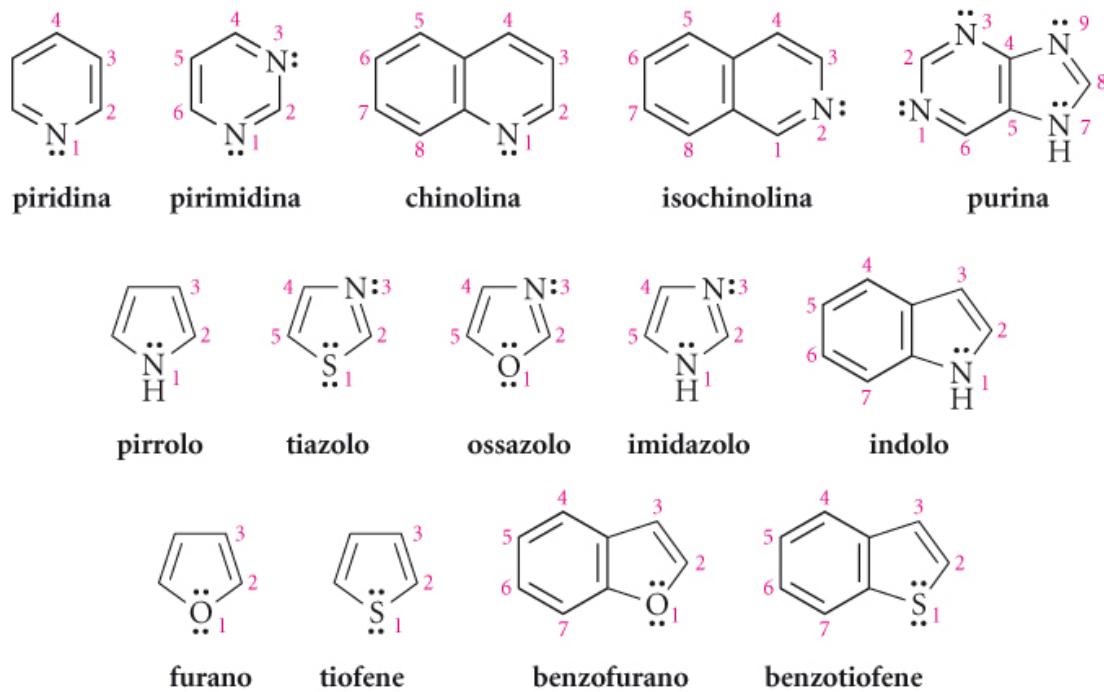
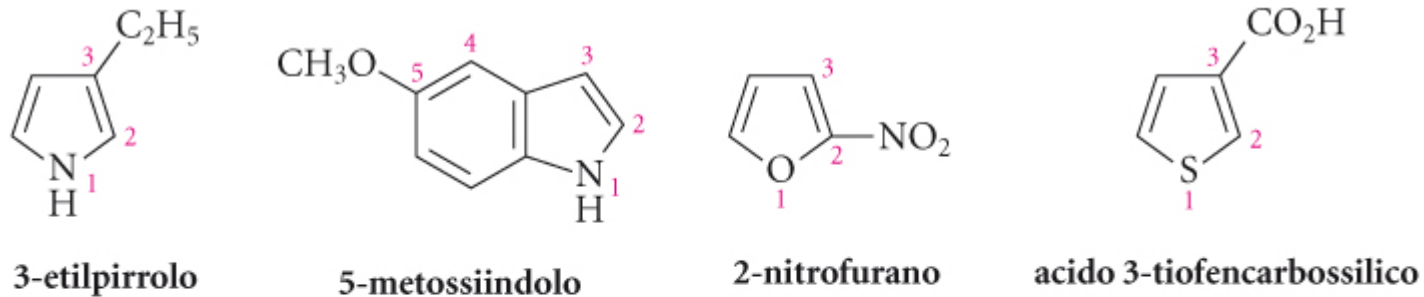


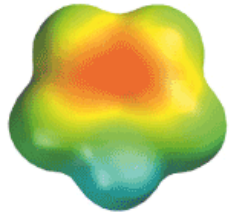
# ETEROCICLI AROMATICI = definizione?



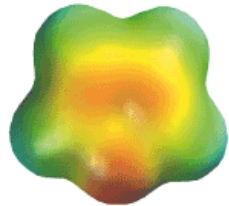
**Figura 25.1** Alcuni importanti composti eterociclici aromatici. I numeri (*in rosso*) sono utilizzati nella nomenclatura dei composti sostituiti.



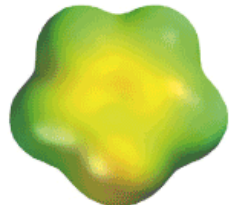
# PIRROLO, FURANO e TIOFENE



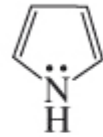
pirrolo



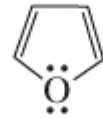
furano



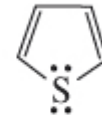
tiofene



pirrolo

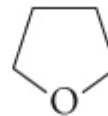


furano

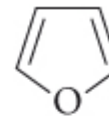


tiofene

## FURANO



tetraidrofurano



furano

momento dipolare:

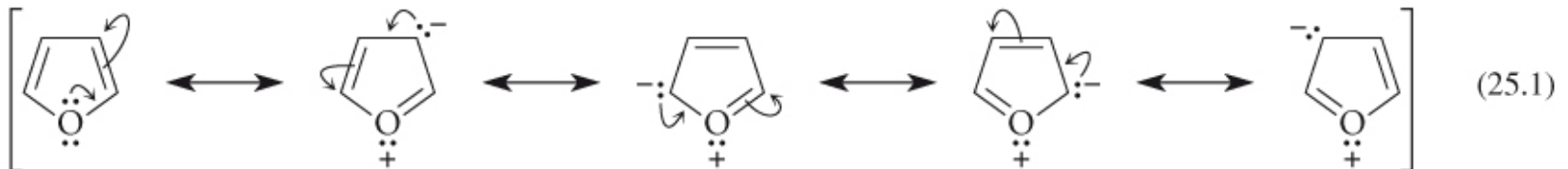
1.7 D

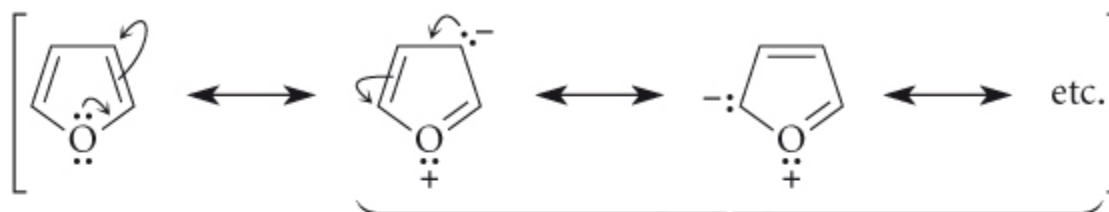
0.7 D

punto di ebollizione:

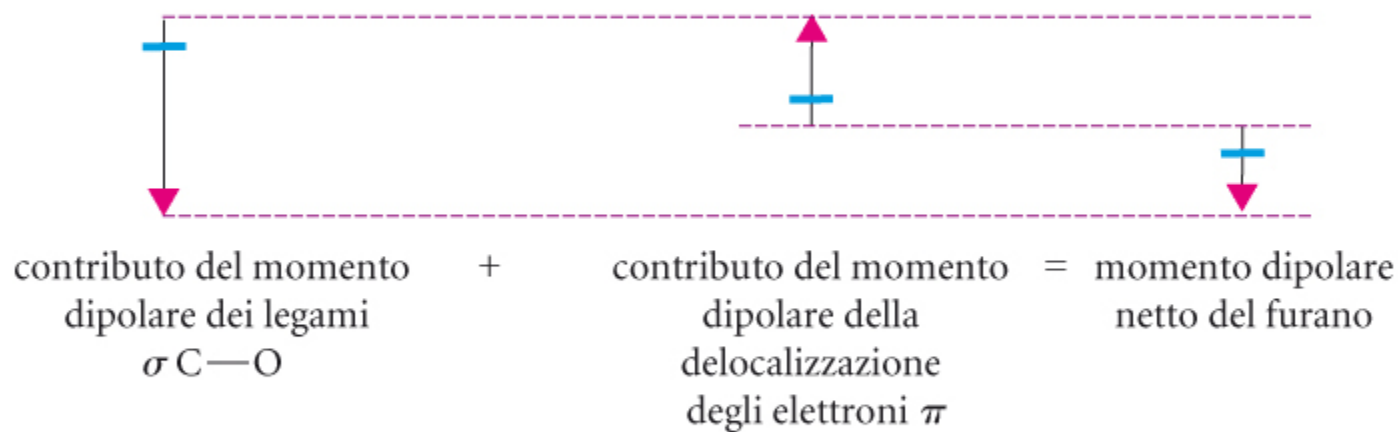
67°C

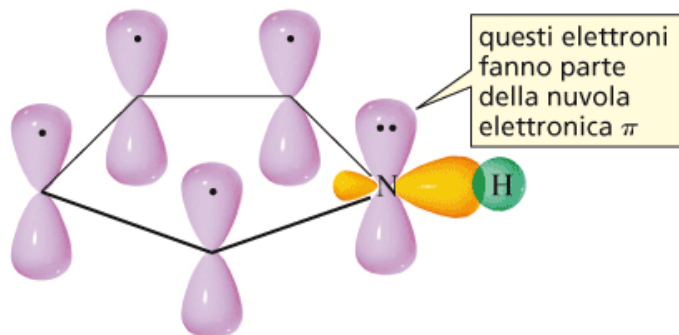
31.4°C



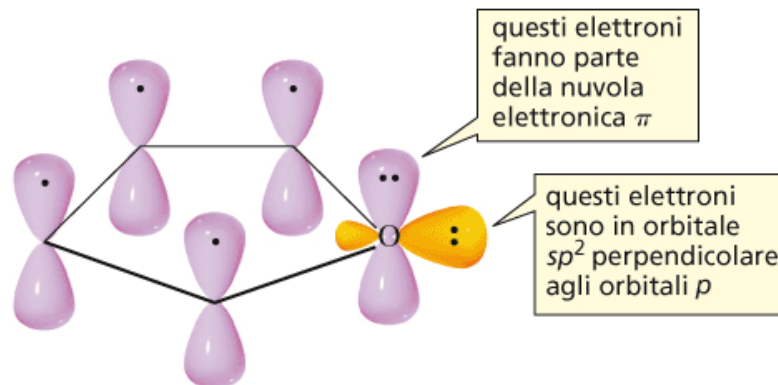


(25.2)





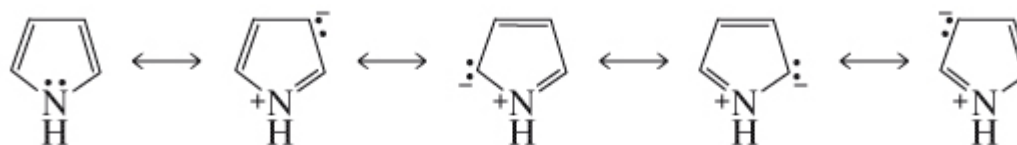
struttura orbitalica del pirrolo



struttura orbitalica del furano



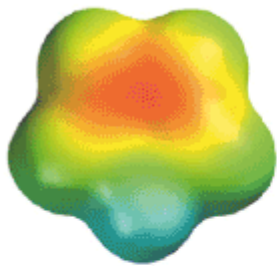
## PIRROLO



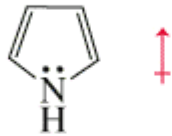
strutture limite di risonanza del pirrolo



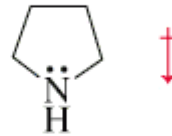
ibrido di risonanza



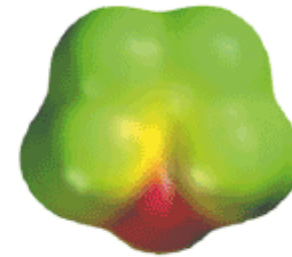
pirrolo



$$\mu = 1.80 \text{ D}$$

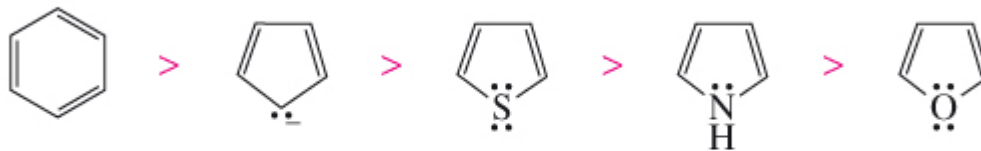


$$\mu = 1.57 \text{ D}$$



pirrolidina

energie relative di delocalizzazione di alcuni composti aromatici



Elettronegatività eteroatomo

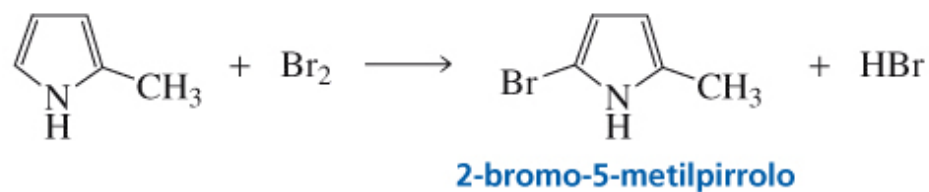
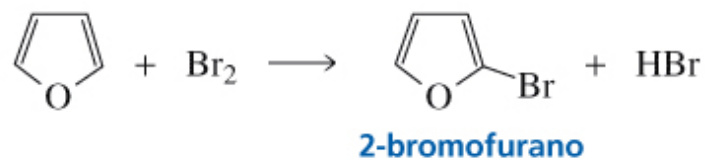


Aromaticità

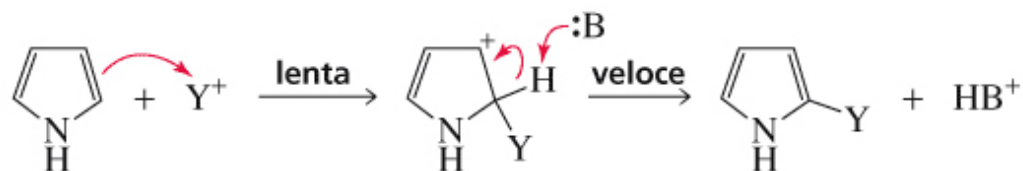
**TABELLA 25.1** Energie empiriche di risonanza di alcuni composti aromatici

| Composto | Energia di risonanza |                        | Composto | Energia di risonanza |                        |
|----------|----------------------|------------------------|----------|----------------------|------------------------|
|          | $\text{kJ mol}^{-1}$ | $\text{kcal mol}^{-1}$ |          | $\text{kJ mol}^{-1}$ | $\text{kcal mol}^{-1}$ |
| benzene  | 138–151              | 33–36                  | tiofene  | 121                  | 29                     |
| piridina | 96–117               | 23–28                  | pirrolo  | 89–92                | 21–22                  |
|          |                      |                        | furano   | 67                   | 16                     |



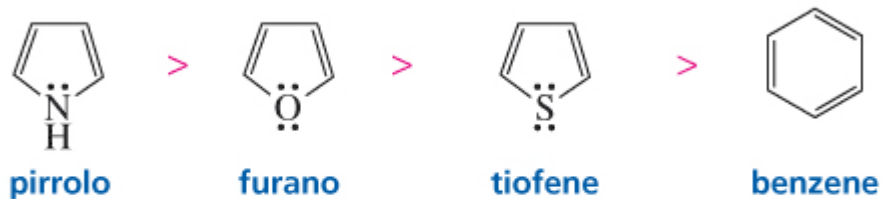


### MECCANISMO DELLA SOSTITUZIONE ELETTROFILA AROMATICA



! Sostituzione in 2 è privilegiata!

# ORDINE di REATTIVITA' nei confronti della S.E.A.



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N dona più volentieri gli elettroni del doppietto

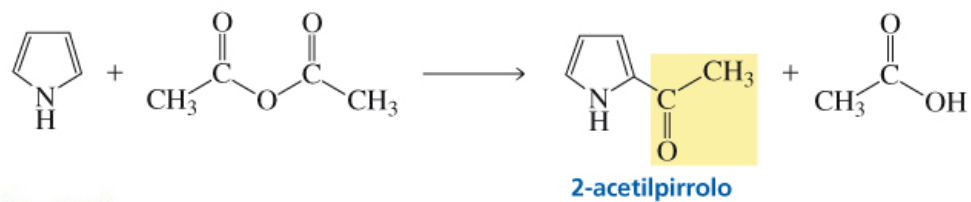
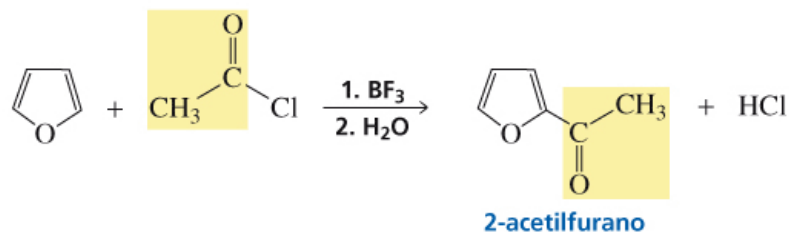
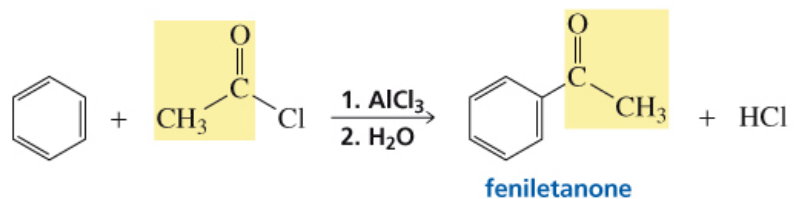
S dona peggio gli elettroni del doppietto: scarso overlap orbitalico 3p-2p

Per l'aromaticità è determinante la stabilità del catione sull'eteroatomo

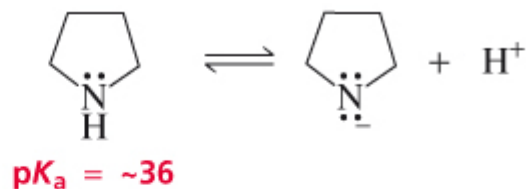
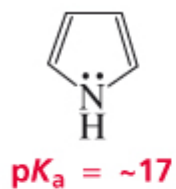
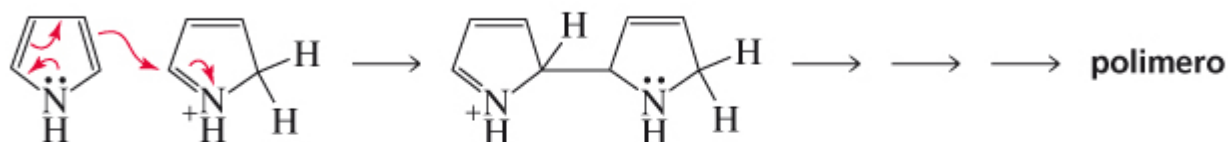
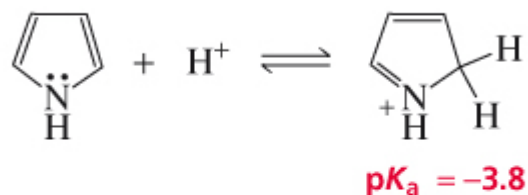
Per il dipolo elettrico è determinante l'entità dell'effetto +M (mesomerico)



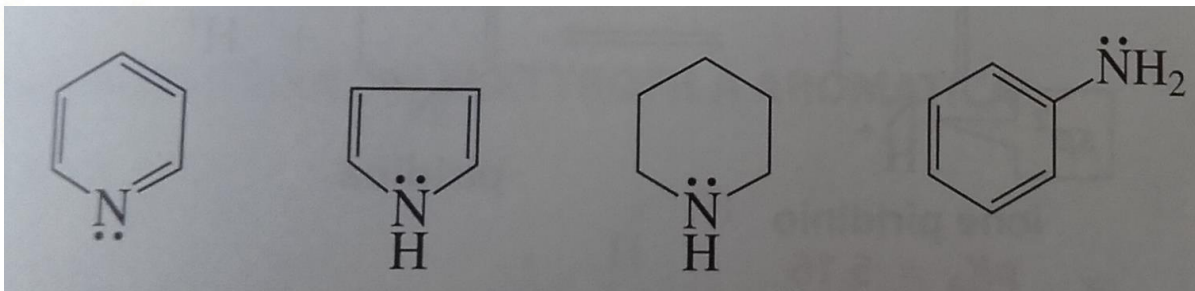
## N.B. Catalizzatore acido di Lewis



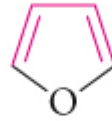
# PROPRIETA' ACIDO-BASE



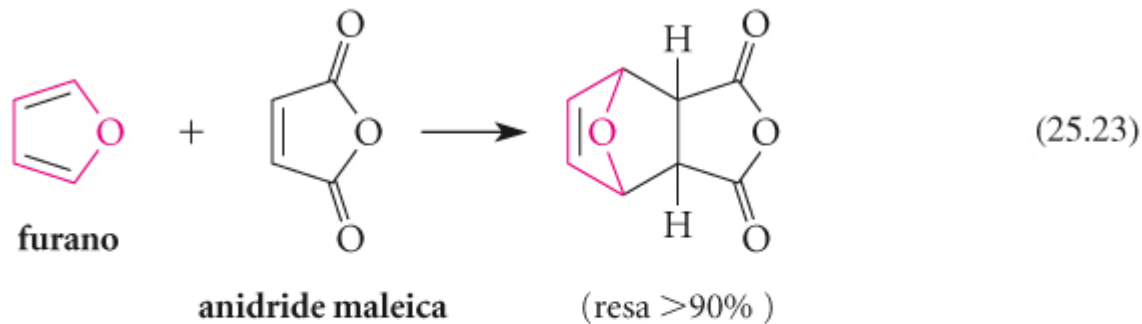
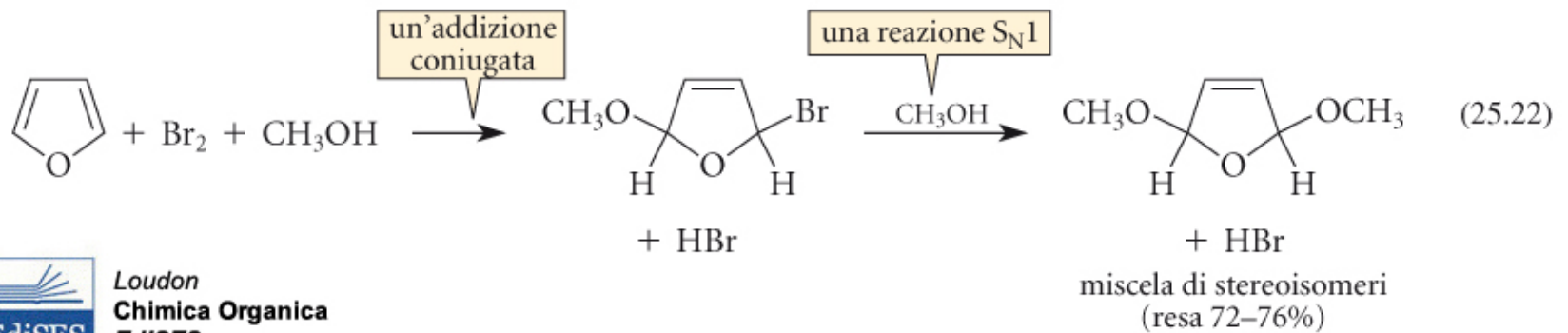
Esercizio: mettere in ordine di basicità crescente:



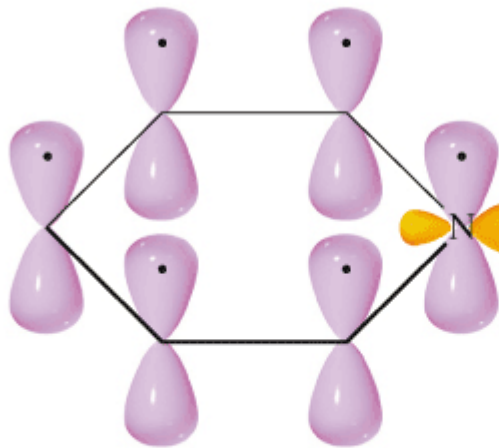
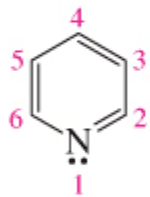
# REATTIVITA' da DIENE CONIUGATO



unità "butadienica" all'interno del furano

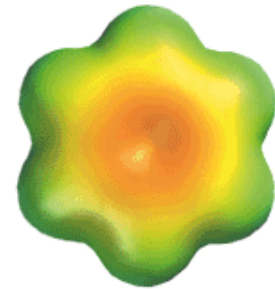


# PIRIDINA

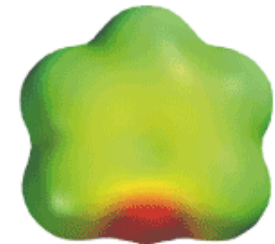


struttura orbitale della piridina

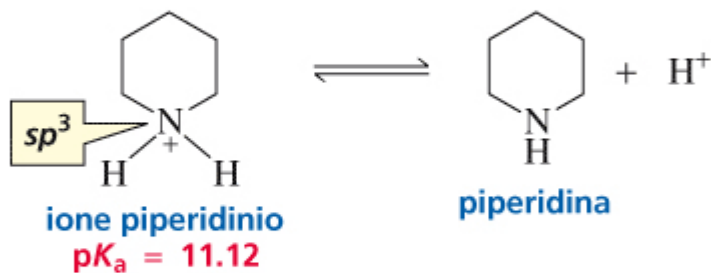
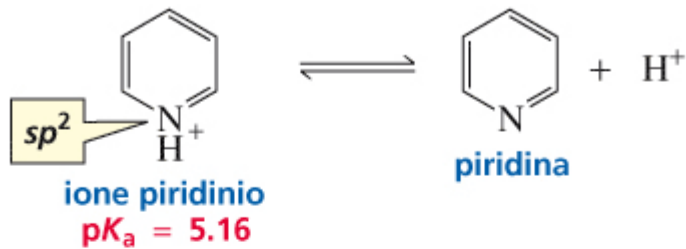
questi elettroni sono in un orbitale  $sp^2$  perpendicolare agli orbitali  $p$

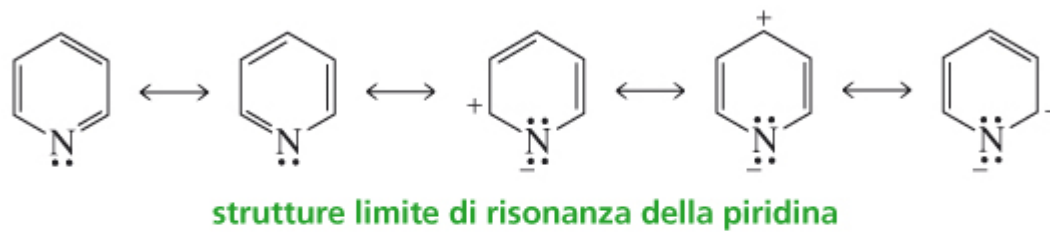
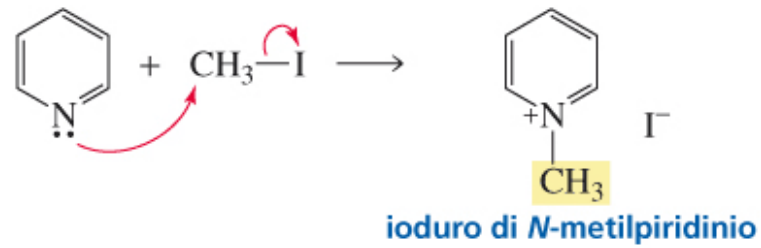
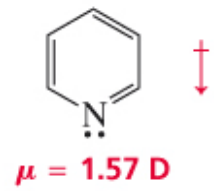


benzene

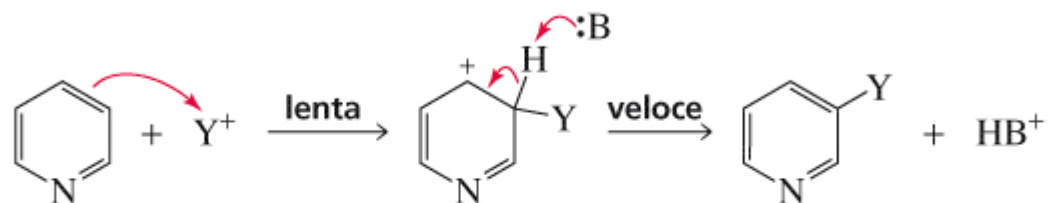


piridina



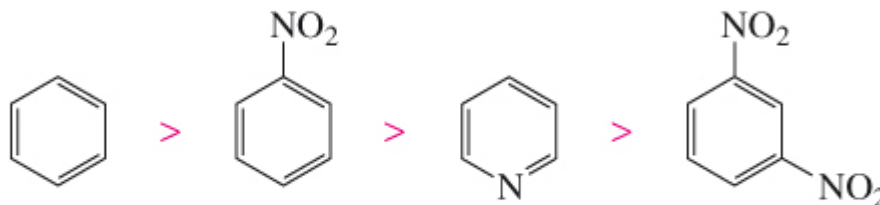


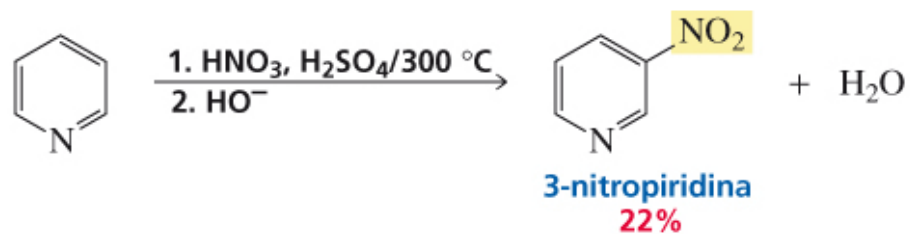
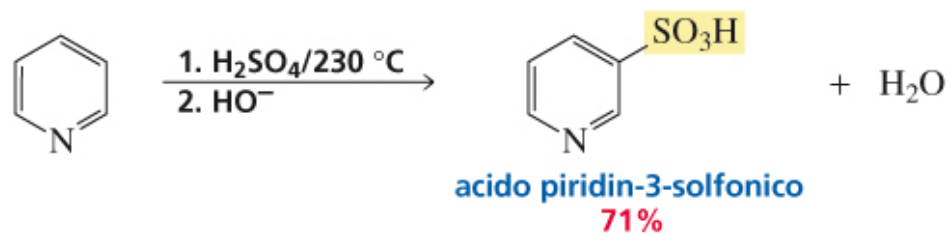
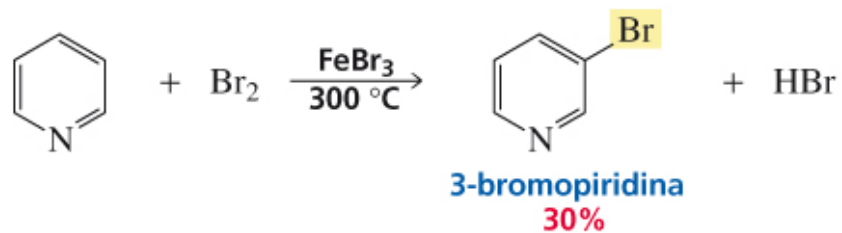
## MECCANISMO DELLA SOSTITUZIONE ELETTROFILA AROMATICA



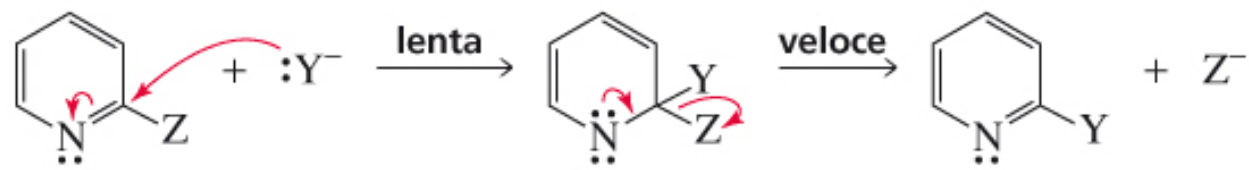
**! PRIVILEGIATA la SOSTITUZIONE in 3 !**

reattività relative verso la sostituzione elettrofila aromatica

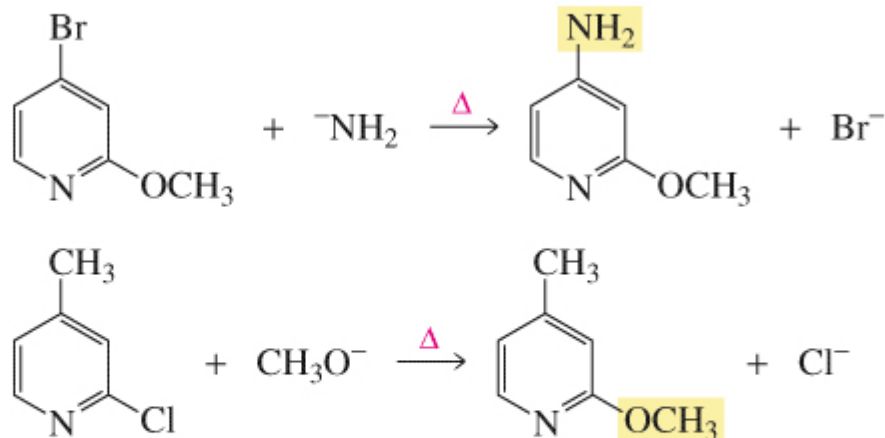




## MECCANISMO DELLA SOSTITUZIONE NUCLEOFILA AROMATICA

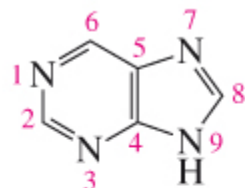


**! PRIVILEGIATA la SOSTITUZIONE in POSIZIONE 2 o 4!**

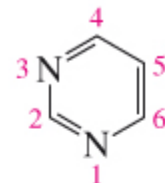




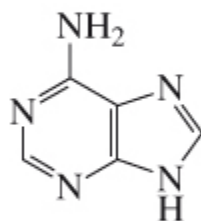
# AMMINE ETEROCICLICHE di IMPORTANZA BIOLOGICA



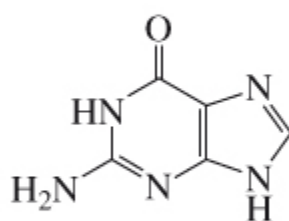
purina



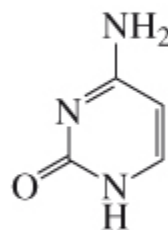
pirimidina



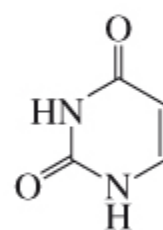
adenina



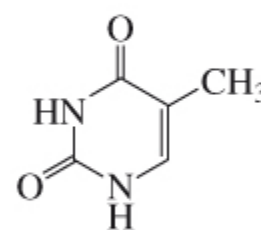
guanina



citosina



uracile

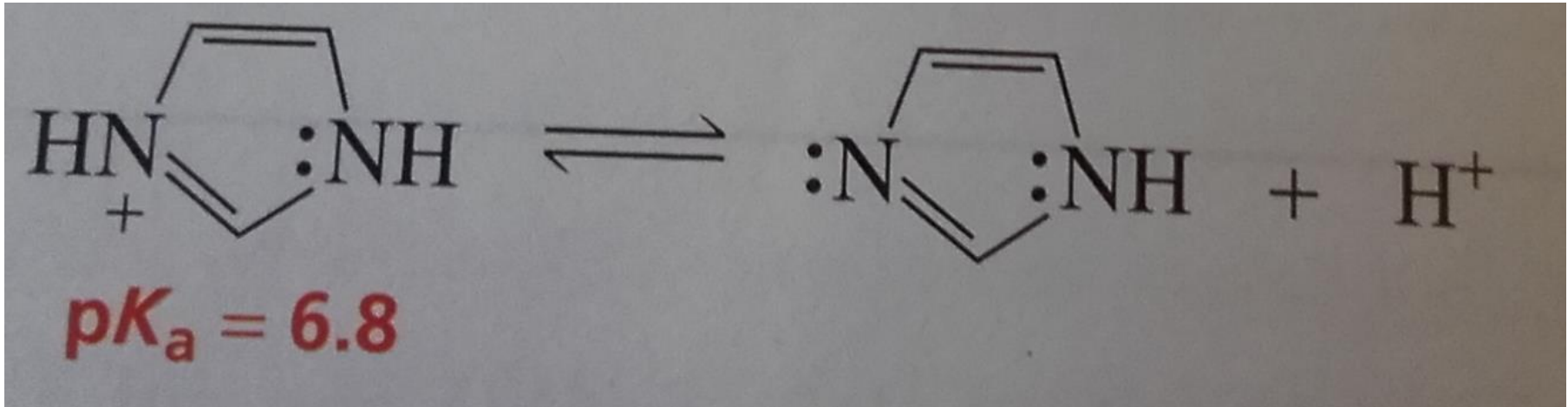


timina

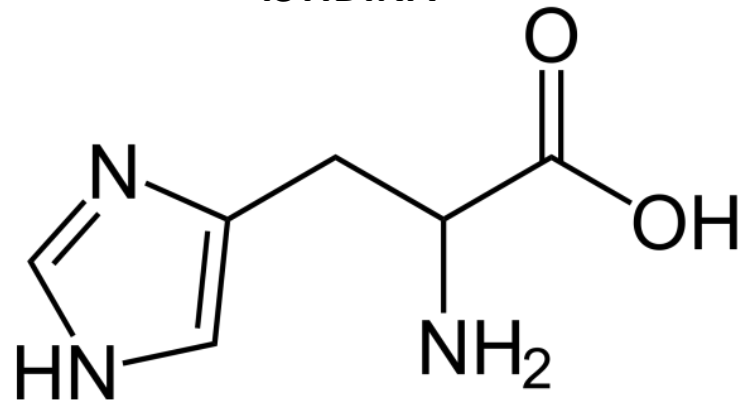


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EdiSES

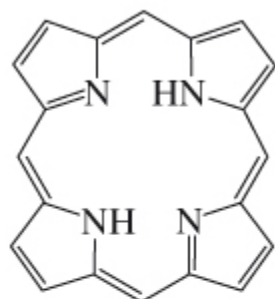
# IMIDAZOLO



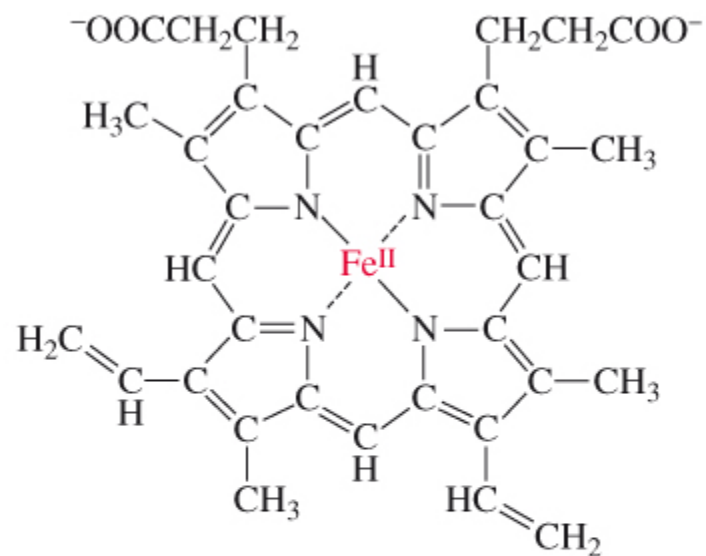
## ISTIDINA



ISTIDINA importante come catalizzatore acido-base: componente di molti enzimi

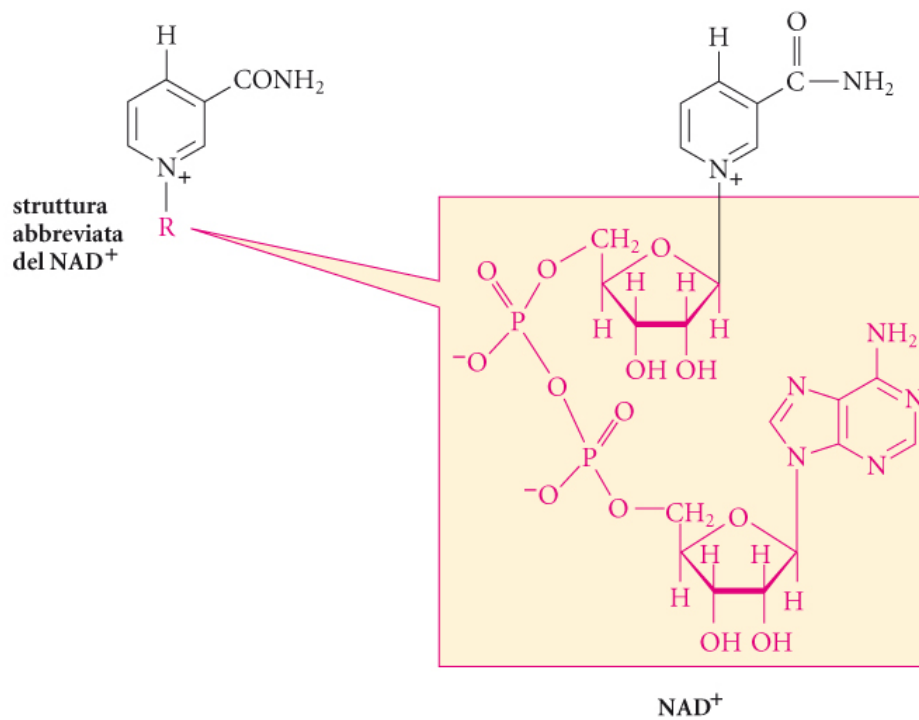


sistema ad anello porfirinico



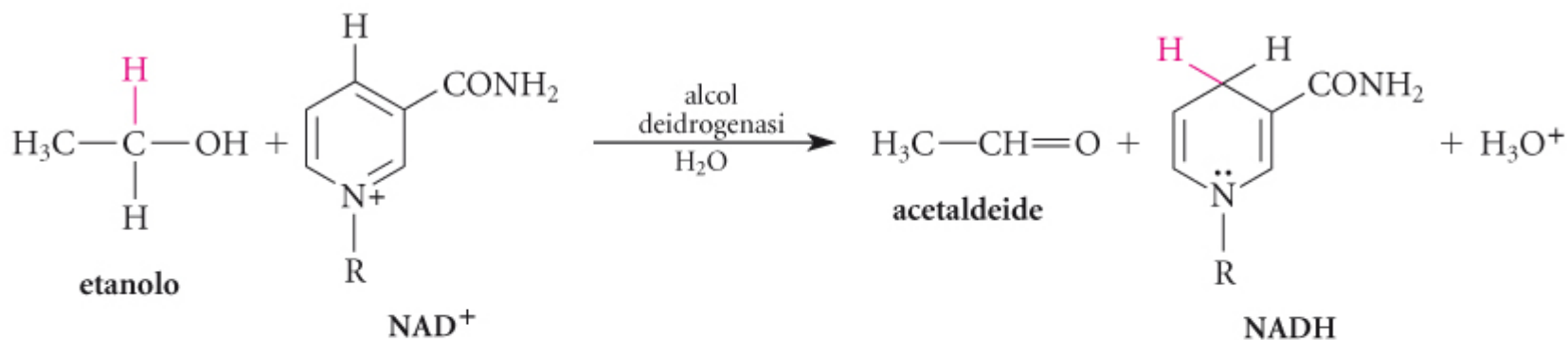
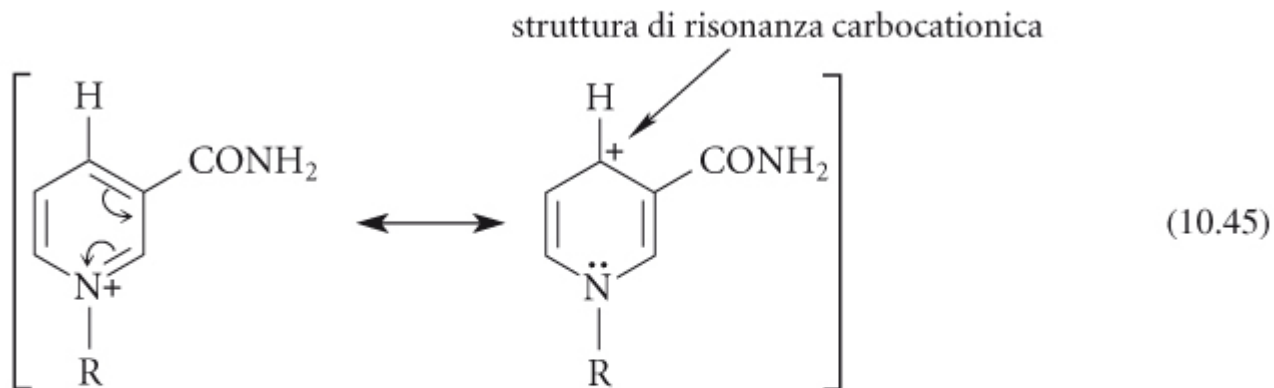
eme

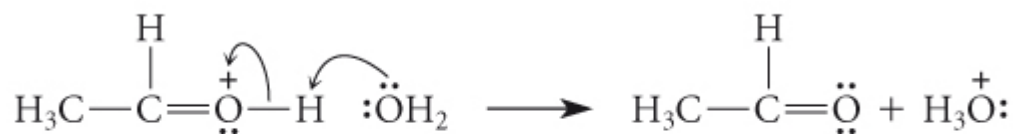
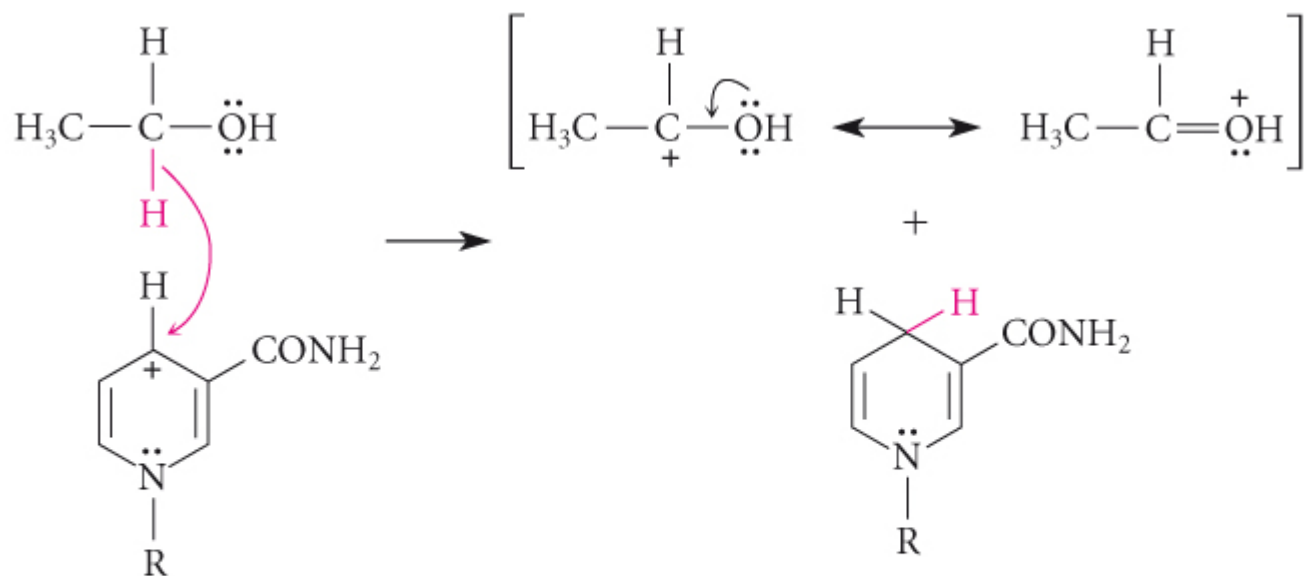
# IONE PIRIDINIO in BIOLOGIA: NICOTINAMMIDE ADENIN DINUCLEOTIDE (NAD<sup>+</sup>)



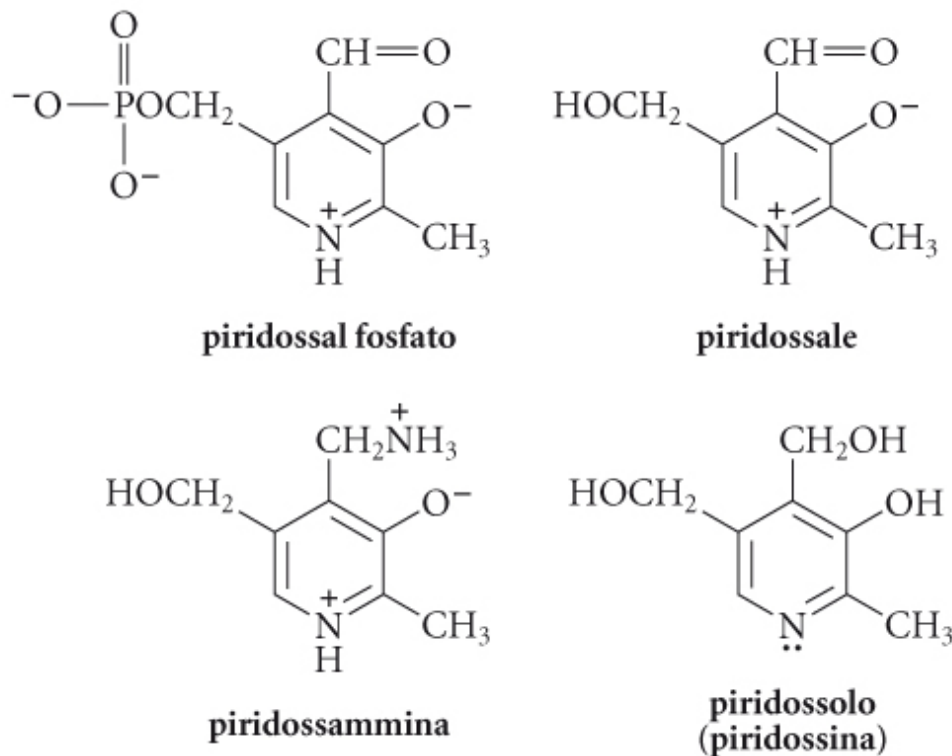
**Figura 10.1** Struttura completa e abbreviata del NAD<sup>+</sup>. La parte in colore della struttura completa è abbreviata come gruppo R.

# NAD<sup>+</sup> coenzima redox (ossidante) più comune in sistemi biologici

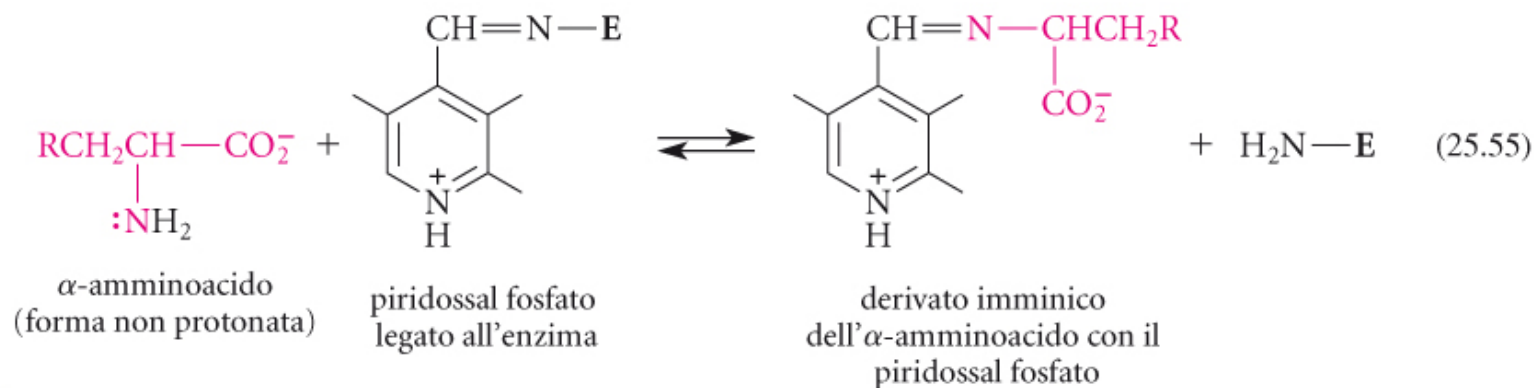
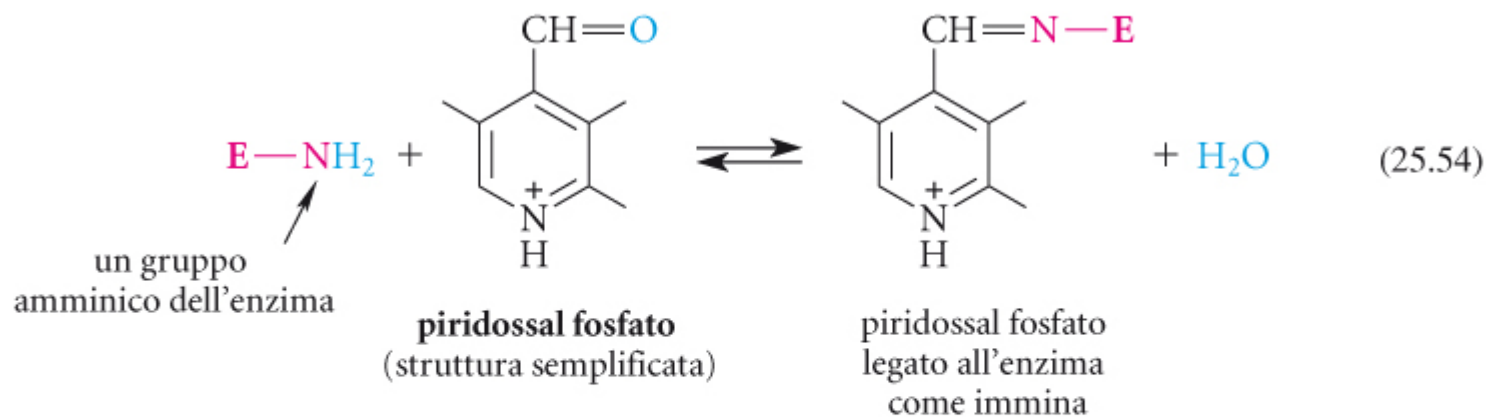




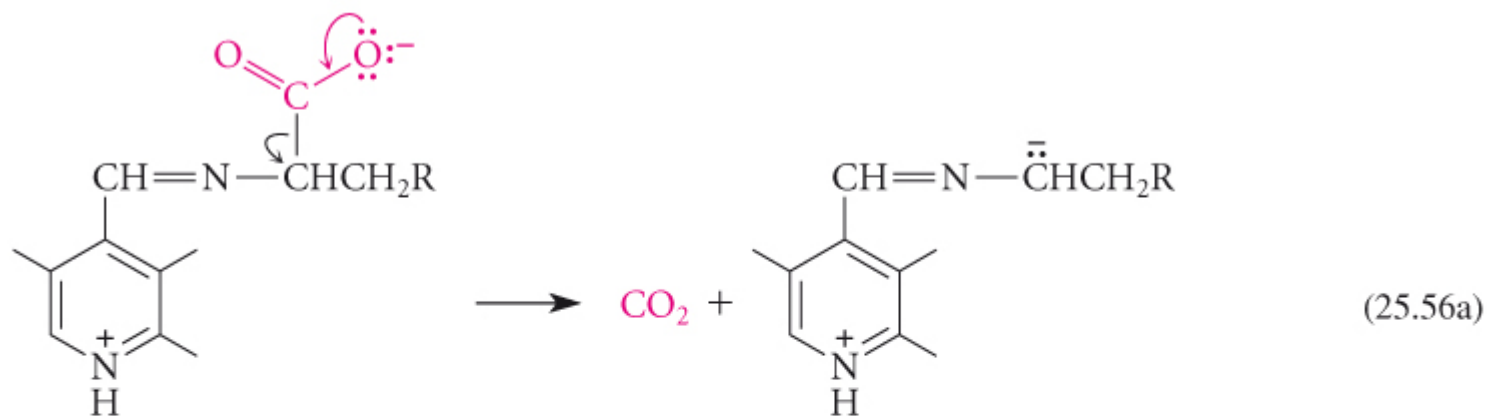
# PIRIDOSSAL FOSFATO (stabilizzatore di carbanioni)



**Figura 25.3** Le varie forme della vitamina B<sub>6</sub>. Il piridossolo è stata la prima forma a essere isolata, ma tutti i composti mostrati possono costituire una fonte della vitamina. (Per esempio, il piridossolo può essere ossidato e fosforilato a piridossal fosfato). Il piridossal fosfato è la forma della vitamina coinvolta in molte trasformazioni biochimiche; la piridossammina fosfato è un intermedio in alcune trasformazioni. Tutti i composti sono mostrati negli stati di ionizzazione prevalenti a pH 7.4 (pH fisiologico).

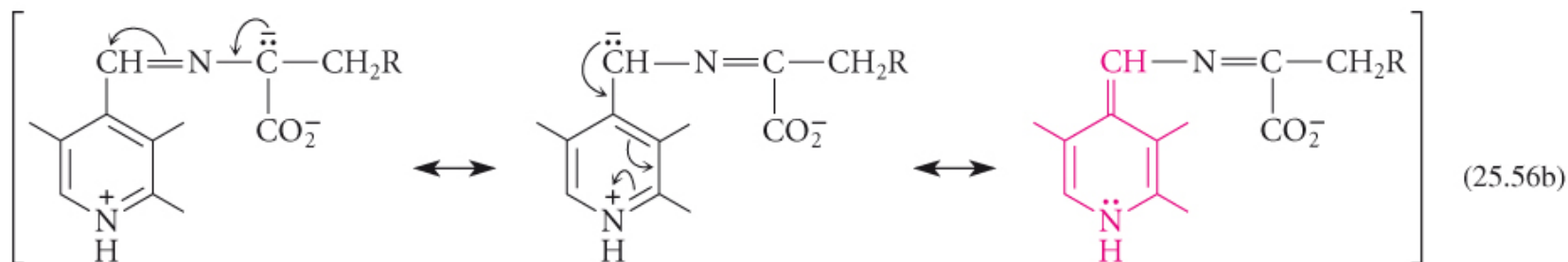






derivato imminico dell' $\alpha$ -amminoacido  
con il piridossal fosfato

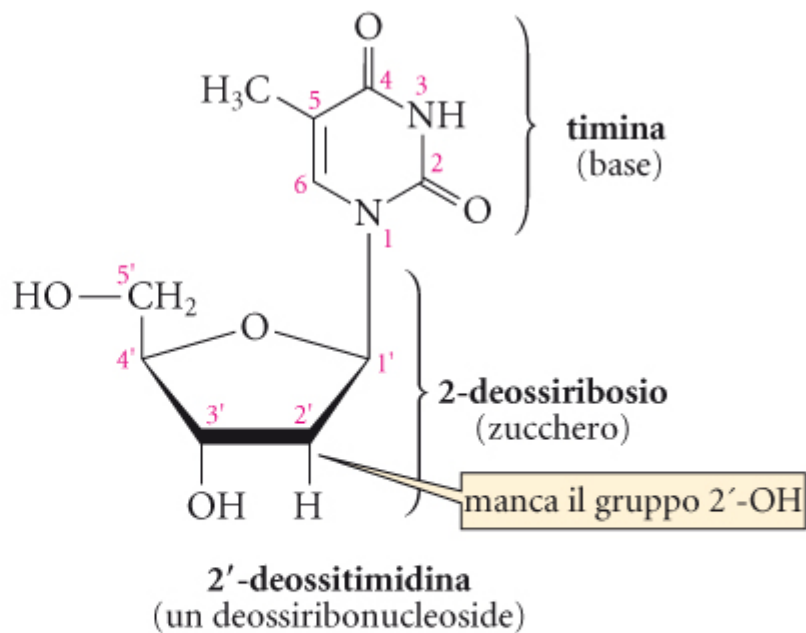
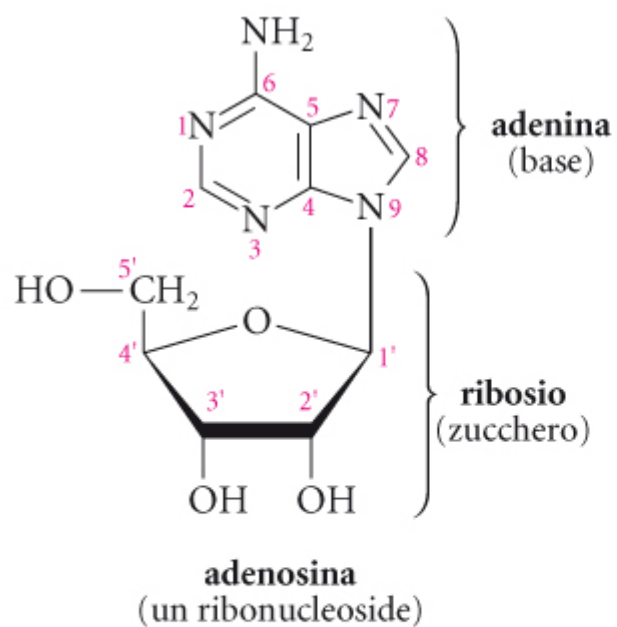
intermedio carboanionico



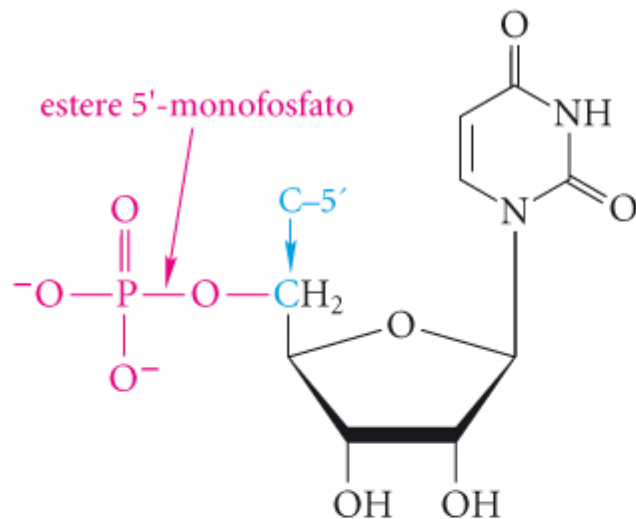
tre delle molte strutture di risonanza dell'intermedio carboanionico

# NUCLEOSIDI, NUCLEOTIDI ed ACIDI NUCLEICI

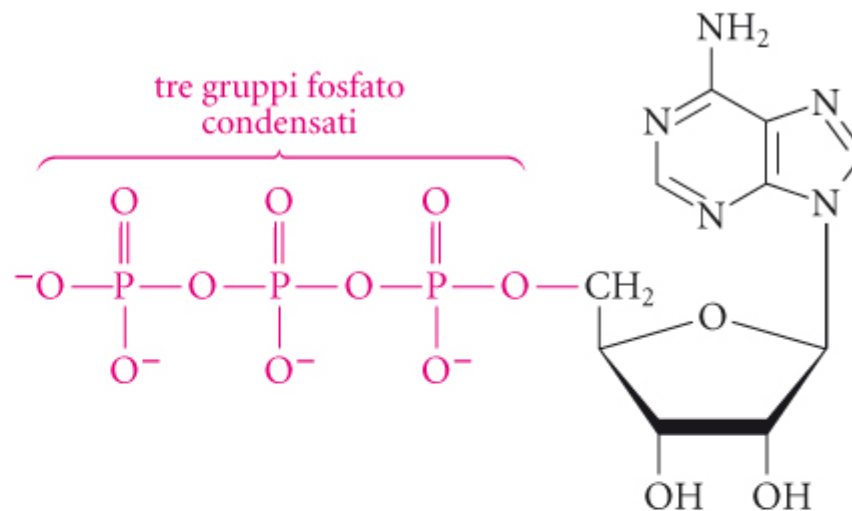
## NUCLEOSIDI



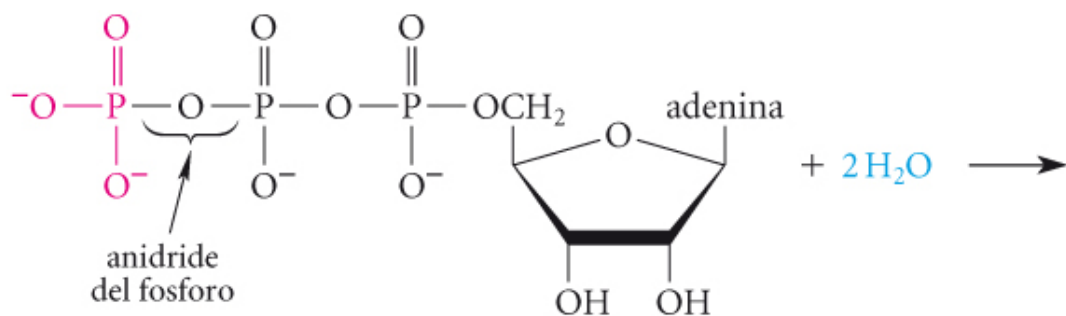
## NUCLEOTIDI = nucleoside fosforilato in 5' (esterificato a gruppo fosfato)



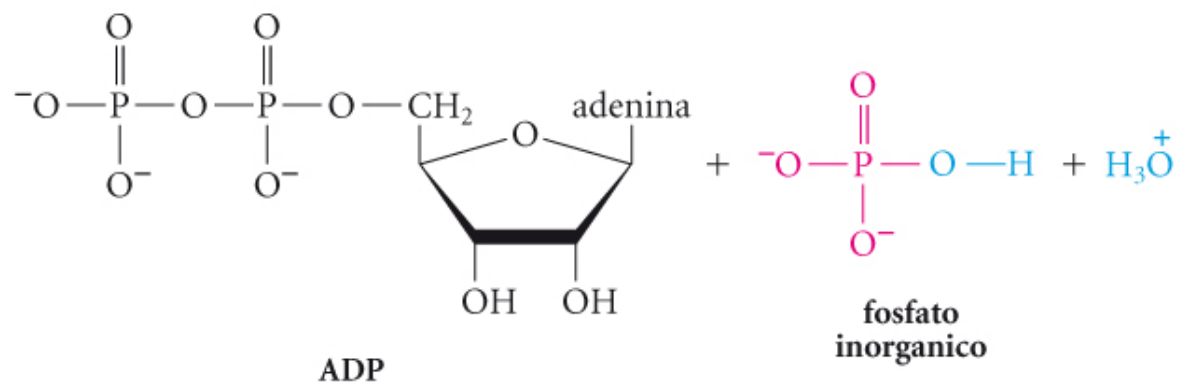
acido uridilico, o UMP  
(uridina monofosfato)



adenosina trifosfato, o ATP

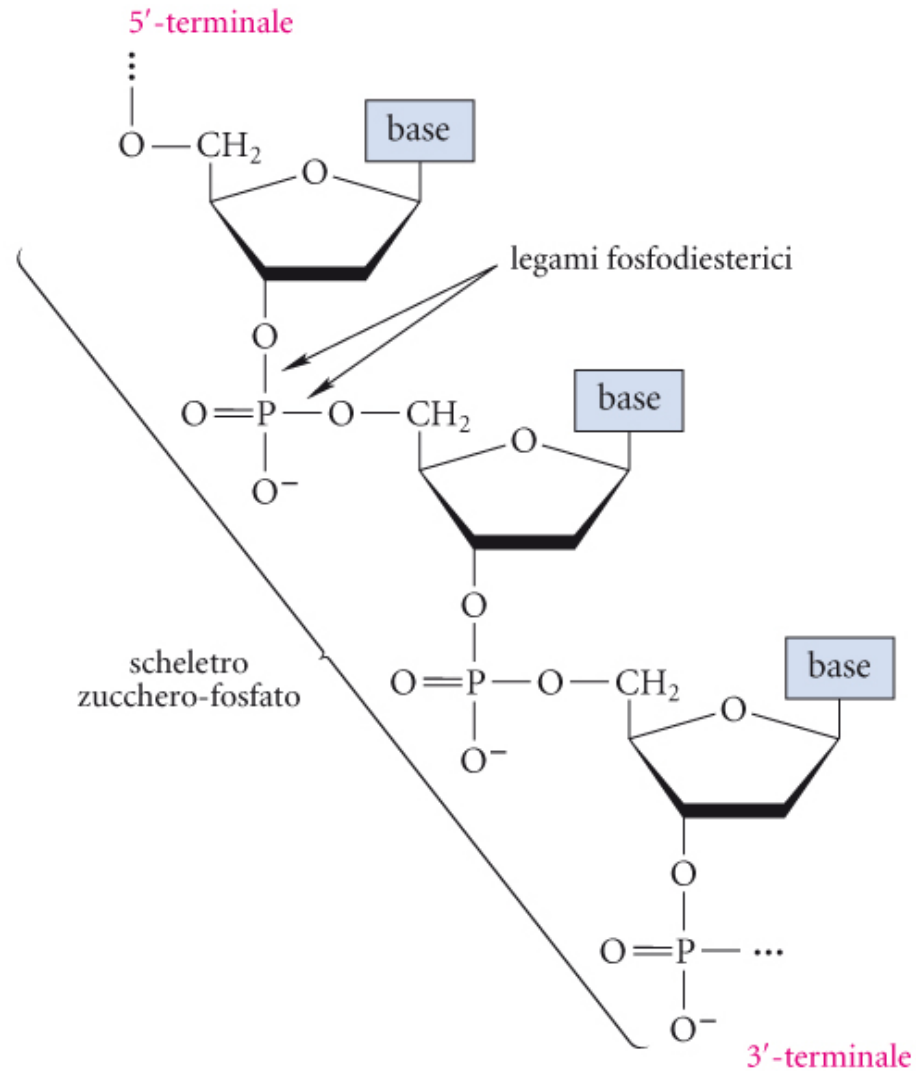


ATP

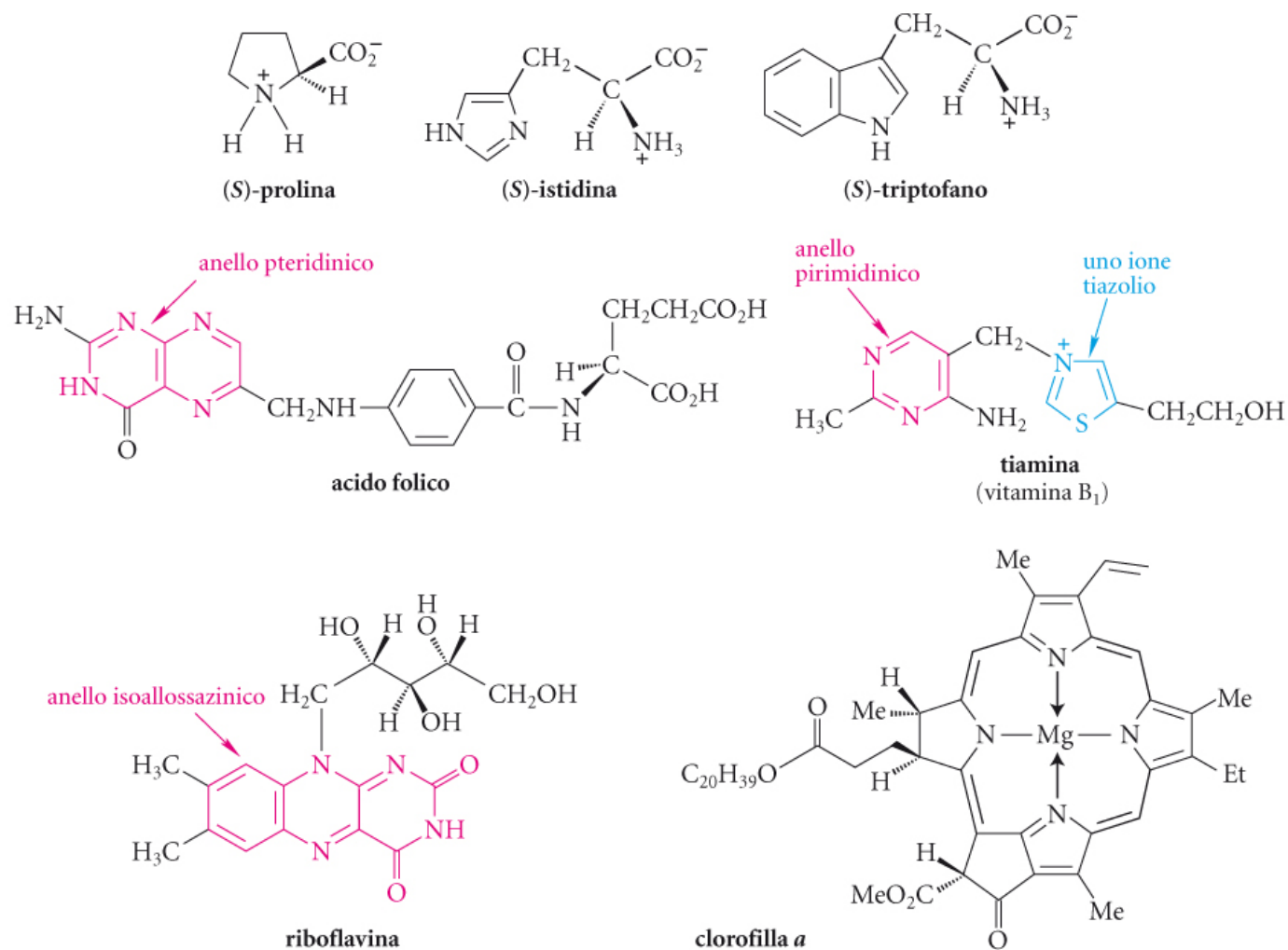


(25.58)

# ACIDI NUCLEICI



**Figura 25.4** 4 Struttura generale del DNA (base = A, T, G, o C; Tabella 25.2). Qui sono mostrati solo tre residui; un tipico filamento di DNA contiene da alcune migliaia a milioni di residui.



**Figura 25.8** Alcuni dei tanti composti eterociclici naturali. Gli enantiomeri *S* di prolina, istidina e triptofano sono  $\alpha$ -amminoacidi proteici. L'acido folico, la tiamina e la riboflavina sono vitamine. Le clorofille sono i pigmenti responsabili del colore verde delle piante. Il gruppo C<sub>20</sub>H<sub>39</sub> è una catena laterale isoprenoidica (vedi Par. 17.6.A). Il NAD<sup>+</sup> (Fig. 10.1, p. 462) e il piridossal fosfato (Fig. 25.3, p. 1241) sono esempi di importanti derivati piridinici naturali.