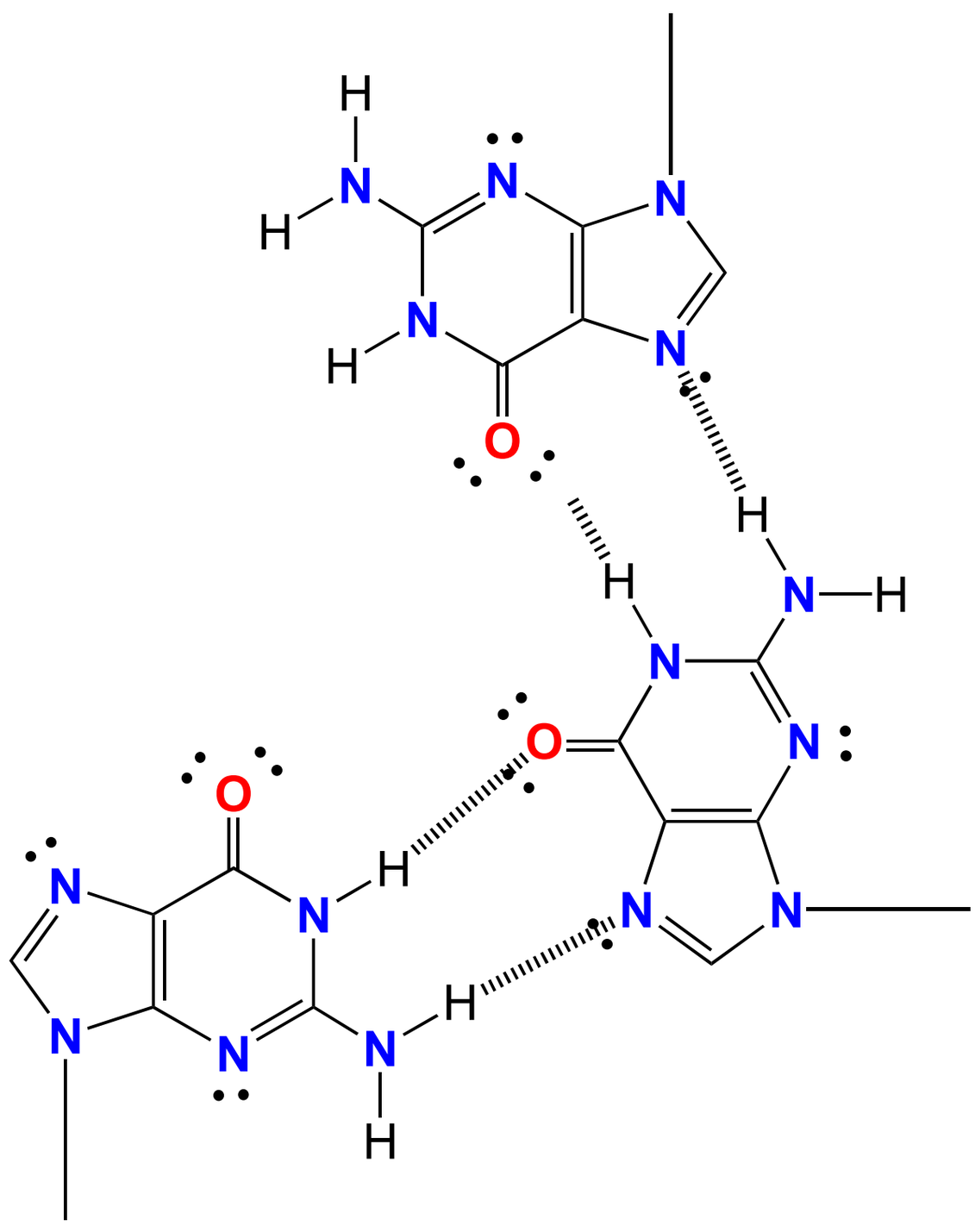
Wild (but good) Base Pairing



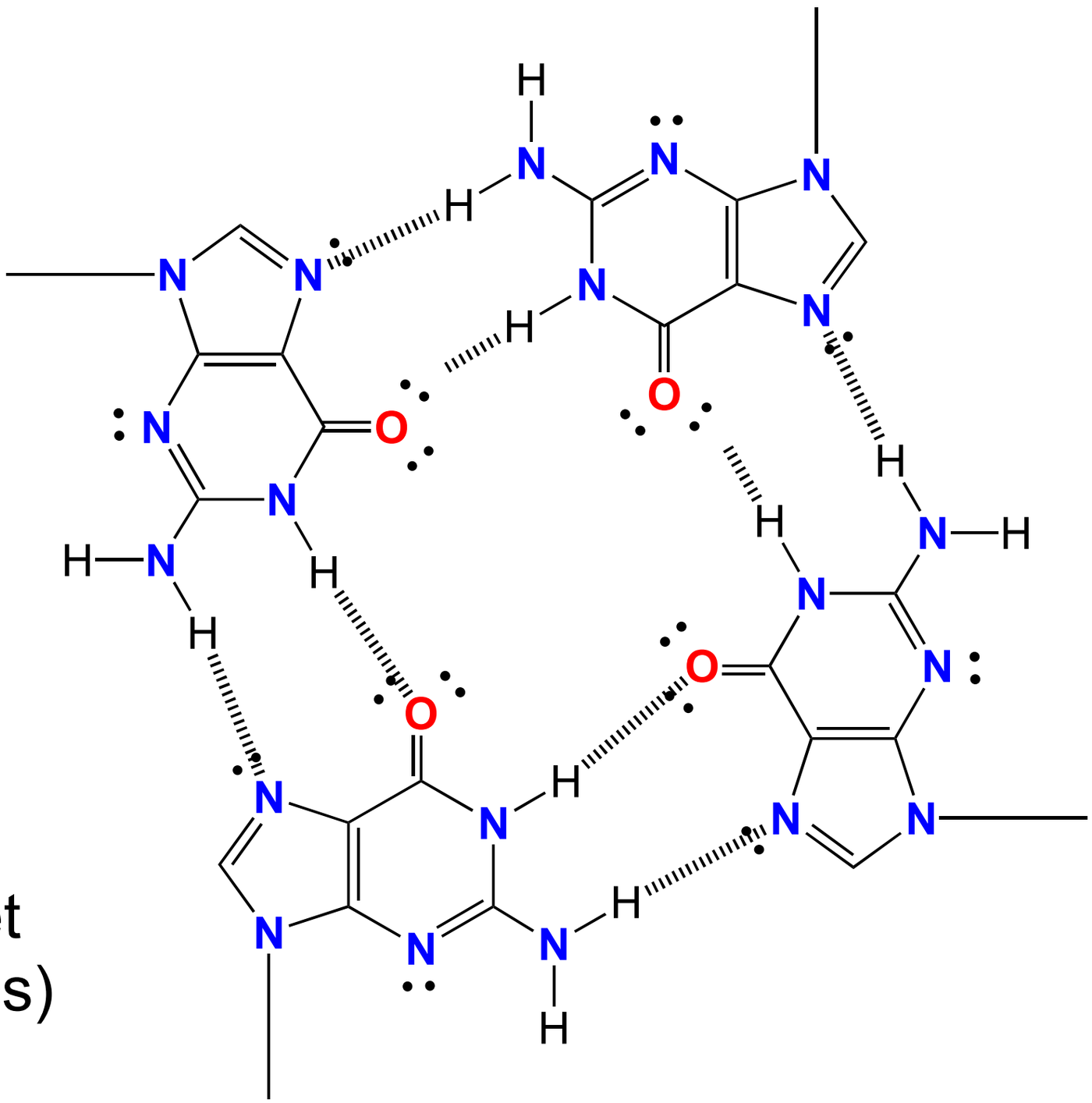
Wild (but good) Base Pairing



Wild (but good) Base Pairing



Wild (but good) Base Pairing



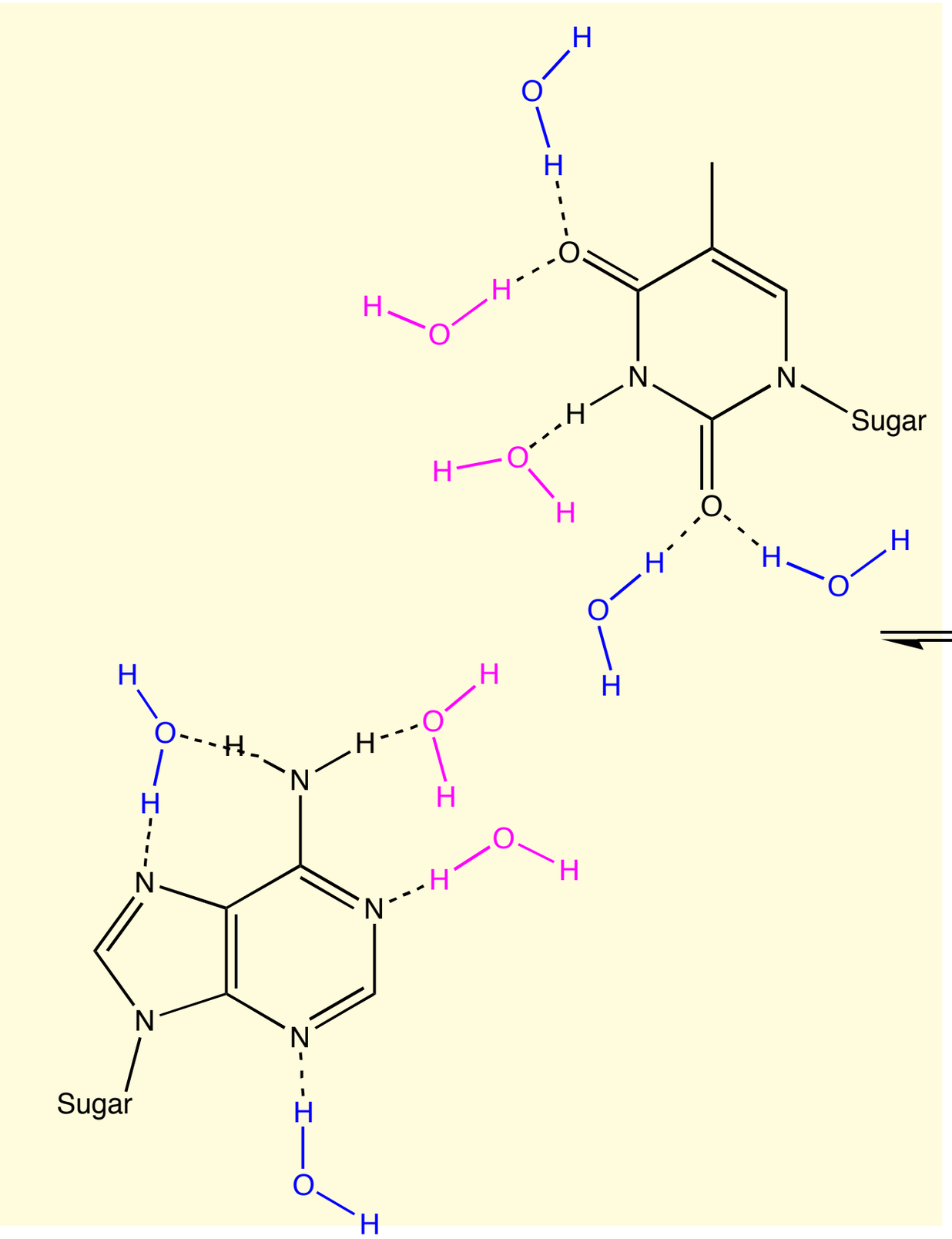
G-quartet
(Telomeres)

What *drives* double helix formation?

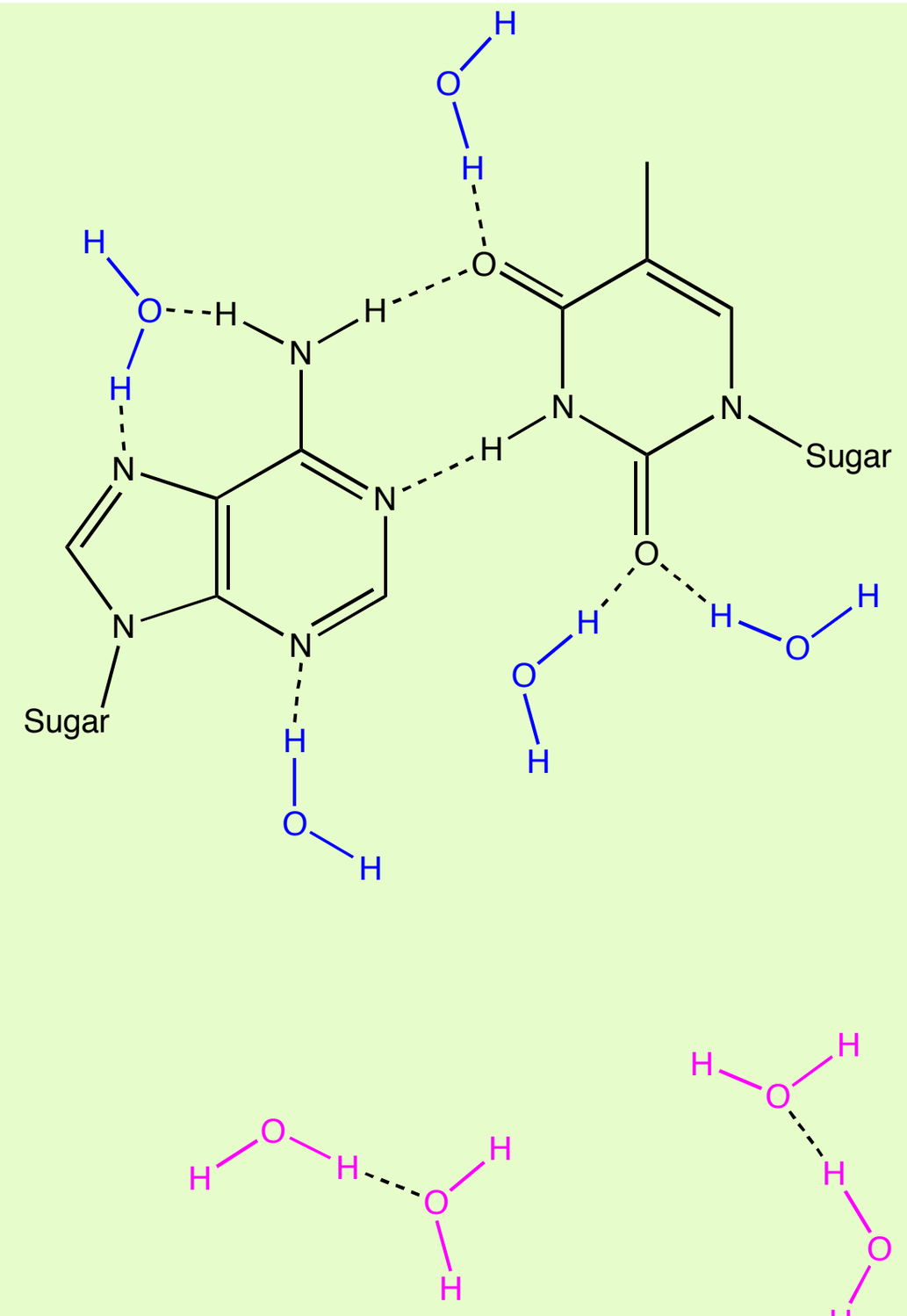
What *drives* double helix formation?

NOT hydrogen bonding

AT Base Pair

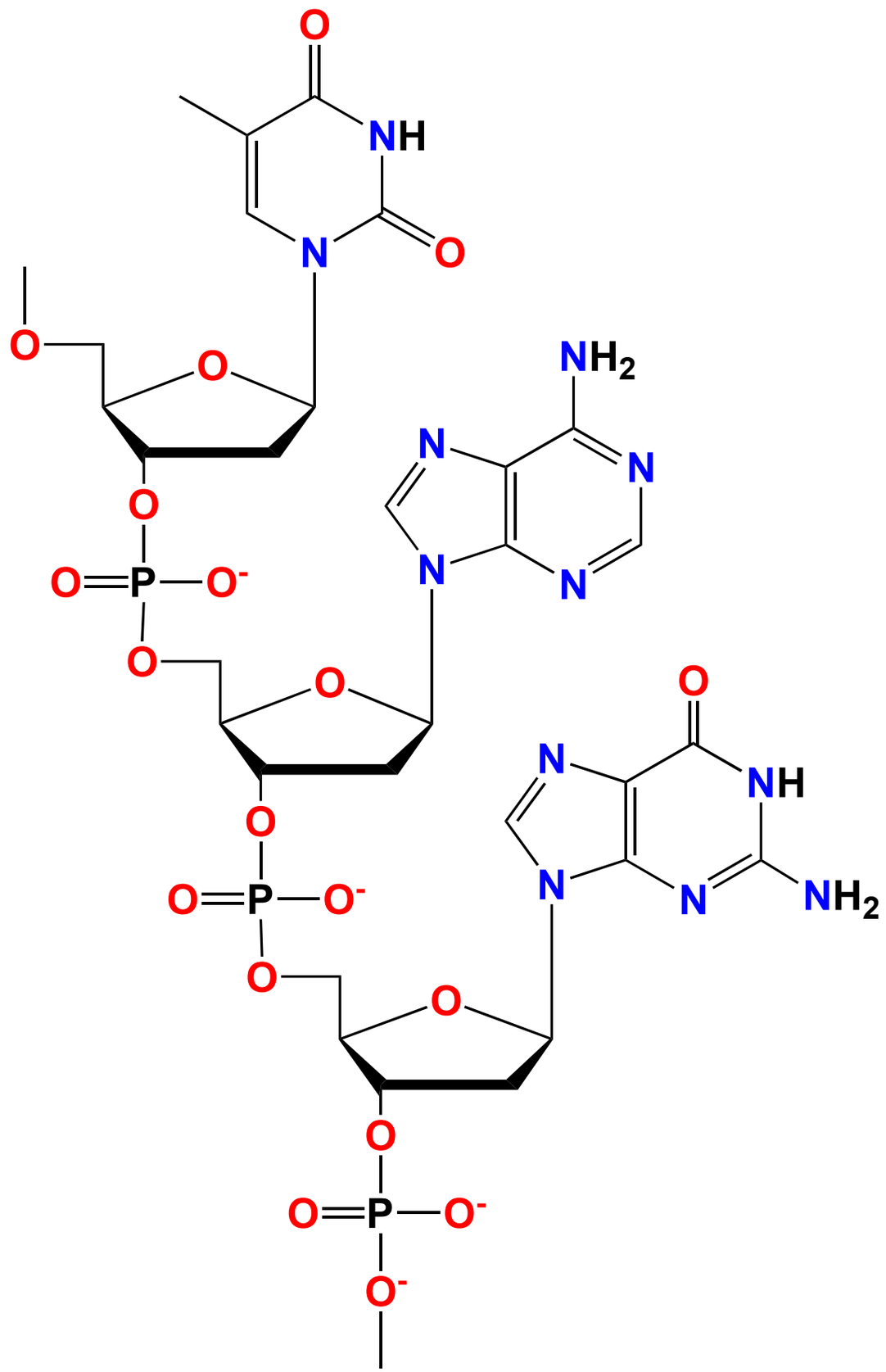


Ten H-Bonds



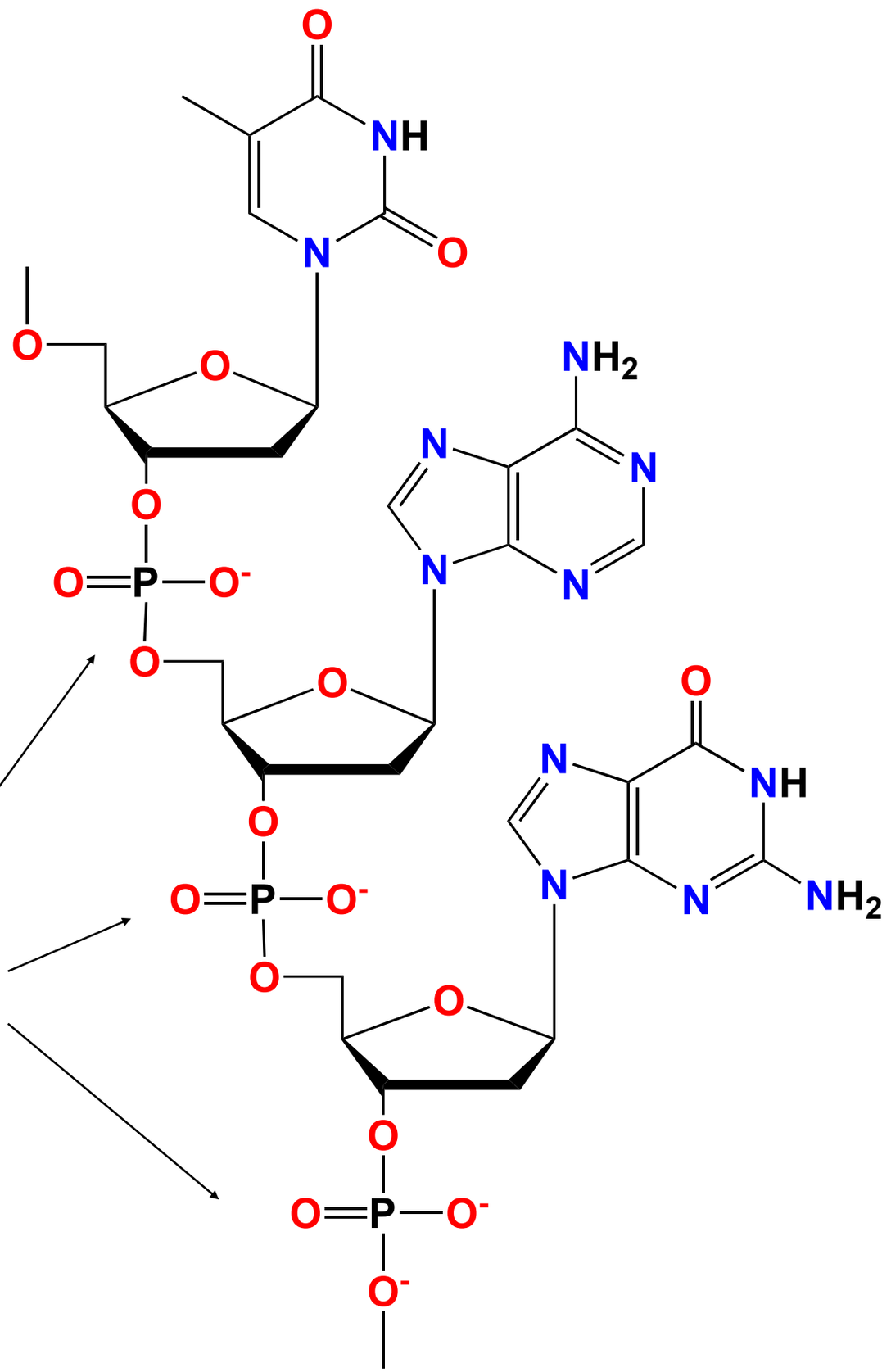
Ten H-Bonds

What *drives* double helix formation?

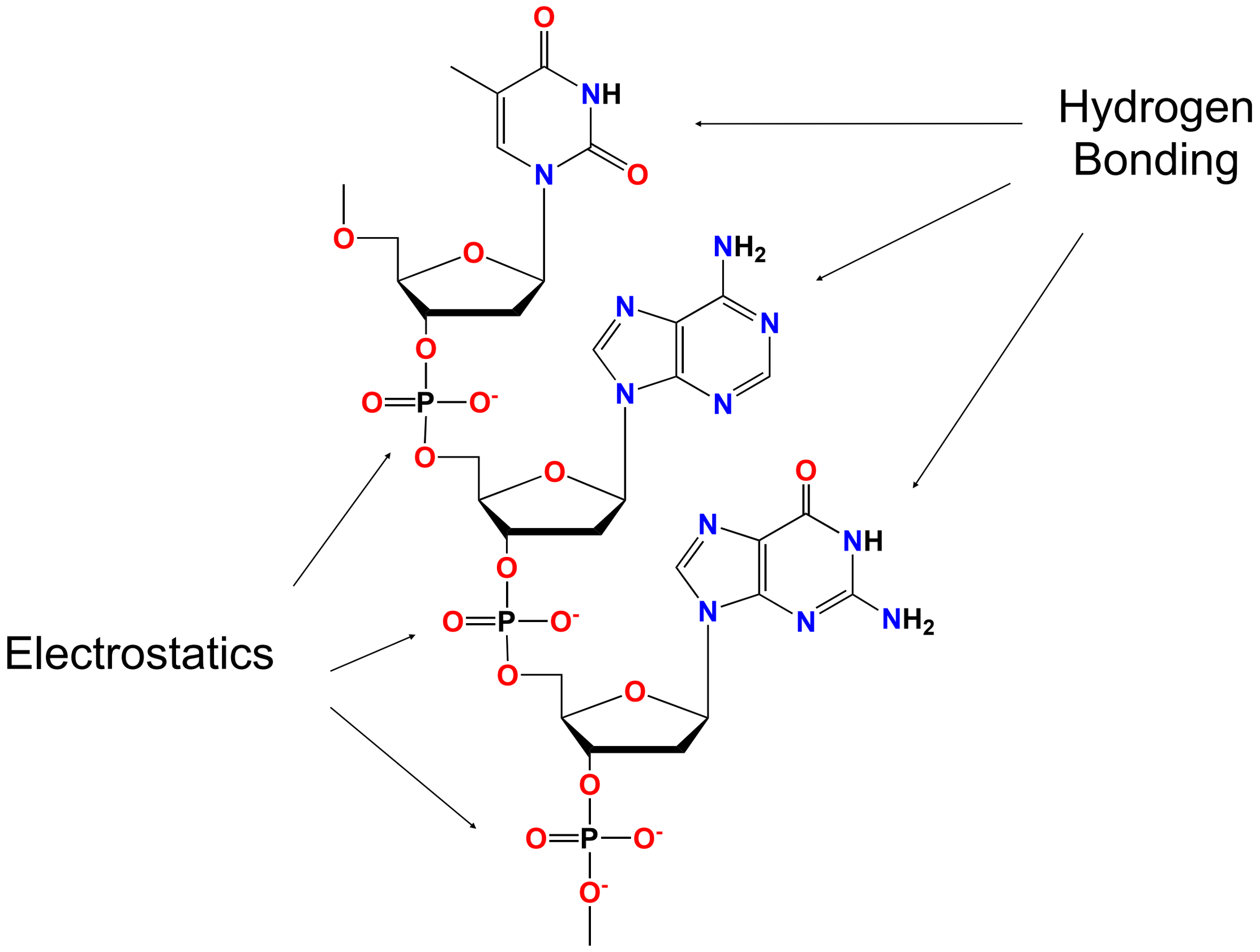


What *drives* double helix formation?

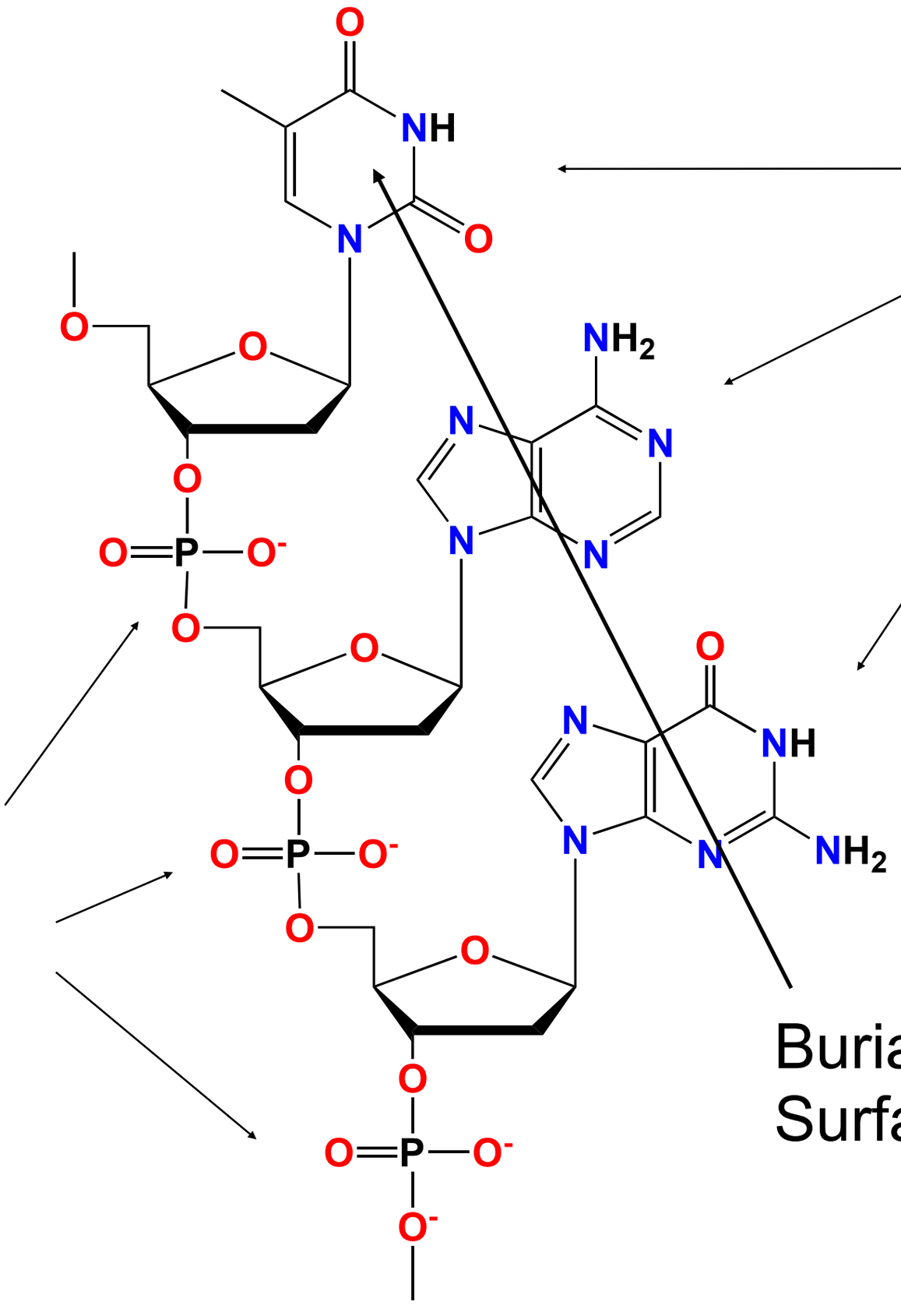
Electrostatics



What *drives* double helix formation?



What *drives* double helix formation?

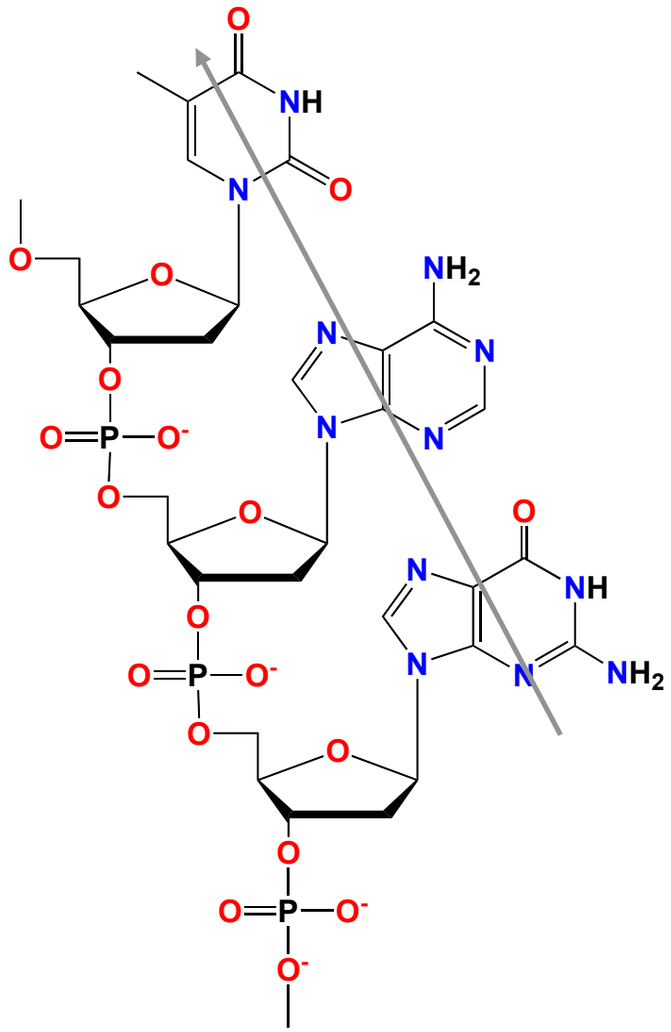


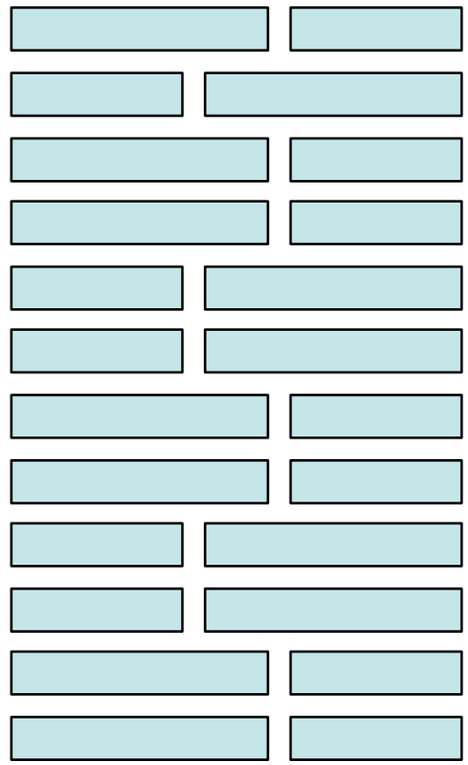
Hydrogen Bonding

Electrostatics

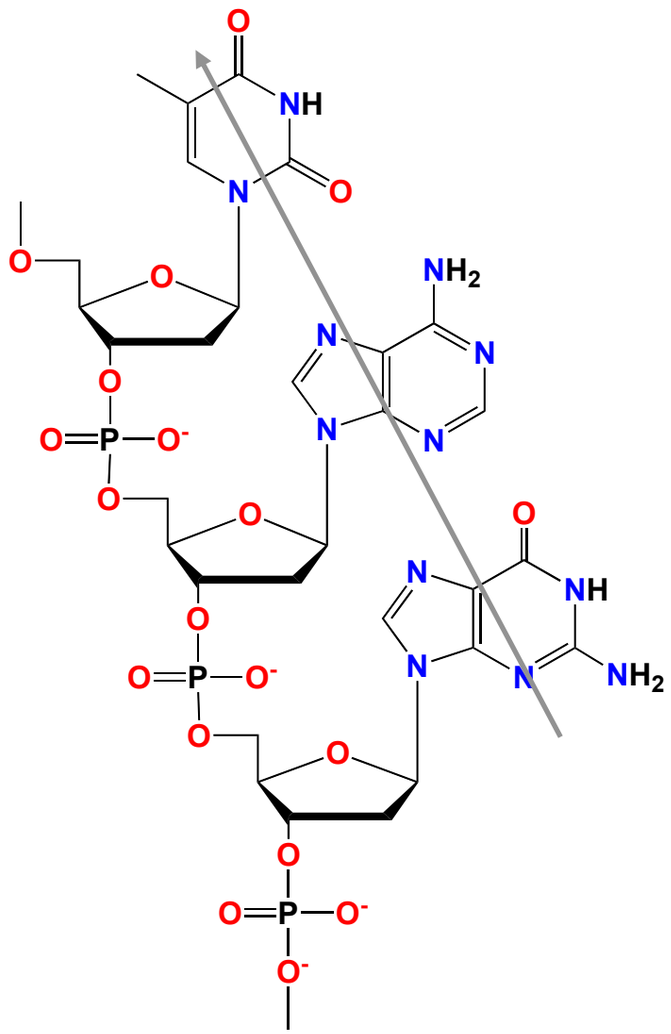
Burial of Hydrophobic Surface & Stacking

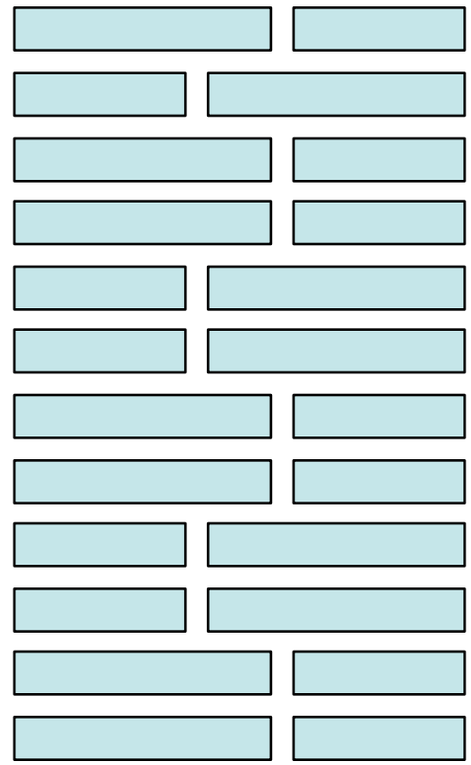
Burial of hydrophobic surface drives helix formation (hydrophobic core / stacking interactions)





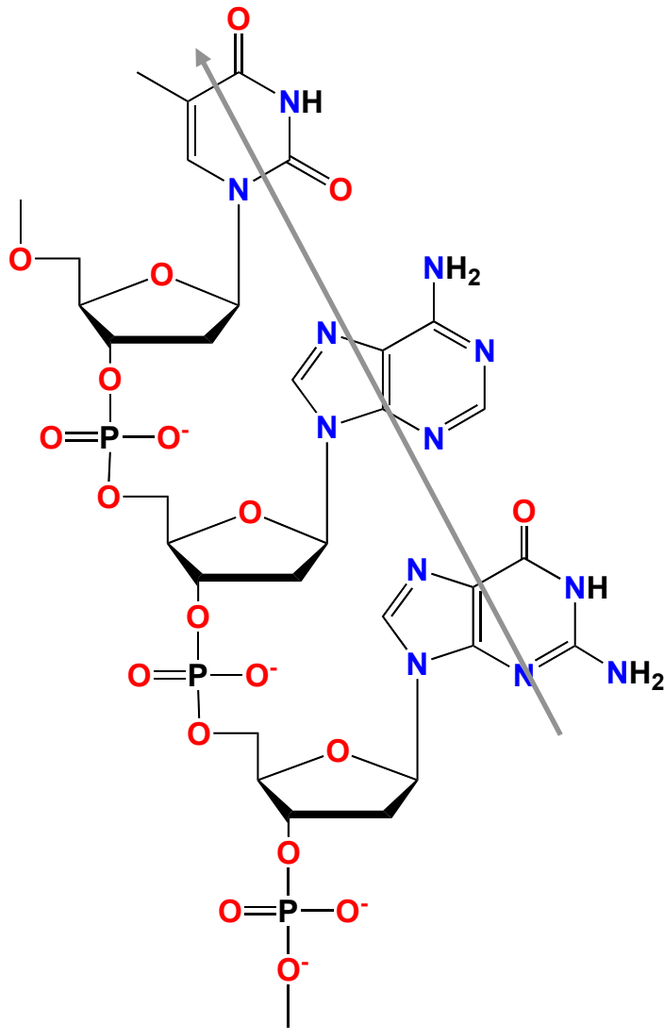
Burial of hydrophobic surface drives helix formation (hydrophobic core / stacking interactions)

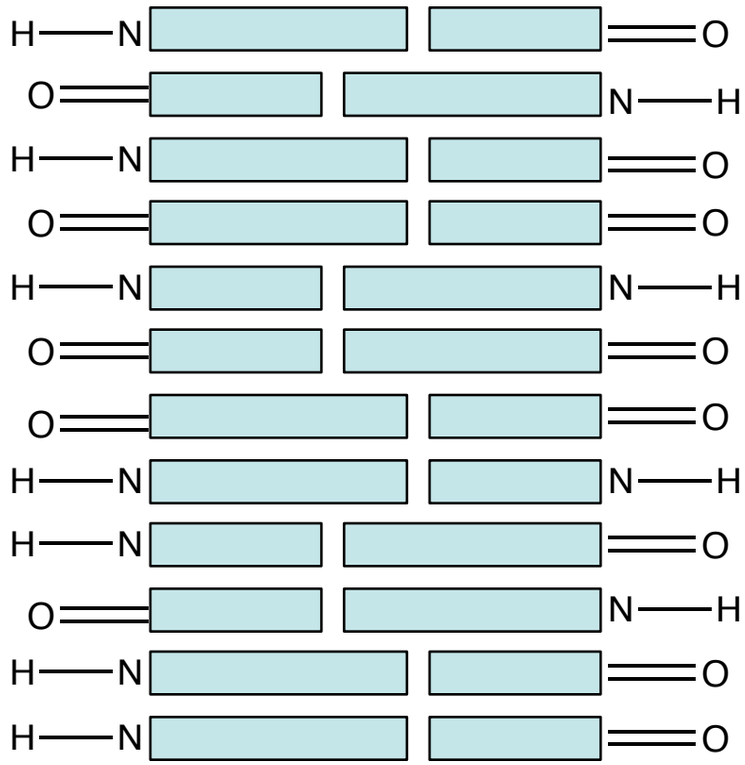




Flat faces are nonpolar

Burial of hydrophobic surface drives helix formation (hydrophobic core / stacking interactions)

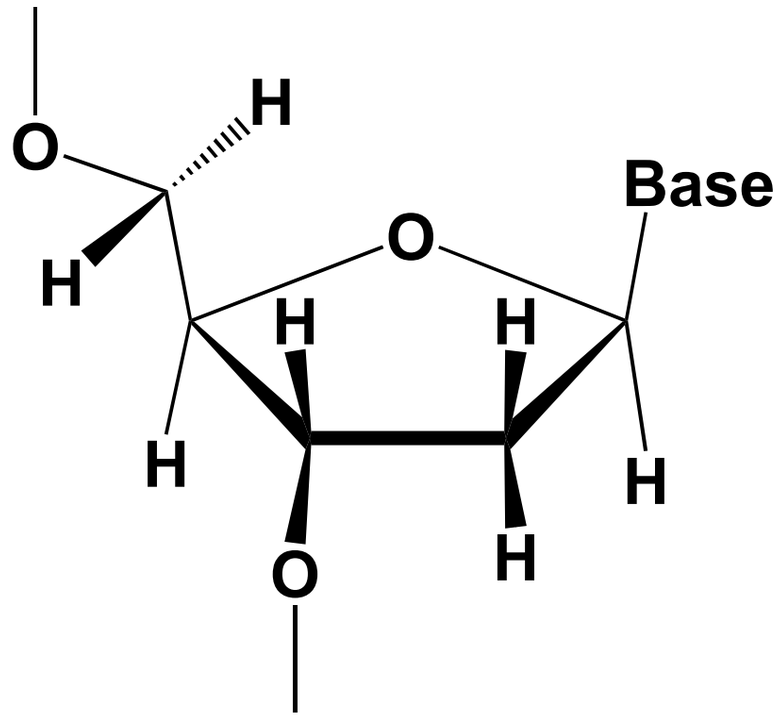




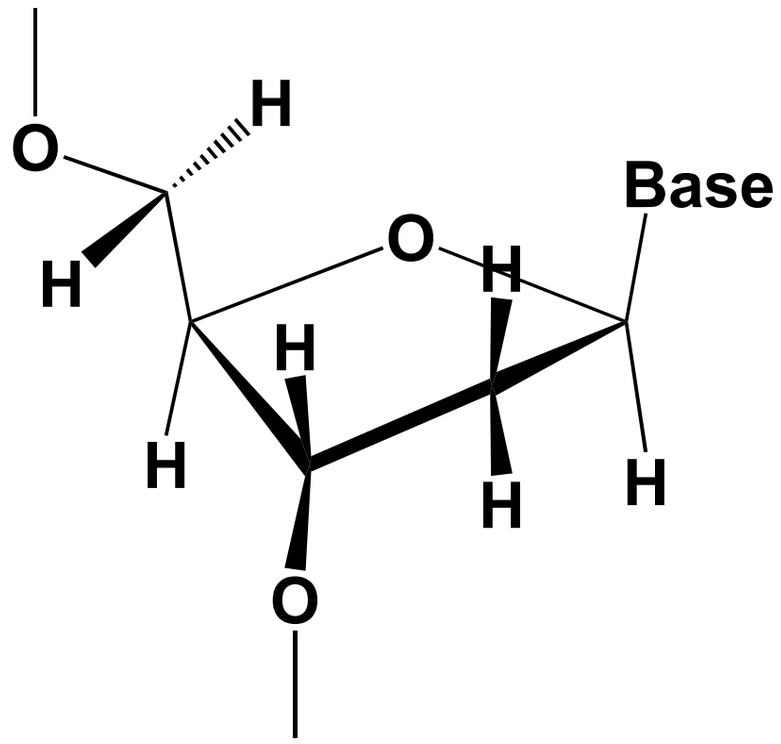
Flat faces are nonpolar
Edges are very polar (can H-bond)

Other chemical constraints

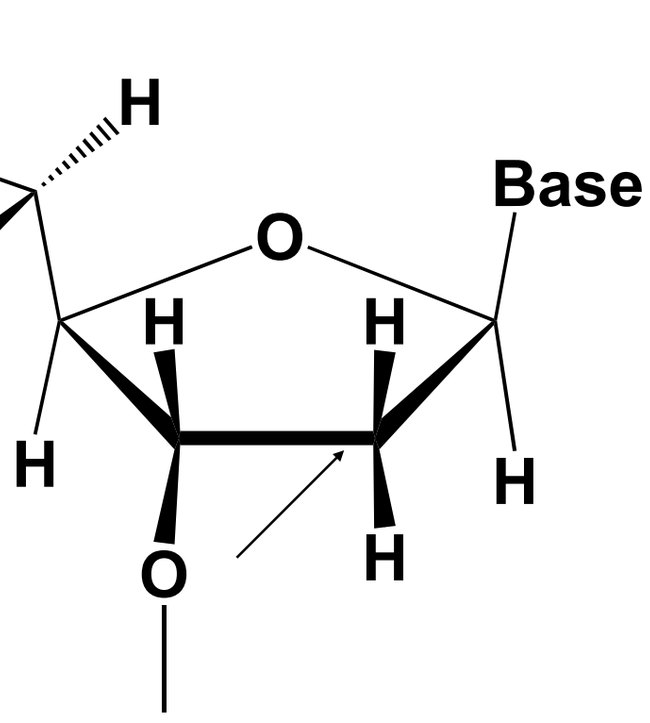
Furanose Sugar Ring

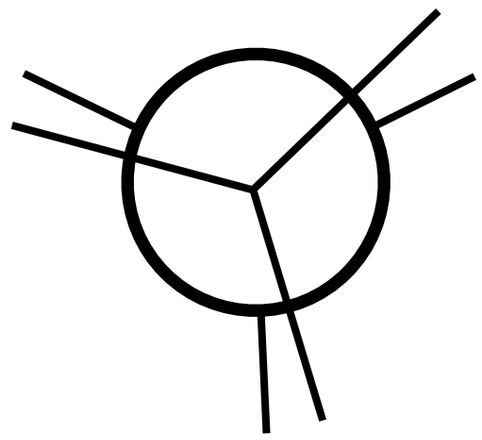


Furanose Sugar Ring

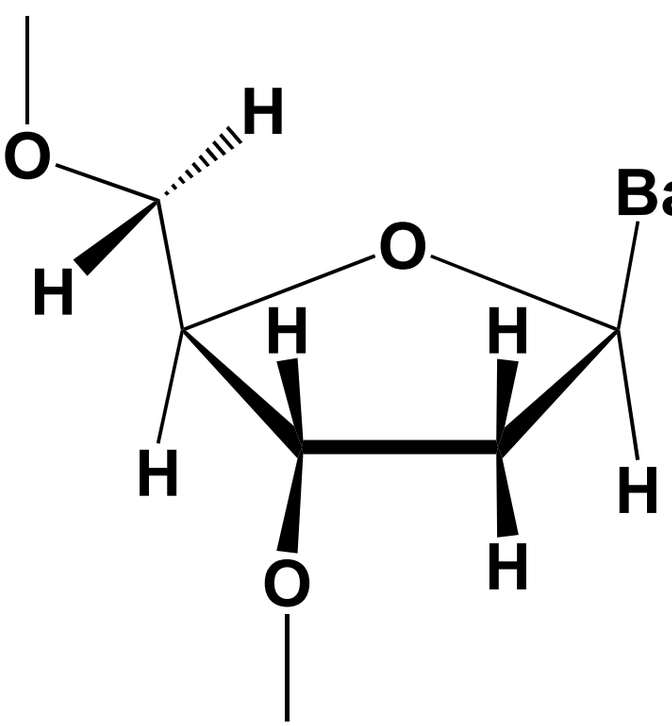


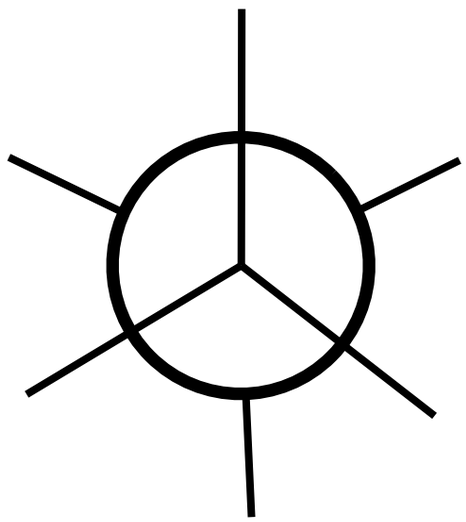
Furanose Sugar Ring



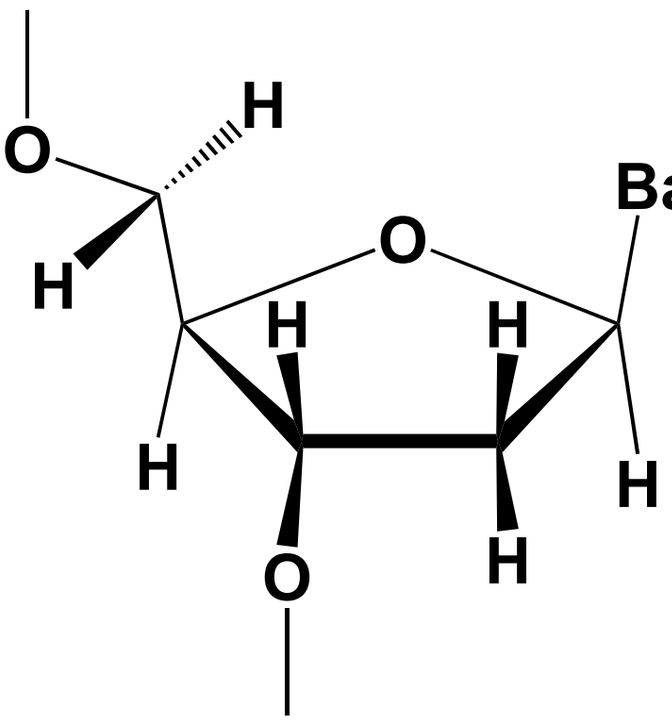


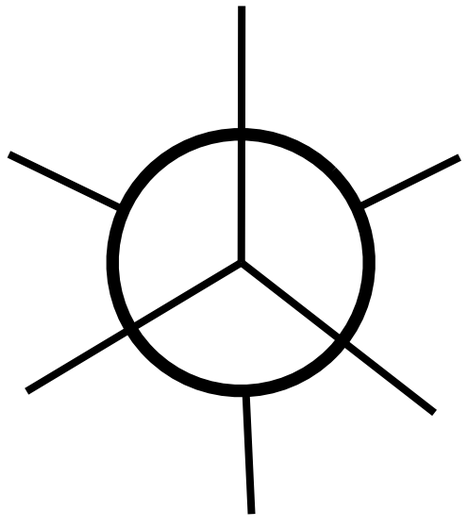
Furanose Sugar Ring

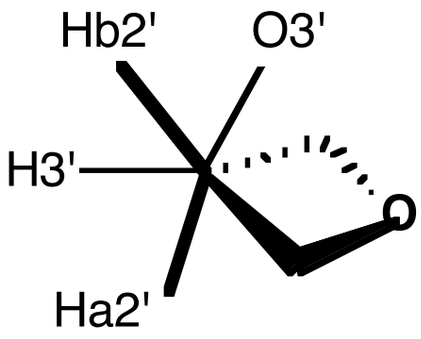


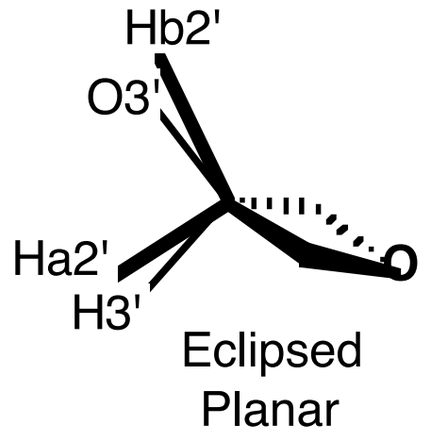


Furanose Sugar Ring

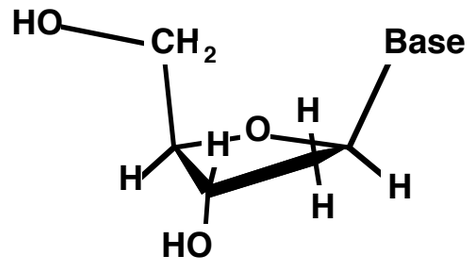




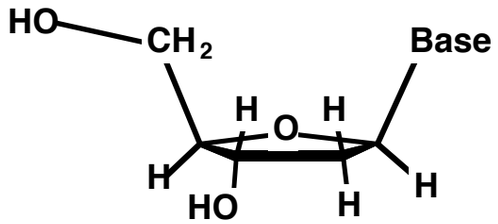




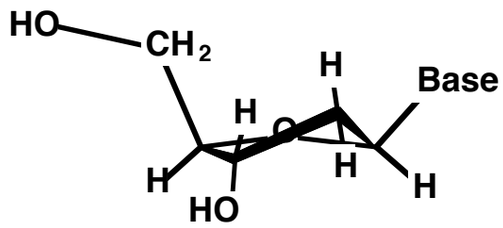
Furanose Sugar Ring



C3' exo



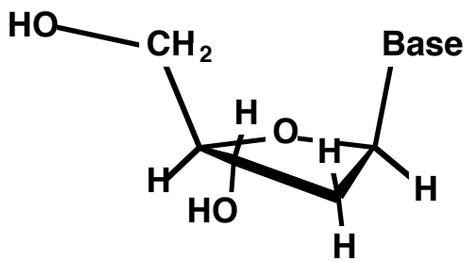
Unpuckered



C2' endo

endo

exo



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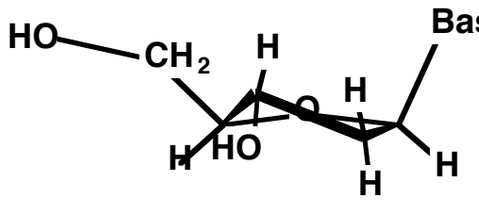
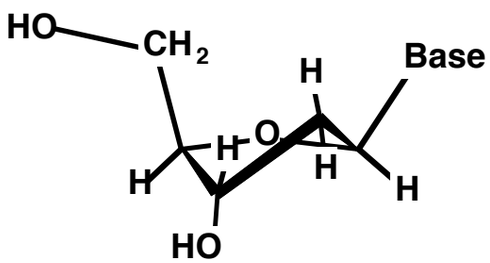
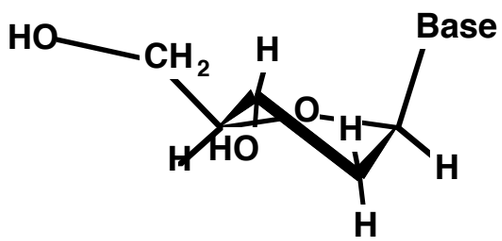


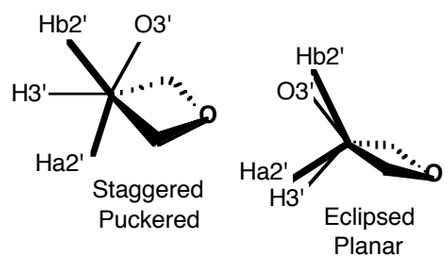
C3' endo

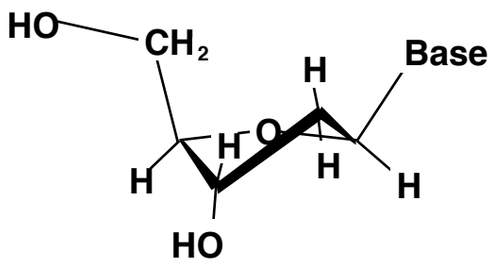


C2' endo - C3' exo



C2' exo - C3' endo





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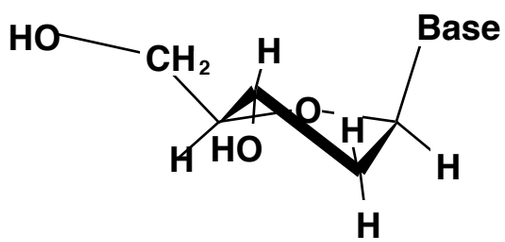


C2' exo – C3' endo

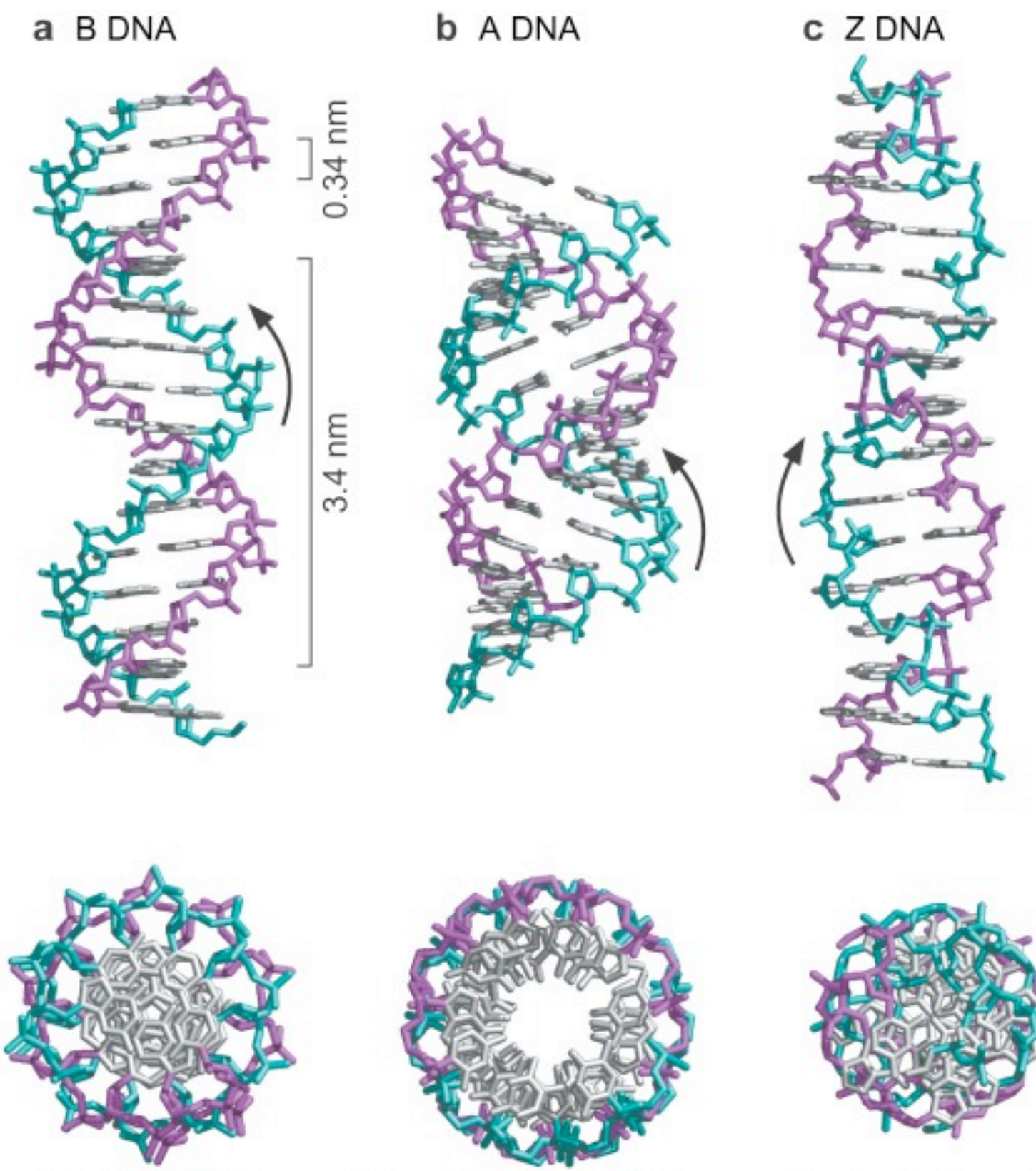


TABLE 6-2 **A Comparison of the Structural Properties of A, B, and Z DNAs as Derived from Single-Crystal X-Ray Analysis**

	Helix Type		
	A	**B**	**Z**
Overall proportions	Short and broad	Longer and thinner	Elongated and slim
Rise per base pair	2.3 Å	3.32 Å	3.8 Å
Helix-packing diameter	25.5 Å	23.7 Å	18.4 Å
Helix rotation sense	Right-handed	Right-handed	Left-handed
Base pairs per helix repeat	1	1	2
Base pairs per turn of helix	~11	~10	12
Rotation per base pair	33.6°	35.9°	−60° per 2 bp
Pitch per turn of helix	24.6 Å	33.2 Å	45.6 Å
Tilt of base normals to helix axis	+19°	−1.2°	−9°
Base-pair mean propeller twist	+18°	+16°	~0°
Helix axis location	Major groove	Through base pairs	Minor groove
Major-groove proportions	Extremely narrow but very deep	Wide and of intermediate depth	Flattened out on helix surface
Minor-groove proportions	Very broad but shallow	Narrow and of intermediate depth	Extremely narrow but very deep
Glycosyl-bond conformation	*anti*	*anti*	*anti* at C, *syn* at G

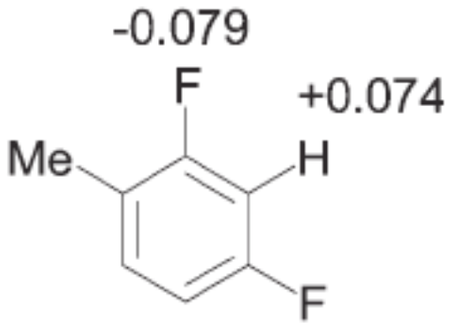
Source: Adapted from Dickerson R. E. et al. 1982. *CSHSQB* 47: 14. Copyright © 1982 Cold Spring Harbor Laboratory Press. Used with permission.

DifluoroToluene

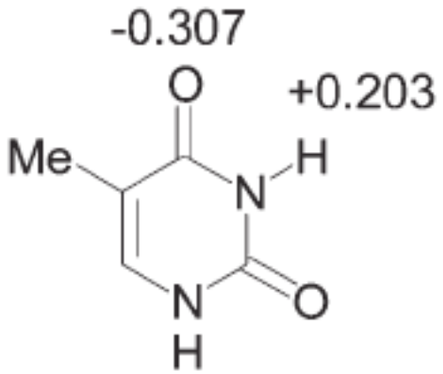
The difluorotoluene debate—a decade later

Eric T. Kool* and Herman O. Sintim

Chem. Commun., 2006, 3665–3675



Difluorotoluene



Thymine

Table 2 Pairing stabilities of 12 bp DNA duplexes containing difluorotoluene or thymine paired opposite natural bases

5′-C T T T T C X T T C T T

3′-G A A A A G Y A A G A A

X.Y	T_m/°C	$\Delta G°_{37}$/kcal mol^{-1}	X.Y	T_m/°C	$\Delta G°_{37}$/kcal mol^{-1}
T.A	42.4	−9.7	A.T	42.4	−9.6
T.G	33.3	−7.5	G.T	34.7	−7.9
T.C	29.5	−6.6	C.T	25.7	−6.0
T.T	29.1	−6.8	T.T	29.1	−6.8
F.A	26.2	−6.2	A.F	27.5	−6.6
F.G	23.6	−6.0	G.F	25.1	−6.4
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F.T	24.0	−5.9	T.F	24.8	−6.4

[a] Conditions: 1 M NaCl, 10 mM phosphate buffer (pH 7.0) with 0.1 mM EDTA, 2.5 μM each strand, monitored at 260 nm. Error in T_m is estimated at ±0.5 °C, and in free energy, ±10%.

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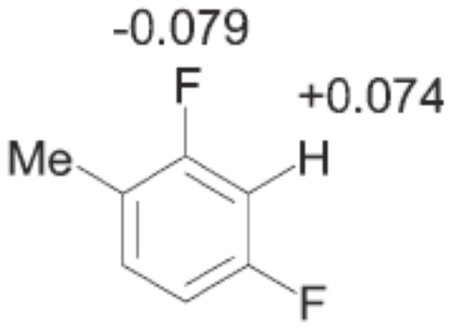
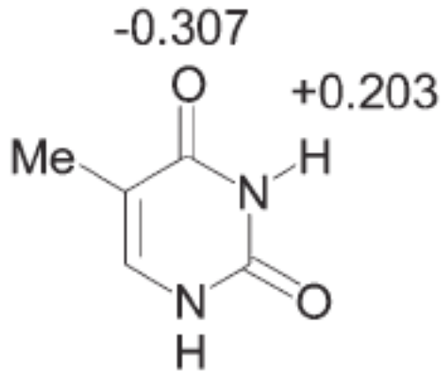


Difluorotoluene



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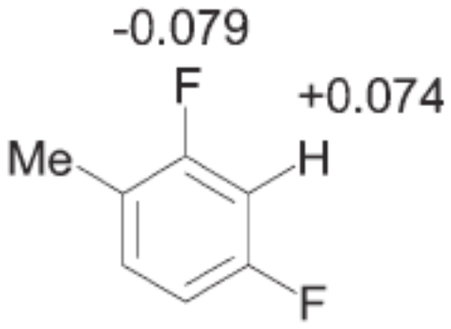

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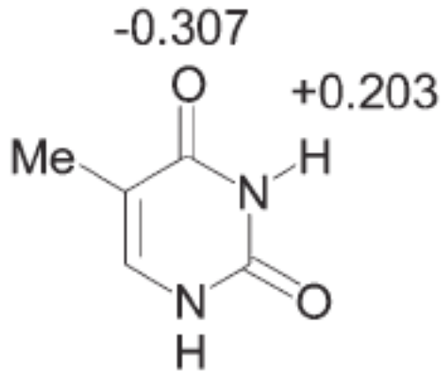

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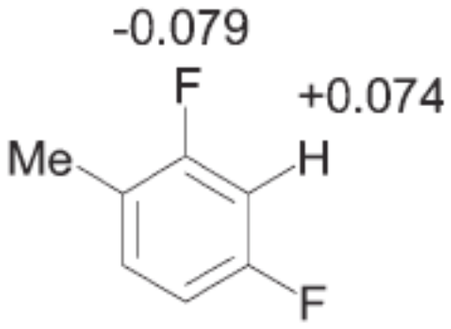
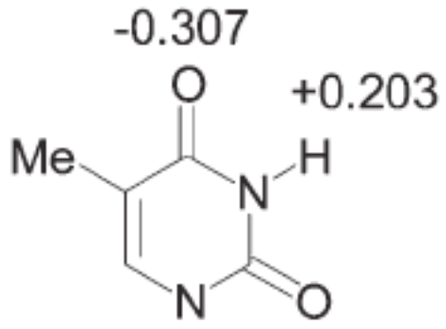


Difluorotoluene



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- DNA polymerase incorporates T opposite A
- DNA polymerase does not incorporate G, C, or A opposite A

DifluoroToluene

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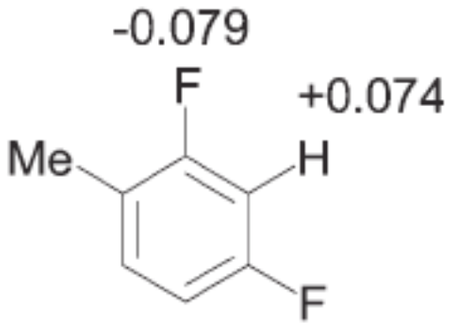
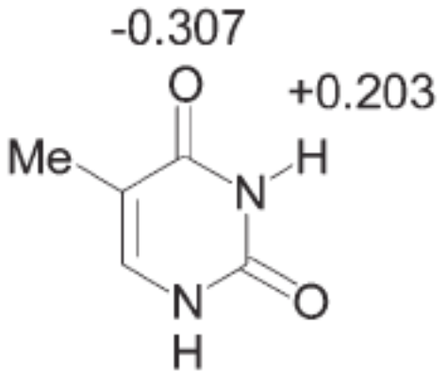


Difluorotoluene



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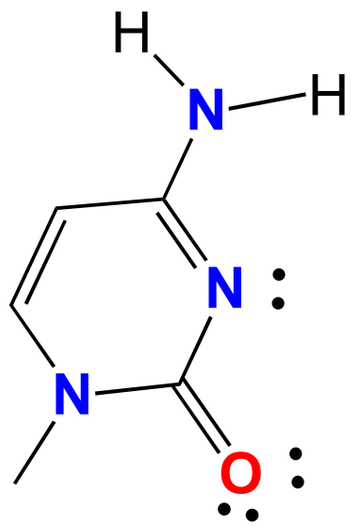
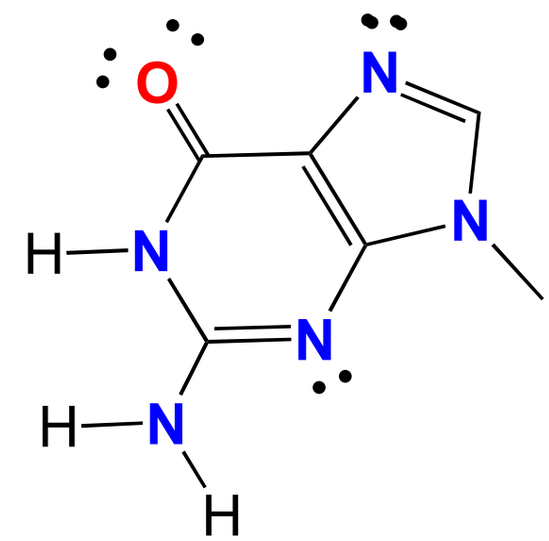
- DNA polymerase incorporates Difluorotoluene opposite A

Why is Watson-Crick so good?

C



G



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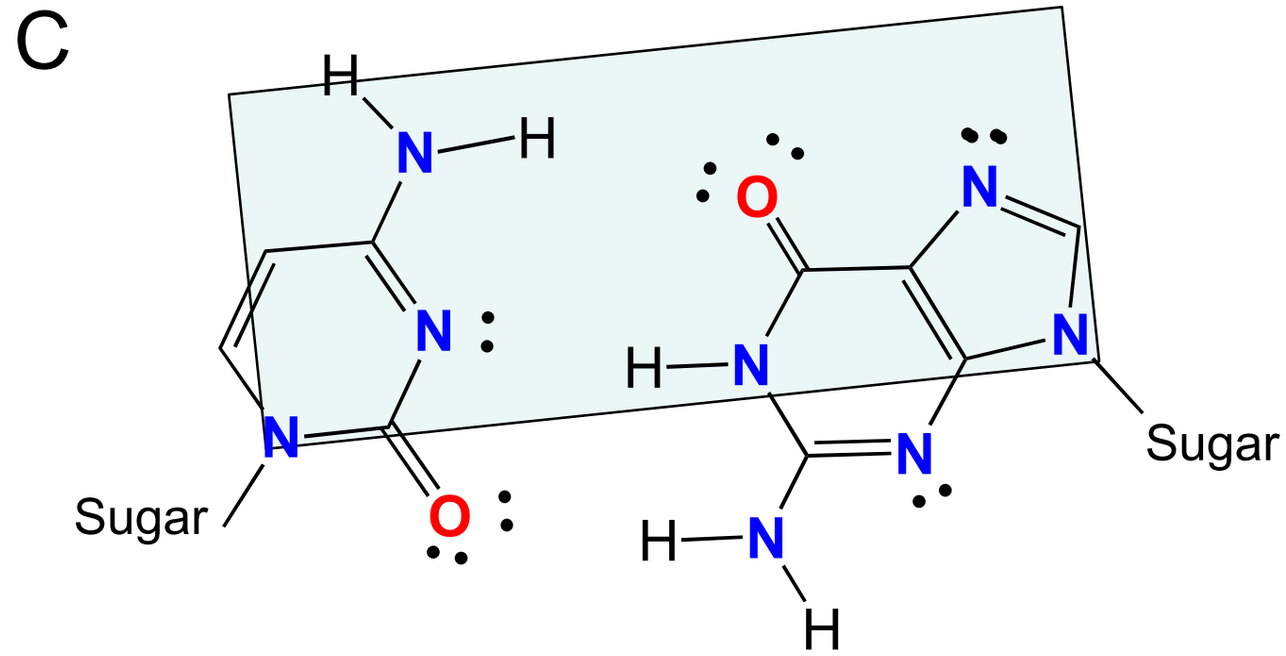

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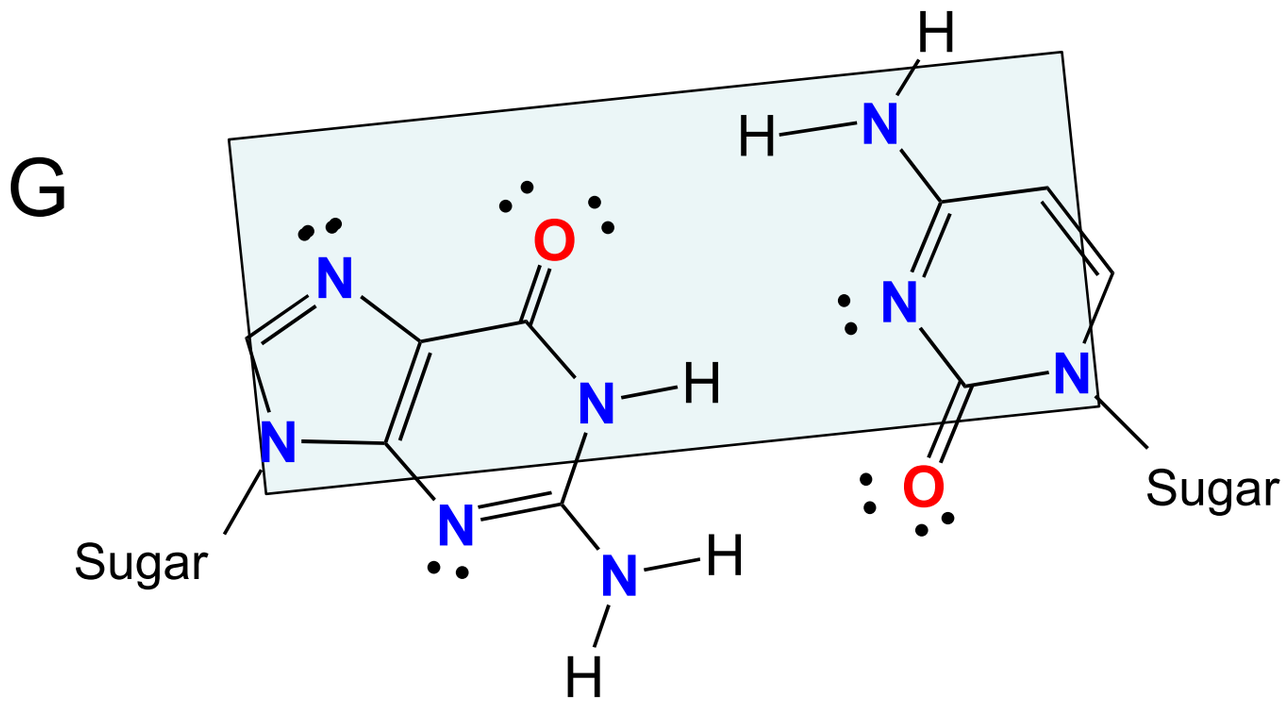

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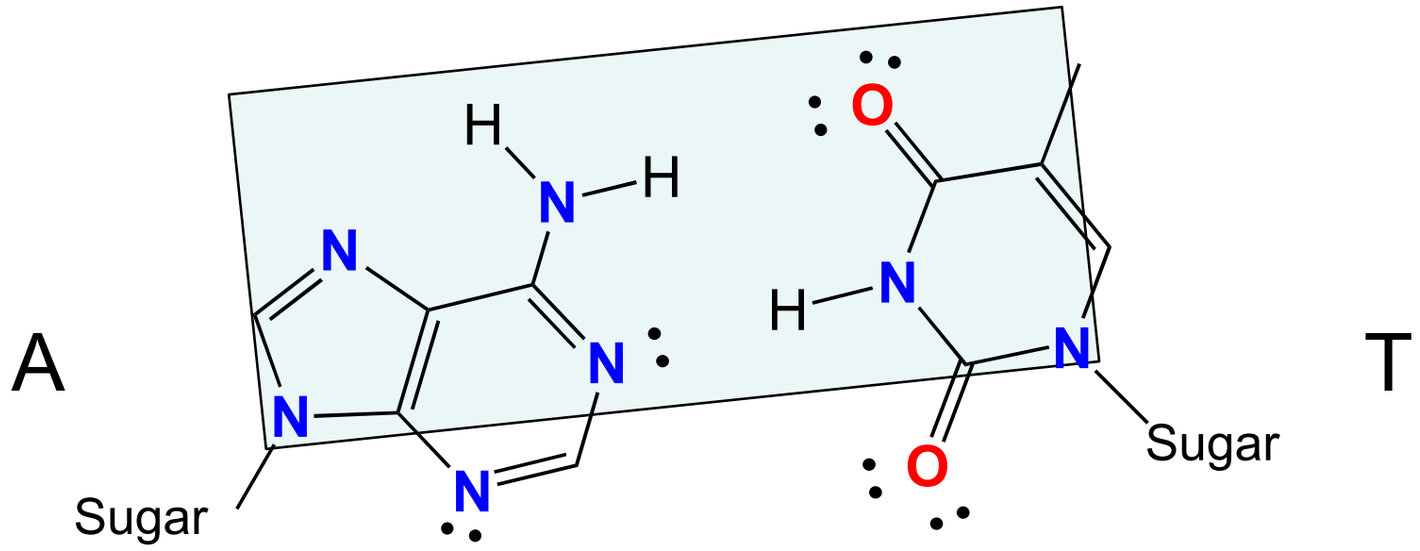

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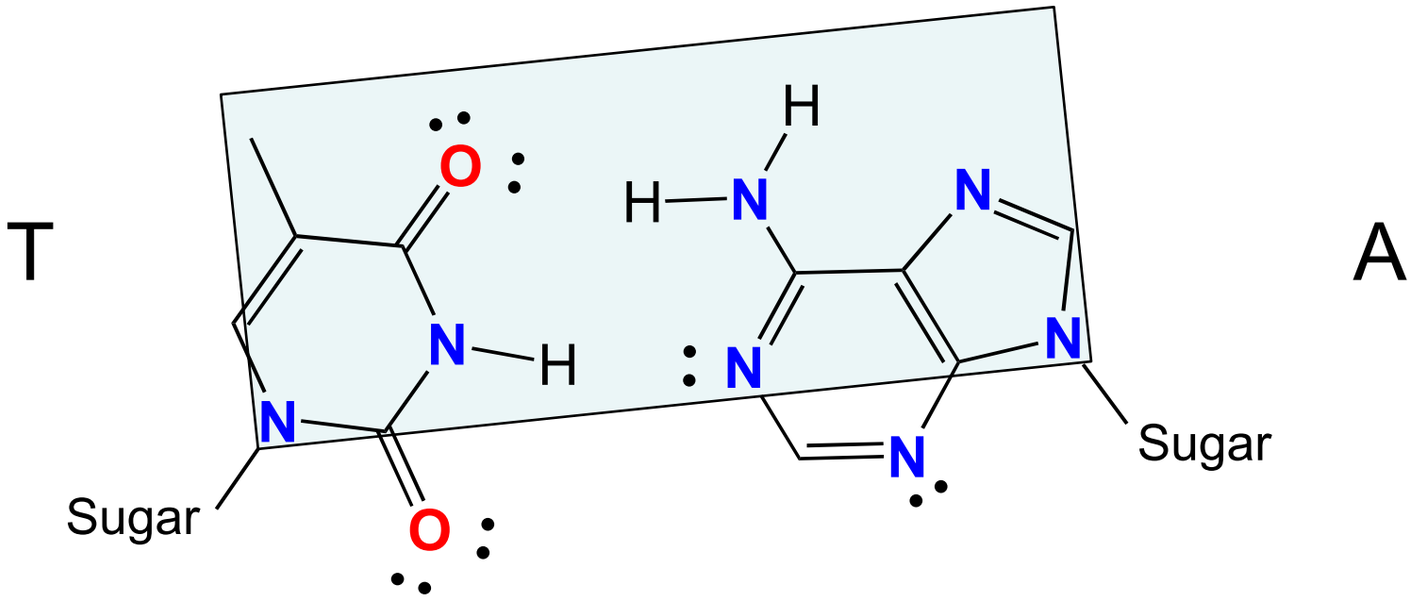

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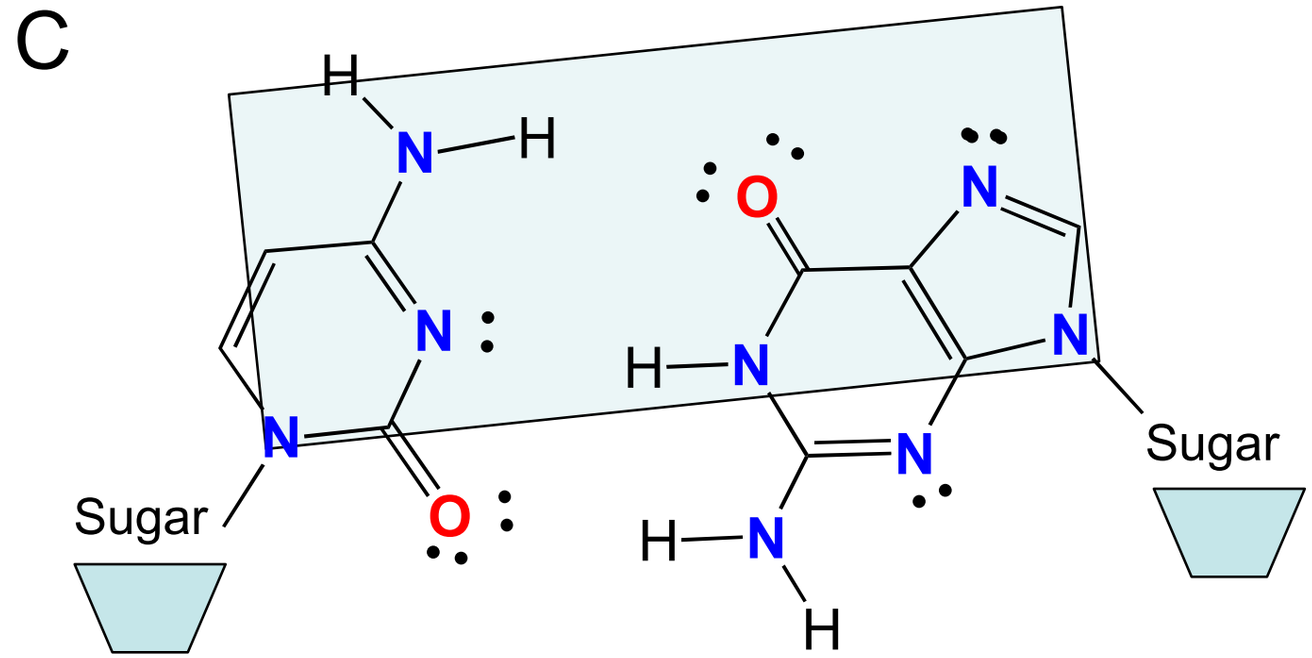

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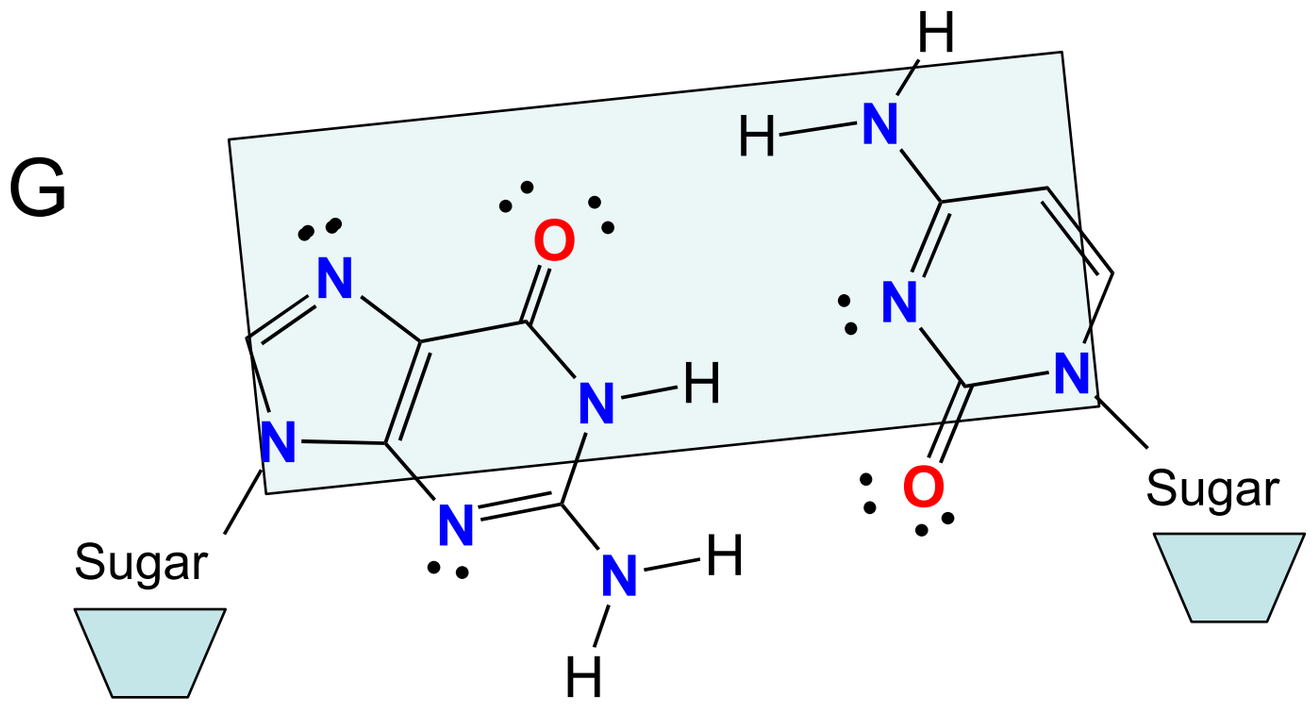

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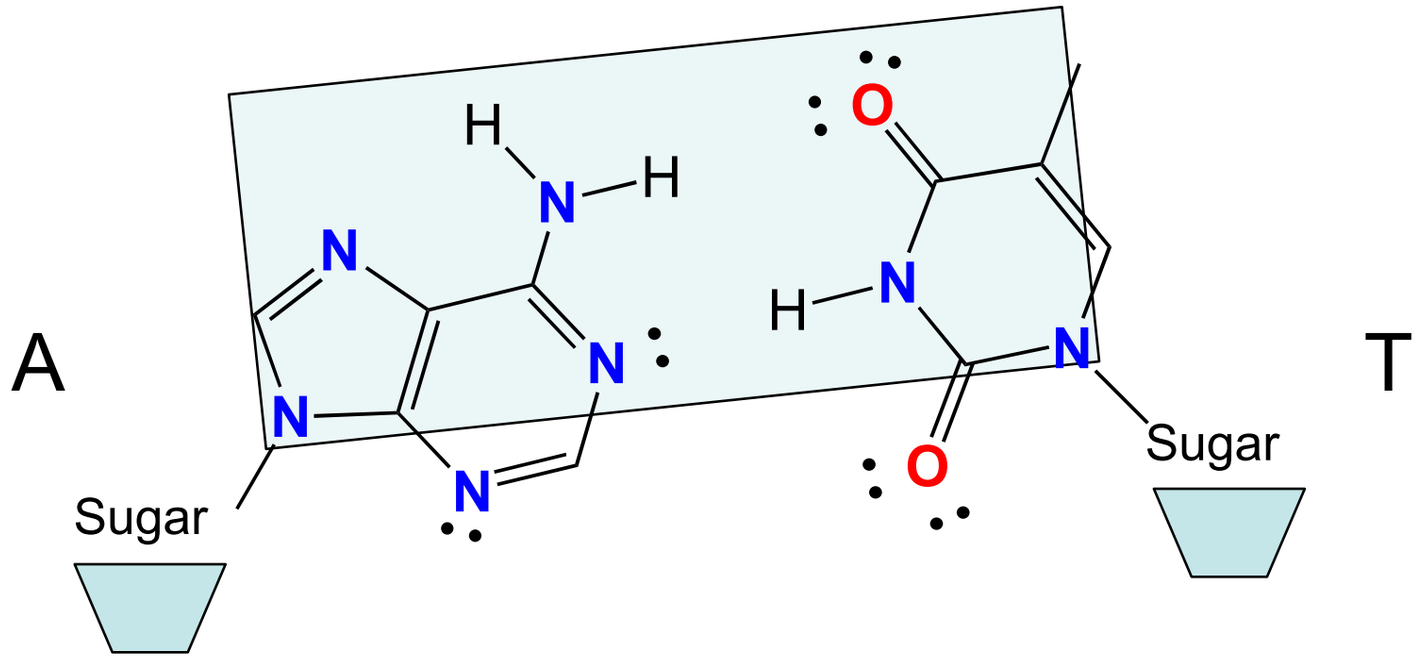

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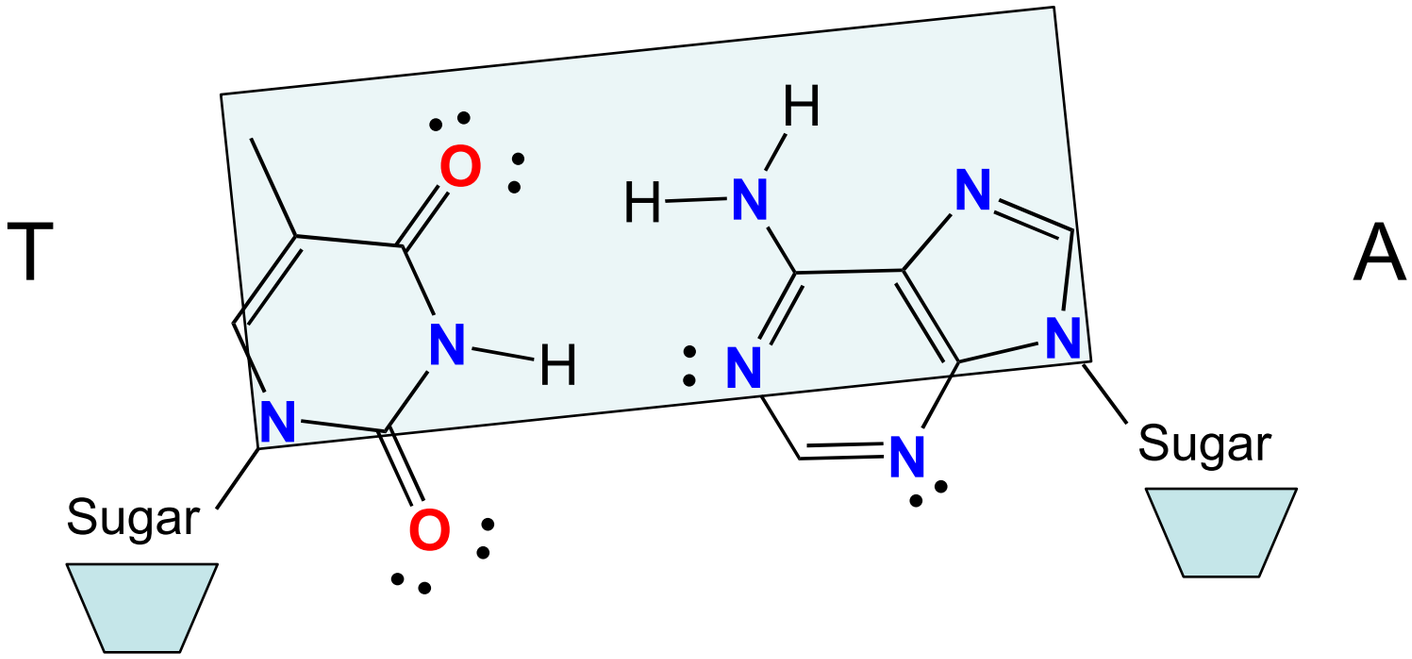
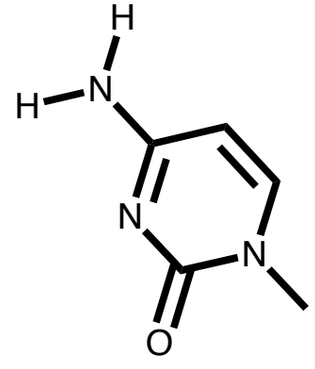
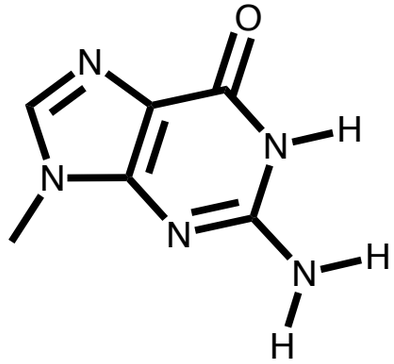
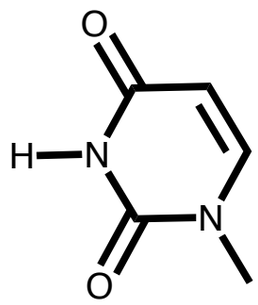
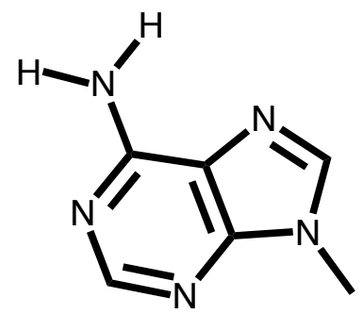


Base Pairs









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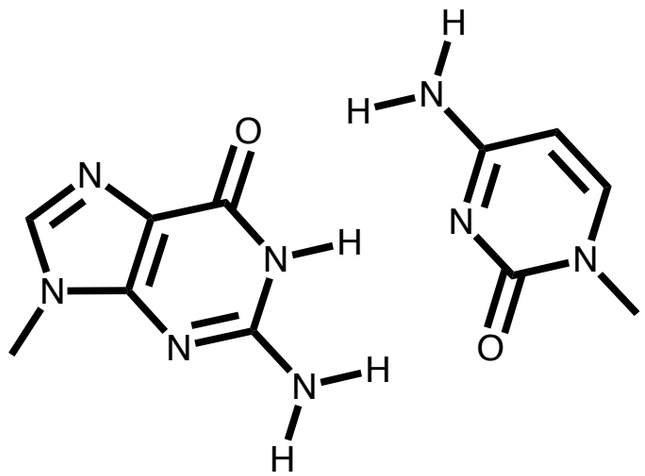

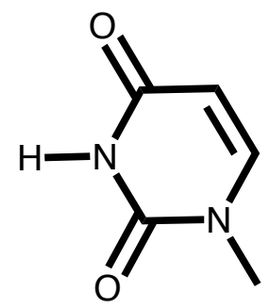

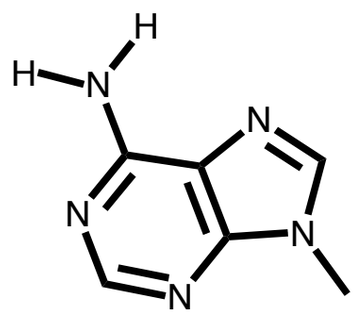

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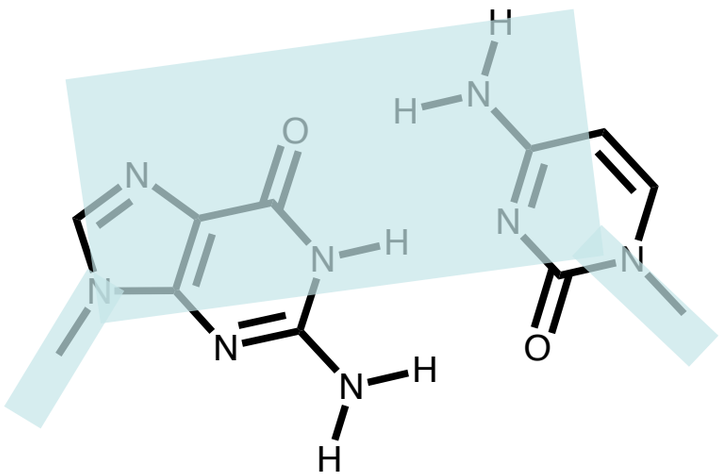

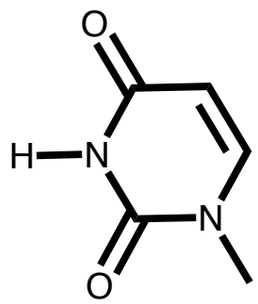

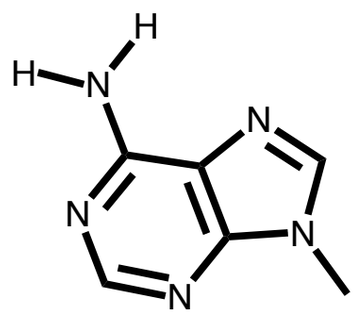

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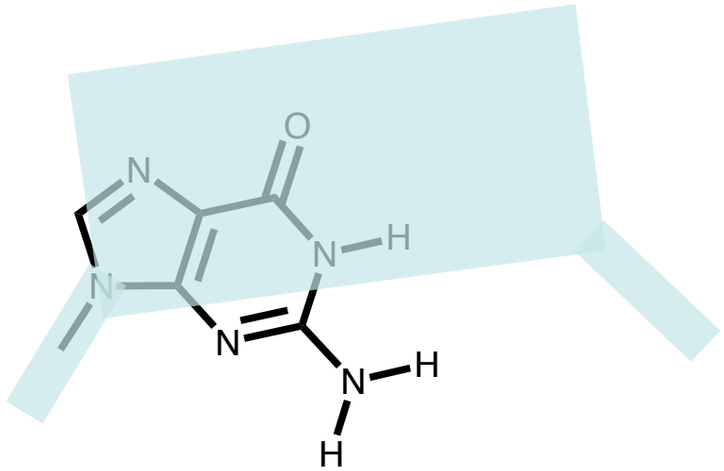

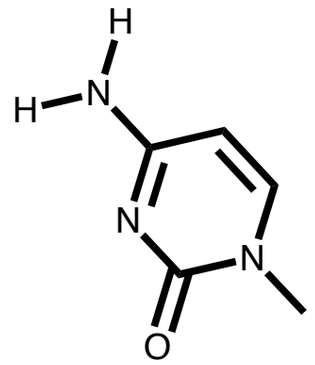

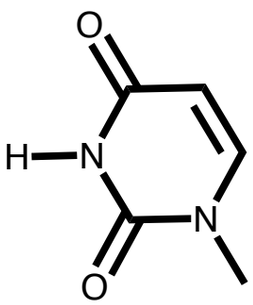

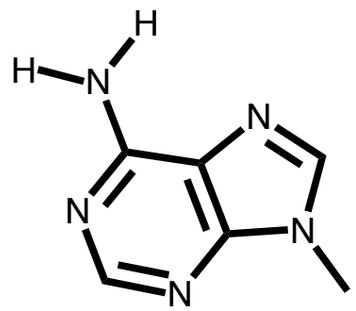

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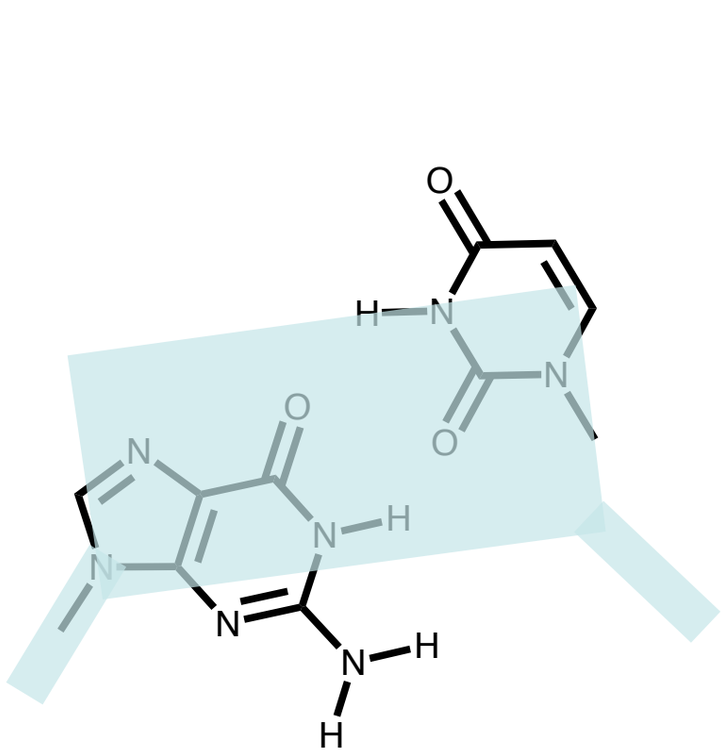

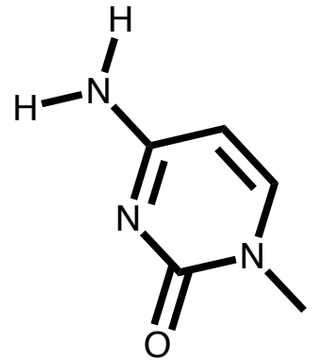

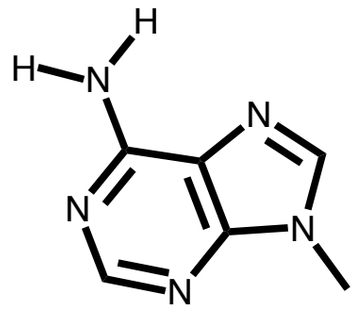

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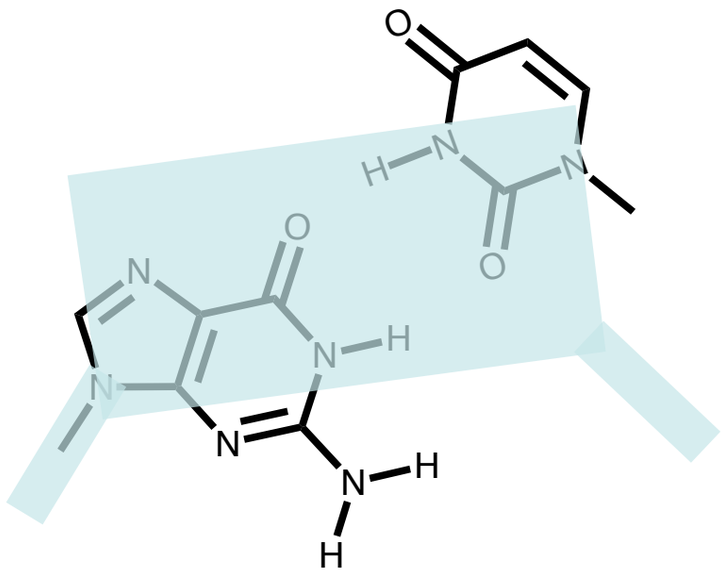

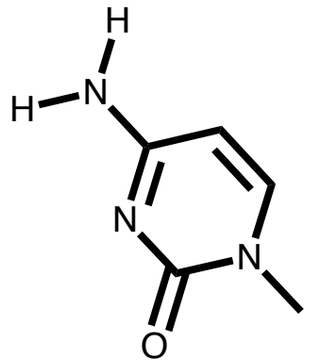

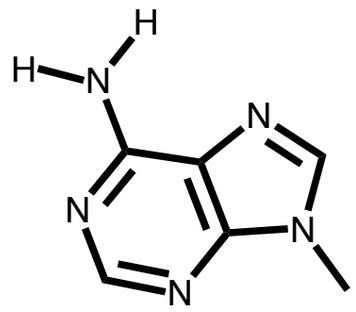

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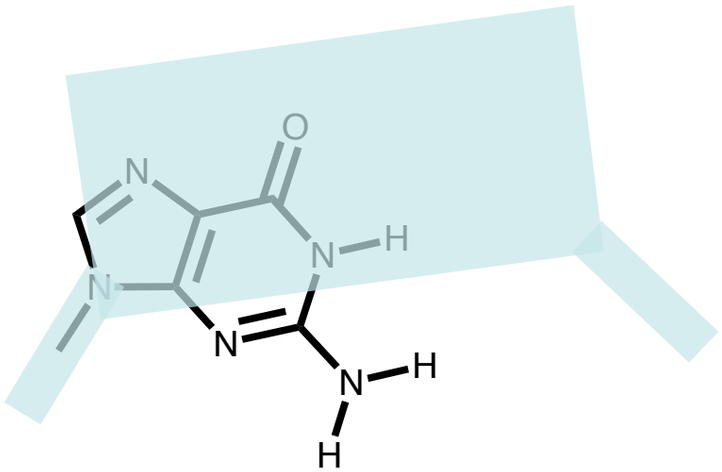

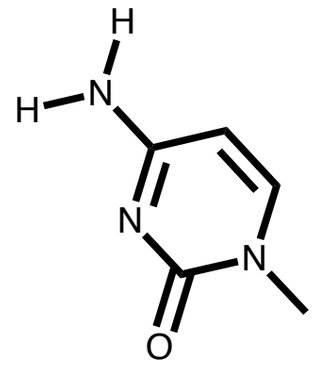

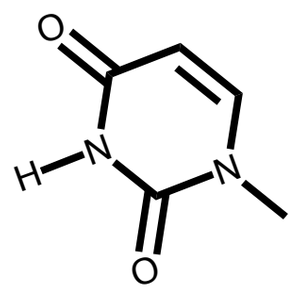

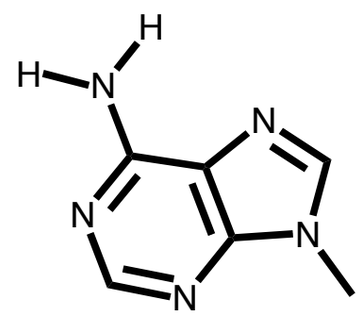

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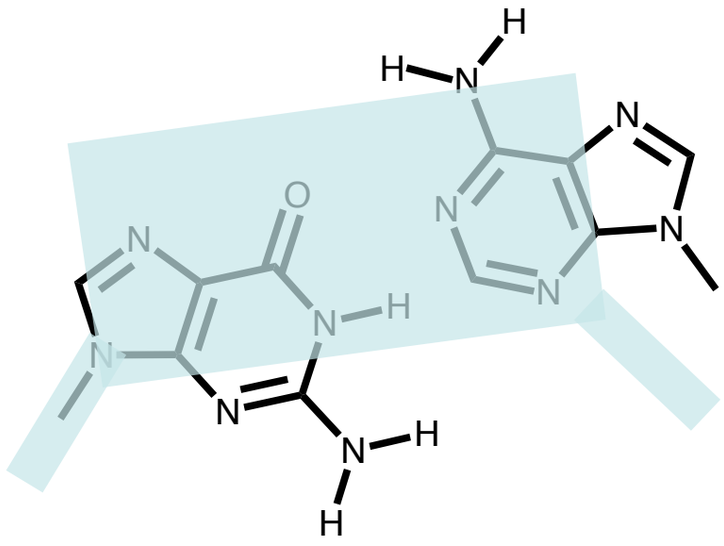

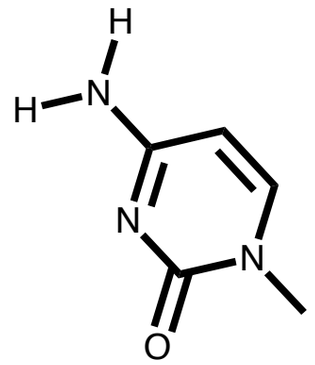

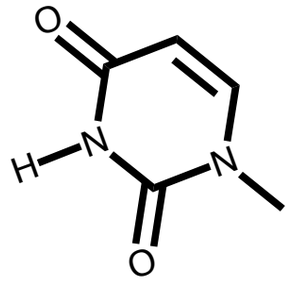

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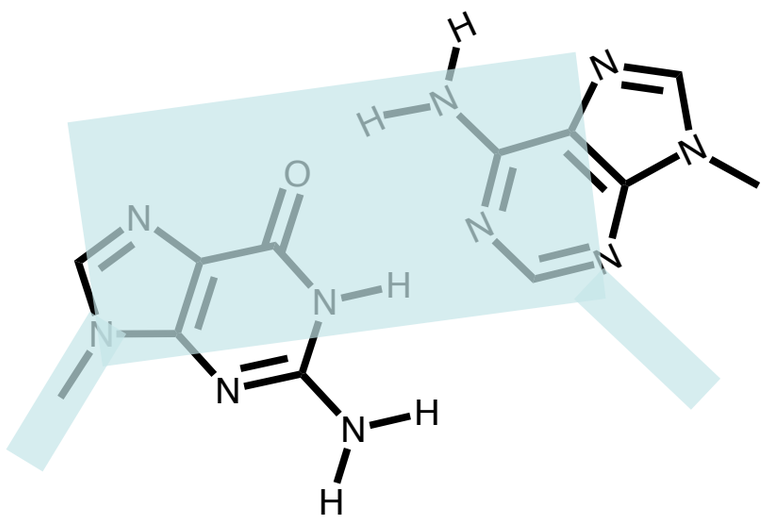

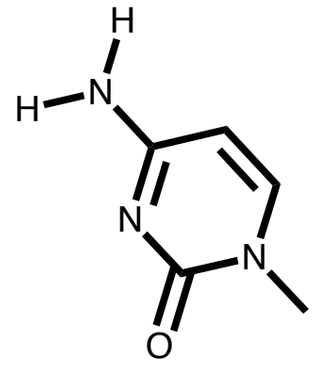

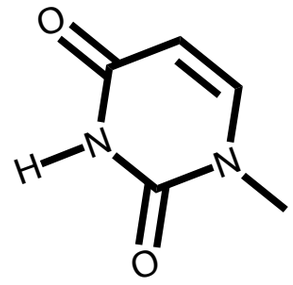

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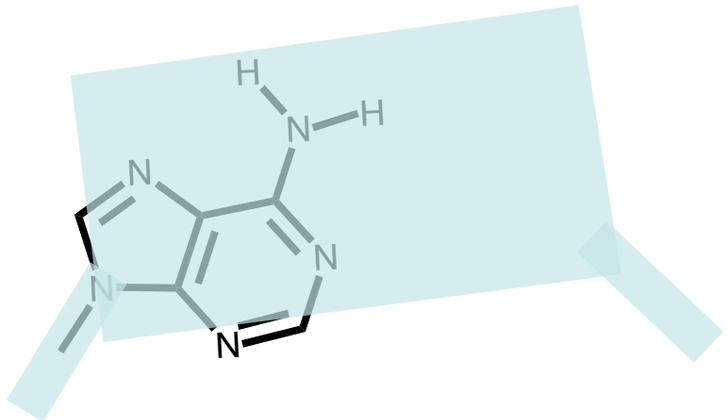

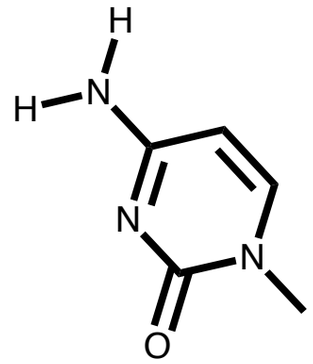

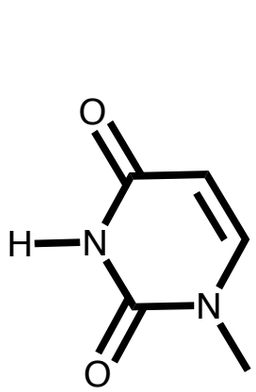

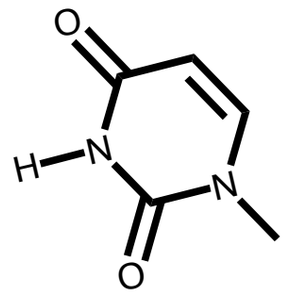

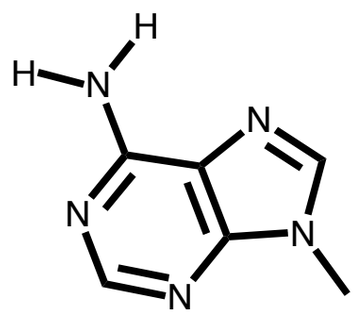

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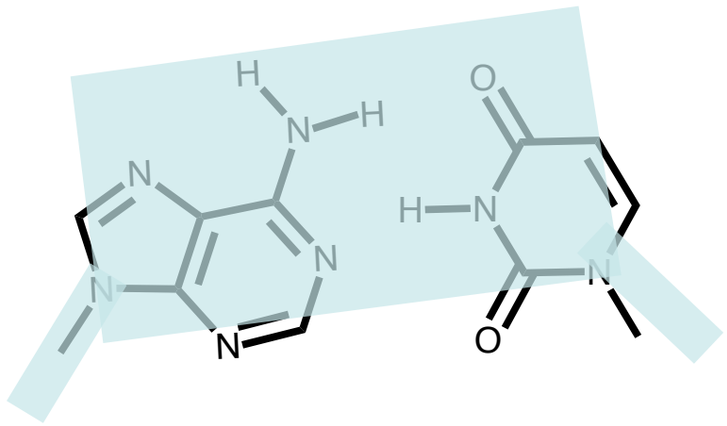

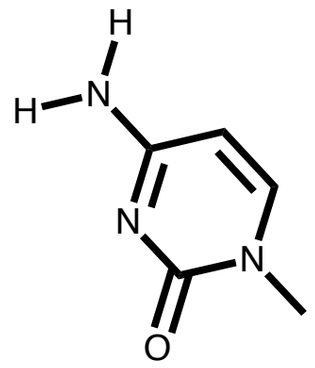

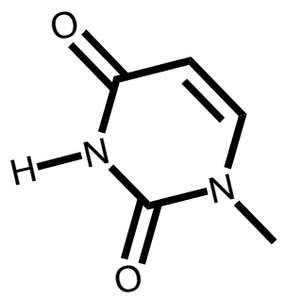

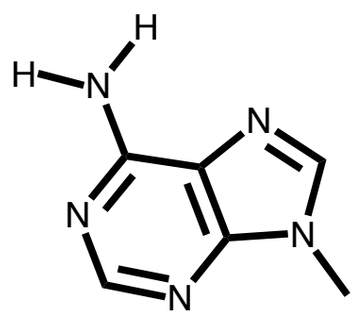

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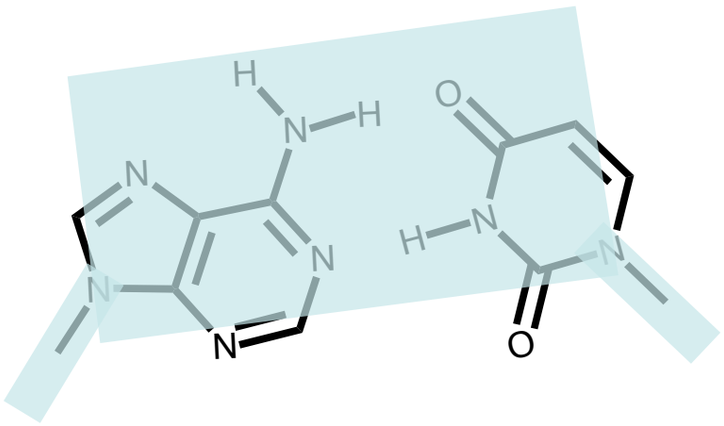
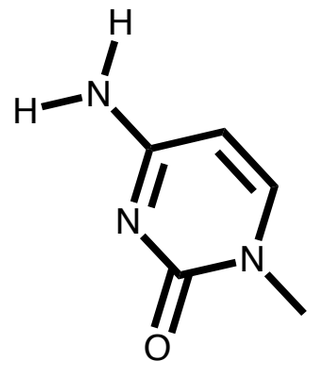
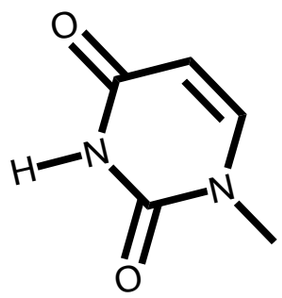
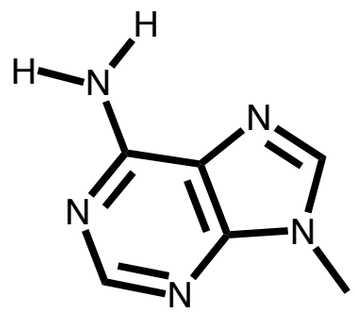




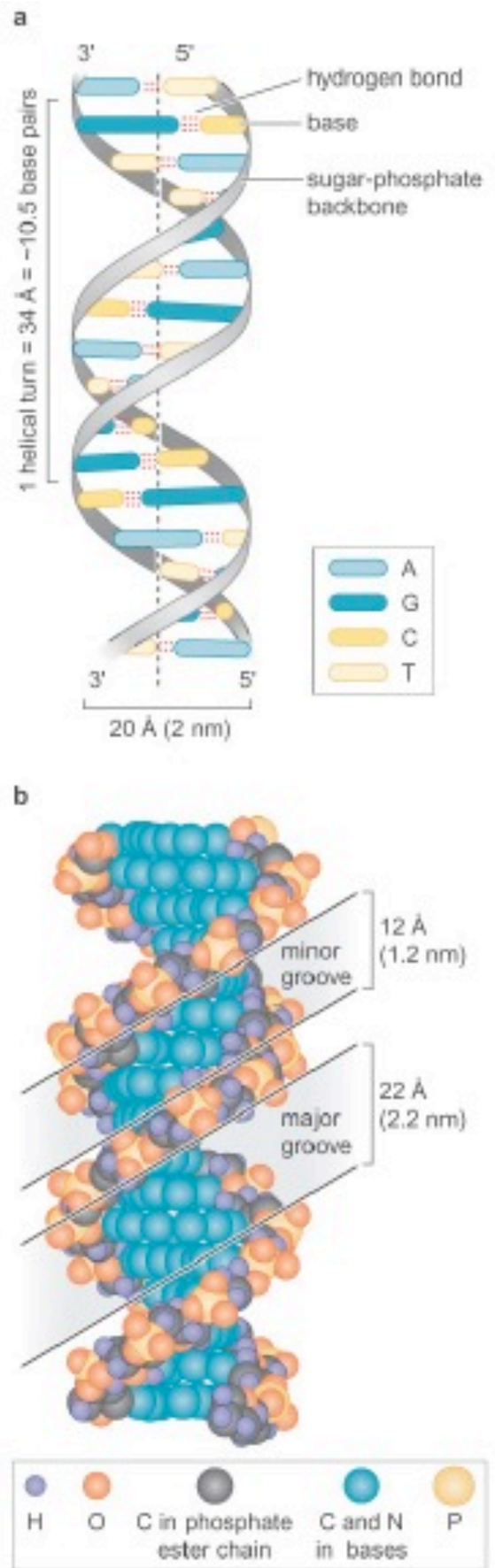




B-form in 3D

A-form in 3D

More in 3D

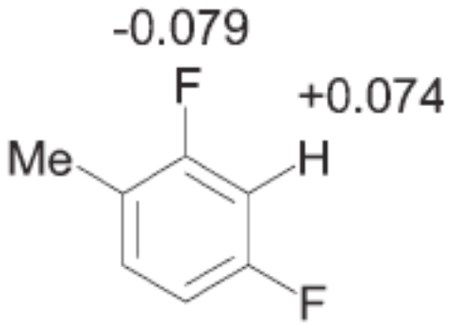


DifluoroToluene

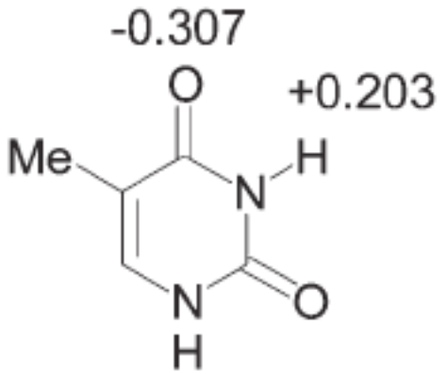
The difluorotoluene debate—a decade later

Eric T. Kool* and Herman O. Sintim

Chem. Commun., 2006, 3665–3675



Difluorotoluene



Thymine

Table 2 Pairing stabilities of 12 bp DNA duplexes containing difluorotoluene or thymine paired opposite natural bases

5′-C T T T T C X T T C T T

3′-G A A A A G Y A A G A A

X.Y	T_m/°C	$\Delta G°_{37}$/kcal mol^{-1}	X.Y	T_m/°C	$\Delta G°_{37}$/kcal mol^{-1}
T.A	42.4	−9.7	A.T	42.4	−9.6
T.G	33.3	−7.5	G.T	34.7	−7.9
T.C	29.5	−6.6	C.T	25.7	−6.0
T.T	29.1	−6.8	T.T	29.1	−6.8
F.A	26.2	−6.2	A.F	27.5	−6.6
F.G	23.6	−6.0	G.F	25.1	−6.4
F.C	23.7	−5.8	C.F	25.1	−6.4
F.T	24.0	−5.9	T.F	24.8	−6.4

[a] Conditions: 1 M NaCl, 10 mM phosphate buffer (pH 7.0) with 0.1 mM EDTA, 2.5 μM each strand, monitored at 260 nm. Error in T_m is estimated at ±0.5 °C, and in free energy, ±10%.

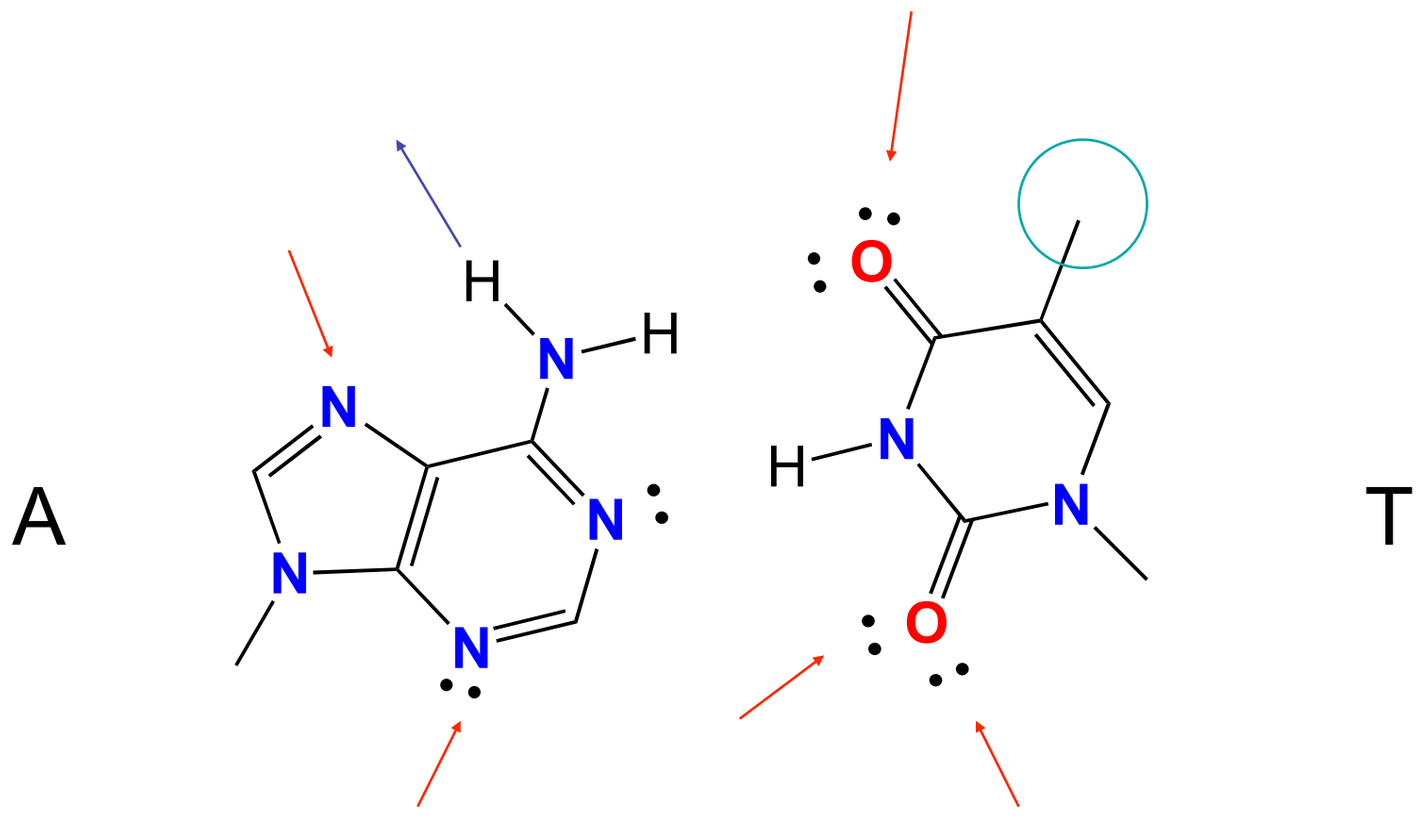
- Difluorotoluene pairs poorly with Adenine, in contrast to the normal partner Thymine

- DNA polymerase incorporates T opposite A
- DNA polymerase does not incorporate G, C, or A opposite A
- DNA polymerase incorporates Difluorotoluene opposite A

Wednesday

Why is the major groove so good?

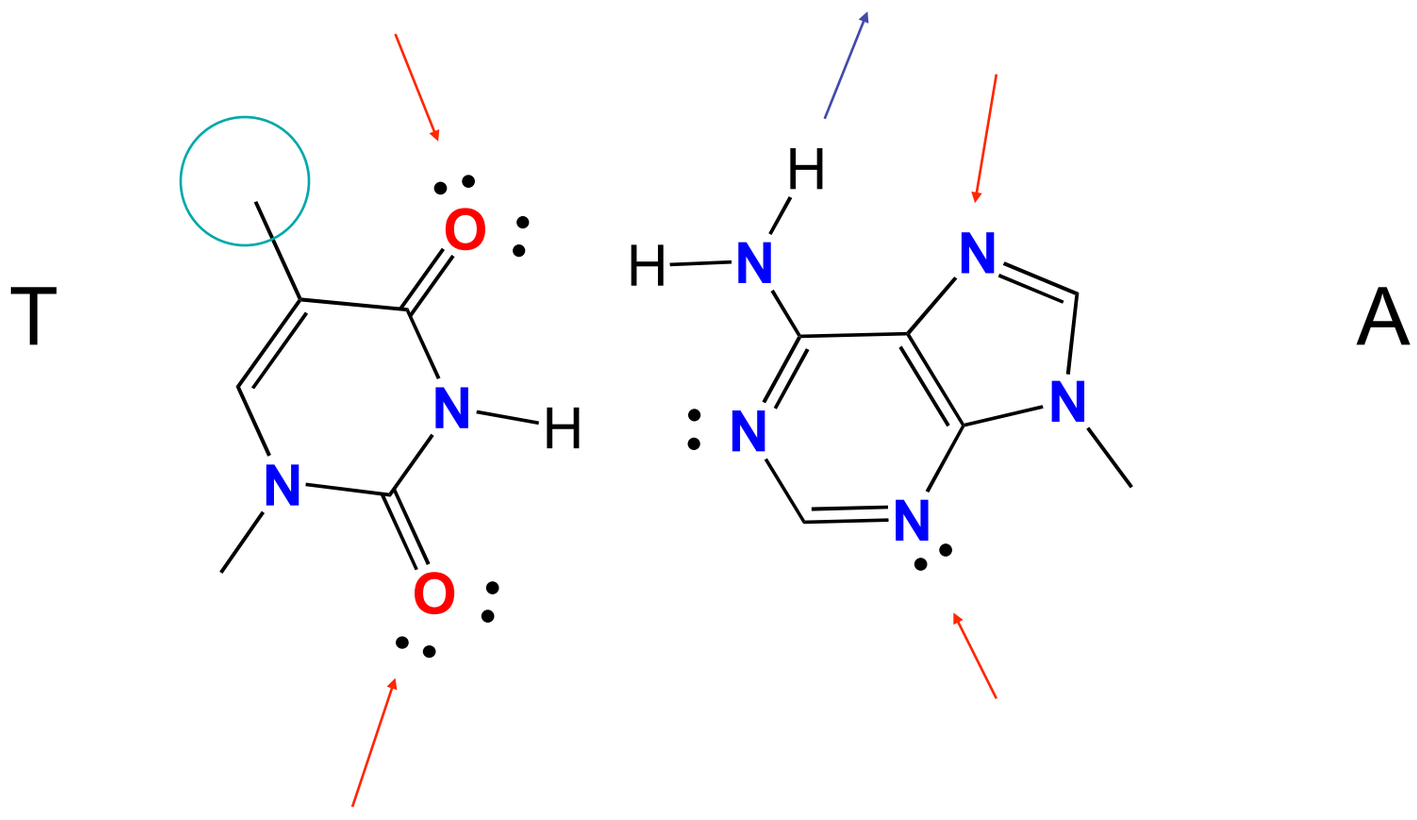
Major Groove



Minor Groove

Why is the major groove so good?

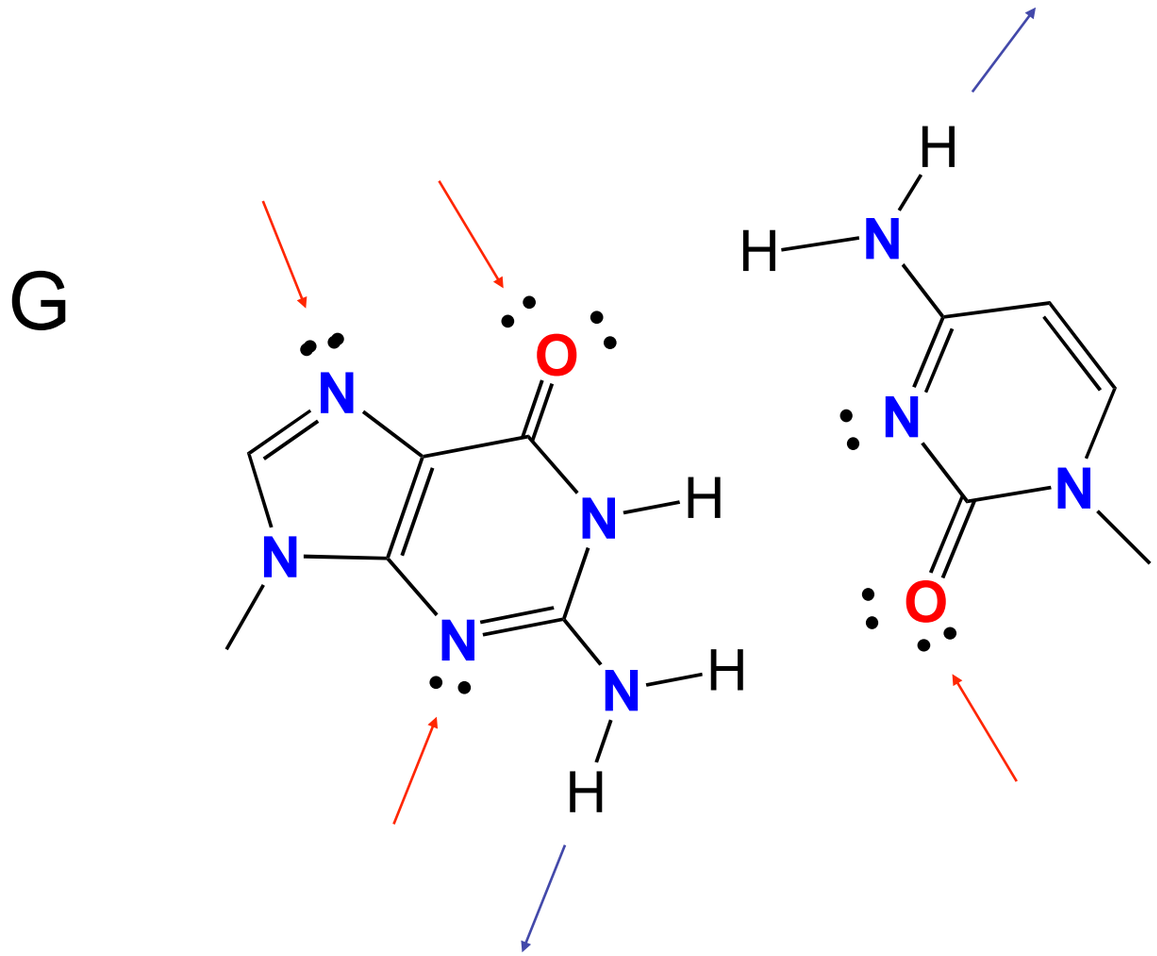
Major Groove



Minor Groove

Why is the major groove so good?

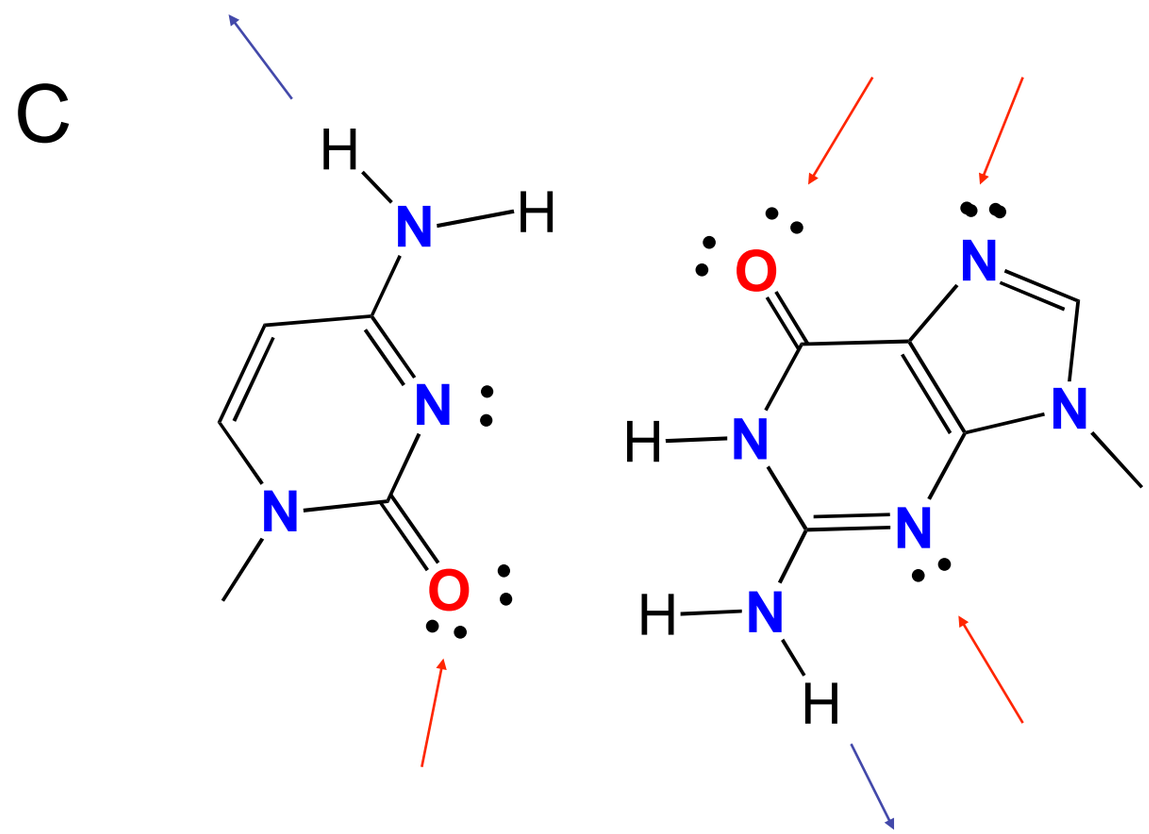
Major Groove



Minor Groove

Why is the major groove so good?

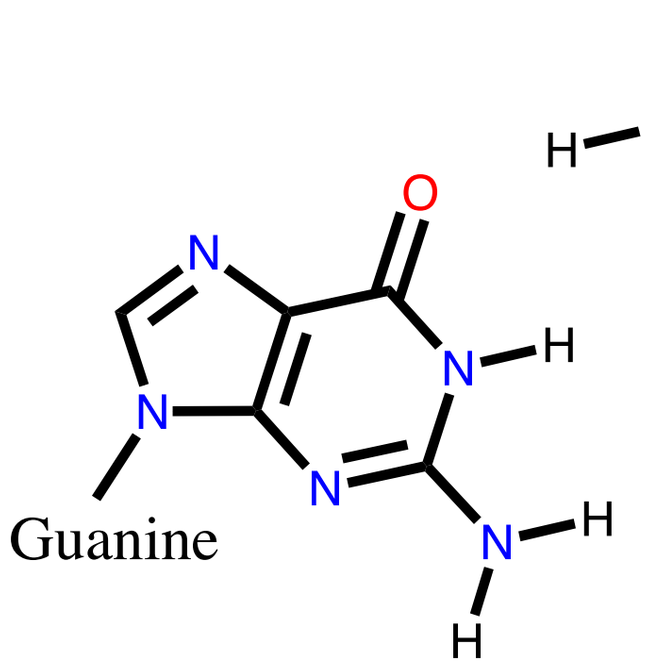
Major Groove



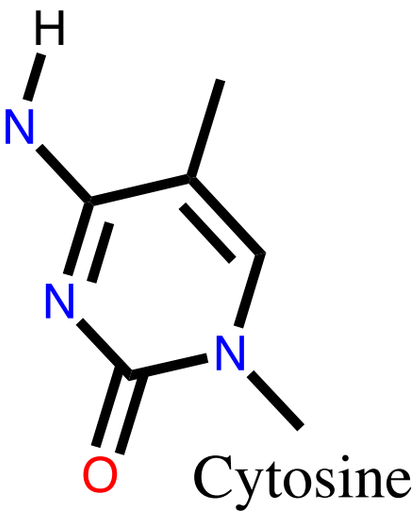
Minor Groove

Sequence-specific binding by proteins

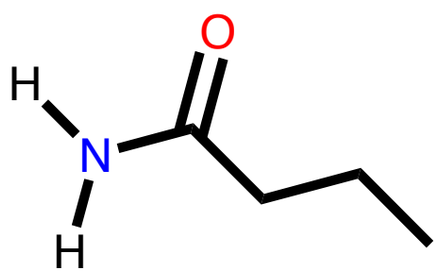
Find “two-fer” interactions

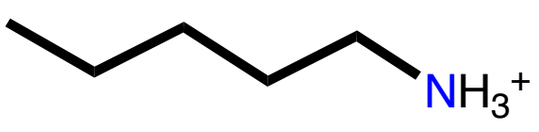


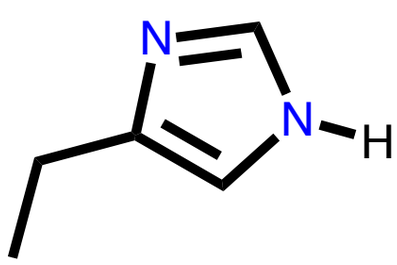
Guanine

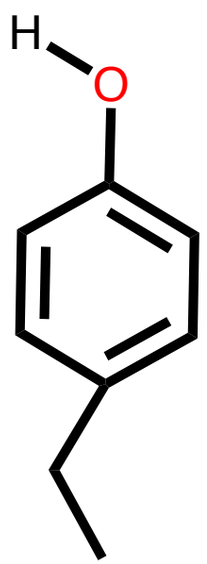


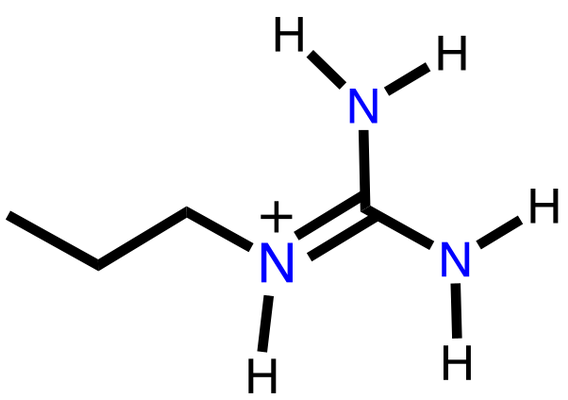
Cytosine





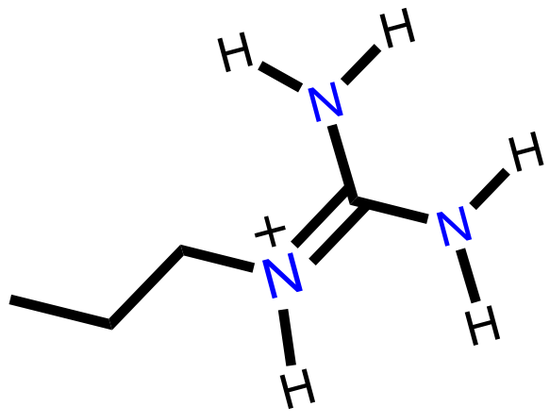


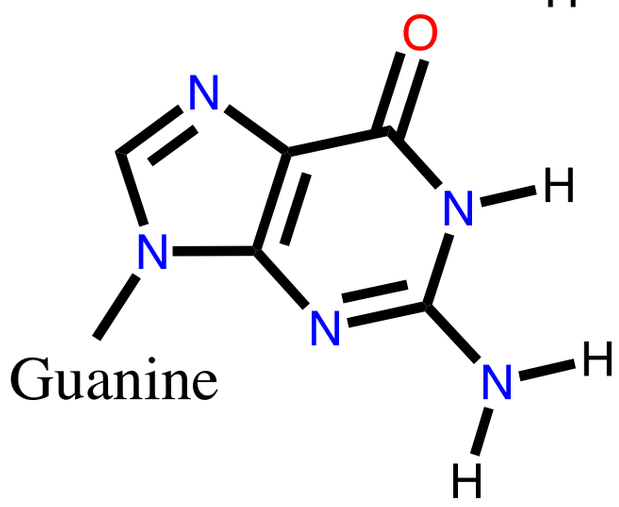




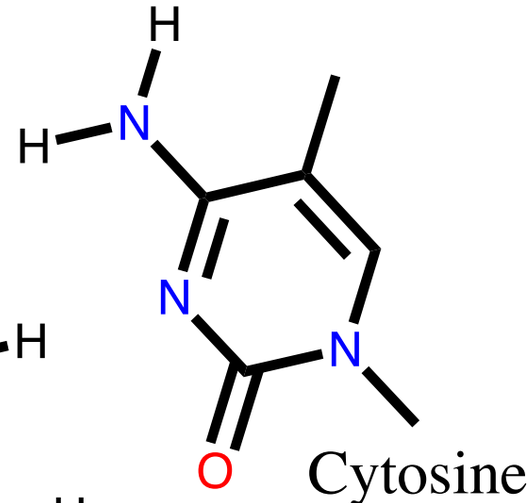
Sequence-specific binding by proteins

Find “two-fer” interactions

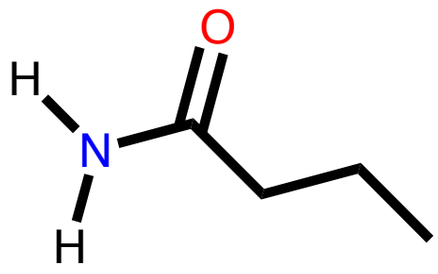


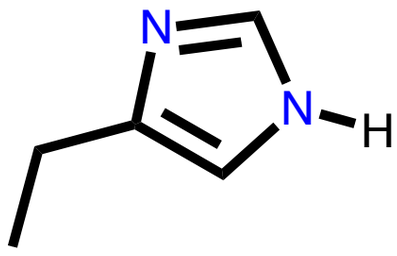


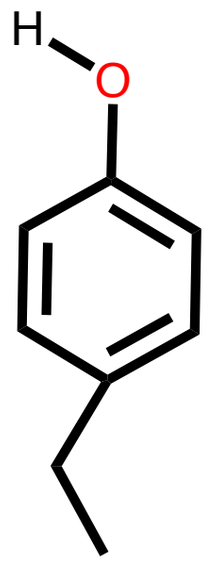
Guanine



Cytosine

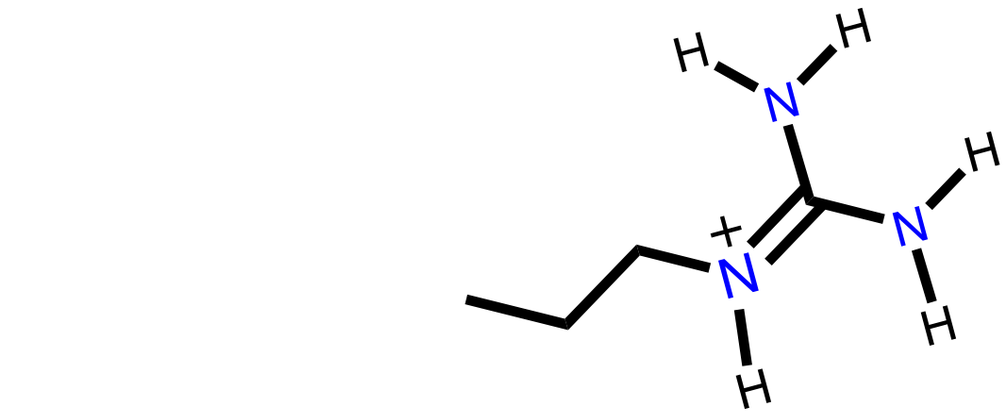


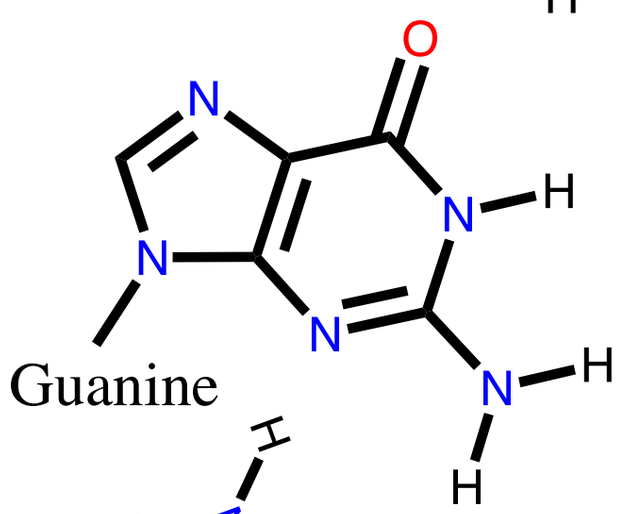




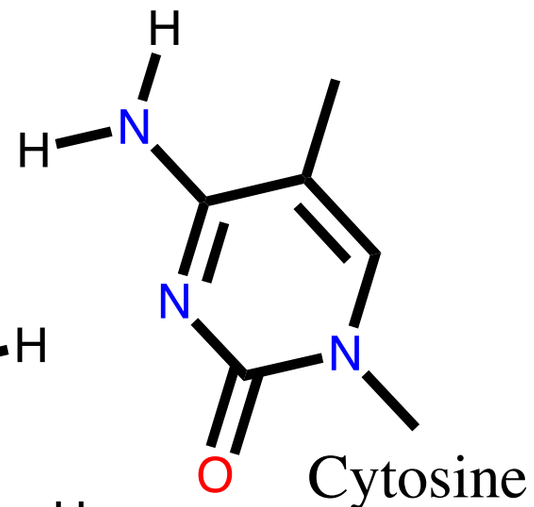
Sequence-specific binding by proteins

Find “two-fer” interactions

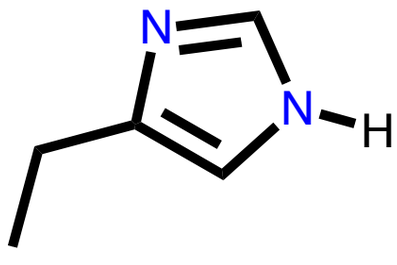


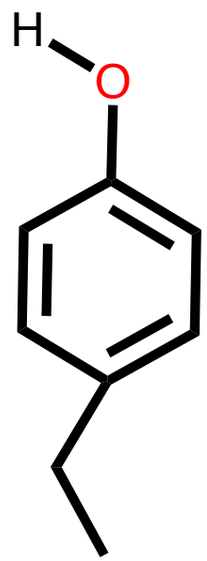


Guanine



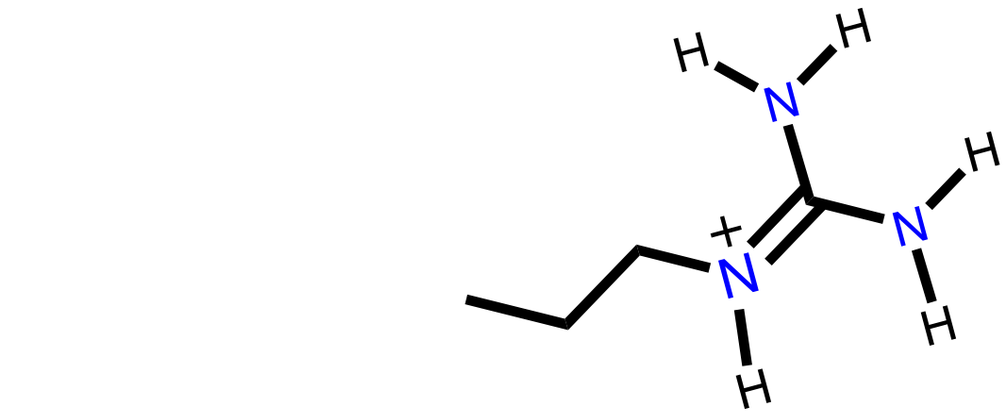
Cytosine

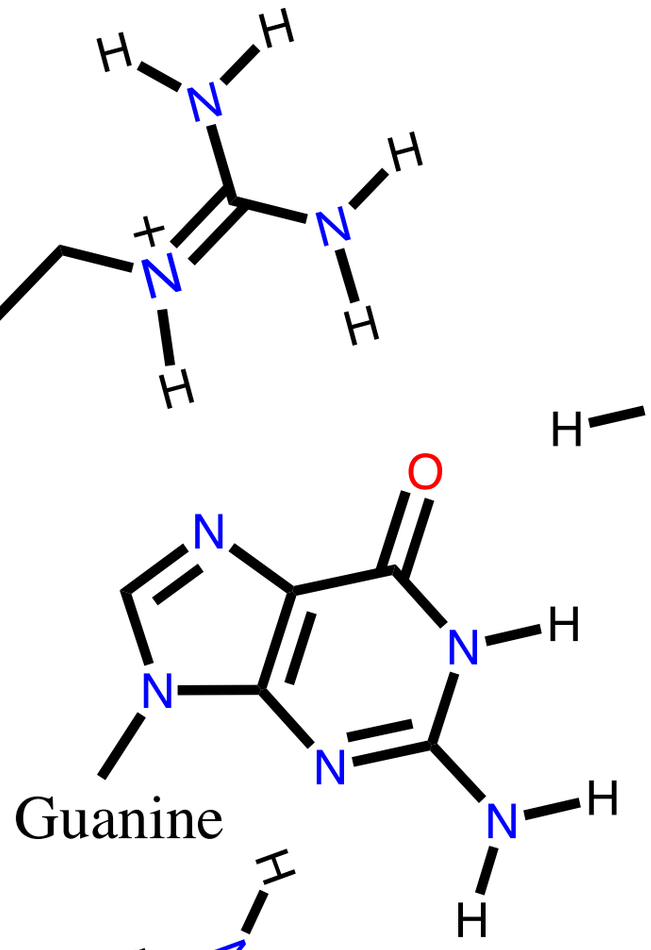




Sequence-specific binding by proteins

Find “two-fer” interactions





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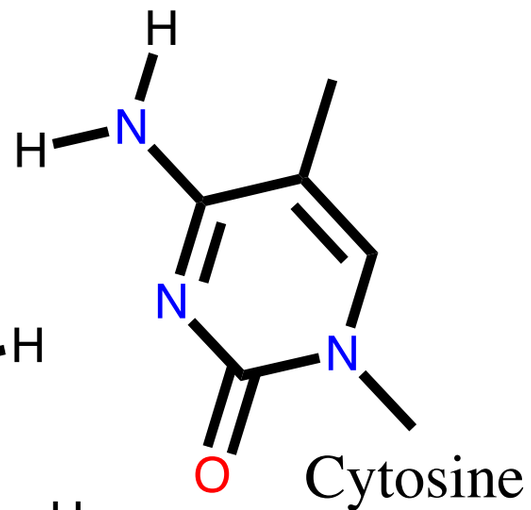

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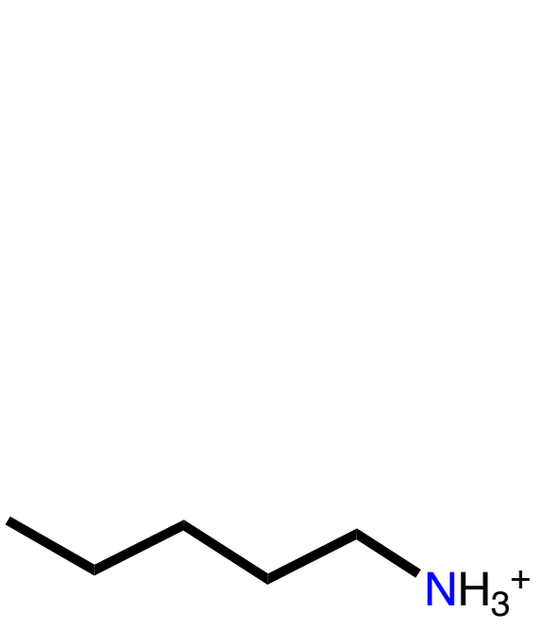
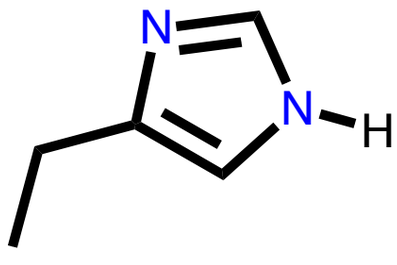
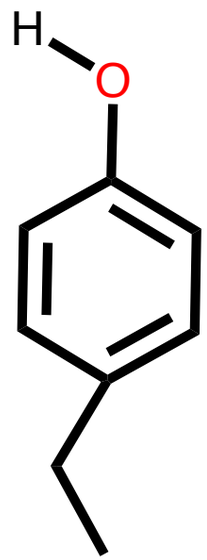


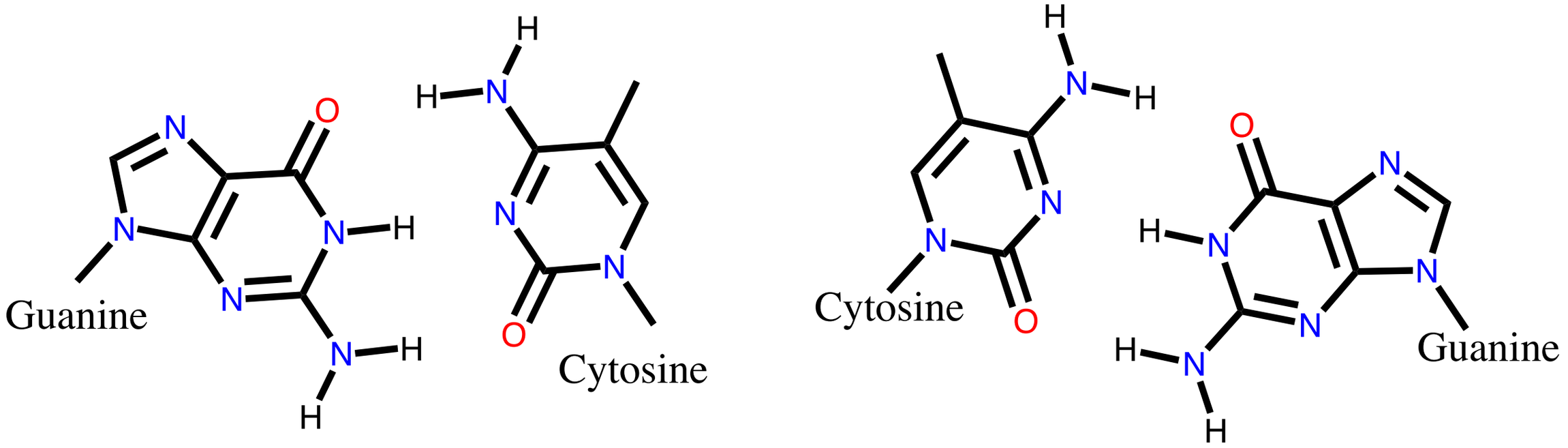


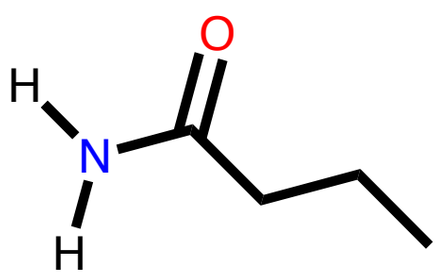


See an example

Sequence-specific binding by proteins

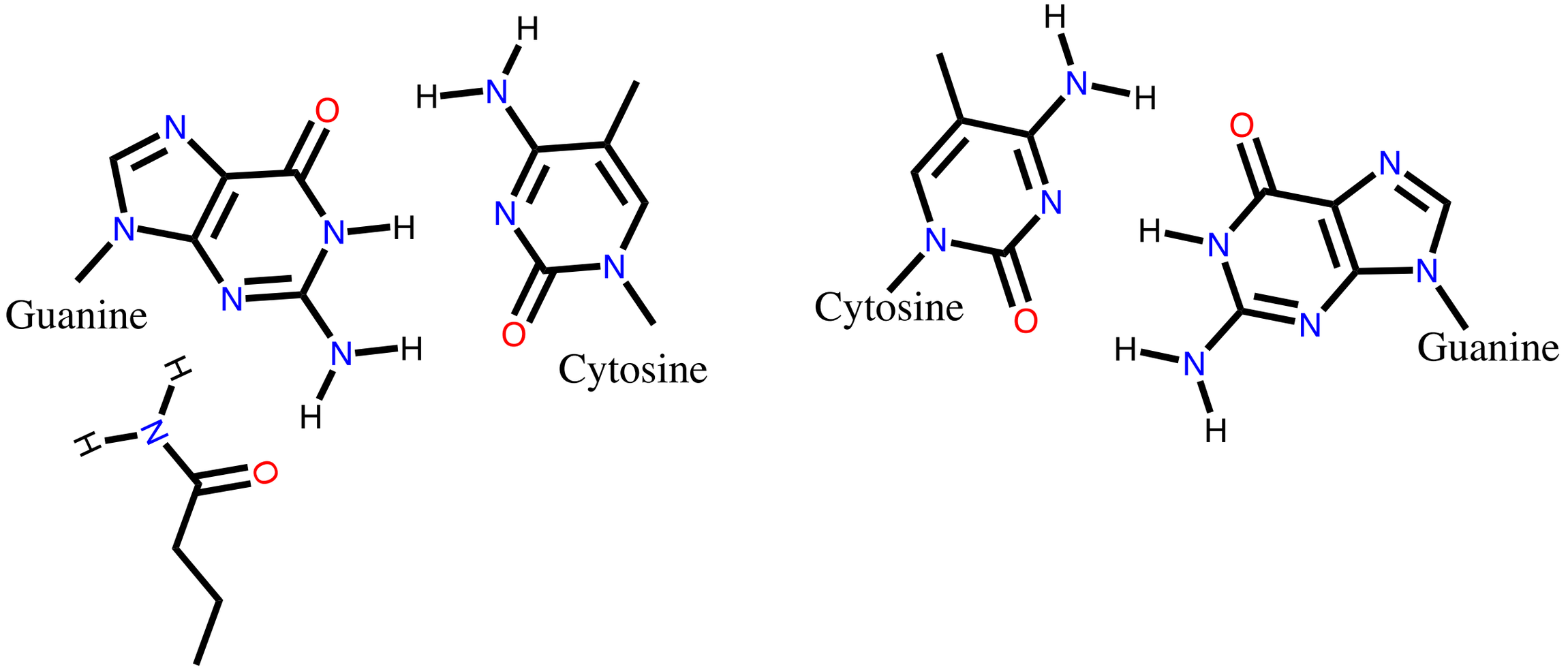
Major groove is better





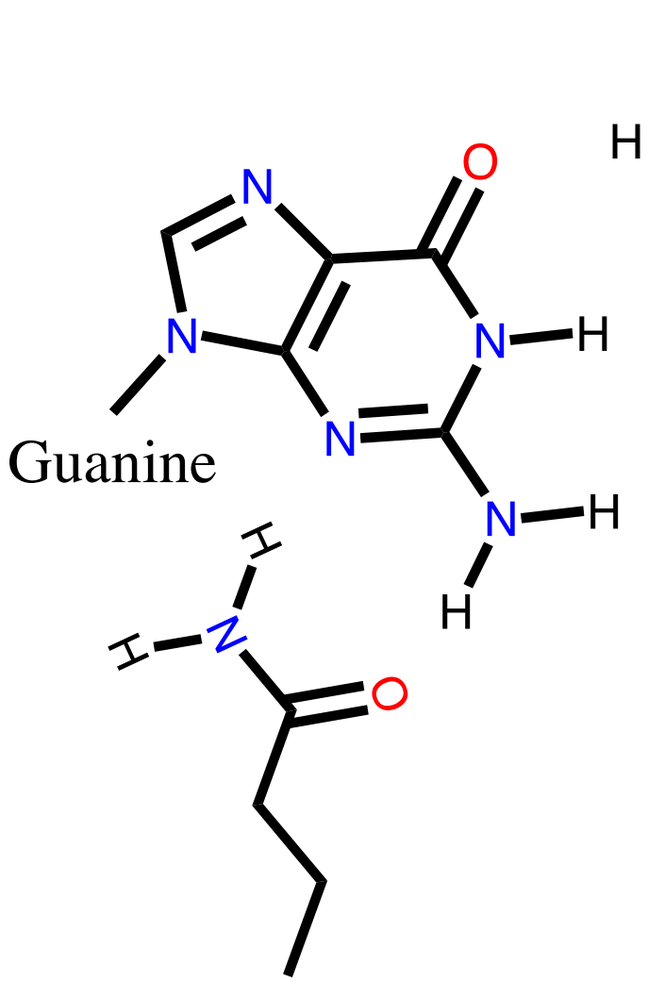
Sequence-specific binding by proteins

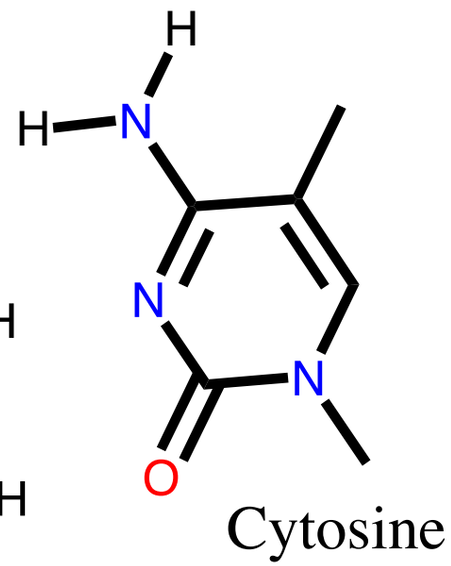
Major groove is better

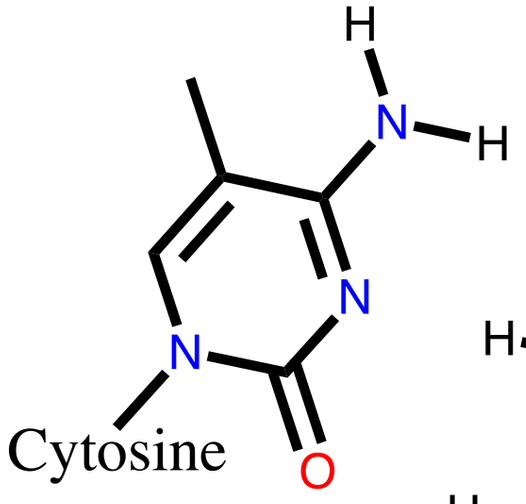


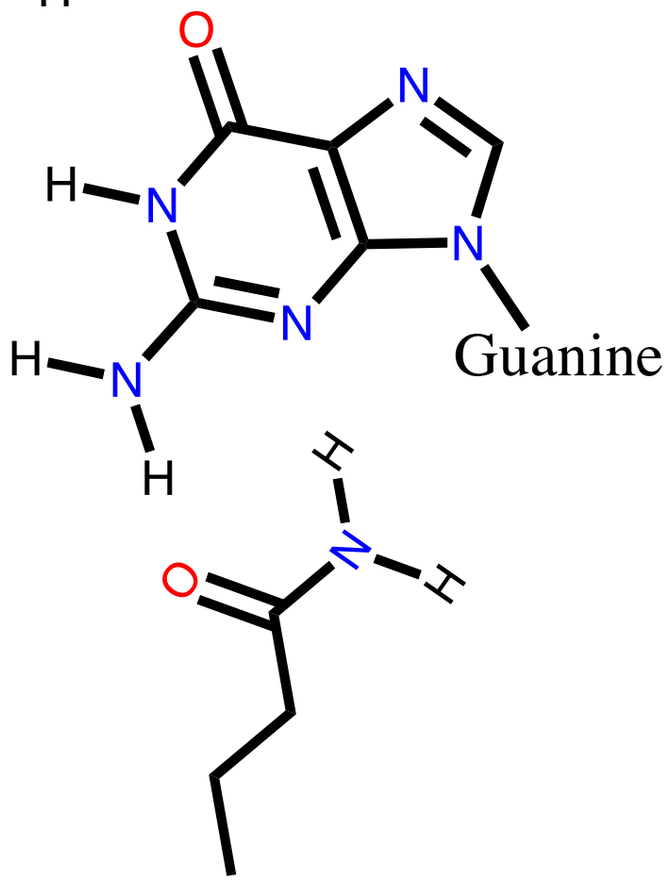
Sequence-specific binding by proteins

Major groove is better



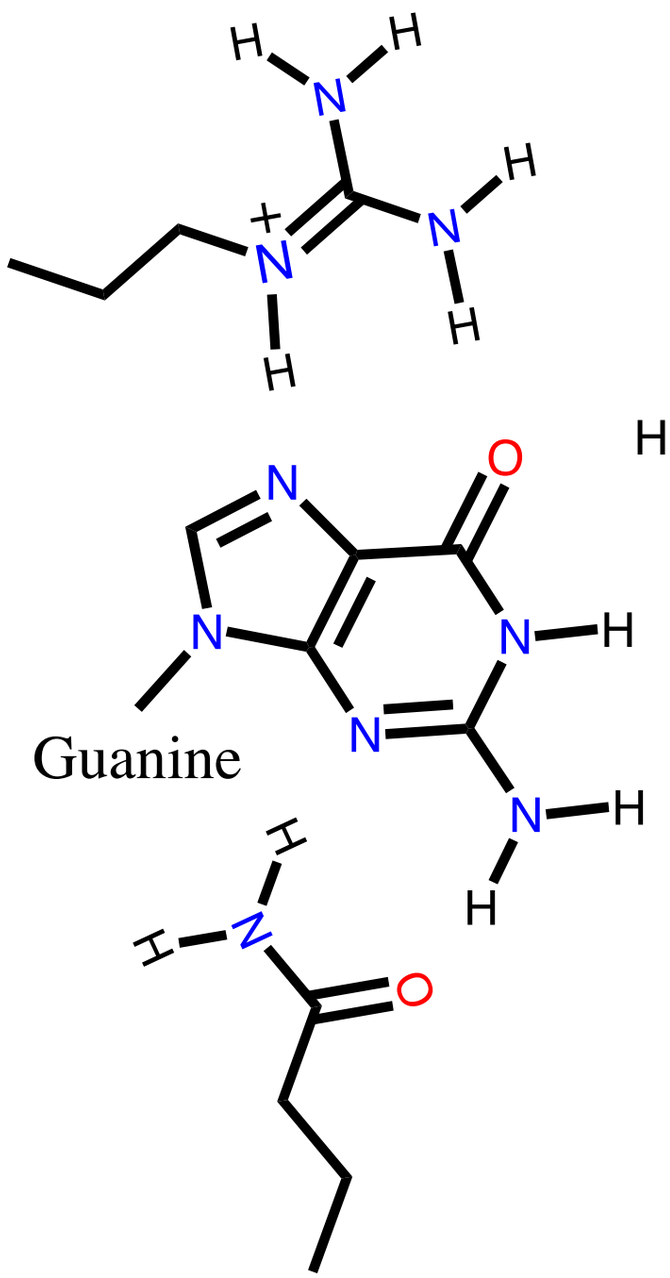




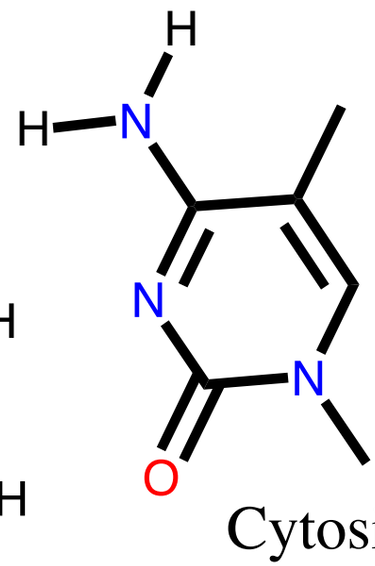


Sequence-specific binding by proteins

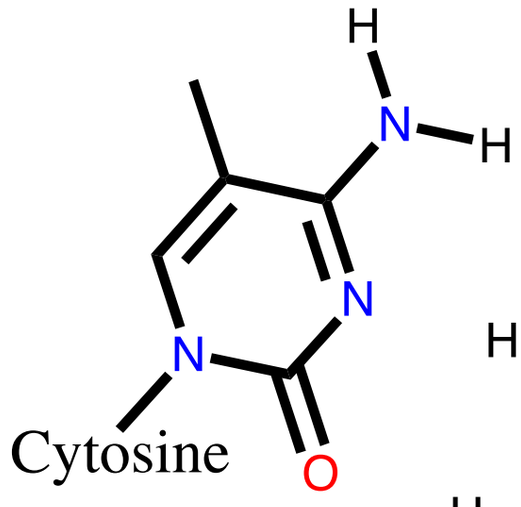
Major groove is better



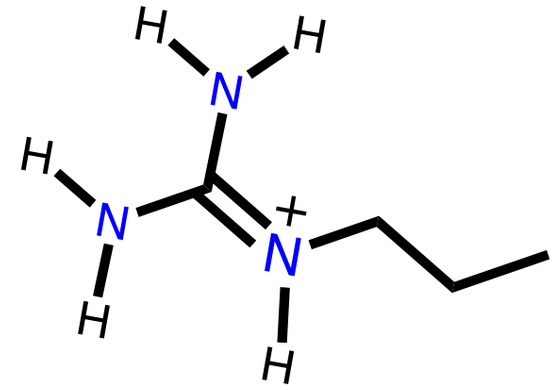
Guanine

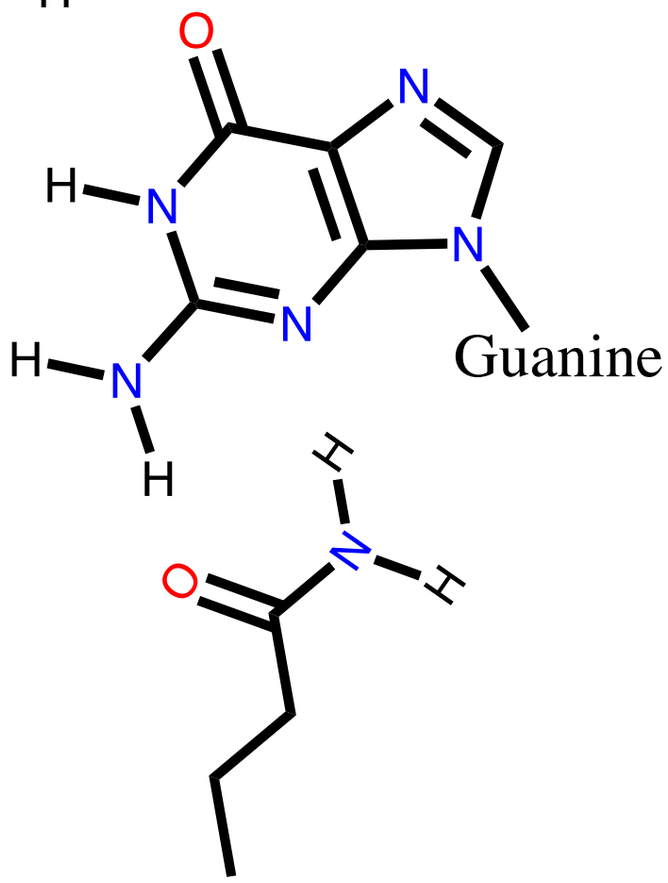


Cytosine



Cytosine

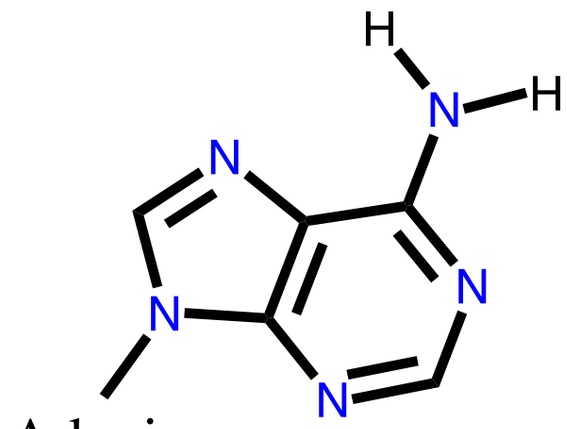




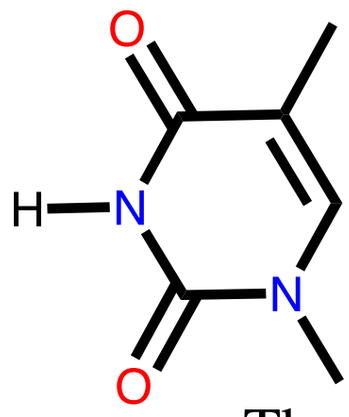
Guanine

Sequence-specific binding by proteins

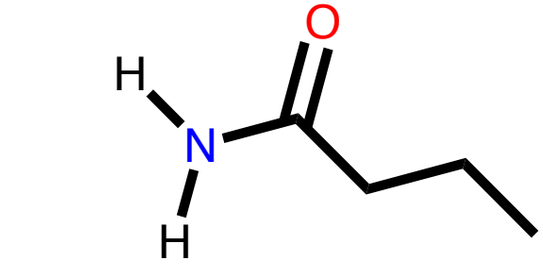
Find “two-fer” interactions

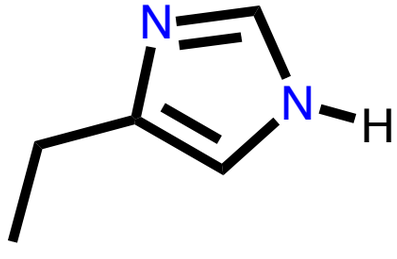


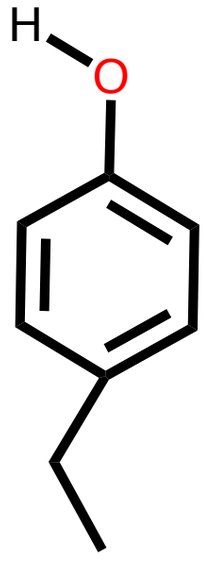
Adenine



Thymine

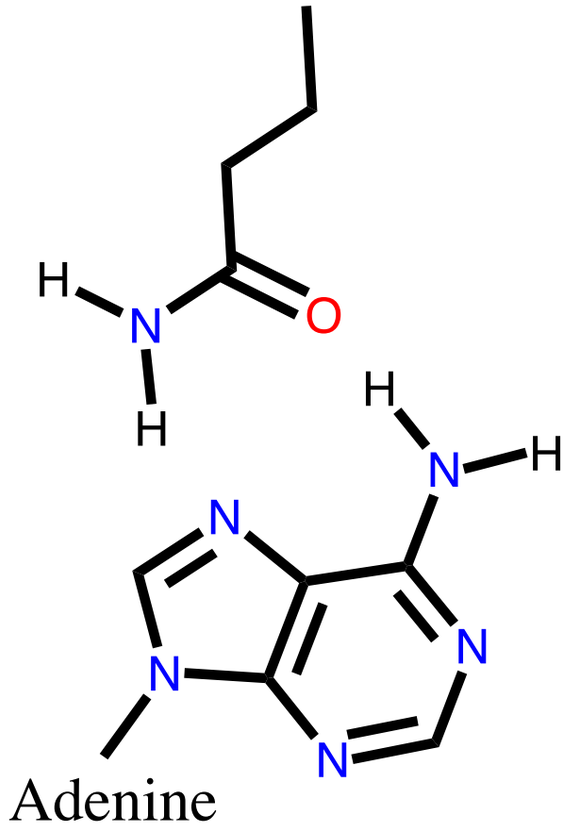






Sequence-specific binding by proteins

Find “two-fer” interactions



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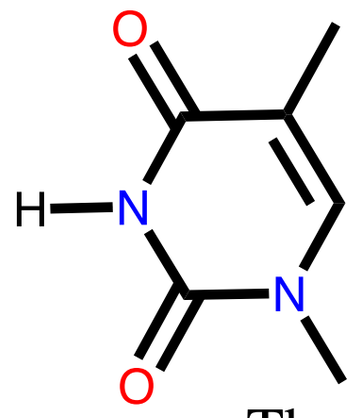
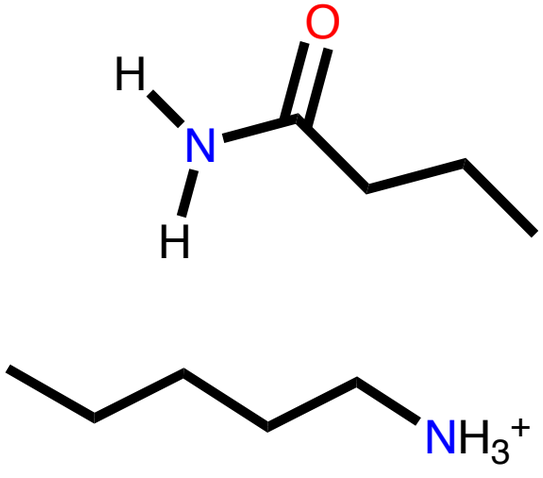
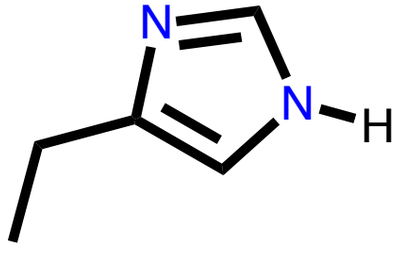
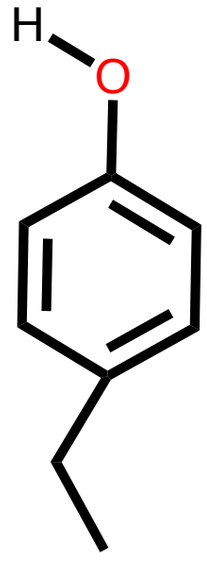


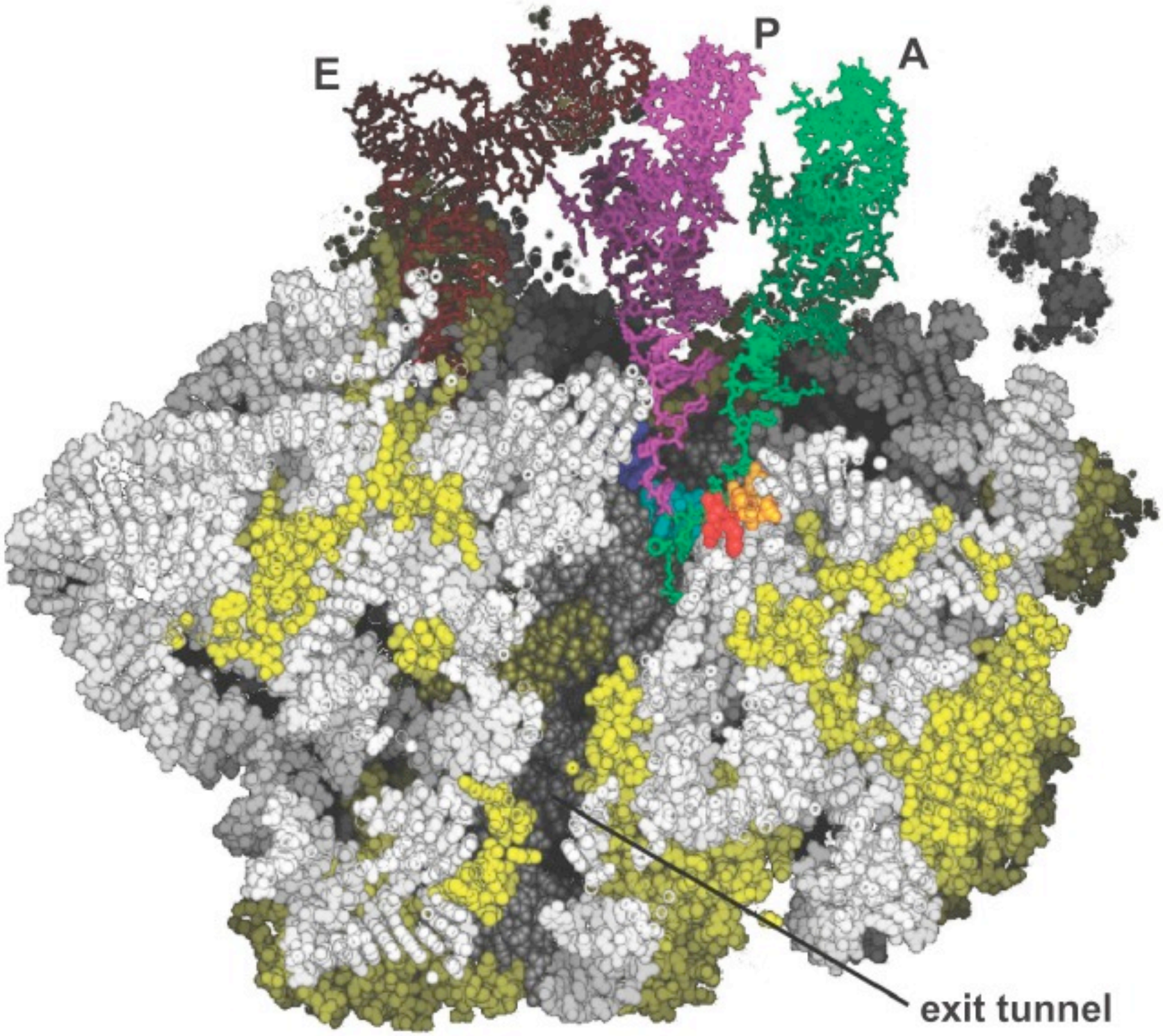
Thymine







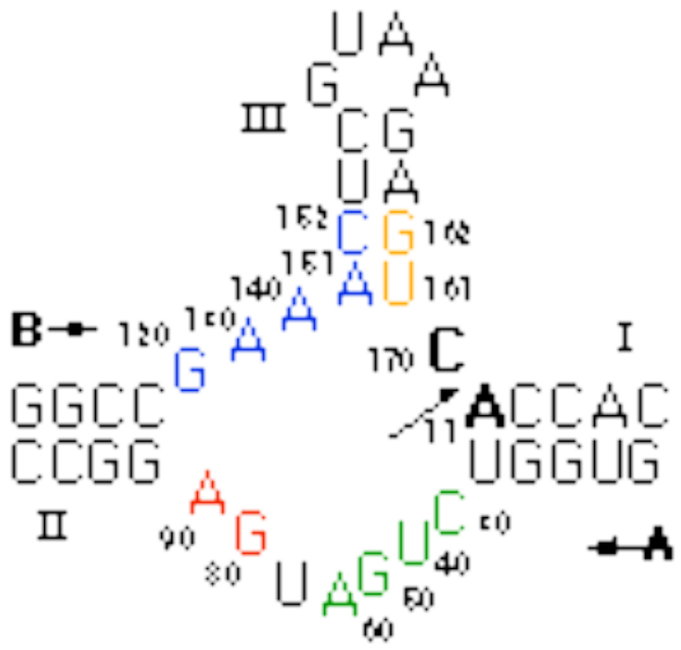
Ribosome



RNA structures are diverse!!

More in 3D

- “Hammerhead” ribozyme



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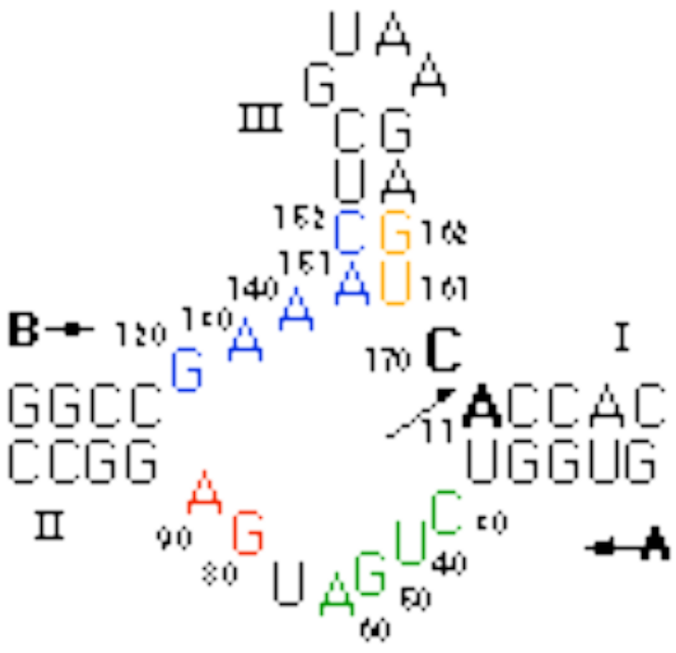
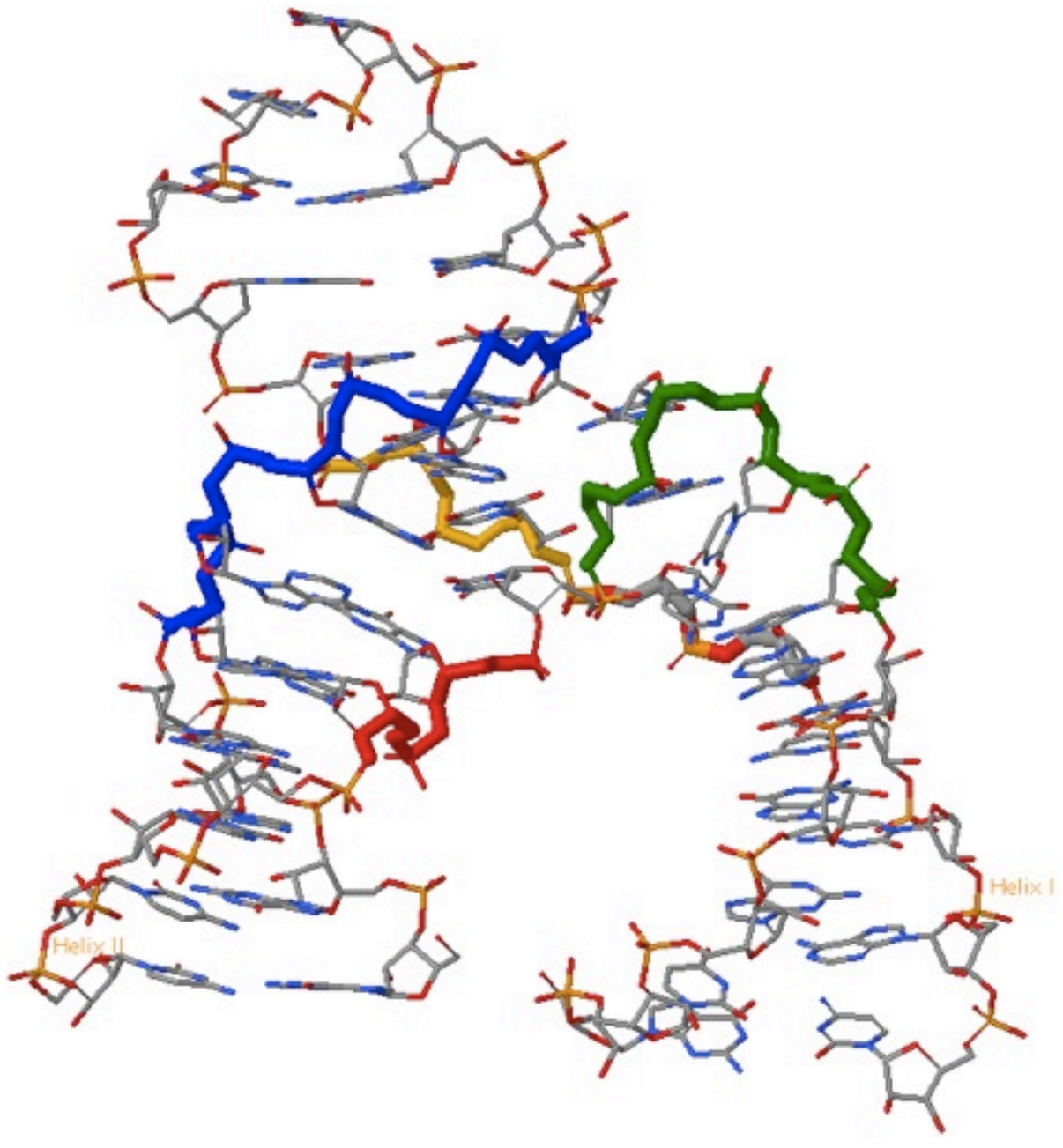
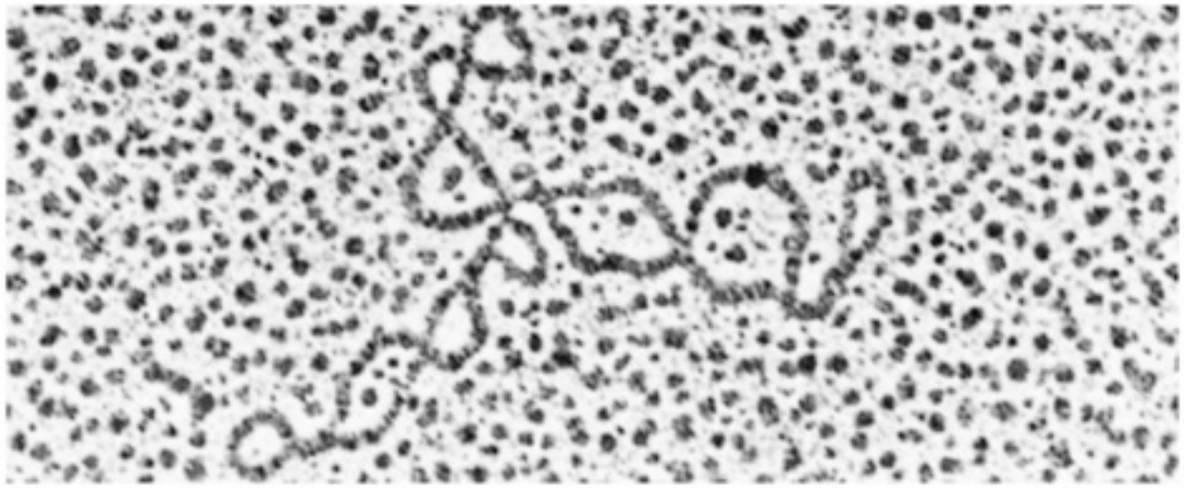
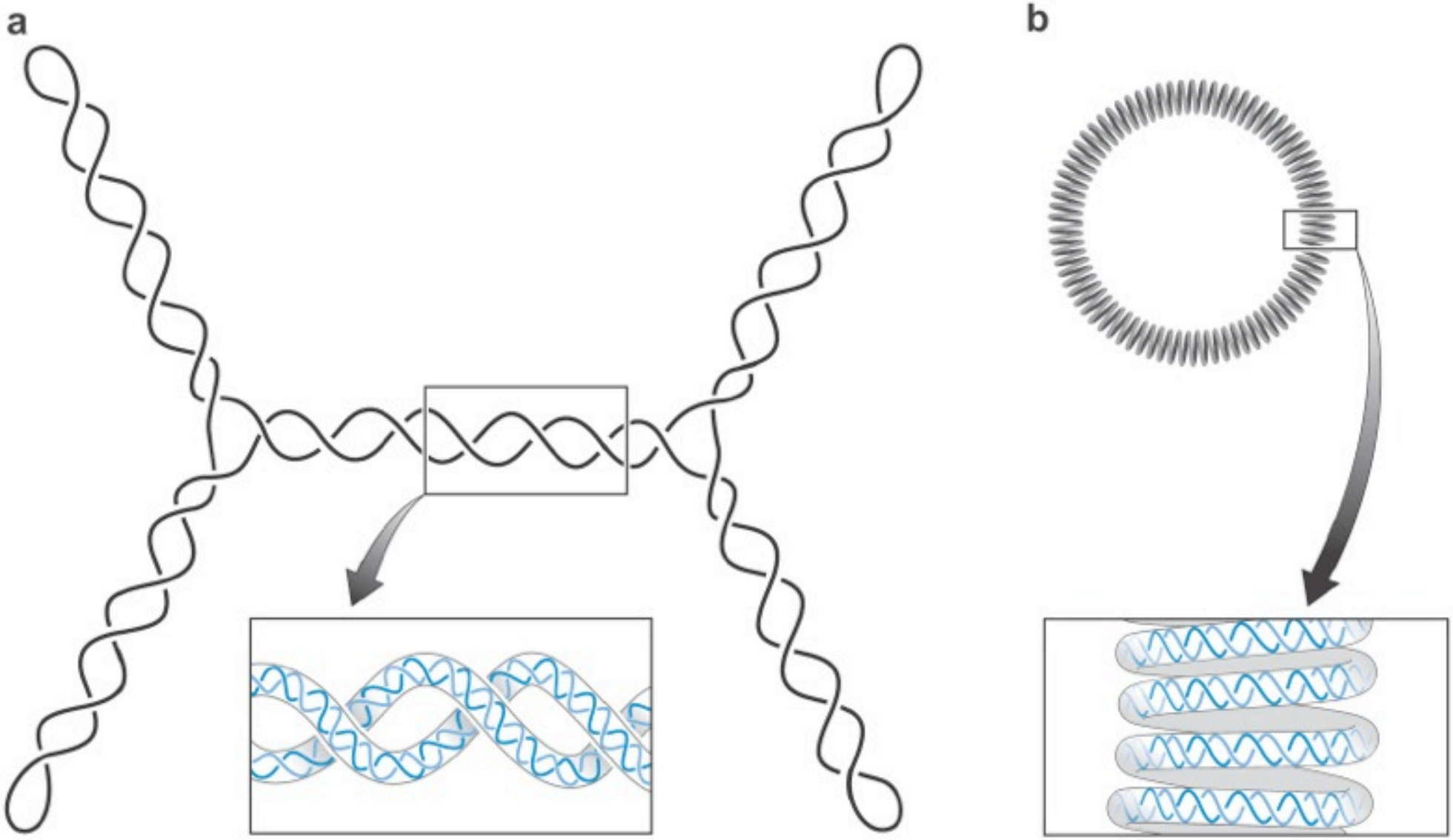


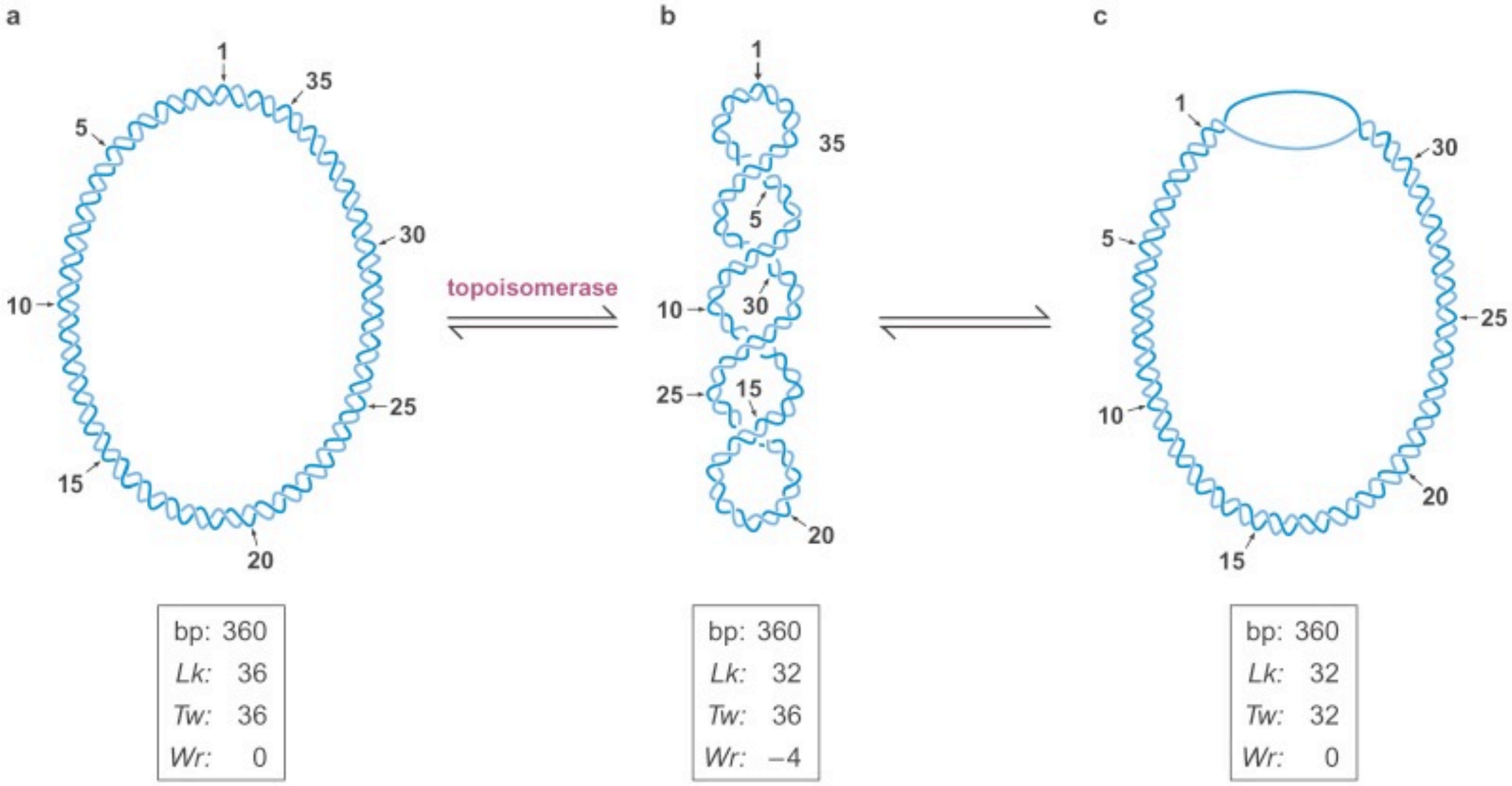


Supercoiling





Supercoiling



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