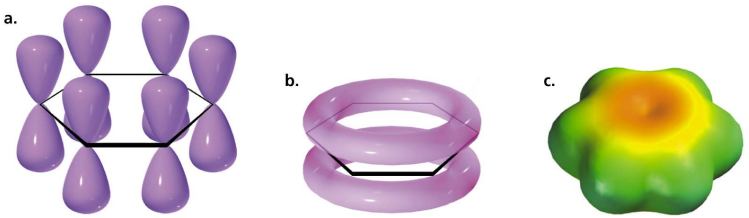
Curso Propedéutico de Química Orgánica

Maestría en Ciencias: Productos Naturales y Alimentos

3ª Parte: Compuestos aromáticos

- Criterios de aromaticidad
- Algunas consecuencias químicas de la aromaticidad
- Radicales libres, propiedades y reactividad
- Polifenoles y antioxidantes



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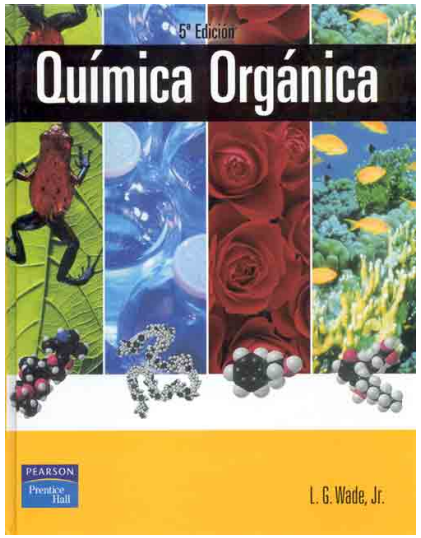
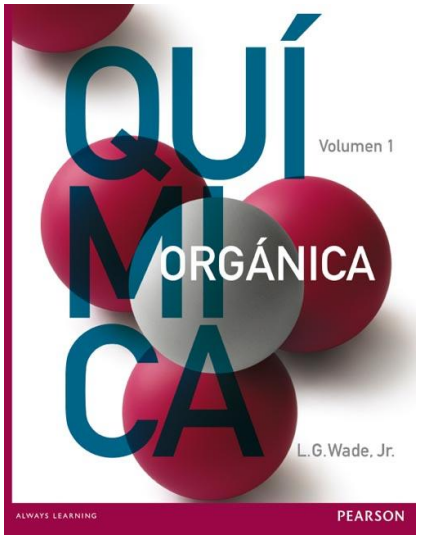
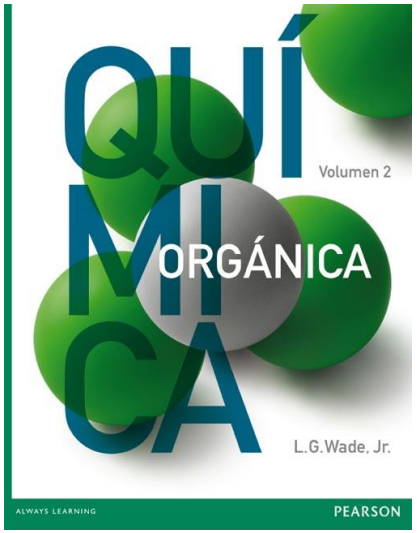
Huajuapan de León, Oaxaca, México


5ª Edición
Química Orgánica
PEARSON
Prentice Hall
L. G. Wade, Jr.


QUÍMICA
Volumen 1
ORGÁNICA
L.G.Wade, Jr.
ALWAYS LEARNING
PEARSON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Volumen 2
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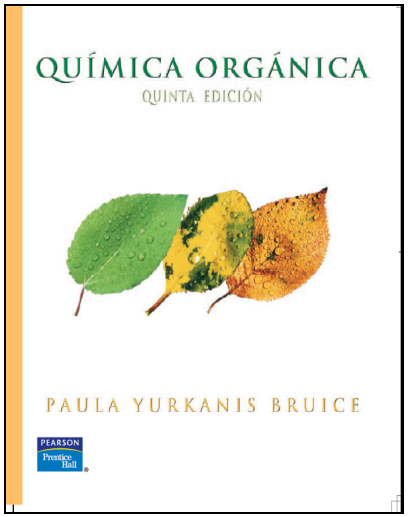
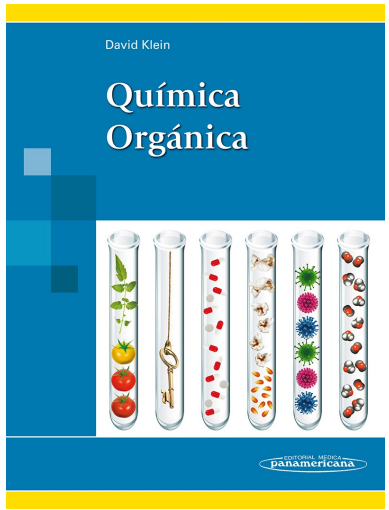
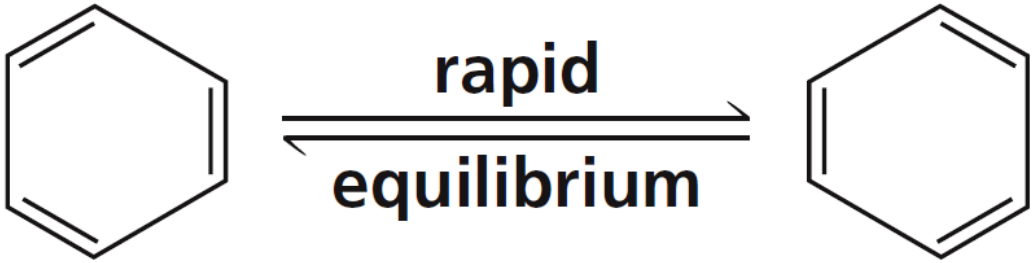

QUÍMICA ORGÁNICA
QUINTA EDICIÓN
PAULA YURKANIS BRUICE
PEARSON
Prentice Hall

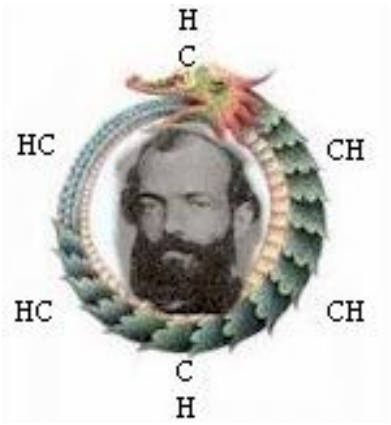

David Klein
Química
Orgánica
panamericana

Kekulé propuso en 1865 una estructura ciclohexatriénica en equilibrio consigo misma. Pero el benceno es una molécula hexagonal completamente simétrica. ¿Cómo explicarlo?

Friedrich August Kekulé von Stradonitz September 7th, 1829 to July 13th, 1896

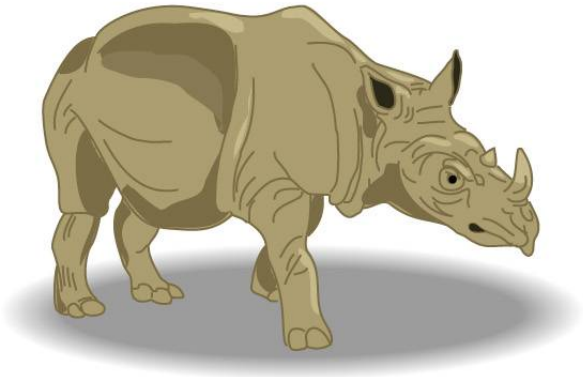


Kekulé structures of benzene



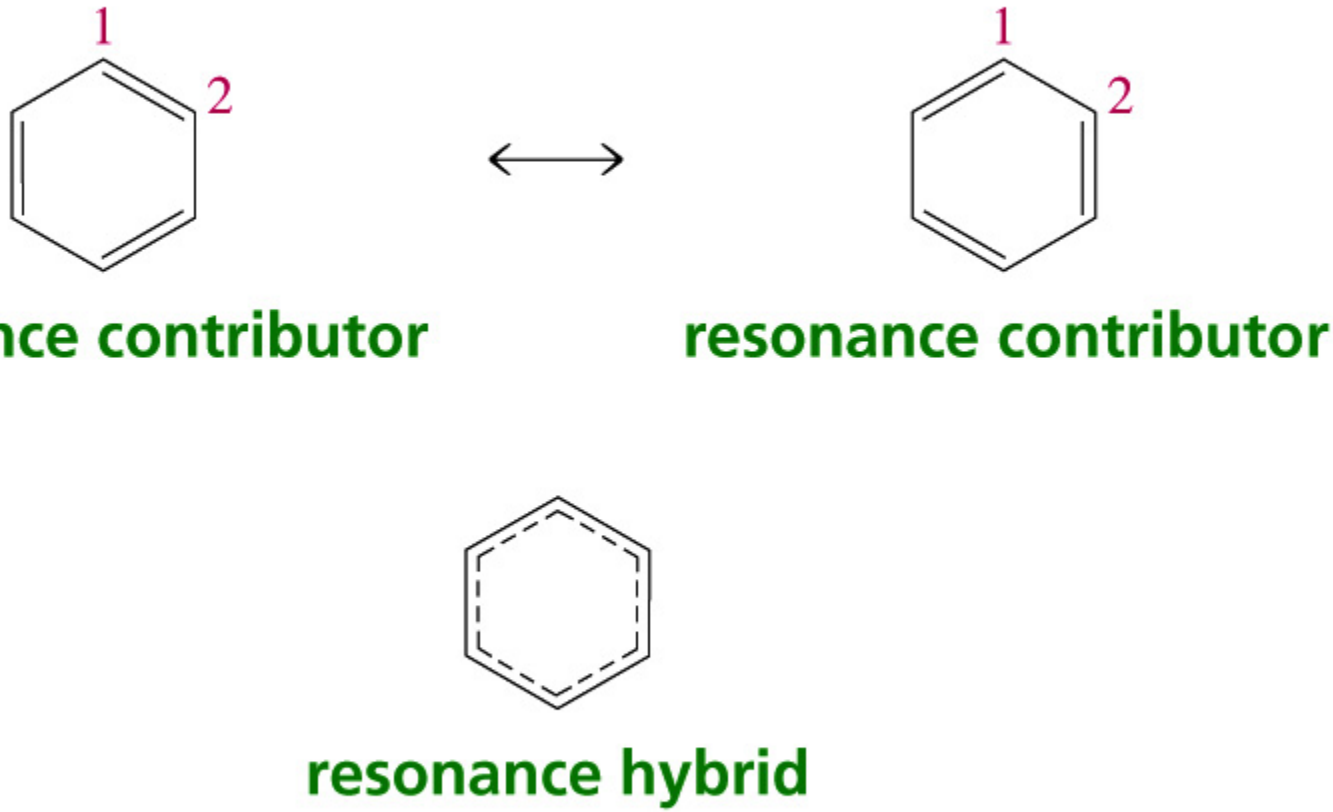
unicorn
resonance contributor

dragon
resonance contributor



rhinoceros
resonance hybrid

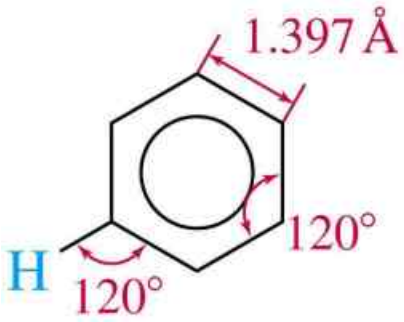
Resonance Contributors and the Resonance Hybrid

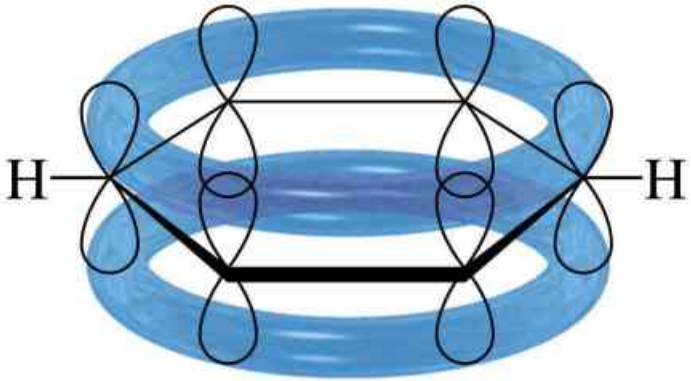


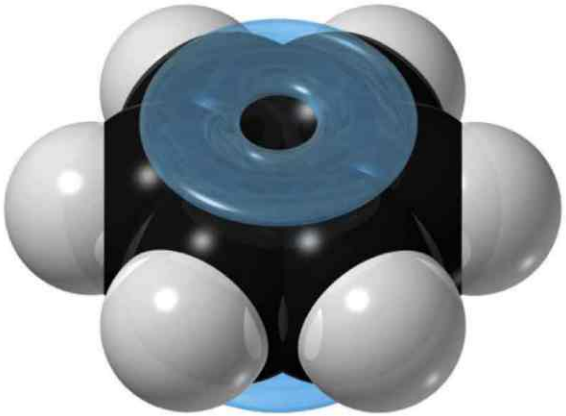
Resonance contributors are imaginary, but the resonance hybrid is real.

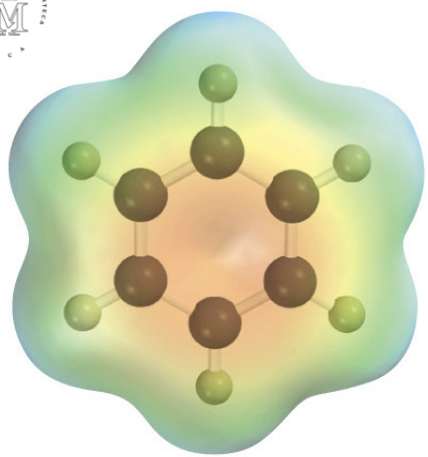
Resonance Structure

Each sp^2 hybridized C in the ring has an unhybridized *p* orbital perpendicular to the ring which overlaps around the ring.

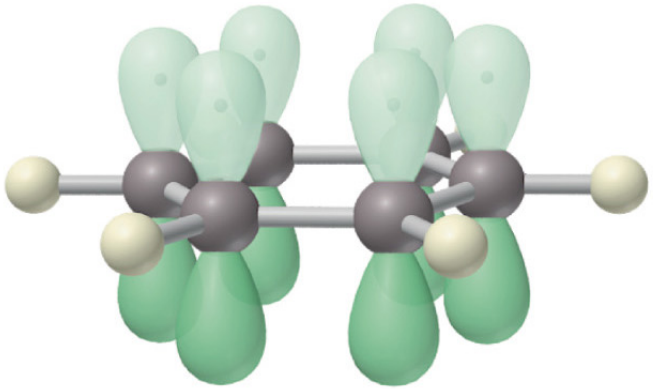




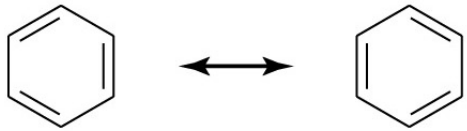




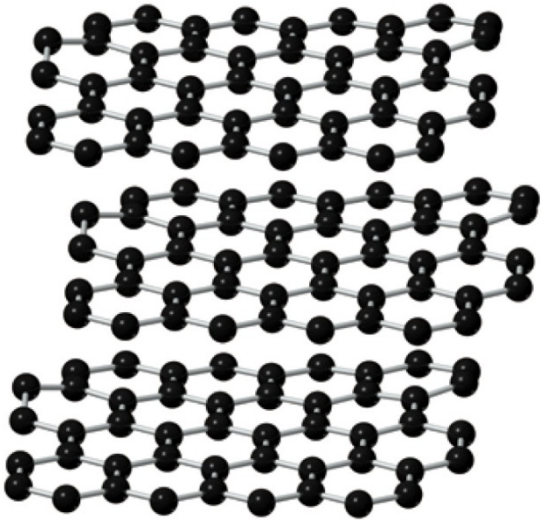
(a)



(b)

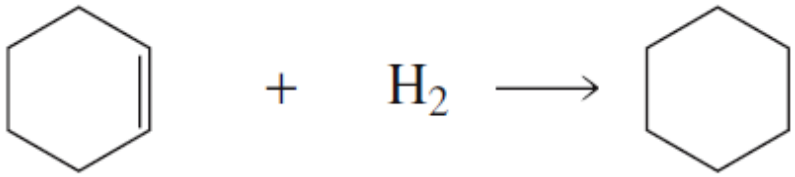


(c)



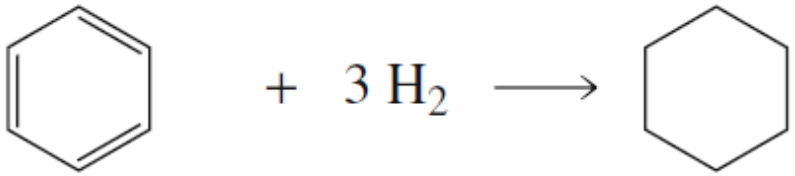
graphite

Resonance energy



cyclohexene

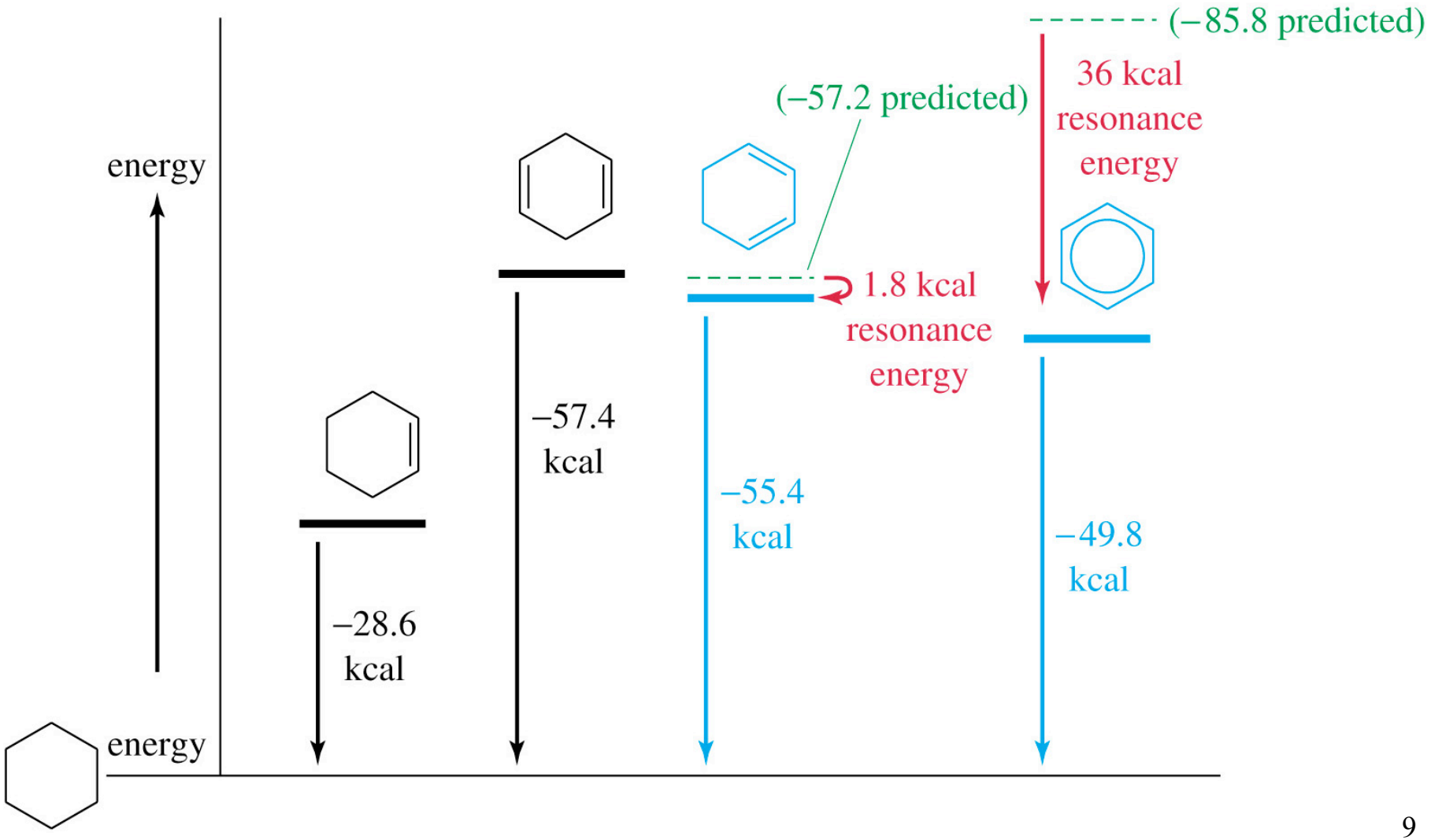
$\Delta H^\circ = -28.6$ kcal/mol (-120 kJ/mol)
experimental



"cyclohexatriene"
hypothetical

$\Delta H^\circ = -85.8$ kcal/mol (-359 kJ/mol)
calculated

Estabilidad del anillo de benceno

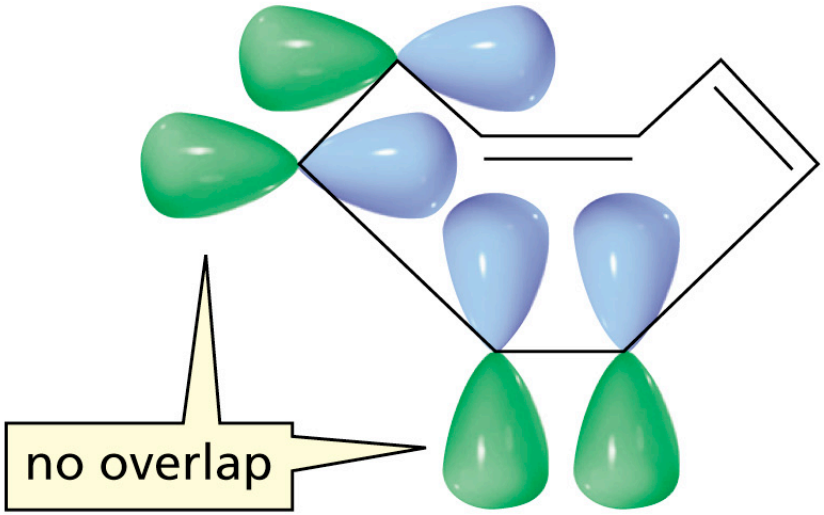


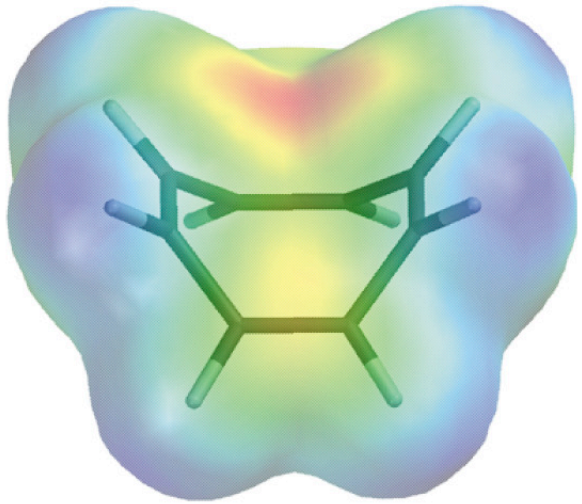
Criterios de aromaticidad

Based on the properties of compounds, there are FOUR criteria about the π system that need to be met in order for the "special" aromatic stabilisation to be observed:

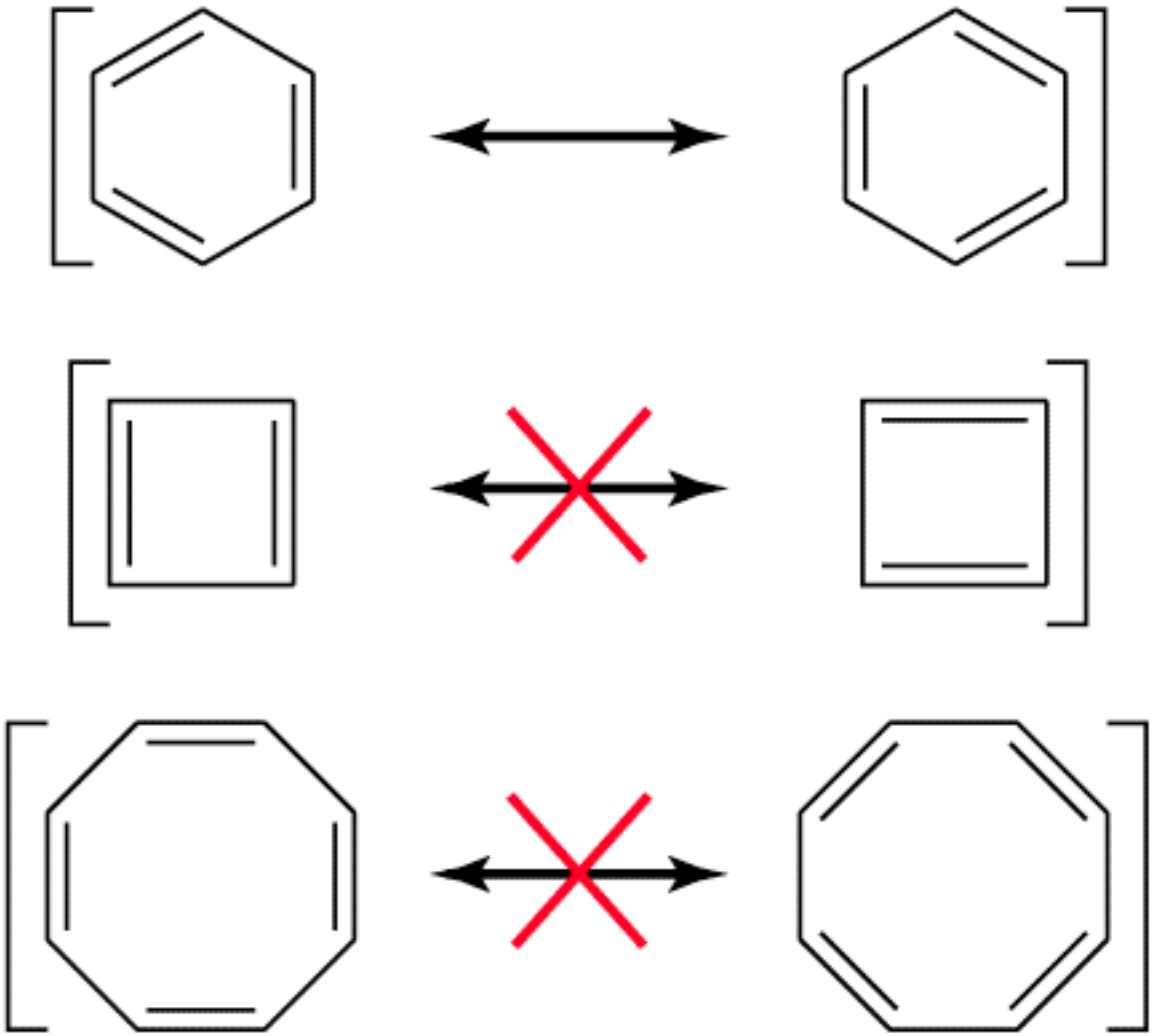
1. **Conjugated** (there needs to one "*p*" orbital from each atom in the cycle, so each atom must be either sp^2 or *sp* hybridised)
2. **Cyclic** (linear systems are not aromatic)
3. **Planar** (so there is good overlap / interaction between the "p" orbitals.... not always easy to consider)
4. The **Huckel Rule**..... 4n+2 π electrons (this is equivalent to an odd number of π−electrons pairs) in the cyclic conjugated system.

π electrons cannot delocalize in nonplanar molecules

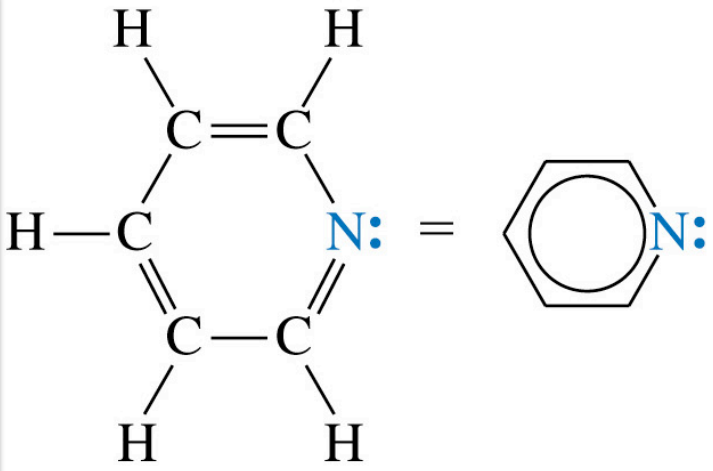




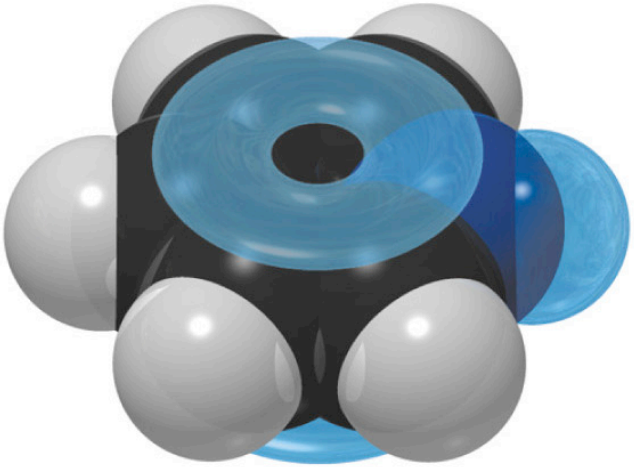
cyclooctatetraene

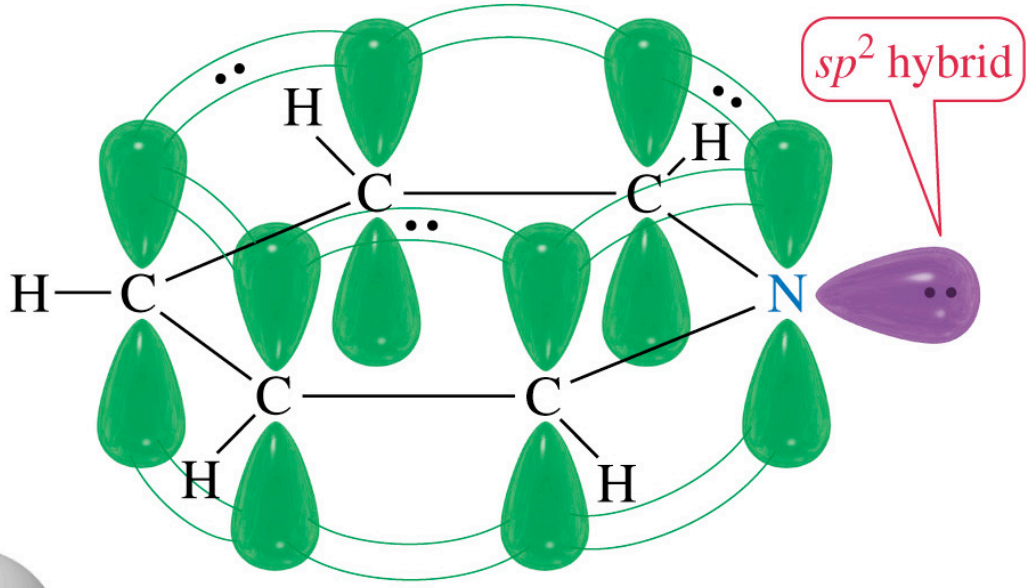


Sistema *pi* de la Piridina

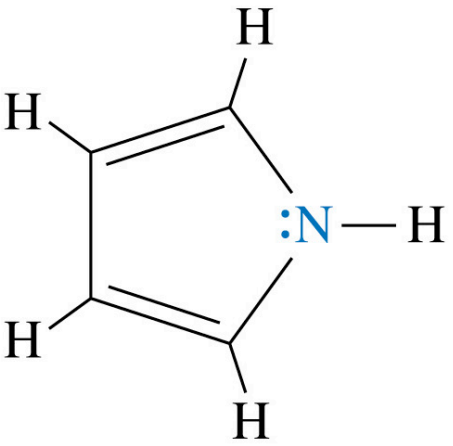


pyridine

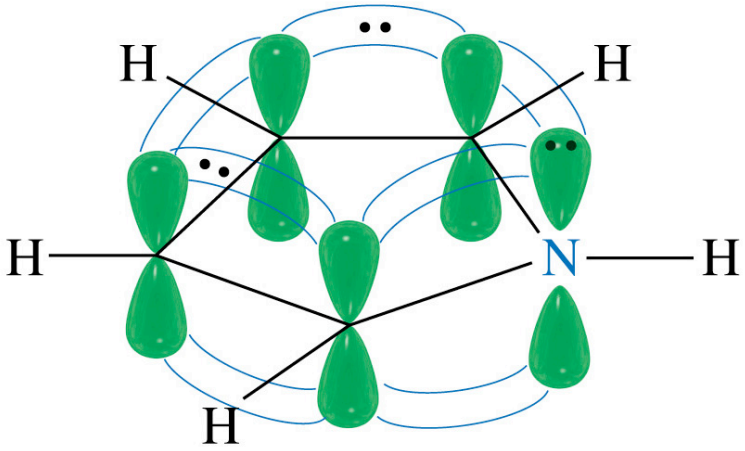




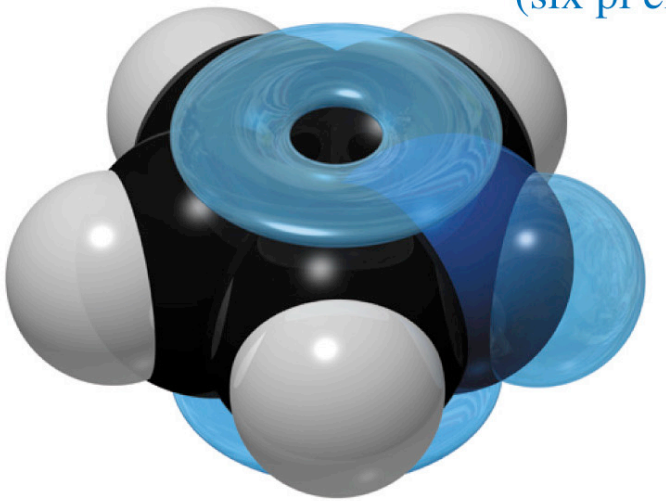
Sistema *pi* del Pirrol



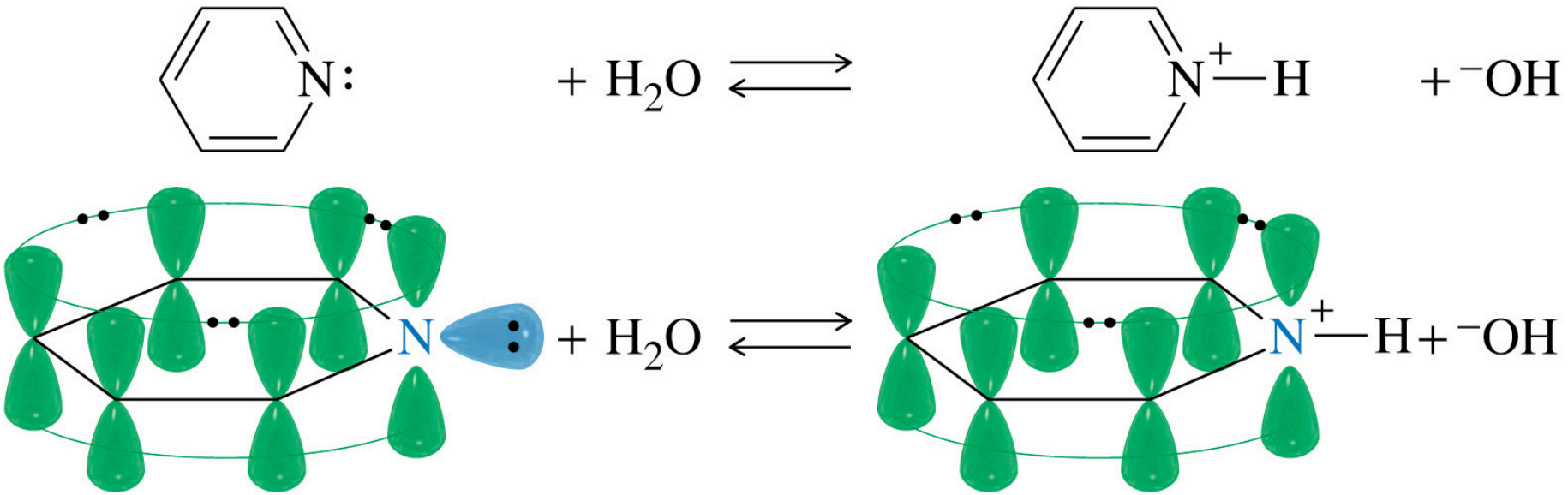
pyrrole



orbital structure of pyrrole
(six pi electrons, aromatic)



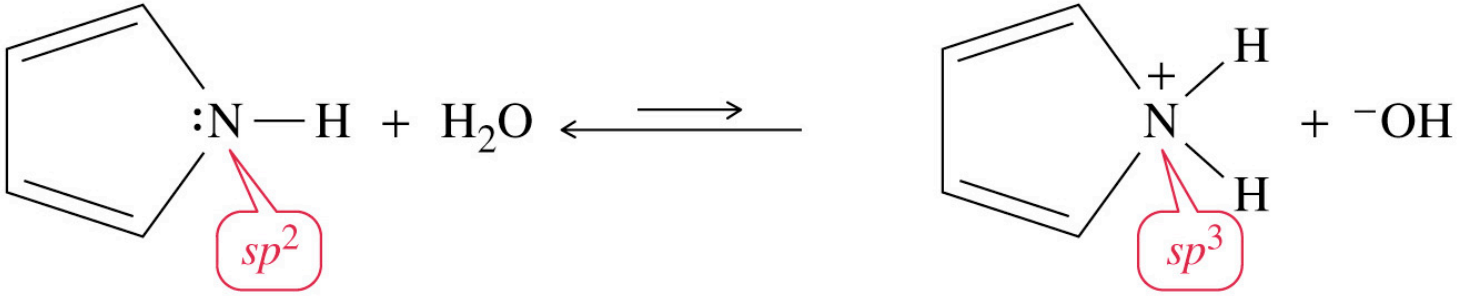
Protonación de la piridina:



pyridine, $pK_b = 8.8$

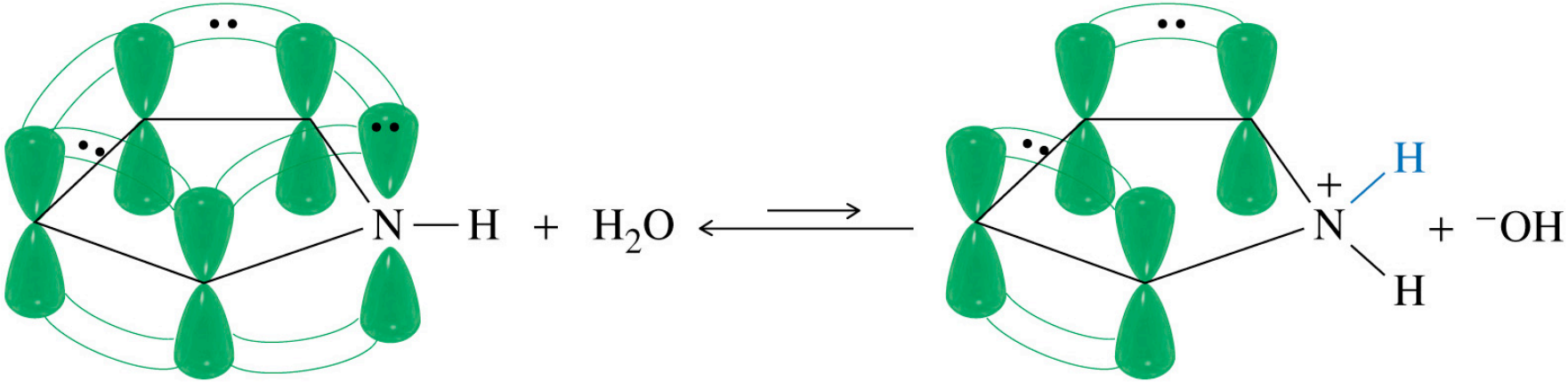
pyridinium ion, $pK_a = 5.2$

Protonación del pirrol:



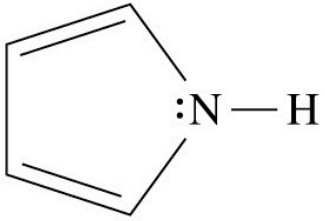
pyrrole, $pK_b = 13.6$
(weak base)

N-protonated pyrrole, $pK_a = 0.4$
(strong acid)

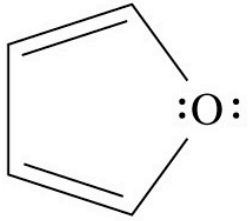


pyrrole
(aromatic)

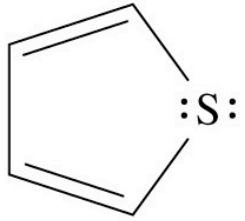
N-protonated pyrrole
(nonaromatic)



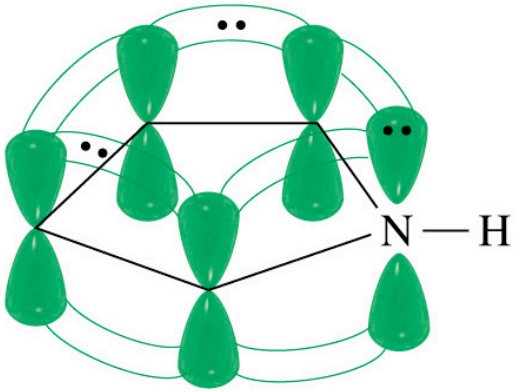
pyrrole



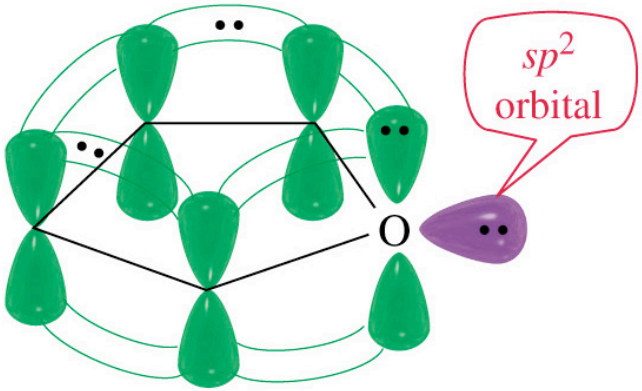
furan



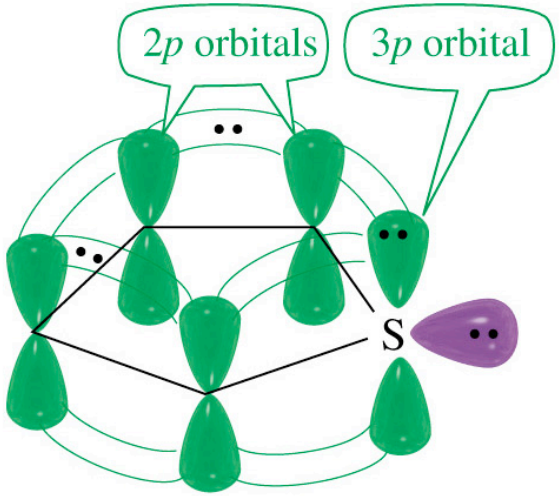
thiophene



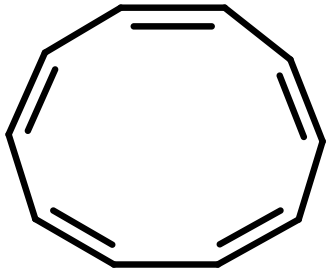
six pi electrons



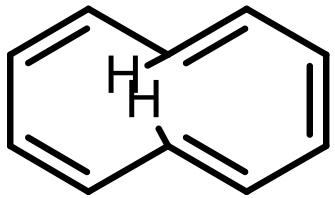
six pi electrons



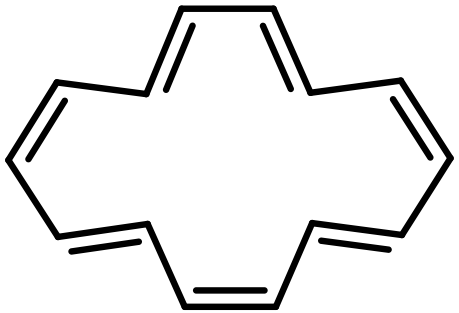
six pi electrons



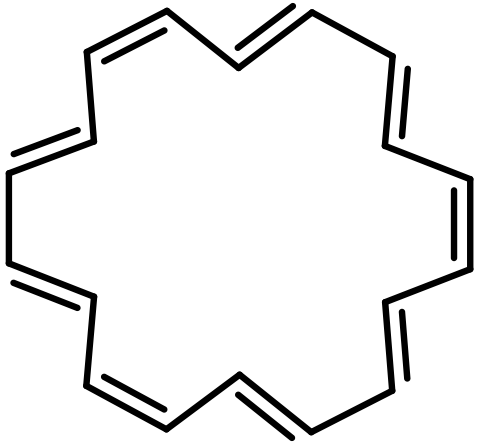
todo cis
no aromático



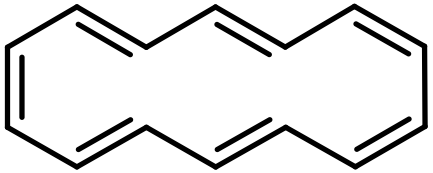
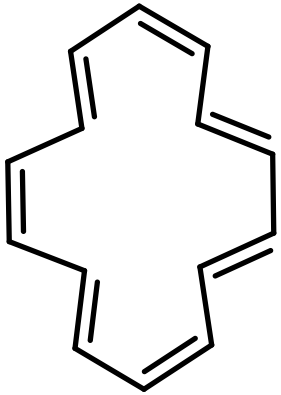
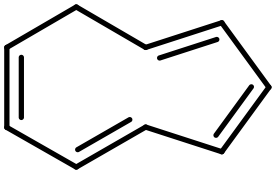
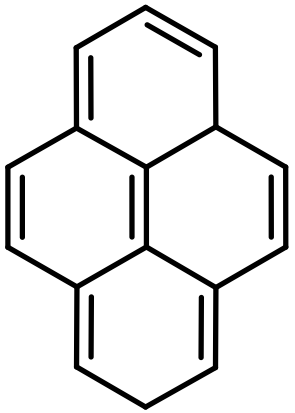
no aromático



[14]anuleno (aromático)



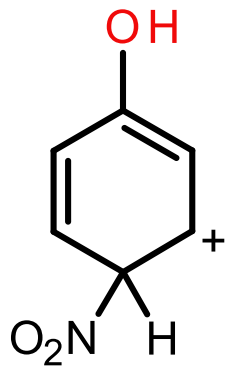
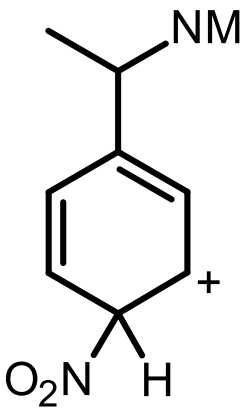
[18]anuleno (aromático)

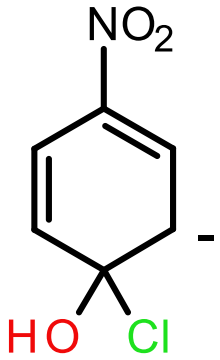
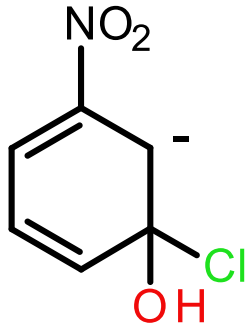





¿Cuál ion, intermediario o molécula de cada par es más estable?

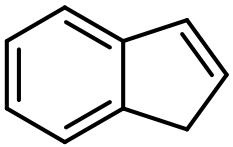
(a)  ó

(b)  ó 

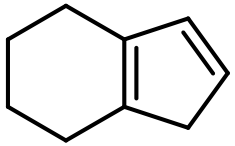
(c)  ó 

(d)  ó 

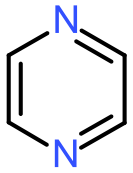
Determine si los compuestos siguientes son aromáticos



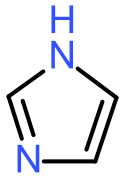
indano



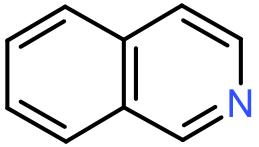
tetrahidroindano



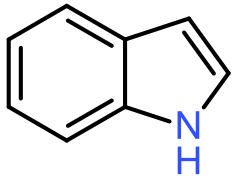
pirazina



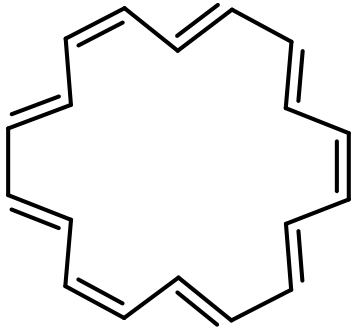
imidazol



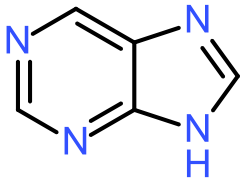
isoquinolina



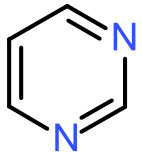
indol



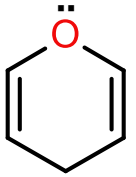
[18]anuleno

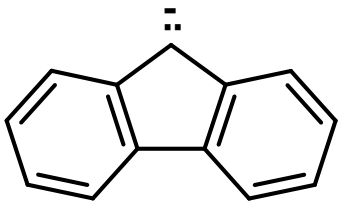


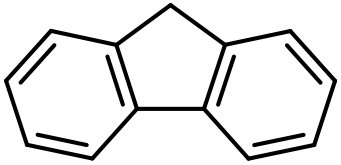
purina



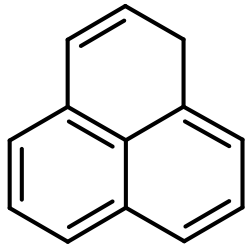
pirimidina



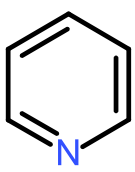




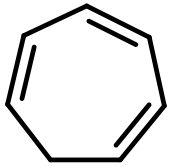
fluoreno



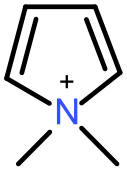
Seleccione el(los) compuesto(s) que mejor describa(n) cada uno de los enunciados siguientes:



A

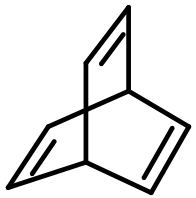


B



C

D



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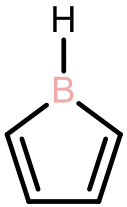
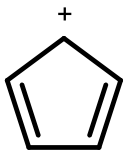
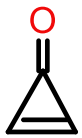


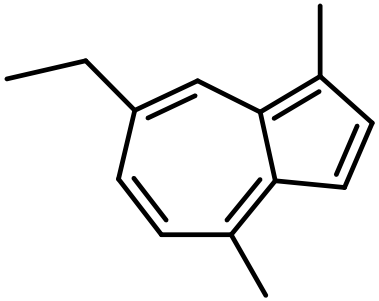
F



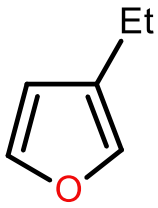
G



H



I

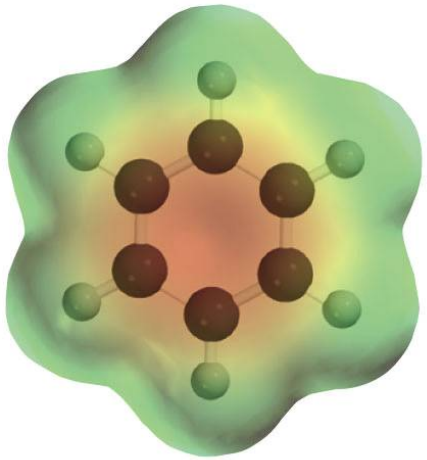


J

- Un sistema neutro, con 4 electrones π, antiaromático.
- Sistema aromático con 6 electrones π.
- Sistema aromático porque n = 2 en la regla de Huckel 4n + 2.
- No aromático, conjugado con 6 electrones π.
- Un hidrocarburo no conjugado.
- No aromático como está dibujado, pero si un H^- se remueve genera un catión aromático.
- No aromático como está dibujado, pero tiene una estructura de resonancia importante que es aromática.
- No aromático como está dibujado, pero tiene una base conjugada aromática.

Algunas consecuencias químicas de la aromaticidad

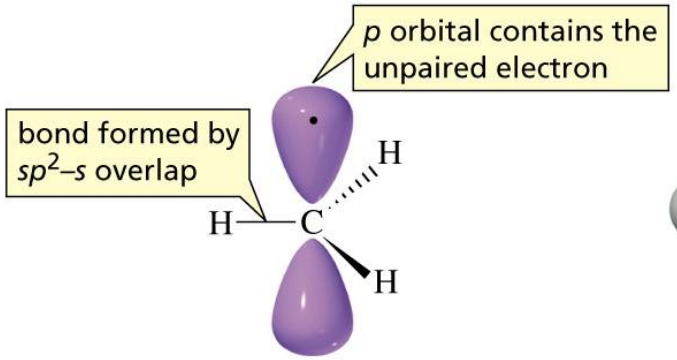
S_EAr
y $S_{Nu}Ar$



benzene

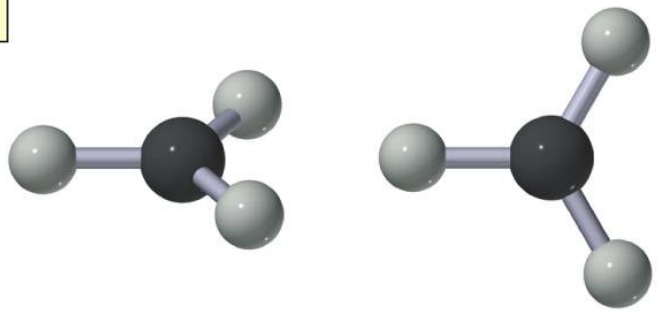
Baja reactividad, alta estabilidad

Radicales libres, propiedades y reactividad



$\cdot CH_3$

methyl radical



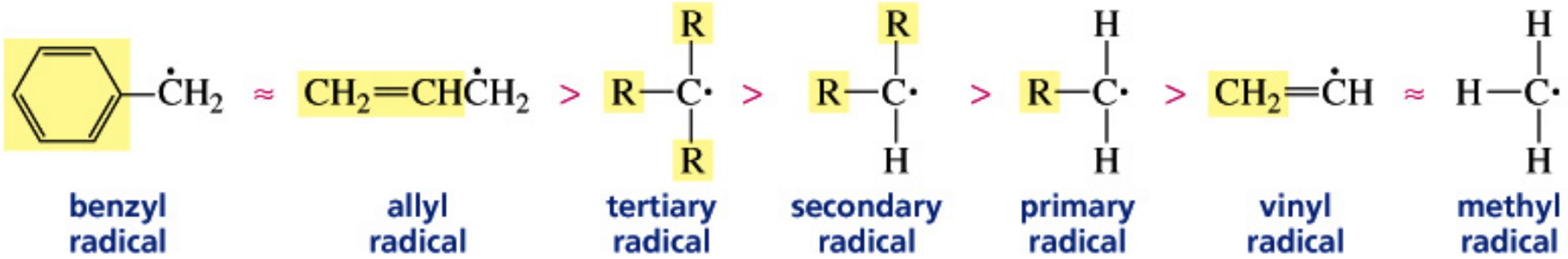
angled side view top view

ball-and-stick models of the methyl radical

electrostatic potential map for the methyl radical

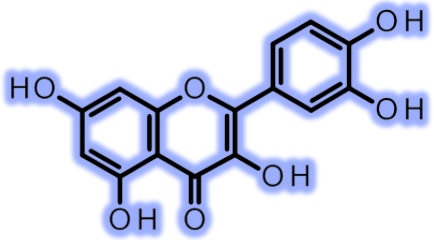
Consider the relative stabilities of radicals

relative stabilities of radicals

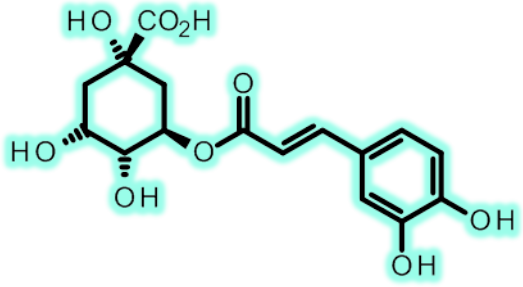


Antioxidant (Antiradical) Compounds

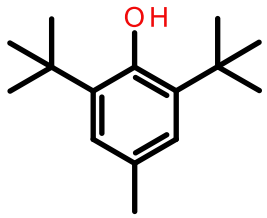
Naturals



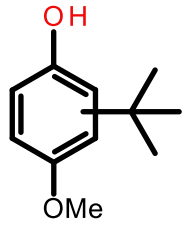
quercetin



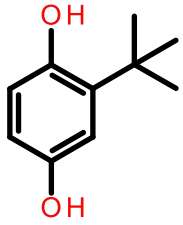
Synthetics



BHT

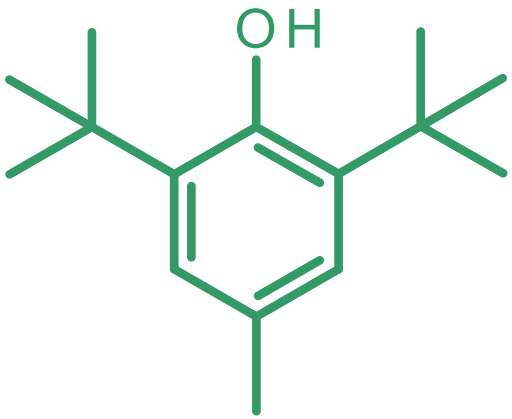


BHA

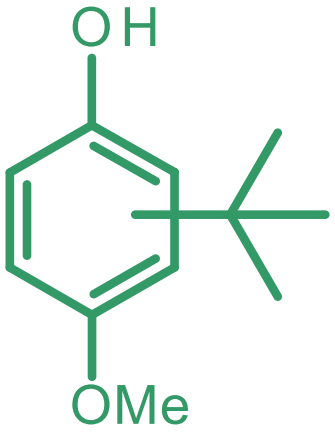


TBHQ

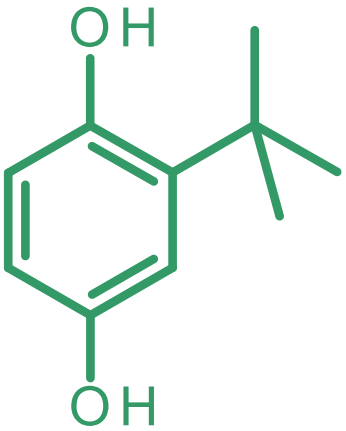
- Polifenoles y antioxidantes


OH

BHT


OH
OMe

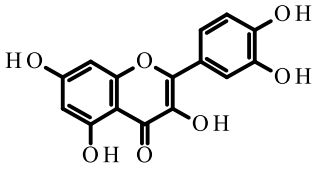
BHA


OH
OH

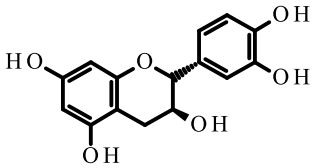
TBHQ


Kellogg's
RICE
CRUNCHY NUT
Kellogg's
FLAKES
GREAT VALUE
Scott's
Porage
Oats
Kellogg's
SPECIAL
Sugar
Cheeri
ORIGINAL
Alpen
JORDANS
COUNTRY
CRISP
Weetabix
NEW
Nesquik
BrunchBa
Kellogg's
VARIETY

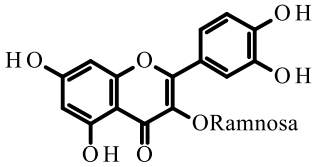
Flavonoides



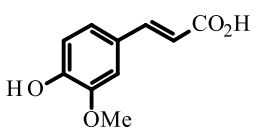
Quercetina



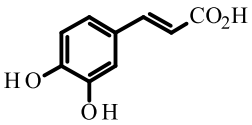
Catequina



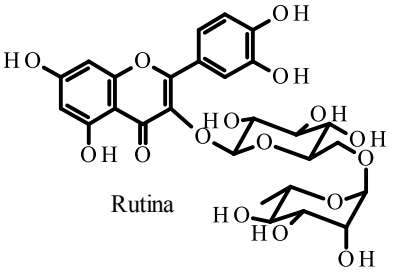
Quercitrina



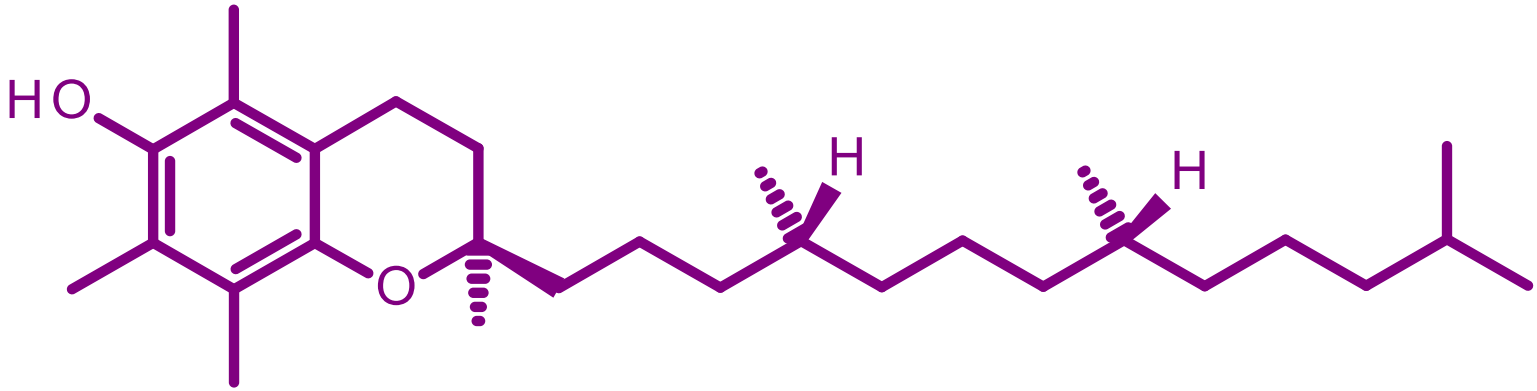
Ácido ferúlico



Ácido cafeico



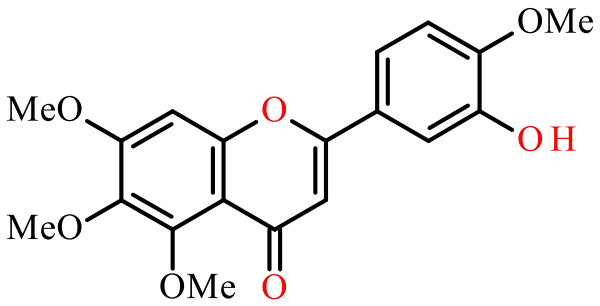
Rutina



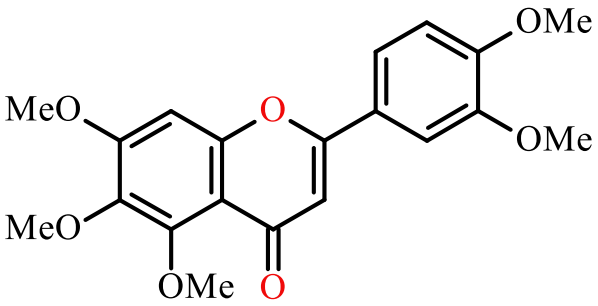
Vitamina E

Corn, nuts, olives green, leafy vegetables, wheat germ


O
OMe
OH

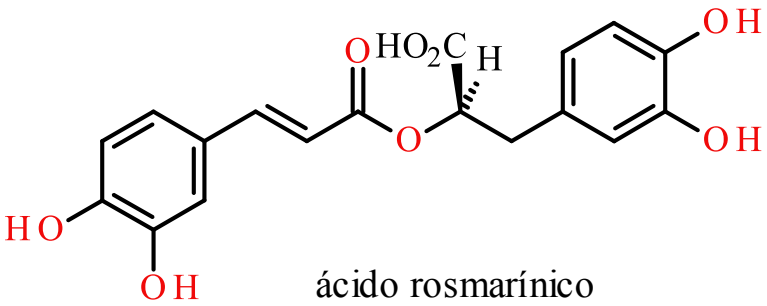


3'-hidroxi-5,6,7,4'tetrametoxiflavona



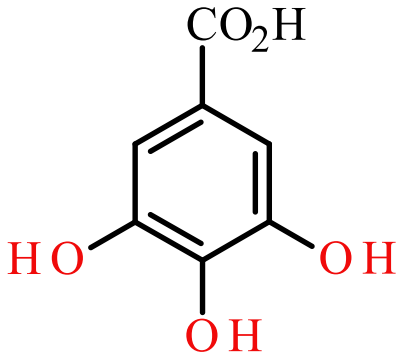
sinensetina

Malus domestica

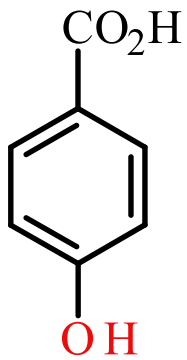


ácido rosmarínico

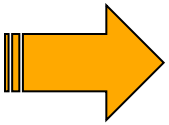
Food Chemistry, **2009**, *113 (1)*, 185-190.



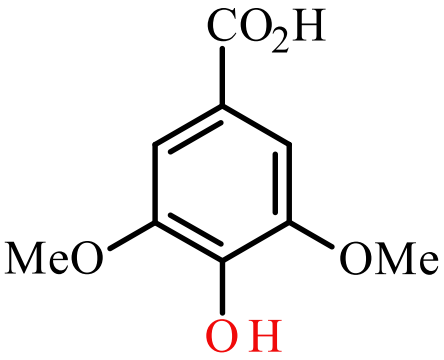
ácido gálico



ácido
p-hidroxibenzoico

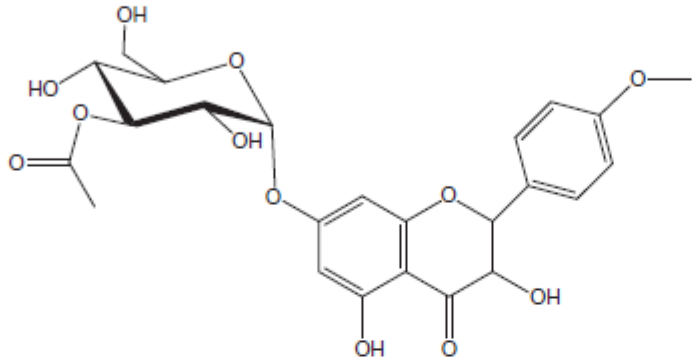


Pouteria sapota
Jacq. H.E. Moore & Stearn

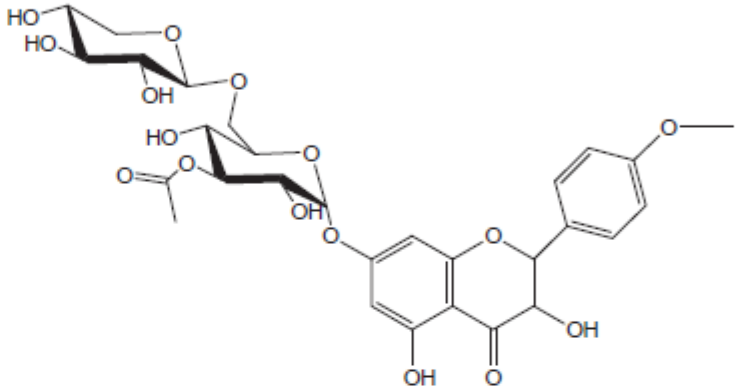


ácido siríngico

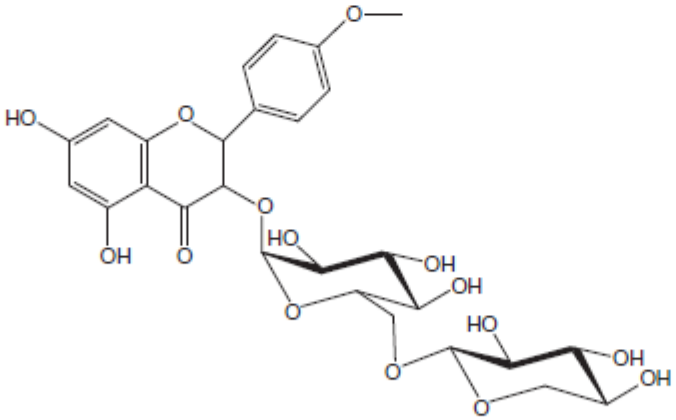
Food Research International. **2011**, *44*, 2175–2181



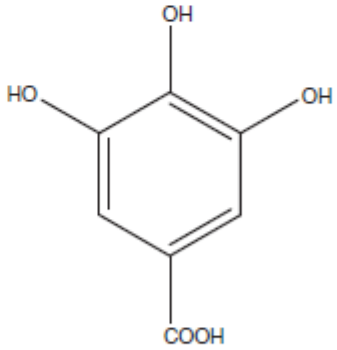
2*R*,3*R*-4'*O*-methyl dihydrokaempferol 7-*O*-[3"-O-acetyl]-β-D-glucopyranoside (**1**)



2*R*,3*R*-4'-*O*-methyl dihydrokaempferol 7-*O*-β-D-β-L-xylopyranosyl-(1'''→6")-[3"-O-acetyl]-β-D-glucopyranoside (**2**)



2*R*,3*R*-4'-*O*-methyl dihydrokaempferol 3-*O*-β-D-β-L-xylopyranosyl-(1 '''→6")-[3"-O-acetyl]-β-D-glucopyranoside (**3**))

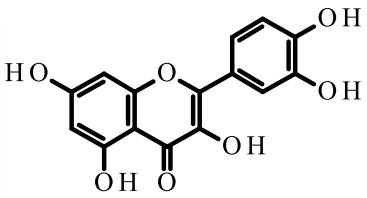


Gallic acid (**4**)

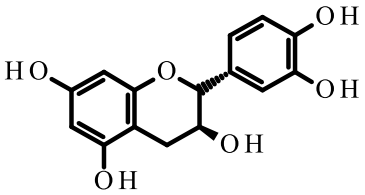
***Pouteria obovata* (R. Br.)**

Food Chemistry. **2011**, *124*, 884-888.

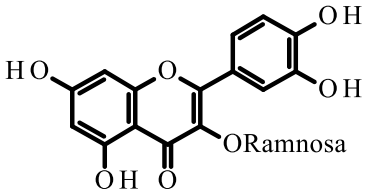
Género Annona



Quercetina

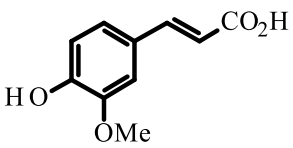


Catequina

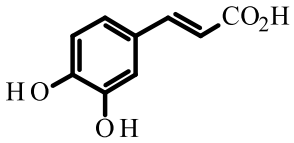


Quercitrina

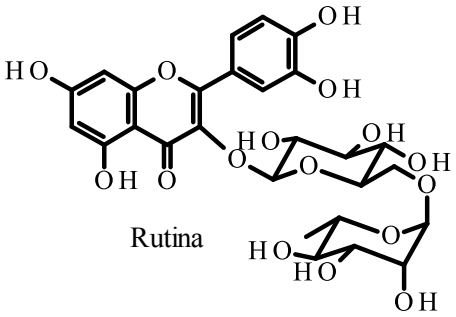
***A. squamosa*[1]**



Ácido ferúlico



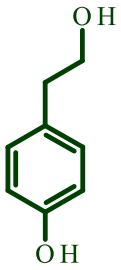
Ácido cafeico



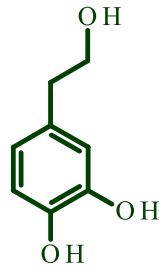
Rutina

***A. crassiflora*[2]**

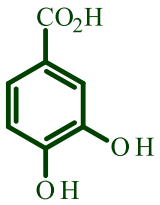
1. *Phytomedicine.* **2007**, *14*, 799-805.
2. *Food Chemistry.* **2007**, *104 (3)*, 1048-1054.



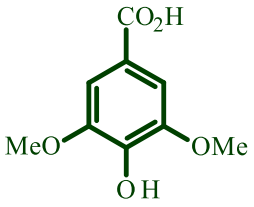
tirosol



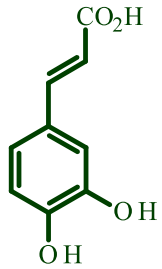
hidroxitirosol



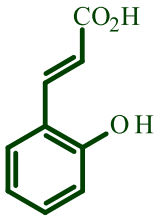
ác. protocatechuico



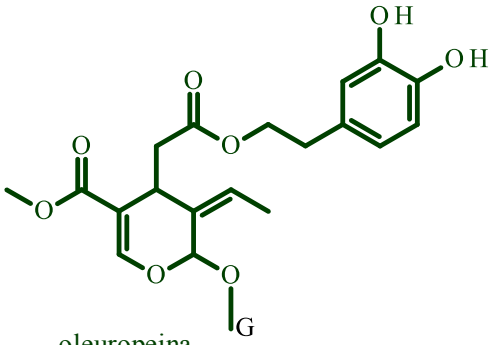
ácido siríngico



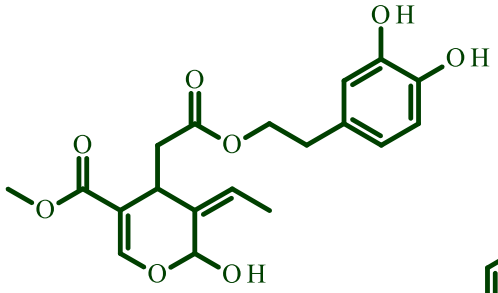
ác. cafeico



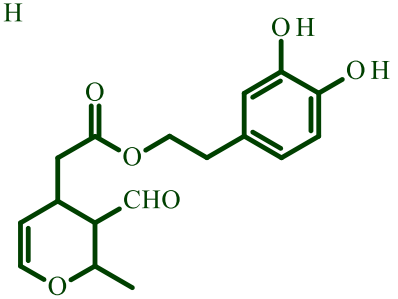
ác. *o*-cumárico

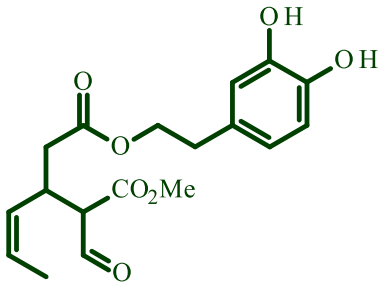


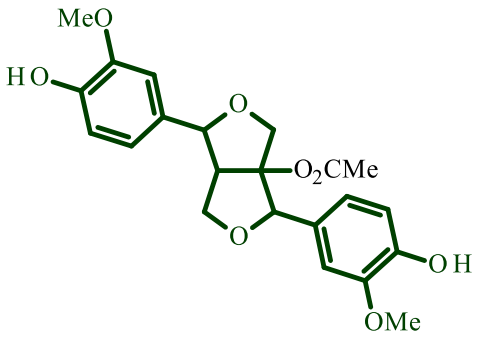
oleuropeina



aglicona oleuropeina

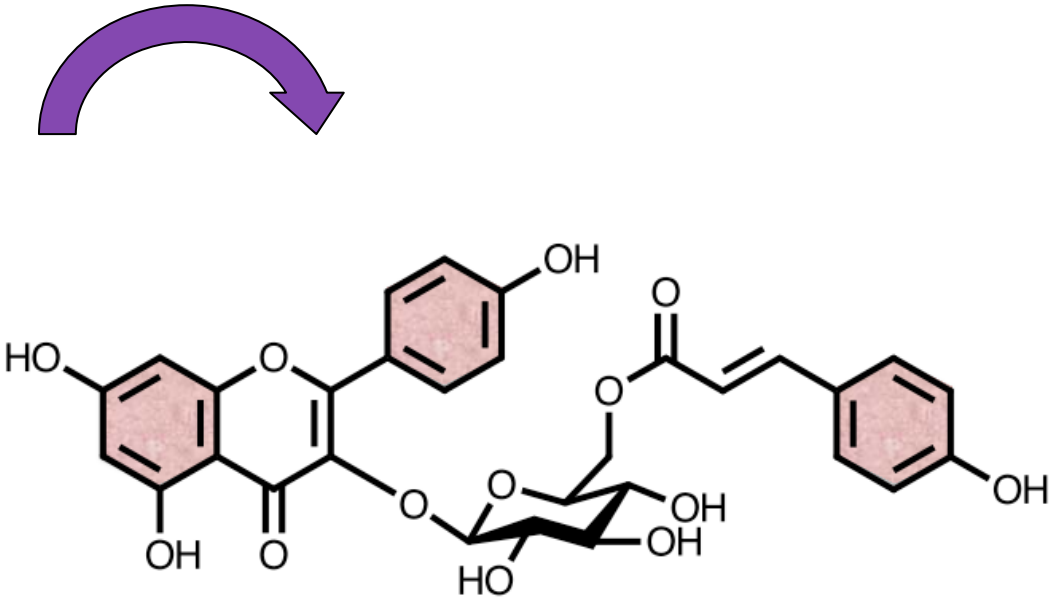






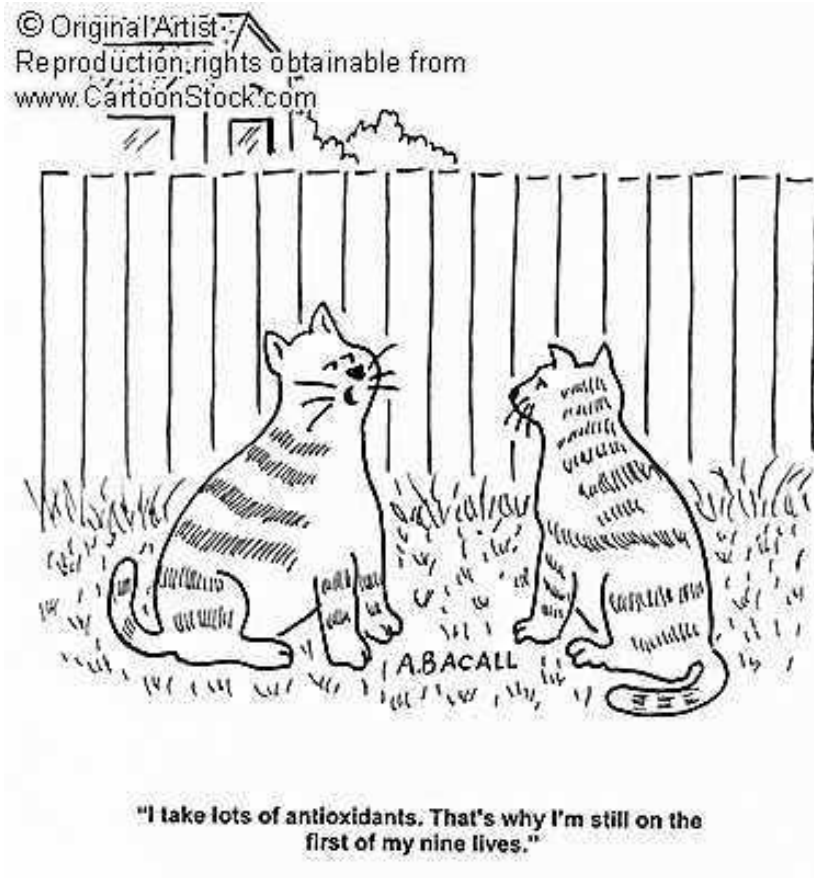
LWT - Food Science and Technology. **2012**, *49*, 267-274.

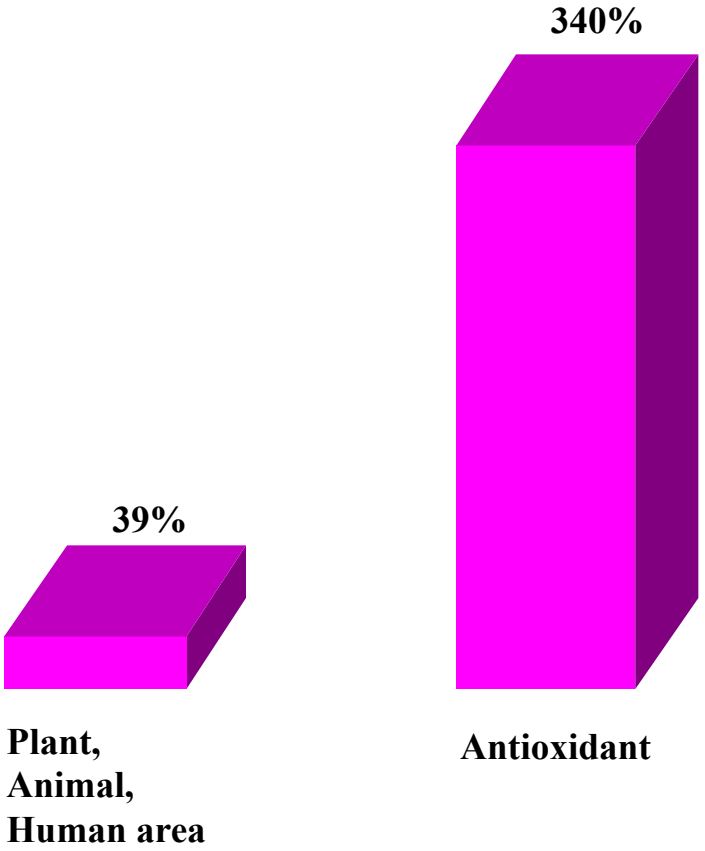
Polyphenolic content, free radical-scavenging activity and isolation of tiliroside from *Heliocarpus terebinthinaceus* (Tiliaceae) seeds



Tiliroside [kaempferol-3-*O*-*β*-D-(6″-*O*-(*E*)-*p*-coumaroyl)glucopyranoside]

Santos-Sánchez, N.F.; Flores-Parra, A.; Valadez-Blanco, R.; Fernández-Rojas, B.; Martínez-Vásquez, J.B.; Salas-Coronado, R. *Journal of Biological Science*. **2014**, *14* (5), 376-380. ISSN 1727-3048. DOI: 10.3923/JBS.2014.376.380.

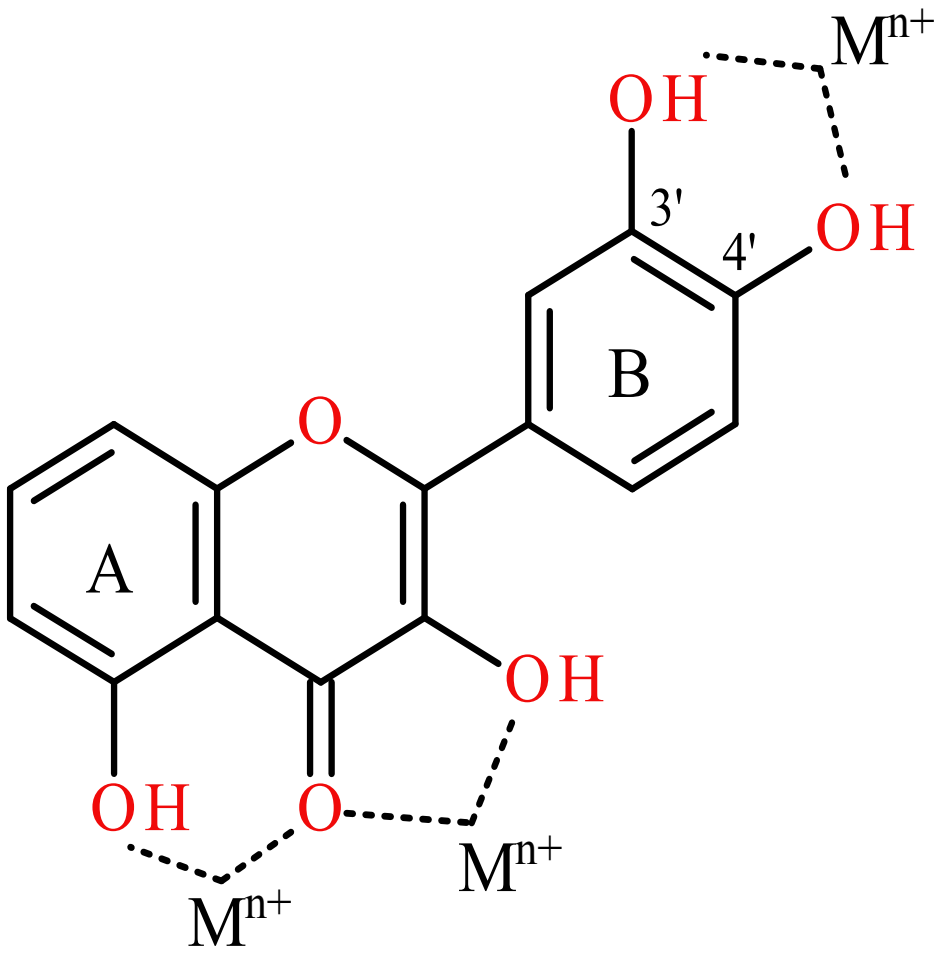




Medline database (2005)

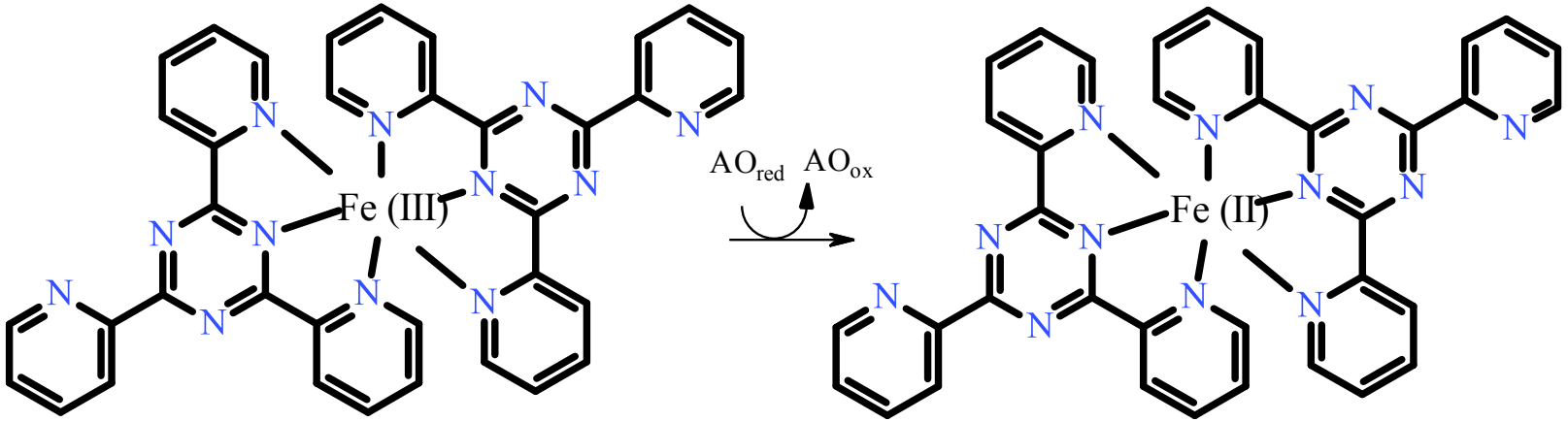
Prior, R.; Wu, X.; Schaich, K. *J. Agric. Food Chem*. **2005**, *53*, 4290-4302.

Sitios de enlace para metales en flavonoides



Prior, R.; Wu, X.; Schaich, K. *J. Agric. Food Chem*. **2005**, *53*, 4290-4302.

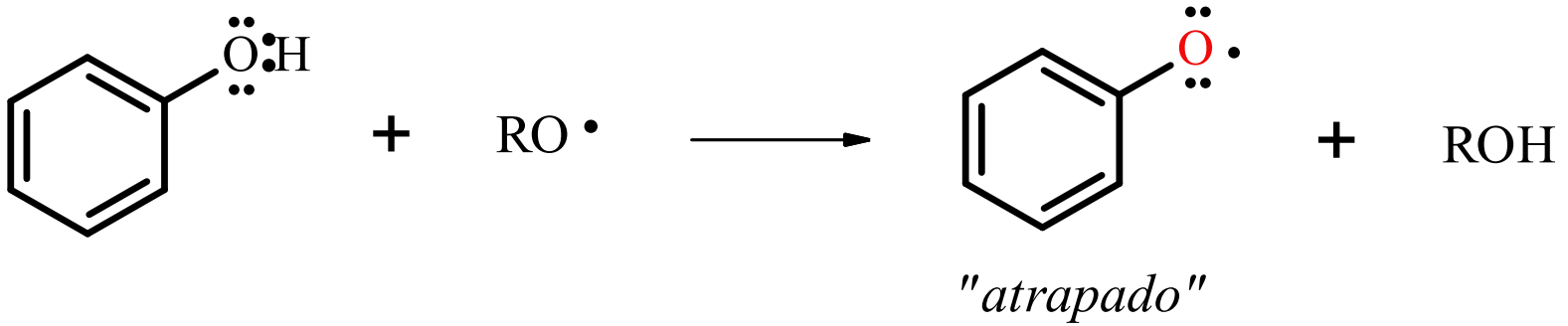
Mecanismo de reacción para el ensayo FRAP frente a un antioxidante (AO)



Fe^{3+}-TPTZ + reducing antioxidant → Fe^{2+}-TPTZ + oxidized antioxidant
(intense blue at 595 nm)

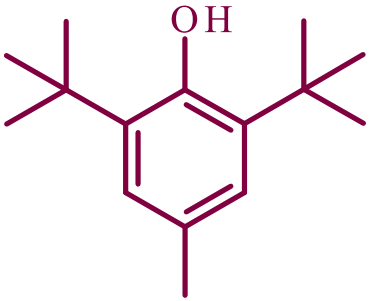
Benzie, I.F.F.; Strain, J.J. *Anal. Biochem*. **1996**, *239*, 70-76.

Un inhibidor que controla la autooxidación se llama antioxidante (conservador o preservador)

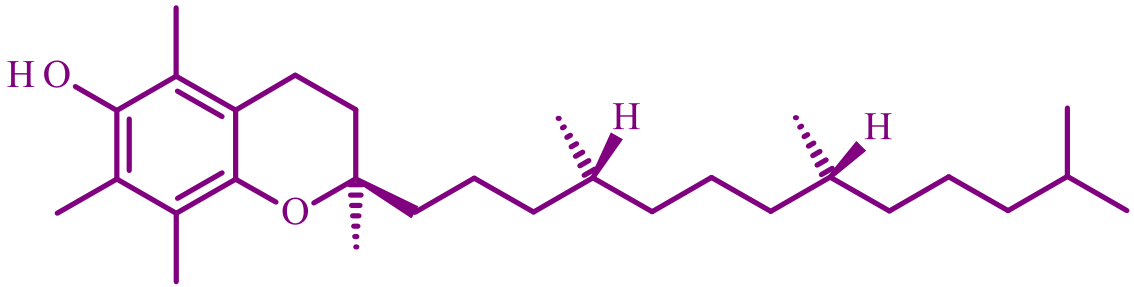


"atrapado"

Fenoles

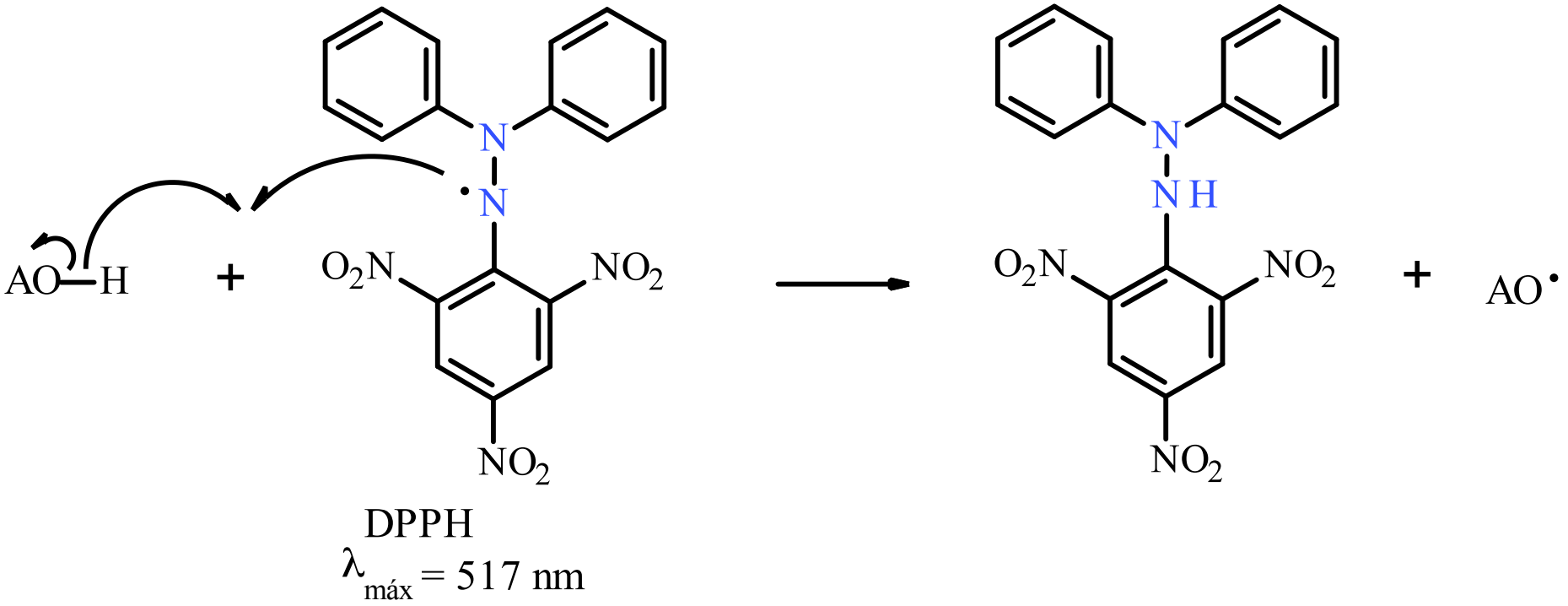


BHT
(butylated hydroxytoluene)



α−tocoferol
(vitamina E)

Determinación de la actividad antioxidante *in vitro*

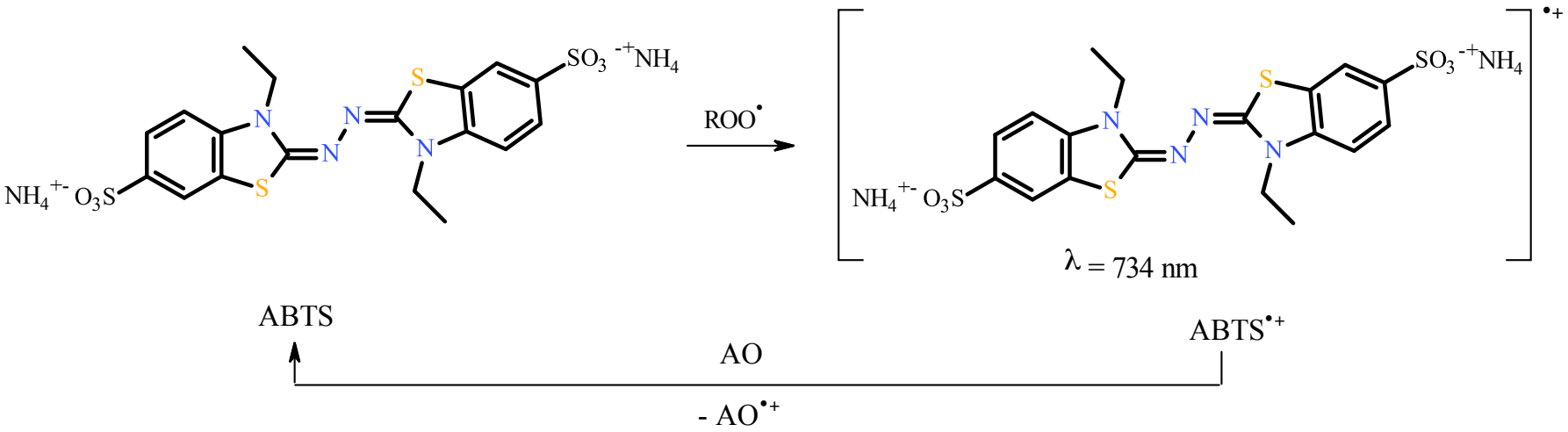


DPPH

$\lambda_{máx} = 517$ nm

1. Roesler, R.; Catharino, R.R.; Malta, L.G.; Eberlin, M.N.; Pastore, G. *Food Chem.* **2007**, *104,* 1048-1054.
2. Julián-Loaeza, A.P.; Santos-Sánchez, N.F.; Valadez-Blanco, R.; Sánchez-Guzmán, B.S.; Salas-Coronado, R. *Ind. Crops Prod*. **2011**, *34*, 1262-1268.

Obtención del catión radical ABTS$^{\bullet+}$, y su reacción con un antioxidante (AO)



Prior, R.; Wu, X.; Schaich, K. *J. Agric. Food Chem*. **2005**, *53*, 4290-4302.


α-glucose
α-fructose