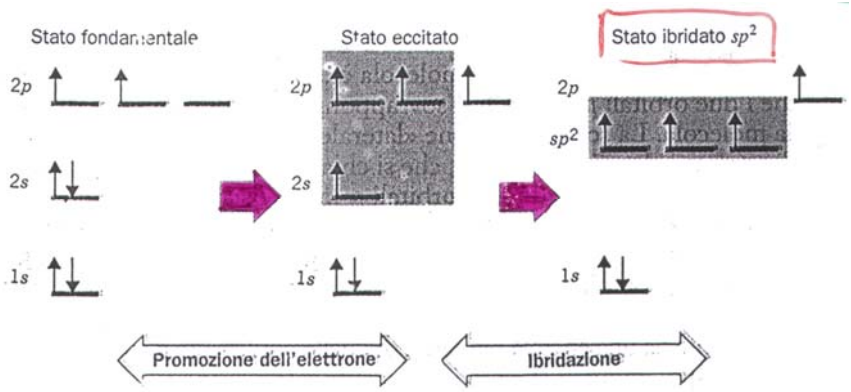
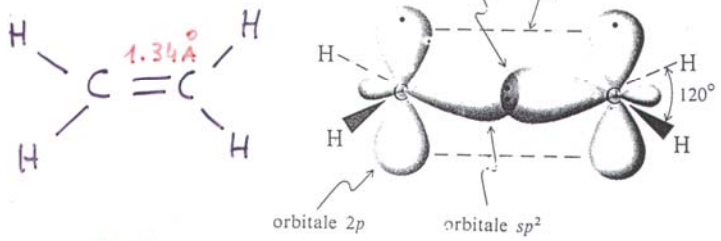
C sp^2

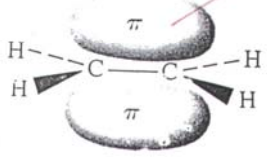
ALCHENI





σ E = 108 Kcal/mol

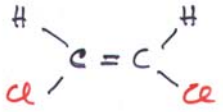
π E = 65 Kcal/mol

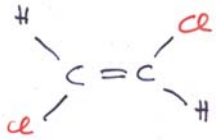


orbitali p non ibridati: è delocalizzati sopra e sotto il piano della molecola

- rotazione – perdita di sovrapposiz. tra gli orb. p.
- Stereoisomeria del doppio legame

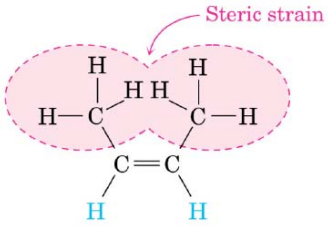
1,2-dicloroetene



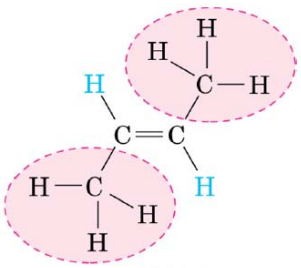


pto fus. −80°C −50

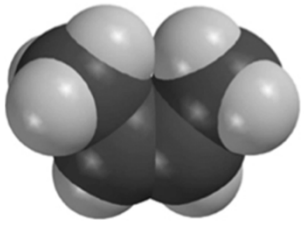
pto ebull. 60°C 48°C

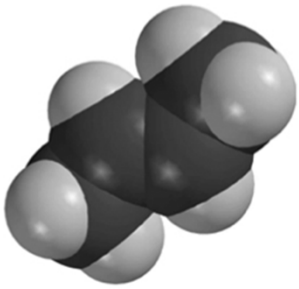


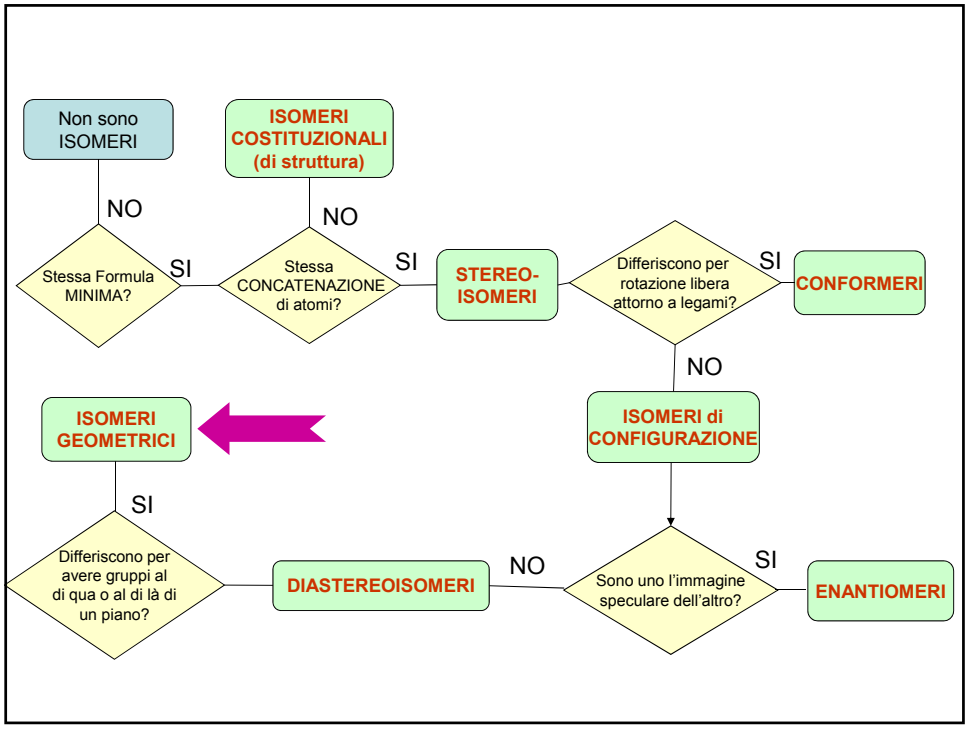
cis-2-Butene

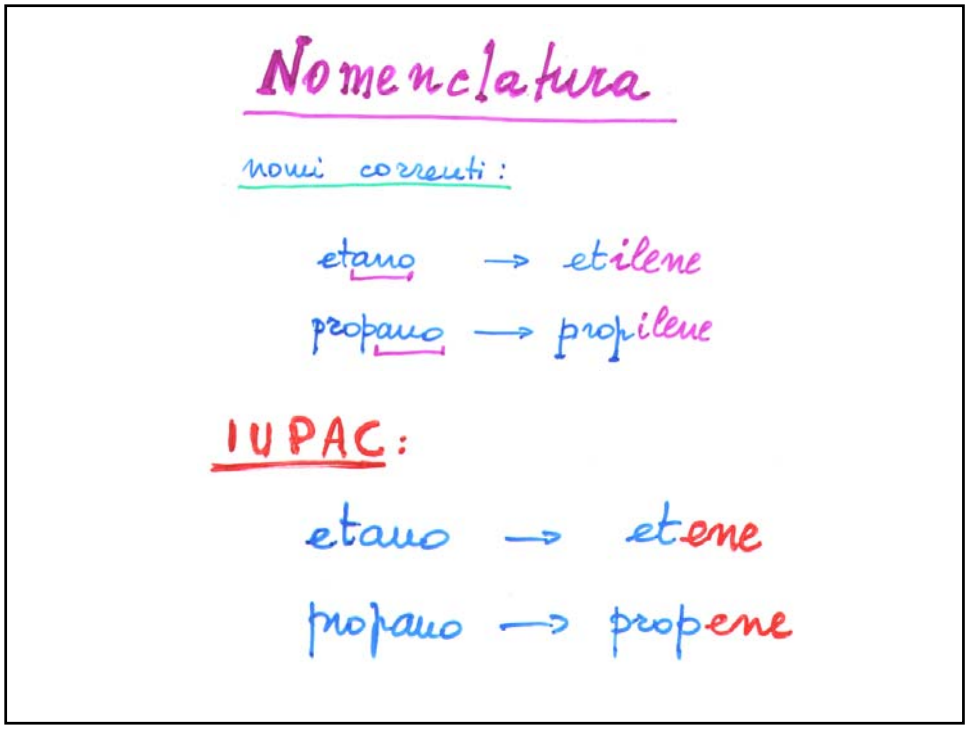


trans-2-Butene

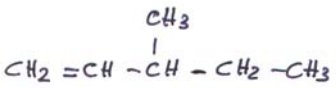


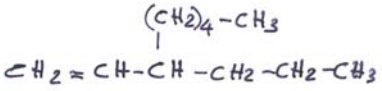



Non sono ISOMERI
NO
ISOMERI COSTITUZIONALI (di struttura)
NO
Stessa Formula MINIMA?
SI
Stessa CONCATENAZIONE di atomi?
SI
STEREO-ISOMERI
Differiscono per rotazione libera attorno a legami?
SI
CONFORMERI
NO
ISOMERI GEOMETRICI
ISOMERI di CONFIGURAZIONE
SI
Differiscono per avere gruppi al di qua o al di là di un piano?
DIASTEREOISOMERI
NO
Sono uno l'immagine speculare dell'altro?
SI
ENANTIOMERI

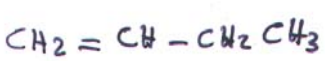

Nomenclatura
nomi correnti:
etano → etilene
propano → propilene
IUPAC:
etano → etene
propano → propene

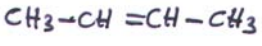
Regola 1: individuare la catena più lunga che contenga il doppio legame ⇒ -ene



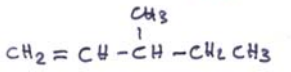


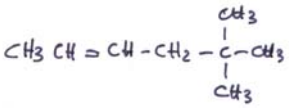
Regola 2: si numera partendo dall'estremità più vicina al doppio legame





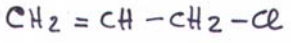
Regola 3. I sostituenti si aggiungono come prefissi; si Assegnano ai sostituenti i numeri più bassi possibile.

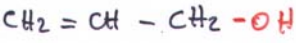


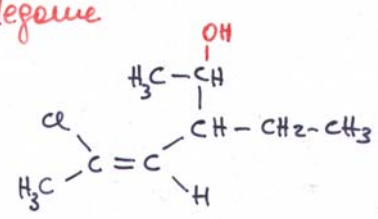


Regola 3.b Il gruppo ossidrile (-OH) ha priorità sul doppio legame

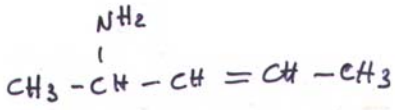
-OH → -olo



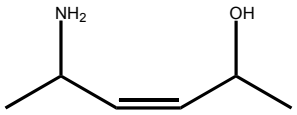




Ammine: anche il gruppo ammidico ha priorità sul doppio legame:



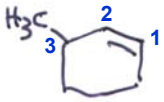
2-ammino-3-pentene

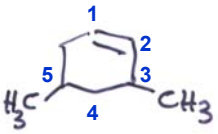


cis-5-ammino-3-esen-2-olo

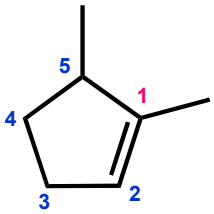
Regola 3.c

Per i cicloalcheni si usa una nomenclatura analoga. Numerare il ciclo in modo da assegnare agli atomi di carbonio coinvolti nel doppio legame i numeri 1 and 2 e al primo sostituente il numero più basso possibile.

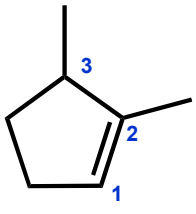




Se c'è un sostituente su uno degli atomi di carbonio del doppio legame, questo diventa numero 1.

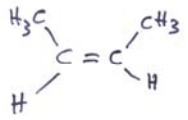


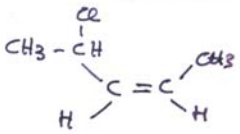
1,5-dimetilciclopentene

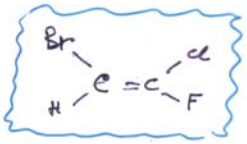


2,3-dimetilciclopentene **NO**

Regola 4. Nel caso di stereoisomeri, assegnare le sigle "cis" o "trans". (2 sostituenti)



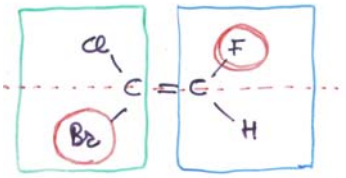




• ingombro sterico

Regola 5: sistema E, Z (più di 2 sostituenti)

Dare priorità con le regole di Cahn-Ingold-Prelog



F > H

Br > Cl

da parti opposte: E

Dalla stessa parte: Z

Regola 6.

alcano → alchile

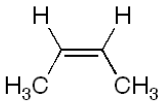
alcene → alchenili

$CH_2=CH-$ vinile

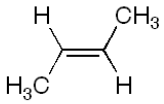
$CH_2=CH-CH_2-$ allile

Stabilità relativa degli alcheni

In generale, gli alcheni ***trans***-disostituiti sono ***più stabili*** dei loro isomeri *cis*



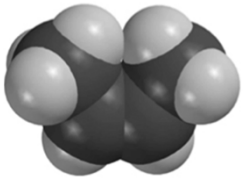
cis-2-butene



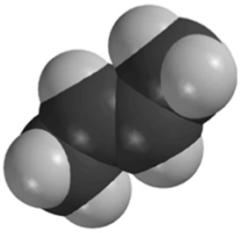
trans-2-butene

l'isomero ***trans*** è ***più stabile*** del *cis* di circa 3 kJ/mole

I *cis*-alcheni sono destabilizzati da effetti sterici (van der Waals)

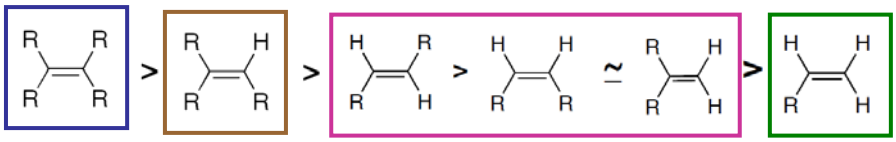


cis-2-butene

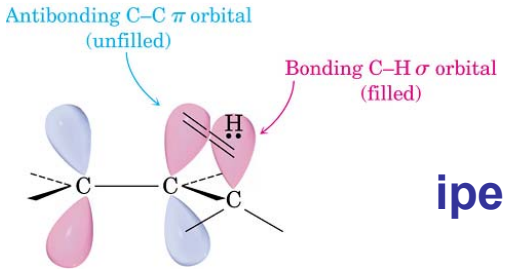


trans-2-butene

In generale, più alto è il numero dei sostituenti al doppio legame, maggiore è la stabilità dell'alchene.



Stabilità crescente



Ciò è dovuto alla

iperconiugazione

The delocalization of σ-electrons or lone pair of electrons into adjacent *π*-orbital or *p*-orbital is called hyperconjugation (or "no bond resonance" or "Baker-Nathan effect").

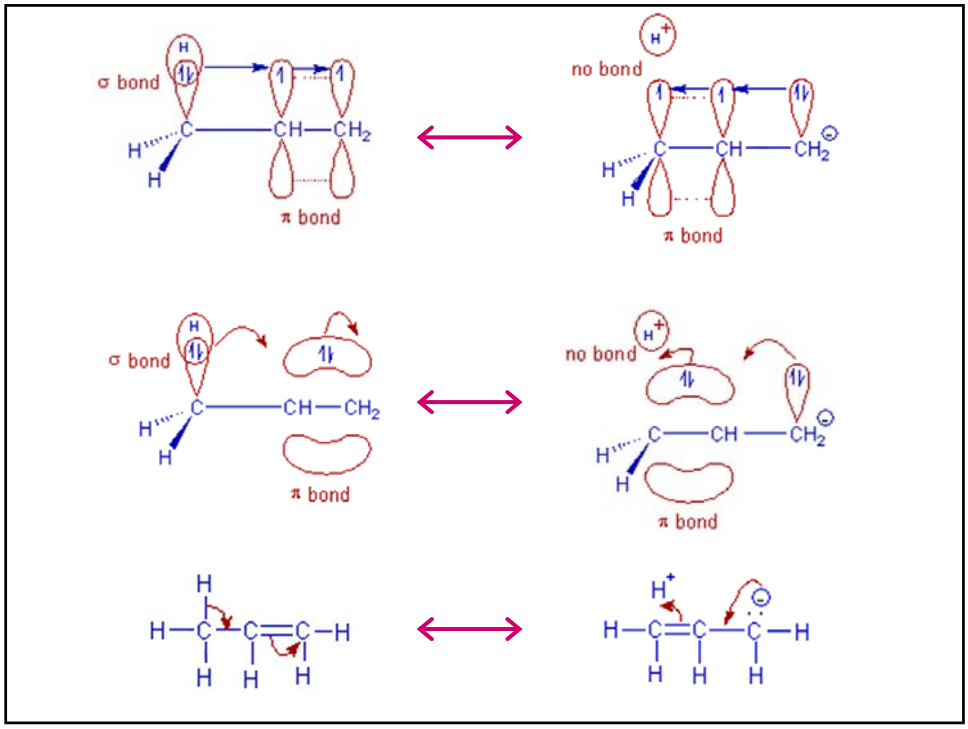
Conditions for hyperconjugation

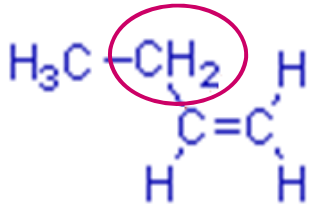
There must be an α-CH group or a lone pair on atom adjacent to sp^2 hybrid carbon or other atoms like nitrogen, oxygen etc.

E.g., alkenes, alkyl carbocations, alkyl free radicals, nitro compounds with α-hydrogen

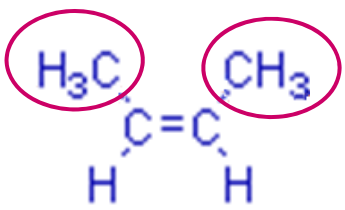
The displacement of σ-electrons towards the multiple bond occurs when **there are hydrogens on the α-carbon** adjacent to the multiple bond. This results in the polarization of the multiple bond.

E.g. in propene, the σ-electrons of C-H bond of methyl group can be delocalized into the π-orbital of the doubly bonded carbon.





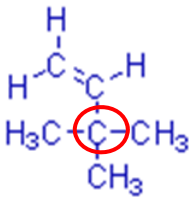
1-butene



2-butene

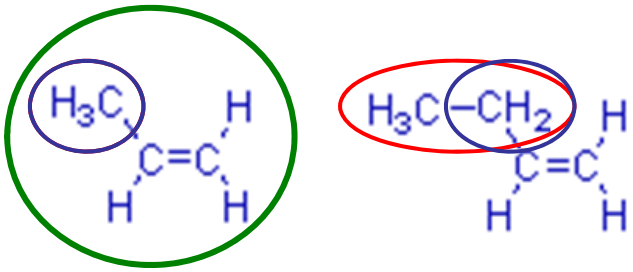
Increasing the substitution of an alkene, increases the number of possible hyperconjugation interactions

but:



no hyperconjugation !!

It is also important to note that the effect of **hyperconjugation** is **stronger** than the inductive effect.



Inductive effect	lower (CH_3)	**higher (C_2H_5)**
Hyperconjugation	**higher (CH_3)**	lower (CH_2)
Stability	**more stable**	less stable

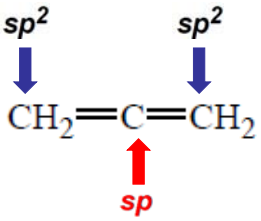
Proprietà chimico-fisiche

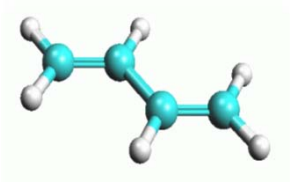
Punto di ebollizione e pto di fusione

		pf	p. eboll.
Etene	$CH_2=CH_2$	-169	-104
Etano	CH_3-CH_3	-183	-88.6
Propene	$CH_3-CH=CH_2$	-185	-47
Propano		-188	-42
cis-2-butene	$CH_3CH=CH-CH_3$	-139	3.7
trans-2-butene		-106	1.0
1-Eptene		-119	94
Eptano		-91	98.4

DIENI E COMPOSTI POLIINSATURI

Cumulati





Coniugati

$CH_2{=}CH{-}CH{=}CH_2$

$H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$

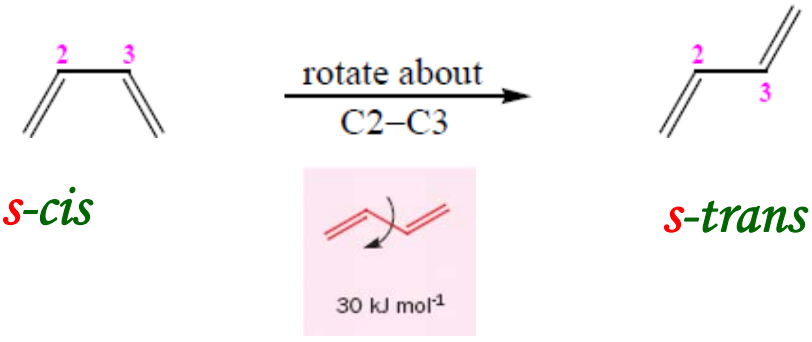
Isolati

Polieni

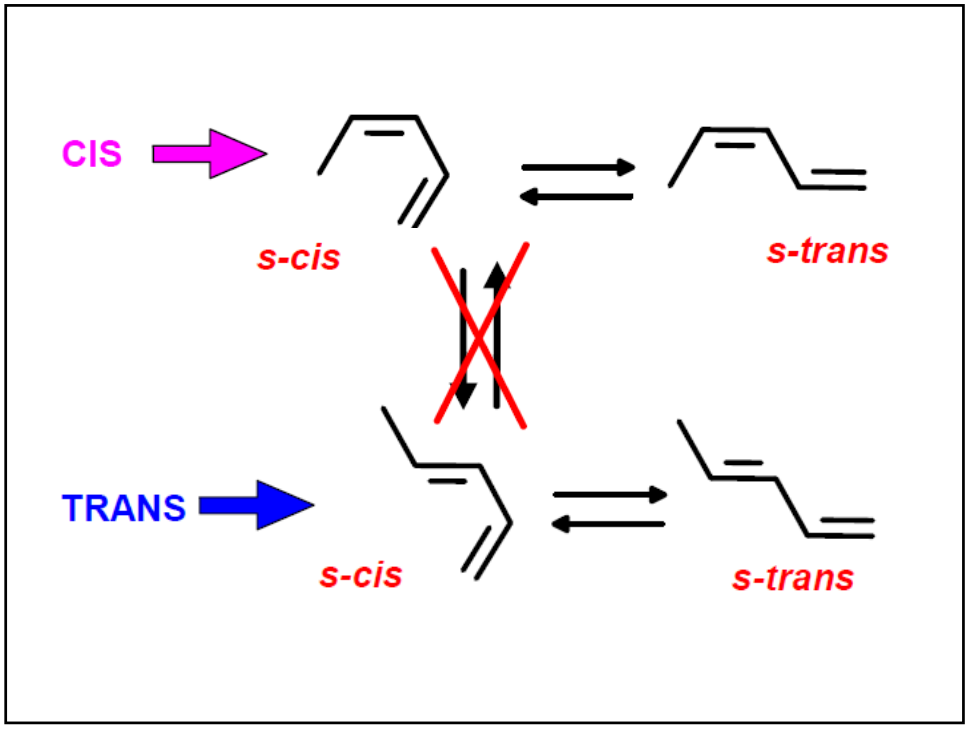
CONFORMAZIONI DEI DIENI CONIUGATI

Nei dieni coniugati, la rotazione attorno al legame semplice che si trova tra i due doppi legami può essere solo di 180°, per permettere che gli atomi di carbonio (tutti ibridati sp^2) stiano sullo stesso piano (e quindi sia possibile la delocalizzazione elettronica).

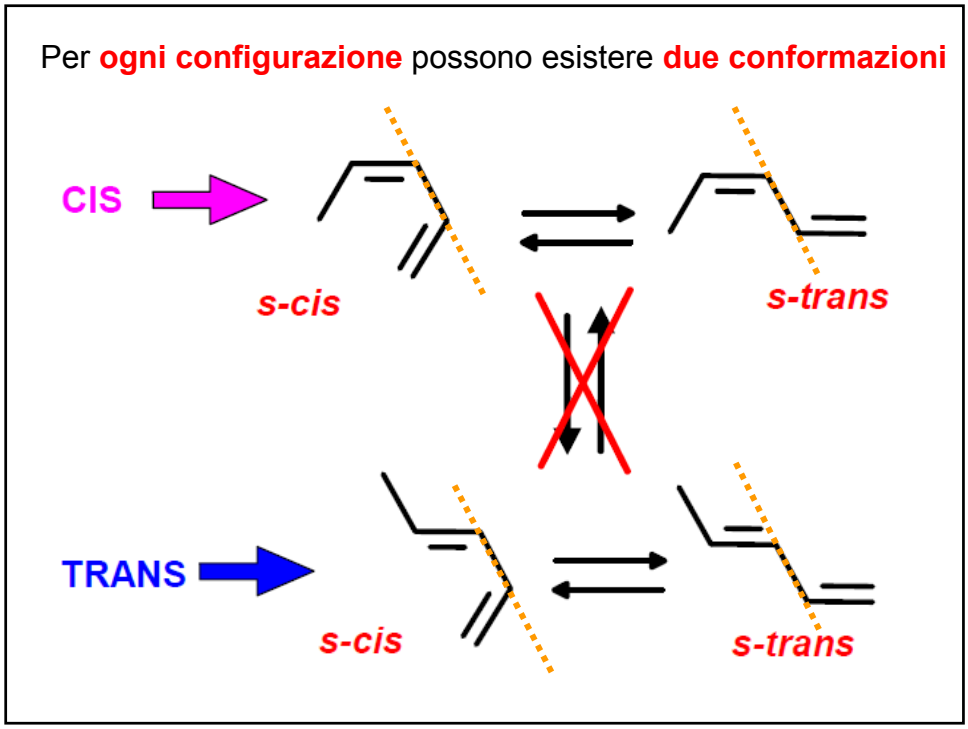
Le conformazioni sono solo DUE

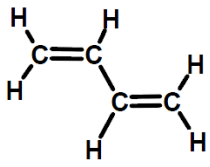


s-cis *s-trans*

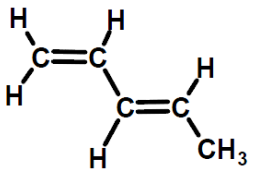


Per **ogni configurazione** possono esistere **due conformazioni**



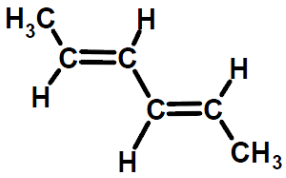


1,3-butadiene



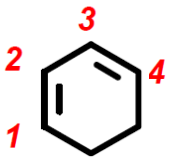
trans-1,3-pentadiene

(E)-1,3-pentadiene

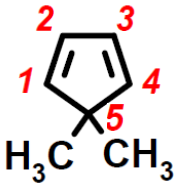


(2-*trans*,4-*trans*)-2,4-esadiene

(2E,4E)-2,4-esadiene

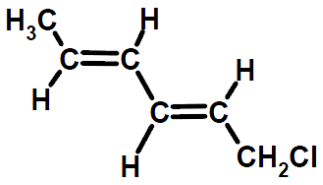


1,3-cicloesadiene



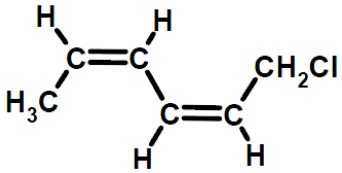
5,5-dimetilciclopentadiene

Scrivere gli isomeri geometrici del **1-cloro-2,4-esadiene**



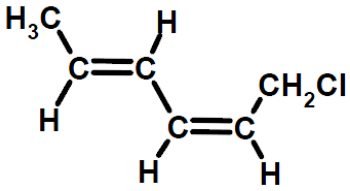
(2-*trans*,4-*trans*)-1-cloro-2,4-esadiene

(2E,4E)-1-cloro-2,4-esadiene



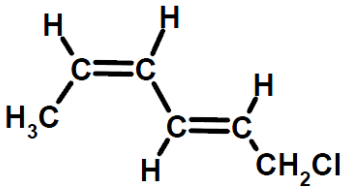
(2-cis,4-cis)-1-cloro-2,4-esadiene

(2Z,4Z)-1-cloro-2,4-esadiene



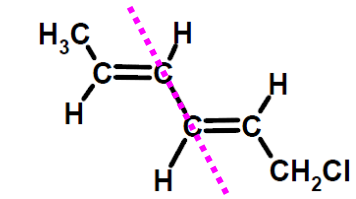
(2-*cis*,4-*trans*)-1-cloro-2,4-esadiene

(2Z,4E)-1-cloro-2,4-esadiene

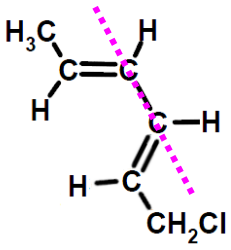


(2-*trans*,4-*cis*)-1-cloro-2,4-esadiene

(2E,4Z)-1-cloro-2,4-esadiene



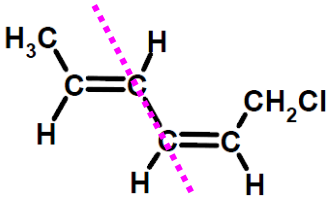
s-trans



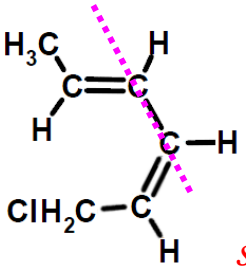
s-cis

(*2-trans,4-trans*)-1-cloro-2,4-esadiene

(*2E,4E*)-1-cloro-2,4-esadiene



s-trans



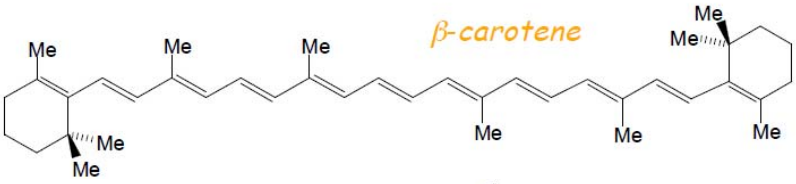
s-cis

(*2-cis,4-trans*)-1-cloro-2,4-esadiene

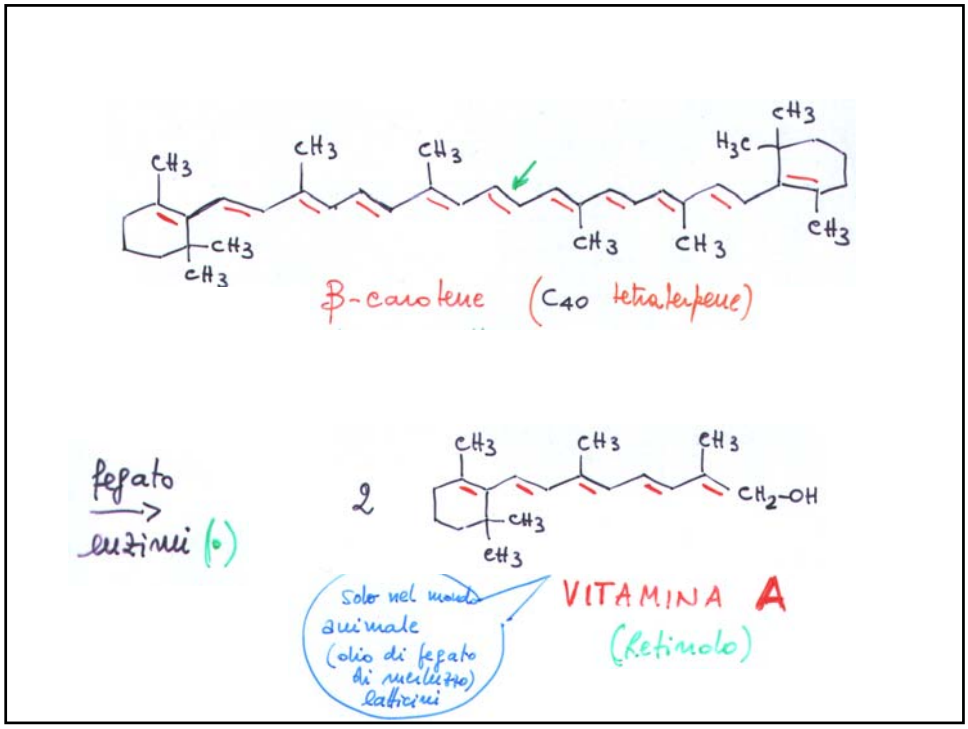
(*2Z,4E*)-1-cloro-2,4-esadiene

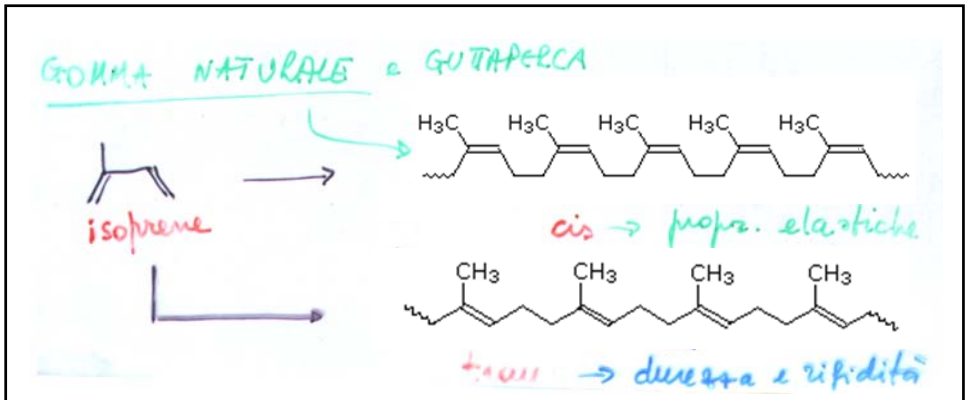
Sistemi π esteri .... in natura

β-carotene

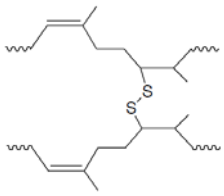


antioxidant believed to protect against cancer, heart disease



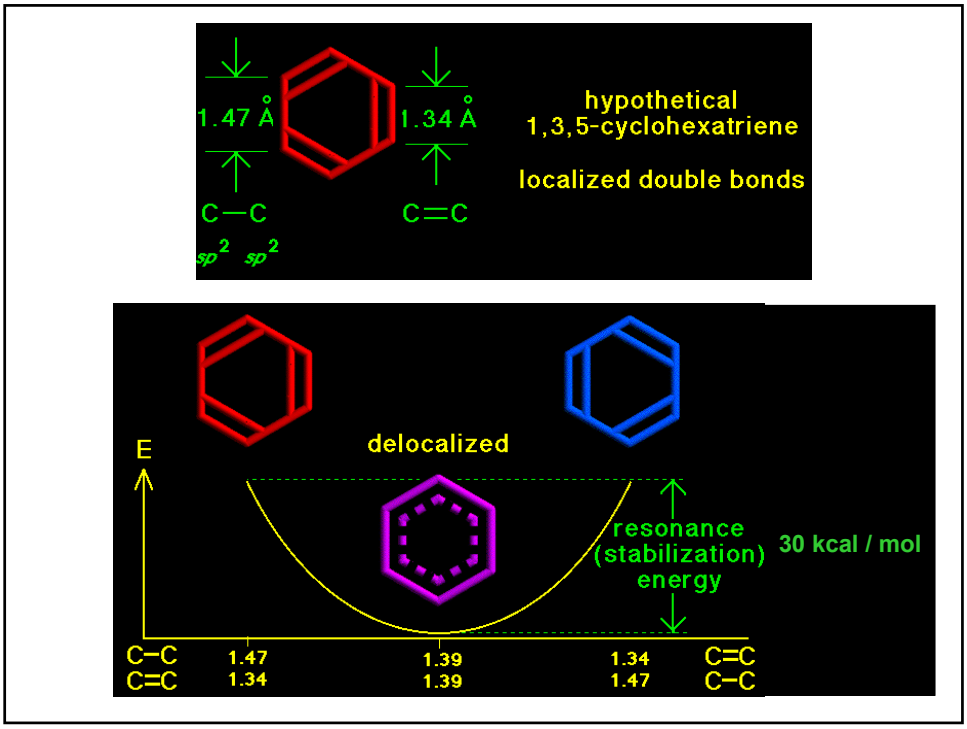


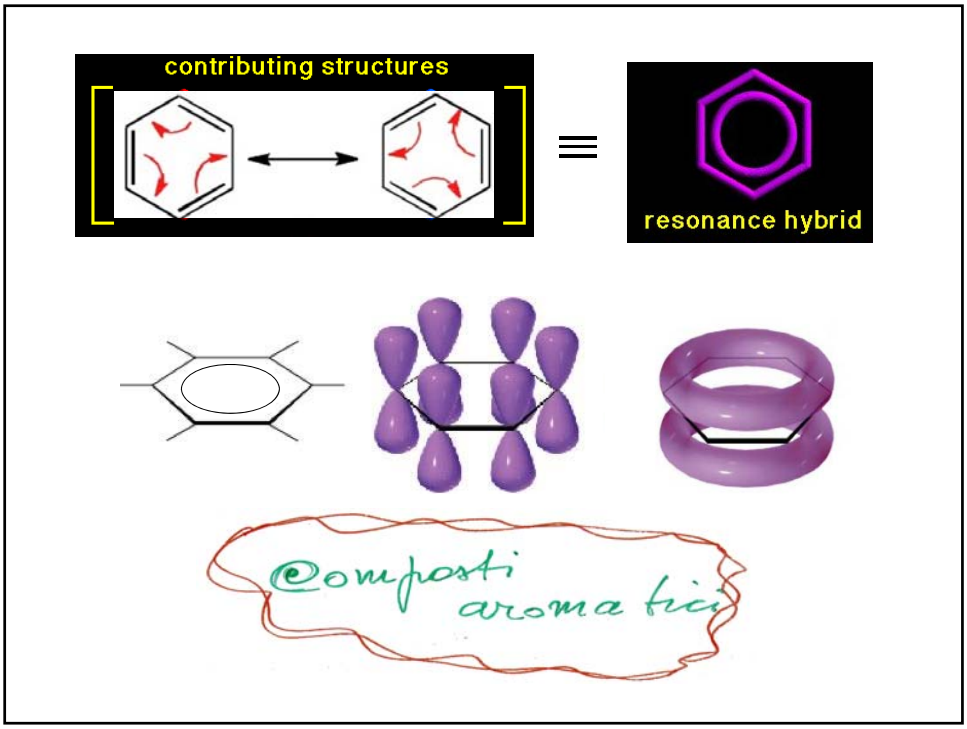
vulcanization (Goodyear, 1839) introduces sulfur crosslinks

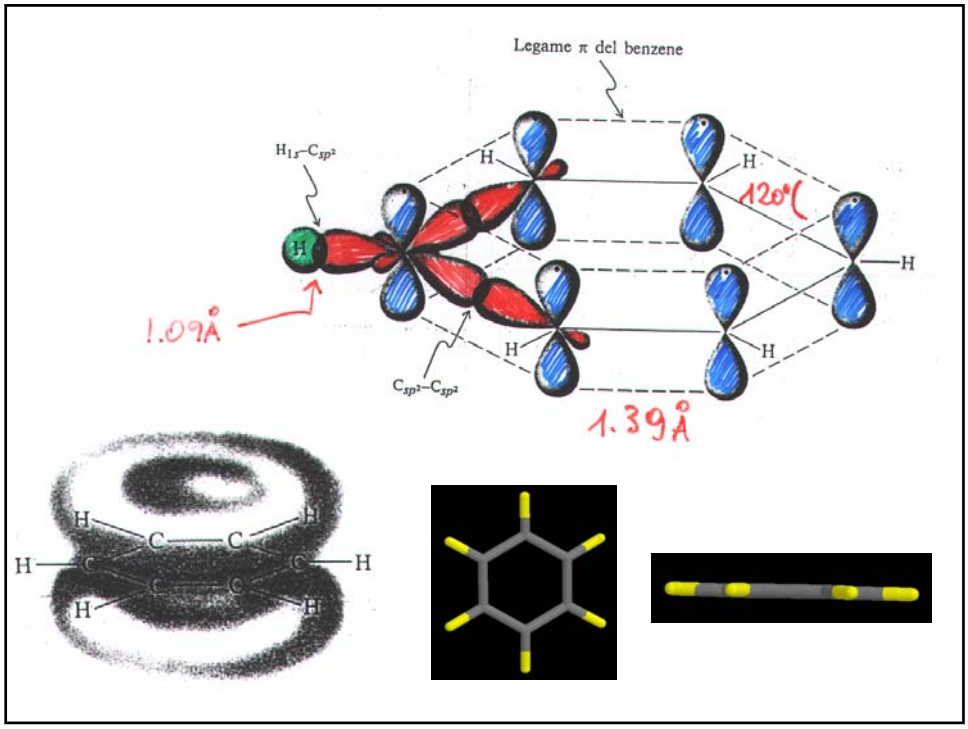


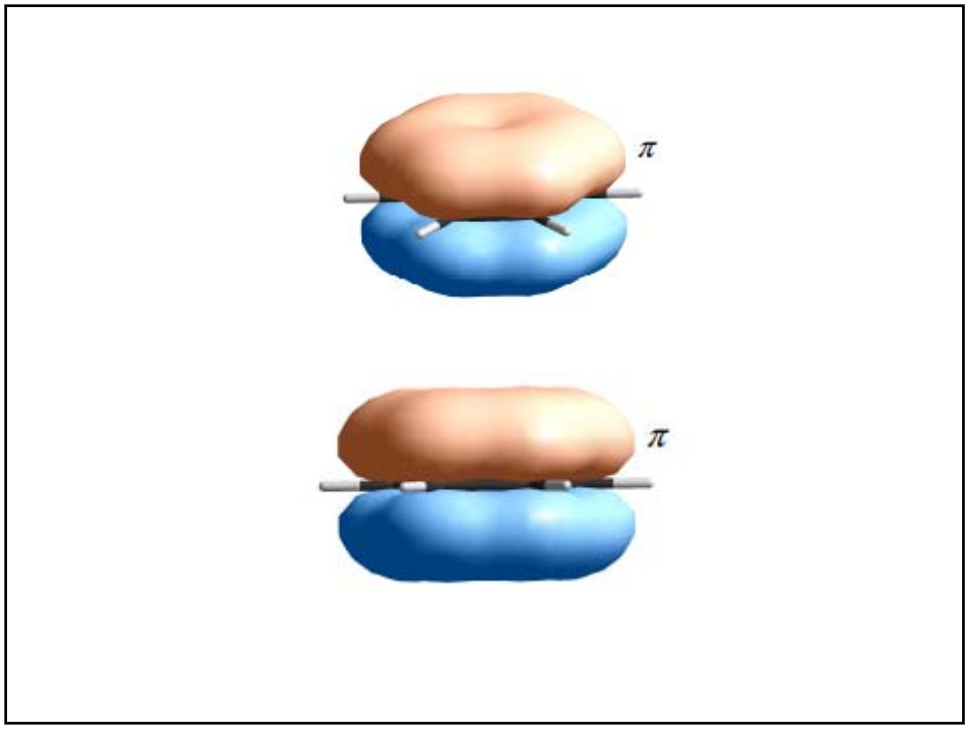
crosslinks separated by ~100 isoprene units

•susceptibility to oxidation and aging


1.47 Å
1.34 Å
C—C
C=C
sp2 sp2
hypothetical
1,3,5-cyclohexatriene
localized double bonds
E
delocalized
resonance
(stabilization)
energy
30 kcal / mol
C—C
C=C
1.47
1.34
1.39
1.39
1.34
1.47
C=C
C—C


contributing structures
resonance hybrid
Composti aromatici

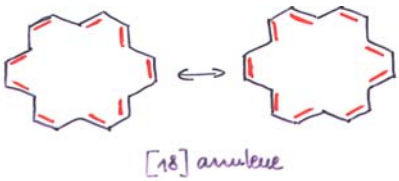

Legame π del benzene
H1s–Csp²
1.09Å
120°
1.39Å
Csp²–Csp²


π
π

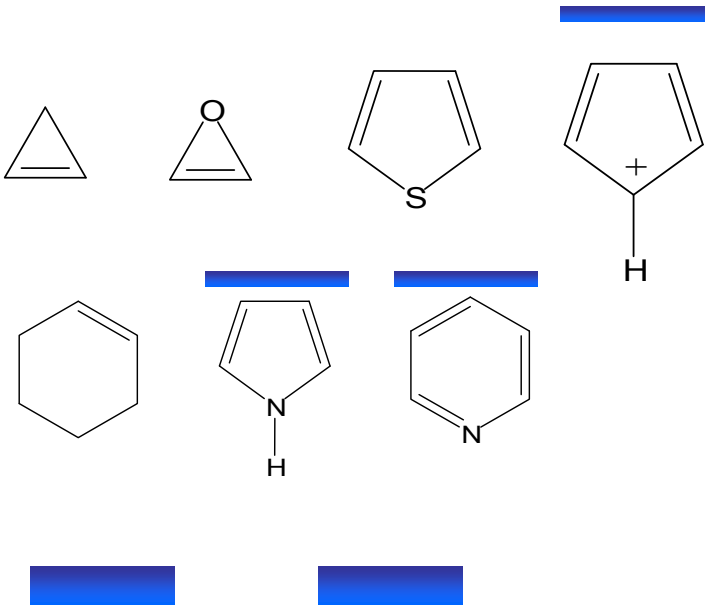
AROMATICITA'

1. La molecola è ciclica
2. La molecola è planare
3. $e^- \pi = 4n + 2$ $\quad n = 0, 1, 2, 3, \ldots$

   Regola di Hückel
4. Orbitali *p* perpendicolari al piano del ciclo



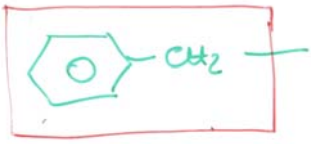
[18] annulene



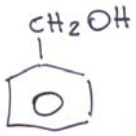
Benzeni sostituiti = ARENI

Ar- gruppi arilici

C_6H_5- fenile



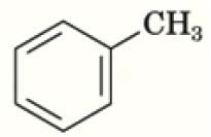
Benzile



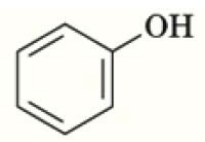
Alcol benzilico

Nomenclatura

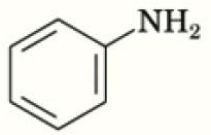
Nomi comuni



toluene

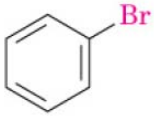


fenolo

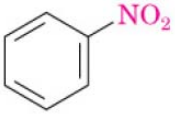


anilina

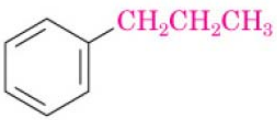
Derivati monosostituiti



Bromobenzene

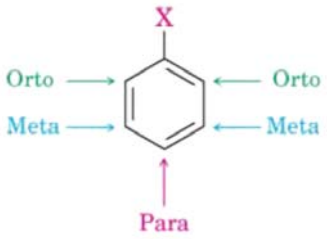


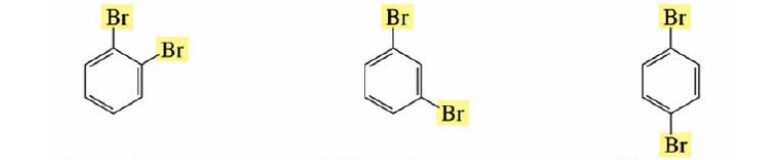
Nitrobenzene



Propilbenzene

Derivati bisostituiti

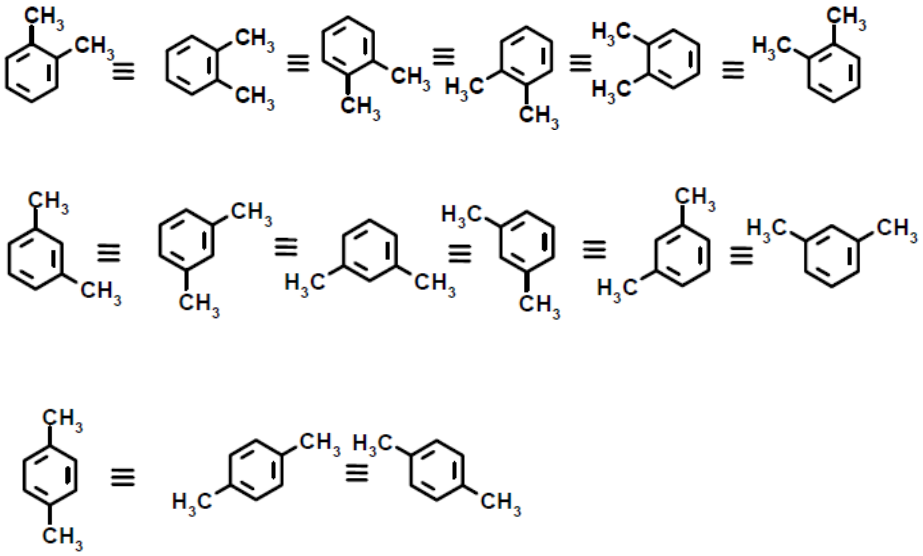




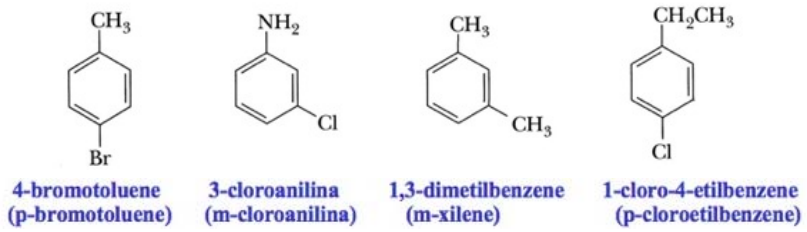
1,2-dibromobenzene
orto-dibromobenzene
o-dibromobenzene

1,3-dibromobenzene
meta-dibromobenzene
m-dibromobenzene

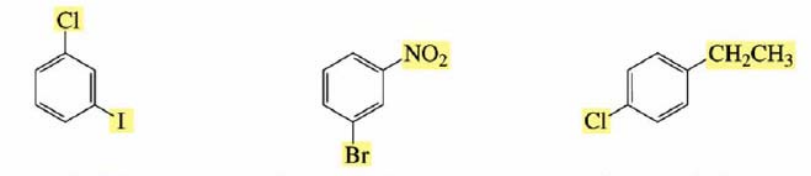
1,4-dibromobenzene
para-dibromobenzene
p-dibromobenzene



Se ci sono due sostituenti diversi, si usa l'ordine alfabetico



4-bromotoluene (p-bromotoluene) | 3-cloroanilina (m-cloroanilina) | 1,3-dimetilbenzene (m-xilene) | 1-cloro-4-etilbenzene (p-cloroetilbenzene)



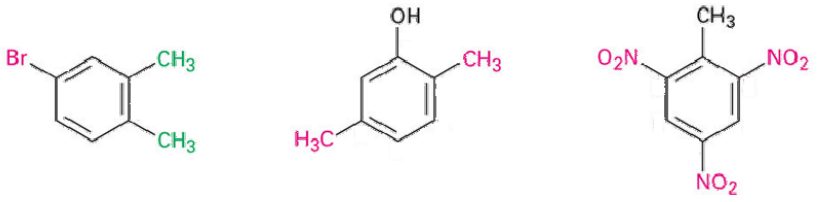
1-chloro-3-iodobenzene
meta-chloroiodobenzene
not
1-iodo-3-chlorobenzene
meta-iodochlorobenzene

1-bromo-3-nitrobenzene
meta-bromonitrobenzene

1-chloro-4-ethylbenzene
para-chloroethylbenzene

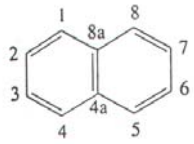
Derivati polisostituiti

Si numera l'anello in modo che i sostituenti abbiano i numeri più bassi possibili.



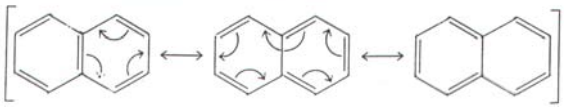
4-bromo-1,2-dimetilbenzene | 2,5-dimetilfenolo | 2,4,6-trinitrotoluene

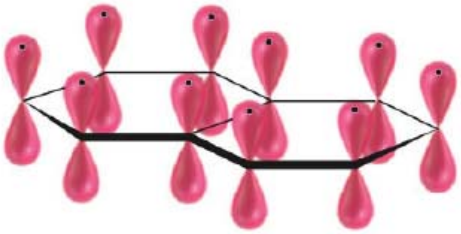
SISTEMI AROMATICI POLICICLICI

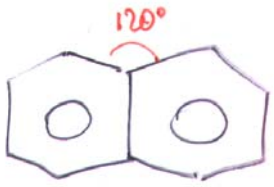


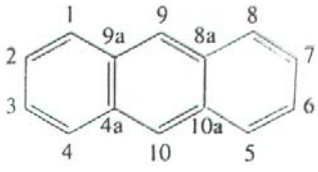
Naftalene

Strutture di risonanza nel naftalene

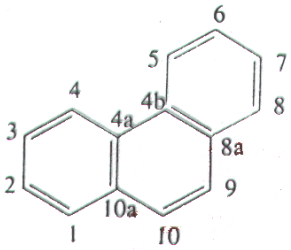




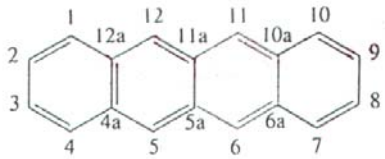




Antracene

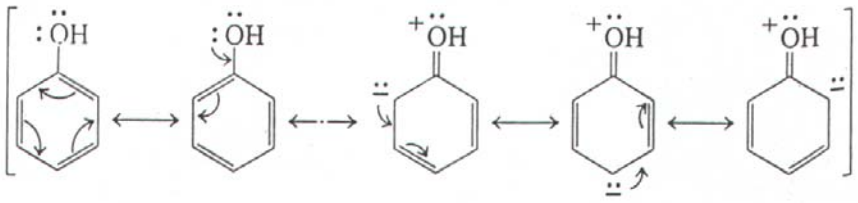


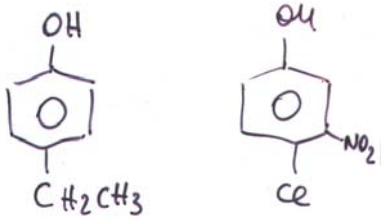
Fenantrene

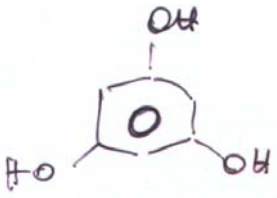


Tetracene
(Naftacene)

I fenoli

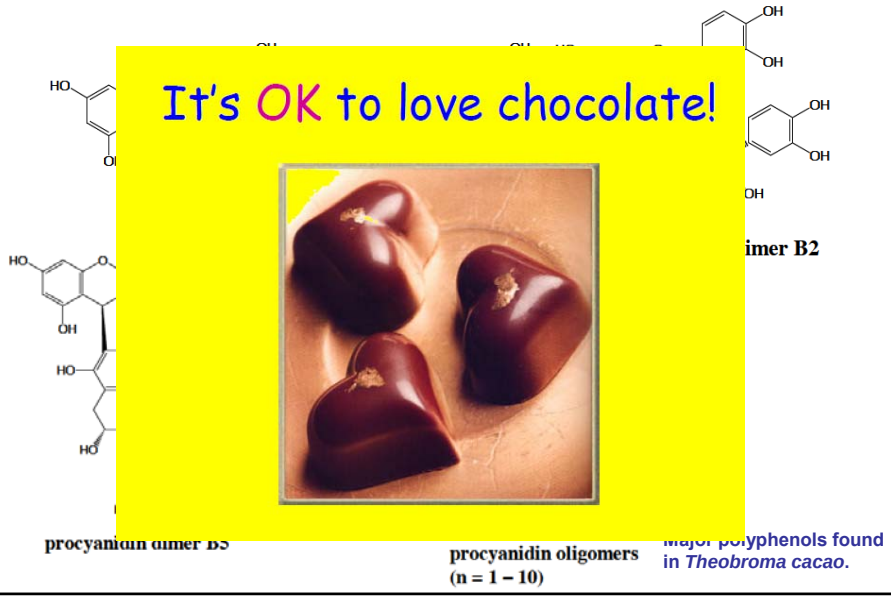




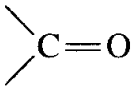


- disinfettanti
- polimeri
- coloranti
- fotografia

Chocolate may be the "food of the gods" containing antioxidants such as polyphenols

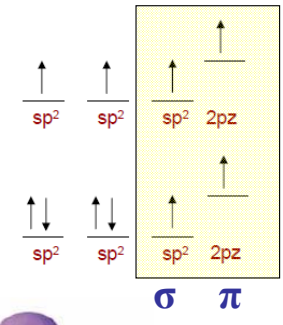


Il gruppo carbonilico

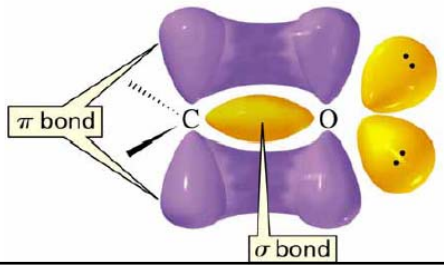


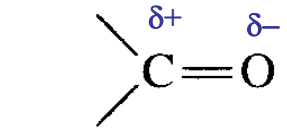
Elettroni di valenza del carbonio : $2s^2\ 2p^2$
con orbitali ibridi sp^2 :

Elettroni di valenza dell'ossigeno : $2s^2\ 2p^4$
con orbitali ibridi sp^2 :

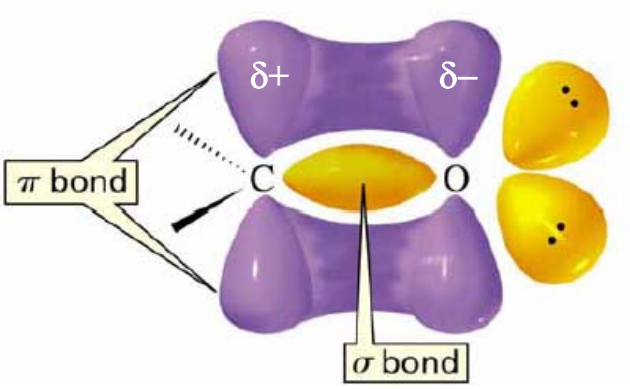


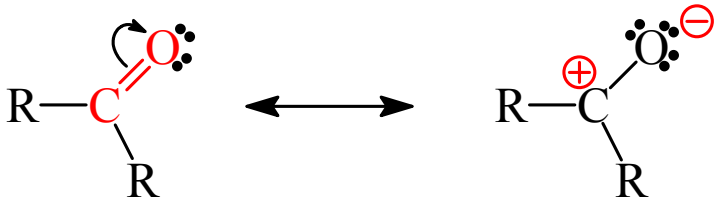
3 regions of electrons
sp^2 hybridization

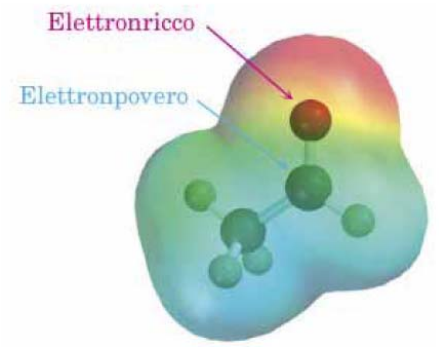


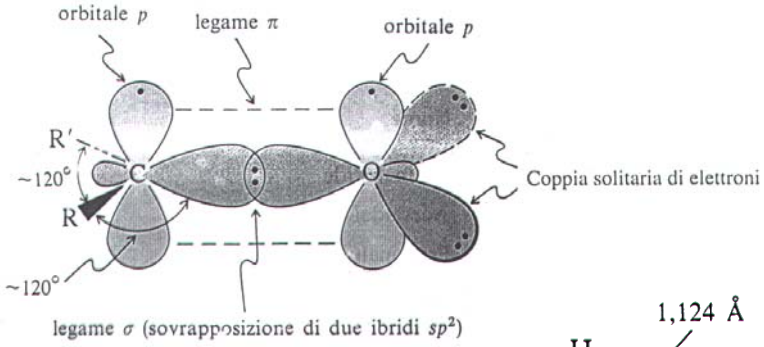

δ+
δ–
C
O

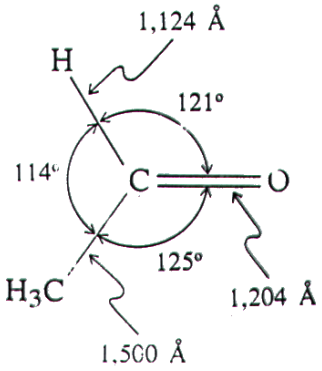
EN: C 2,5 O 3,5


δ+
δ–
π bond
C
O
σ bond


R
C
O
R
R
C
O
R

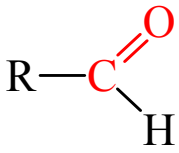

Elettronricco
Elettronpovero



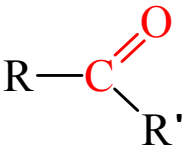


I composti carbonilici:

aldeidi e chetoni



aldeide



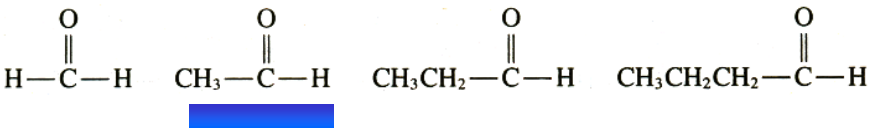
chetone

R, R' = alchile, arile

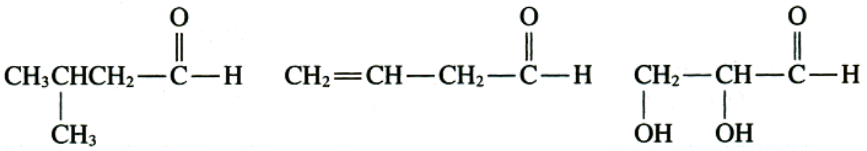
Nomenclatura

La desinenza delle **aldeidi** è ***-ale***

- Si individua la catena di atomi di carbonio più lunga contenente il gruppo carbonilico e si sostituisce la desinenza *–o* dell'alcano con ***– ale***.
- I sostituenti della catena si numerano a partire dal carbonio carbonilico che per definizione è **C1**.
- La funzione aldeidica ha priorità rispetto a quella chetonica.

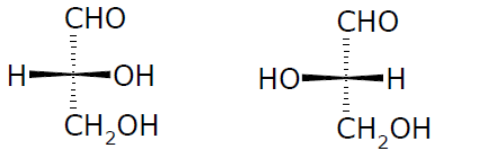


metanale (formaldeide) | etanale (acetaldeide) | propanale (propionaldeide) | butanale (*n*-butirraldeide)

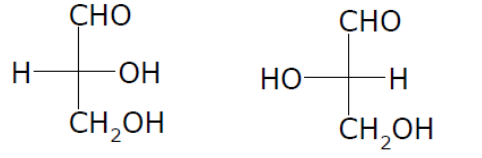


3-metilbutanale | 3-butenale | 2,3-diidrossipropanale (gliceraldeide)

Gli **zuccheri** si definiscono della serie D e L basandosi sulla configurazione dell'unico stereocentro della gliceraldeide.

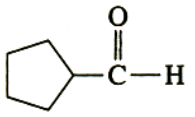


D-Gliceraldeide | **L-Gliceraldeide**

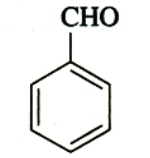


R-(+) | S-(–)

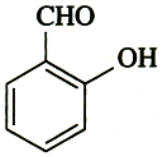
Quando il gruppo –CHO è legato ad un anello, il composto prende il nome di **carbaldeide** e il carbonio carbonilico è il C1.



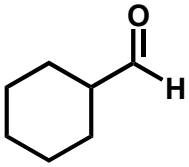
ciclopentancarbaldeide
(formilciclopentano)



benzaldeide
(benzencarbaldeide)



aldeide salicilica
(2-idrossibenzencarbaldeide)

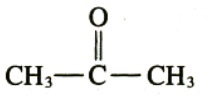


cicloesancarbaldeide

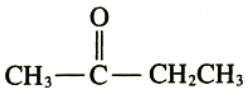
Nomenclatura

La desinenza dei chetoni è ***-one***

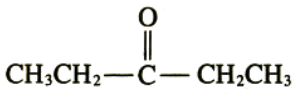
- Si individua la catena di atomi di carbonio più lunga contenente il gruppo carbonilico e si sostituisce la desinenza –*o* dell'alcano con ***– one***.
- Al carbonio carbonilico spetta il numero più basso della catena a prescindere dalla presenza di altri sostituenti o dei gruppi funzionali –OH, C=C o C≡C.



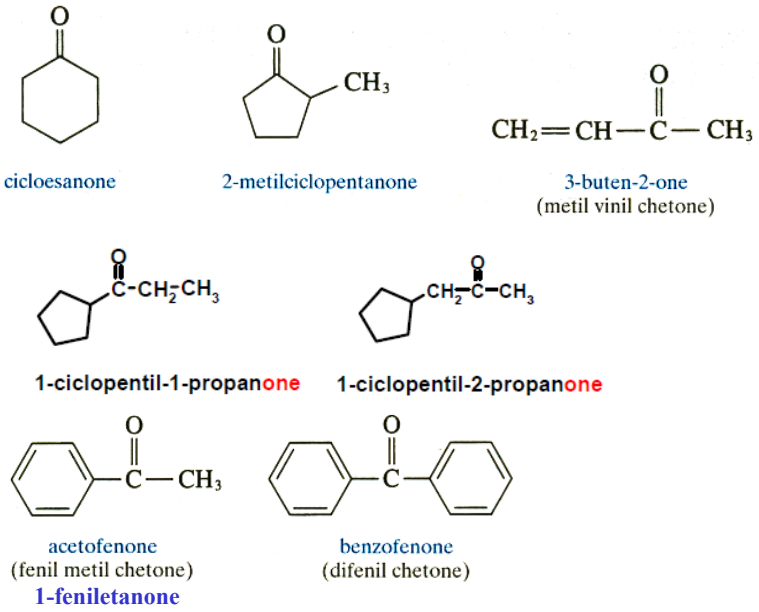
propanone
(acetone)



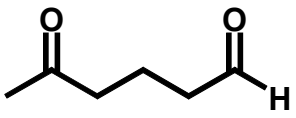
2-butanone
(etil metil chetone)



3-pentanone
(dietil chetone)



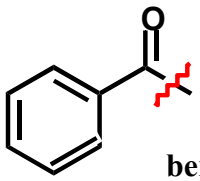
Quando un chetone è contemporaneamente presente con una funzione aldeidica ci si riferisce ad esso con il termine **osso**.



5-ossoesanale

RC– è chiamato alcanoile o **acile**

HC– è chiamato **formile**



benzoile

CH_3C– è chiamato **acetile**

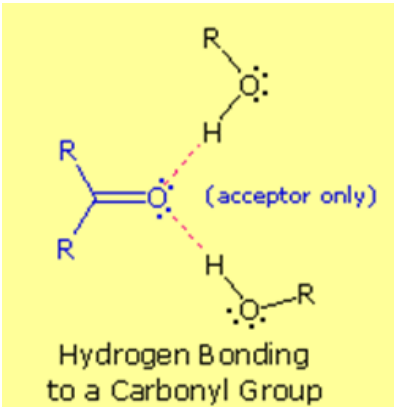
Formula	Nome	pf (°C)	pe (°C)	Solubilità in acqua
HCHO	Formaldeide	−92	−21	Molto solubile
CH_3CHO	Acetaldeide	−125	21	∞
CH_3CH_2CHO	Propanale	−81	49	Molto solubile
$CH_3(CH_2)_2CHO$	Butanale	−99	76	Solubile
$CH_3(CH_2)_3CHO$	Pentanale	−91,5	102	Poco solubile
$CH_3(CH_2)_4CHO$	Esanale	−51	131	Poco solubile
C_6H_5CHO	Benzaldeide	−26	178	Poco solubile
$C_6H_5CH_2CHO$	Fenilacetaldeide	33	193	Poco solubile
CH_3COCH_3	Acetone	−95	56,1	∞
$CH_3COCH_2CH_3$	2-Butanone	−86	79,6	Molto solubile
$CH_3COCH_2CH_2CH_3$	2-Pentanone	−78	102	Solubile
$CH_3CH_2COCH_2CH_3$	3-Pentanone	−39	102	Solubile
$C_6H_5COCH_3$	Acetofenone	21	202	Insolubile
$C_6H_5COC_6H_5$	Benzofenone	48	306	Insolubile

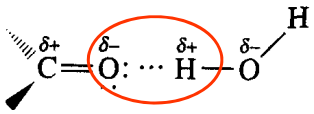
Proprietà chimico-fisiche di aldeidi e chetoni

Composto	Nome	pf (°C)	pe (°C) (1 atm)	Densità d_4^{20} (g mL^{-1})	Solubilità in acqua (g 100 mL^{-1} H_2O)
Alcoli monossidrilici					
CH_3OH	Metanolo	−97	64,7	0,792	∞
CH_3CH_2OH	Etanolo	−117	78,3	0,789	∞
$CH_3CH_2CH_2OH$	Alcol propilico	−126	97,2	0,804	∞
$CH_3CH(OH)CH_3$	Alcol isopropilico	−88	82,3	0,786	∞
$CH_3CH_2CH_2CH_2OH$	Alcol butilico	−90	117,7	0,810	8,3
$CH_3CH(CH_3)CH_2OH$	Alcol isobutilico	−108	108,0	0,802	10,0
$CH_3CH_2CH(OH)CH_3$	Alcol *sec*-butilico	−114	99,5	0,808	26,0
$(CH_3)_3COH$	Alcol *terz*-butilico	25	82,5	0,789	∞
$CH_3(CH_2)_3CH_2OH$	Alcol pentilico	−78,5	138,0	0,817	2,4

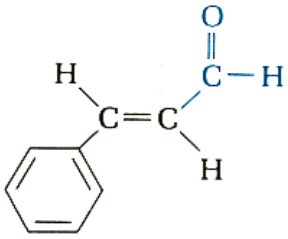
Aldehydes and ketones are not hydrogen bond donors (they can't donate a proton); therefore, they have lower boiling points than alcohols of similar molecular weight.

Aldehydes and ketones are hydrogen bond acceptors; this makes them have considerable solubilities in water.



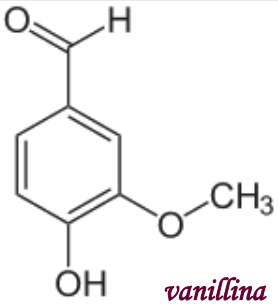


Aldeidi in natura



aldeide cinnamica

trans-3-fenil-2-propenale

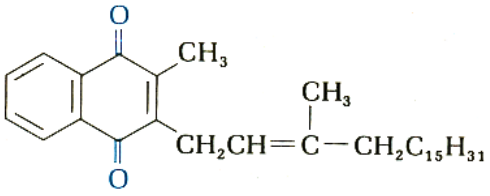


vanillina

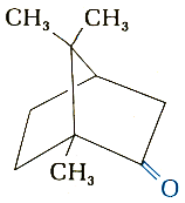
4-idrossi-3-metossibenzaldeide

benzaldeide

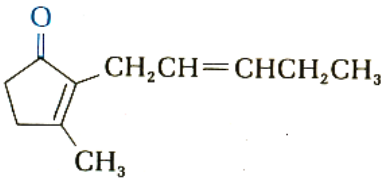
Chetoni in natura



vitamina K



canfora

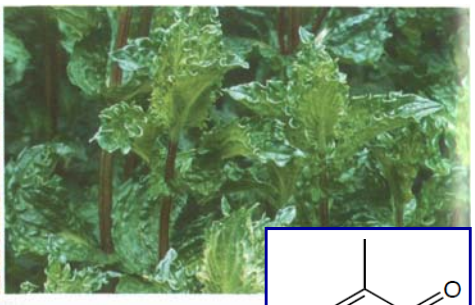


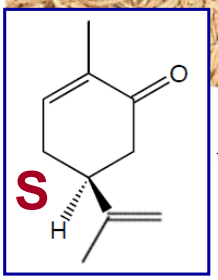
jasmone
(essenza di gelsomino)

Chetoni in natura

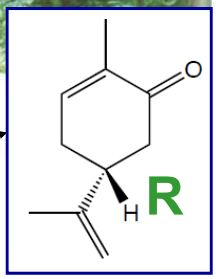
cumino

menta





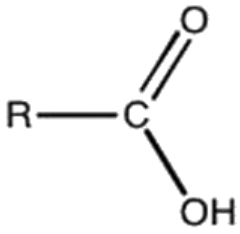
carvone



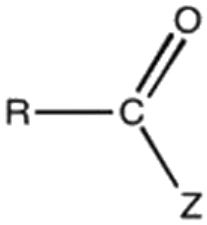
Zibetto africano (*Viverra Civetta*)

Ciclo a 17 termini

Acidi carbossilici



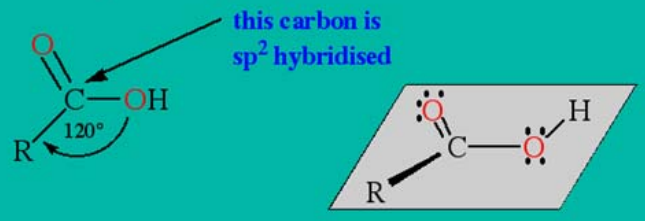
RCOOH



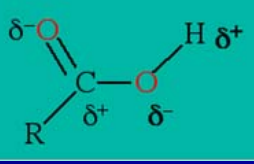
Z = OR, NRR', X, …..

Structure and bonding

- Carbon sp^2 hybridised
- Carboxylic acid group is PLANAR

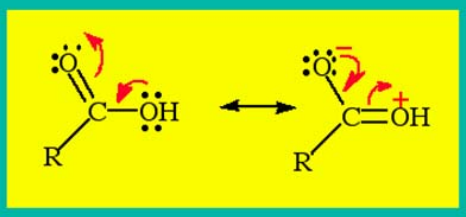


- O—H bond strongly polarised

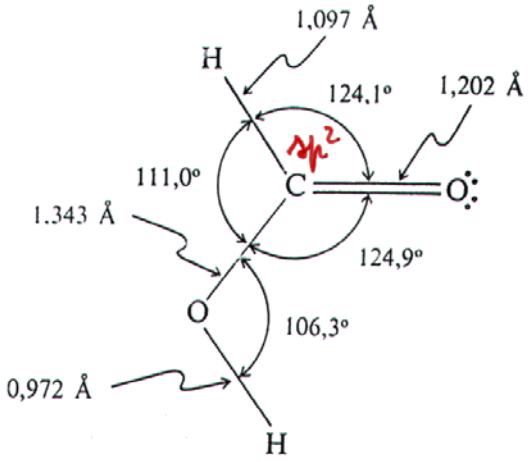


Resonance in carboxyl groups

- Lone pair on oxygen can "delocalise" onto the carbonyl oxygen



- Results in longer C=O and shorter C—OH bond

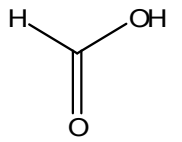


Nomenclatura

Trovare la catena più lunga di atomi di carbonio contenente il gruppo COOH.

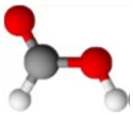
Sostituire la –o finale del nome dell'alcano con –oico, facendo precedere la parola da acido.

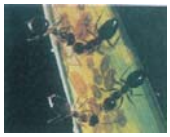
Il carbonio 1 è quello del carbossile



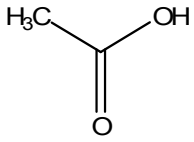
Acido metanoico

Acido formico





Venne ottenuto per la prima volta nel 1670 dalla distillazione distruttiva di formiche

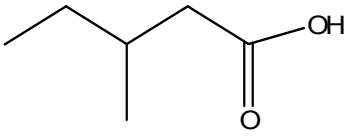


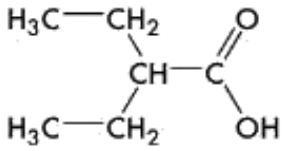
Acido etanoico

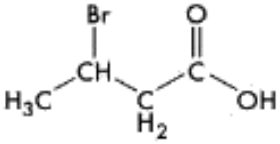
Acido acetico

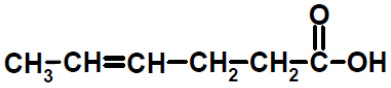
Some common names

Common	IUPAC	Formula
Formic	methanoic	$HCOOH$
Acetic	ethanoic	CH_3COOH
Propionic	propanoic	CH_3CH_2COOH
Butyric	butanoic	$CH_3(CH_2)_2COOH$
Capric	decanoic	$CH_3(CH_2)_8COOH$
Lauric	dodecanoic	$CH_3(CH_2)_{10}COOH$
Steric	octadecanoic	$CH_3(CH_2)_{16}COOH$

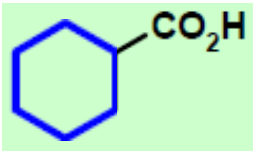




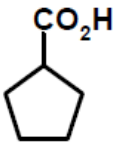


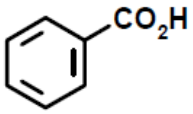


Quando il carbossile è legato ad un anello deve essere nominato esplicitamente come acido **alcan**carbossilico.



acido cicloesancarbossilico



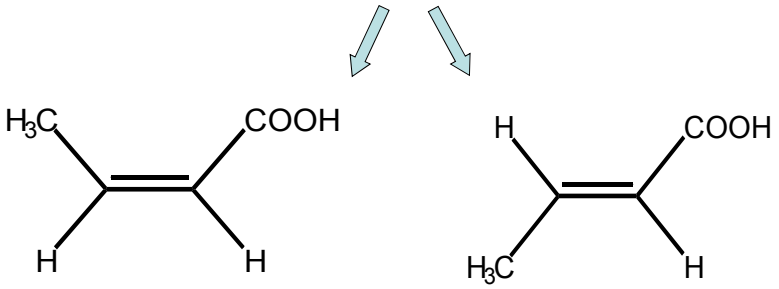


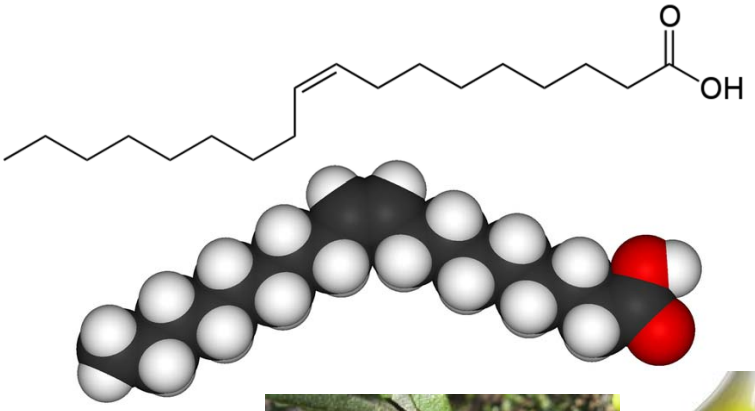
Acido benzencarbossilico
Acido benzoico

Acidi carbossilici insaturi

H_2C=CHCOOH

CH_3CH=CHCOOH

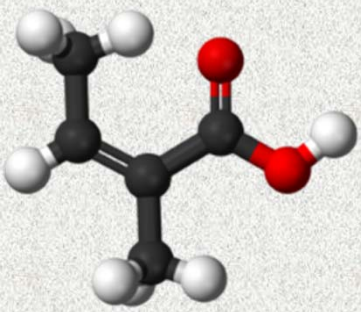




acido oleico

acido *cis*-9-ottadecenoico

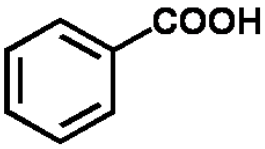
Acidi organici dell'altro mondo …..

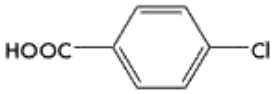


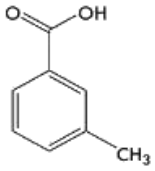
Acido angelico

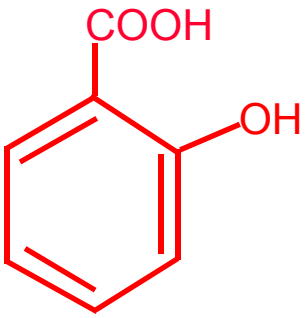
Angelica Archangelica e *Angelica Sylvestris*

Acidi carbossilici aromatici



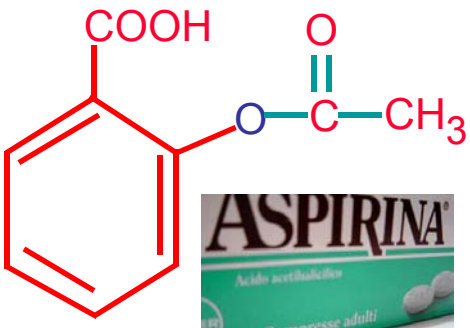






acido *o*-idrossi-benzoico

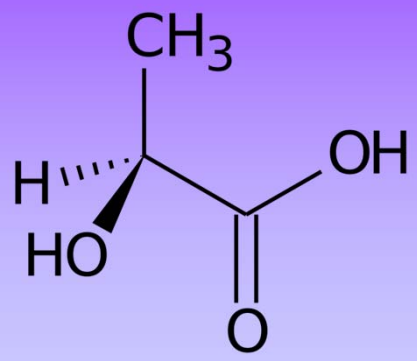
acido salicilico

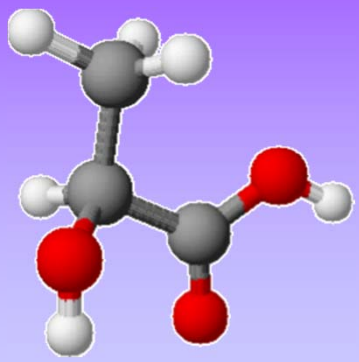


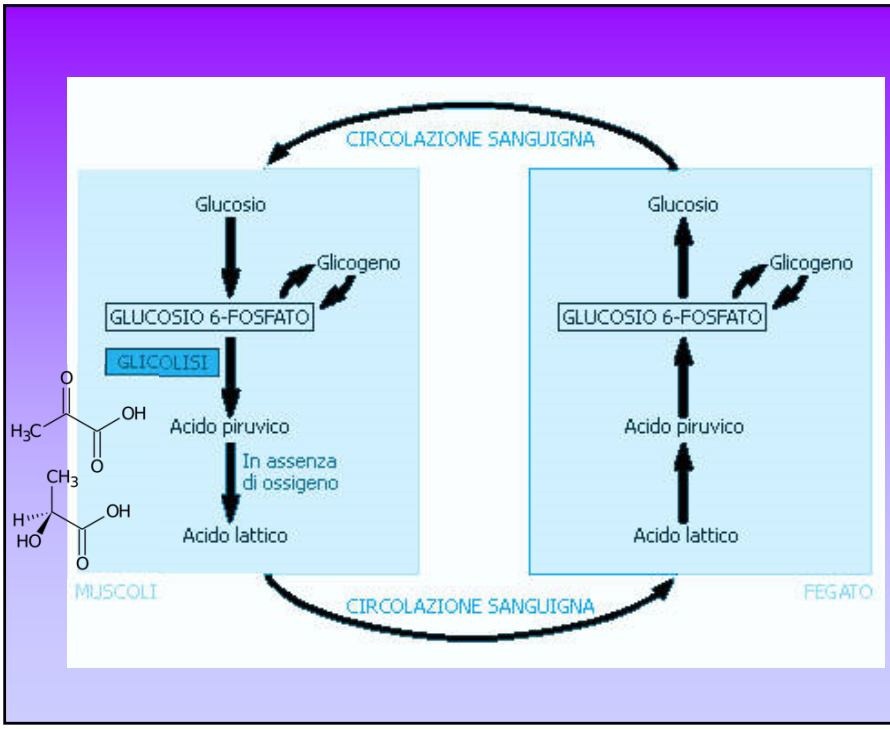
acido acetil-salicilico

Idrossiacidi

Acido lattico







Acidi **bi**carbossilici

Se in una molecola i gruppi carbossilici sono due, *entrambi* devono far parte della catena principale, di cui costituiscono le estremità.

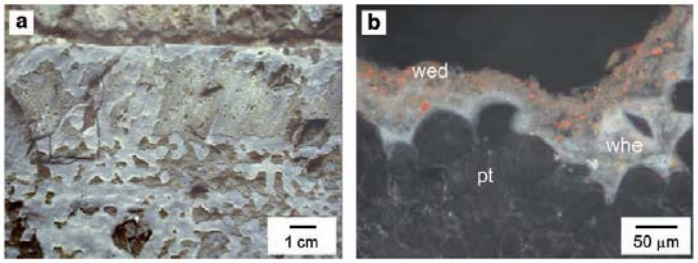
Acidi bicarbossilici alifatici

Formula	*Nome comune*	*Fonte*	*Nome IUPAC*
HOOC—COOH	acido ossalico	piante della famiglia *ossalica* (ad esempio l'acetosella)	
HOOC—CH_2—COOH	acido malonico	mele	
HOOC—$(CH_2)_2$—COOH	acido succinico	ambra (dal latino *succinum*)	
HOOC—$(CH_2)_3$—COOH	acido glutarico	glutine	
HOOC—$(CH_2)_4$—COOH	acido adipico	grassi (dal latino *adeps*)	
HOOC—$(CH_2)_5$—COOH	acido pimelico	grassi (dal greco *pimelé*)	

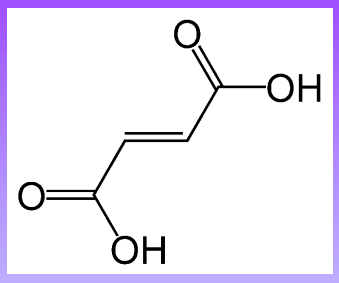
Acido ossalico HOOC-COOH

Rabarbaro

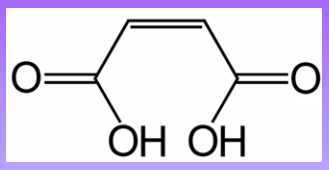
PATINE AD OSSALATO DI CALCIO SU MONUMENTI MARMOREI



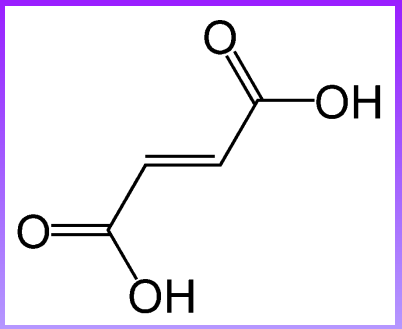
Pellicole ad ossalati di calcio sul paramento murario del Palazzo Pubblico. a: aspetto macroscopico. b: microstratigrafia in sezione sottile trasversale, luce riflessa campo scuro (pt = substrato lapideo; whe = pellicola a whewellite parzialmente solfatata; wed = pellicola a weddellite con pigmenti di ocre rosse e brune e raro nero di carbone).



Acido fumarico



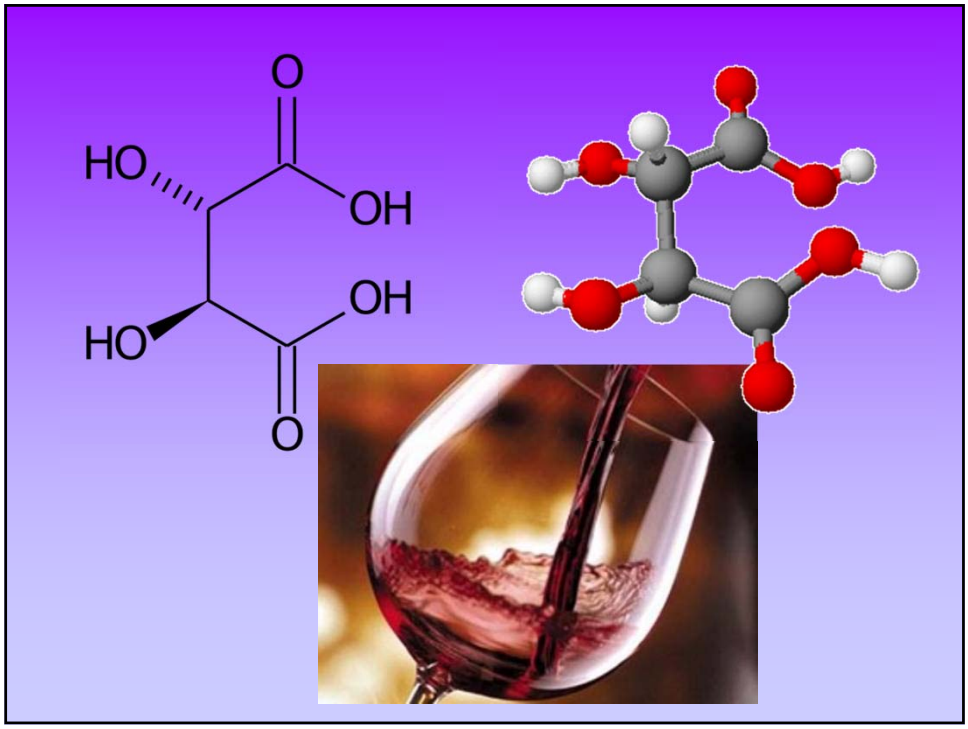
Acido maleico



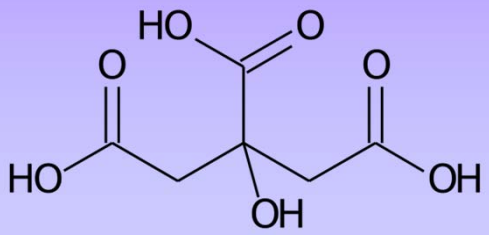
Fumaria officinalis

E297

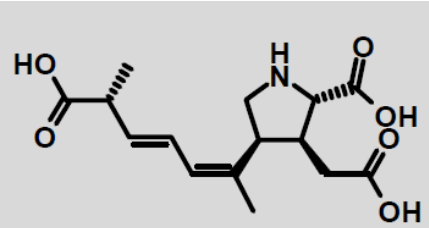
Usato come acido e stabilizzante strutturale in una grande varietà di prodotti. E' anche usato come fonte di acido nel lievito in polvere



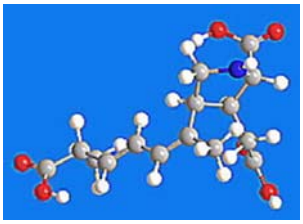
Acidi **poli**carbossilici



Acido citrico



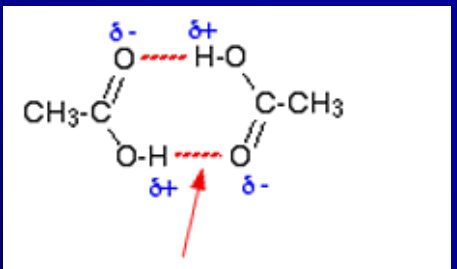
Acido Domoico



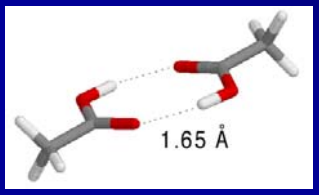
Neurotossina prodotta da un'alga marina. Si diffonde nella catena alimentare uccidendo leoni marini e balene e provocando problemi di digestione e memoria nell'uomo (Amnesic Shellfish Poisoning)

Legami a idrogeno

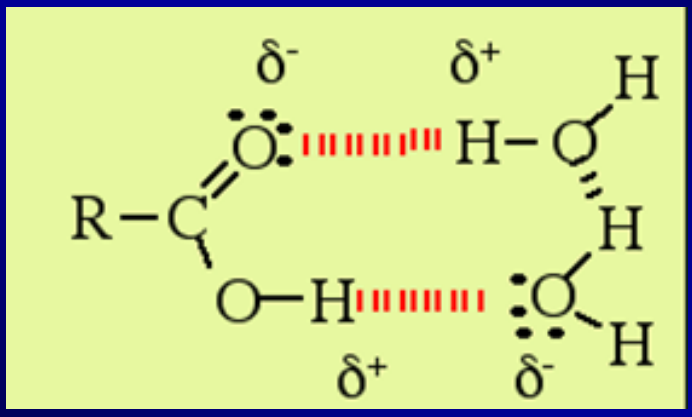
Gli acidi carbossilici formano dimeri nei quali le due unità sono tenute saldamente insieme da due legami idrogeno:



Hydrogen bond between the fairly positive hydrogen atom and a lone pair on the fairly negative oxygen atom.



Solubilità in acqua



Proprietà chimico-fisiche

• I primi termini della serie sono liquidi incolori con odori pungenti o sgradevoli.

• Composti **polari** e, come gli alcoli, **formano legami idrogeno** con se stessi o con altre molecole.

• Di conseguenza: **punti di ebollizione elevati**, più elevati degli alcoli di pari peso molecolare.
[es. l'acido acetico e l'alcol propilico hanno lo stesso peso formula (60) e bollono rispettivamente a 118°C e 97°C].

Proprietà chimico-fisiche

Nome	p.e. °C		p.f. °C	Solubilità, g/100 g di H_2O a 25 °C
formico	101	PM 46	8	
acetico	118		17	completamente
propanoico	141		−22	miscibili (∞)
butanoico	164		−8	
esanoico	205		−1,5	1,0
ottanoico	240		17	0,06
decanoico	270		31	0,01
benzoico	249		122	0,4 (ma 6,8 a 95 °C)

CH_3OH	Metanolo	64,7		−97	∞
CH_3CH_2OH	Etanolo	78,3	PM 46	−117	∞
$CH_3CH_2CH_2OH$	Alcol propilico	97,2		−126	∞
$CH_3CH(OH)CH_3$	Alcol isopropilico	82,3		−88	∞
$CH_3CH_2CH_2CH_2OH$	Alcol butilico	117,7		−90	8,3
$CH_3CH(CH_3)CH_2OH$	Alcol isobutilico	108,0		−108	10,0

HCHO	Formaldeide	−21		−92	Molto solubile
CH_3CHO	Acetaldeide	21	PM 44	−125	∞
CH_3CH_2CHO	Propanale	49		−81	Molto solubile
$CH_3(CH_2)_2CHO$	Butanale	76		−99	Solubile
$CH_3(CH_2)_3CHO$	Pentanale	102		−91,5	Poco solubile
$CH_3(CH_2)_4CHO$	Esanale	131		−51	Poco solubile

Proprietà fisiche degli acidi carbossilici

Nome	Struttura	p.f. (°C)	p.e. (°C)	Solubilità (g/100 g di H_2O a 25°C)
Acido formico	HCOOH	8.4	101	∞
Acido acetico	CH_3COOH	16.6	118	∞
Acido propionico	CH_3CH_2COOH	−21	141	∞
Acido butanoico	$CH_3(CH_2)_2COOH$	−5	162	∞
Acido pentanoico	$CH_3(CH_2)_3COOH$	−34	186	4,97
Acido esanoico	$CH_3(CH_2)_4COOH$	−4	202	0,97
Acido eptanoico	$CH_3(CH_2)_5COOH$	−8	223	0,24
Acido ottanoico	$CH_3(CH_2)_6COOH$	17	237	0,068
Acido nonanoico	$CH_3(CH_2)_7COOH$	15	255	0,026
Acido decanoico	$CH_3(CH_2)_8COOH$	32	270	0,015

Proprietà fisiche degli acidi dicarbossilici

Nome	Struttura	p.f. (°C)	p.e. (°C)	Solubilità (g/100 g di H_2O a 25°C)
Acido ossalico	HOOCCOOH	189	150 (sublima)	s
Acido malonico	$HOOCCH_2COOH$	136	Decompone	m. sol.
Acido succinico	$HOOC(CH_2)_2COOH$	185	235	p. sol.
Acido glutarico	$HOOC(CH_2)_3COOH$	98	200	m. sol.
Acido adipico	$HOOC(CH_2)_4COOH$	151	337	p. sol.
Acido pimelico	$HOOC(CH_2)_5COOH$	106	decompone	p. sol.
Acido ftalico	$1,2\text{-}C_6H_4(COOH)_2$	231		p. sol.
Acido maleico	*cis*-HOOCCH=CHCOOH	130,5		m. sol.
Acido fumarico	*trans*-HOOCCH=CHCOOH	302		p. sol.

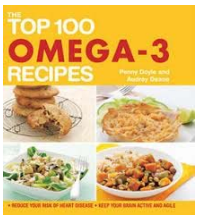
Acidi grassi

Sono acidi monocarbossilici alifatici con numero pari di atomi di carbonio, da C_4 a C_{22} e oltre.

I doppi legami degli acidi grassi insaturi naturali hanno tutti configurazione *cis*.

Essendo alcuni acidi grassi insaturi considerati essenziali, questi si classificano anche in base alla loro appartenenza a determinati processi metabolici:

Omega-3 quando l'ultimo doppio legame è presente sul terzo carbonio a partire dalla fine.

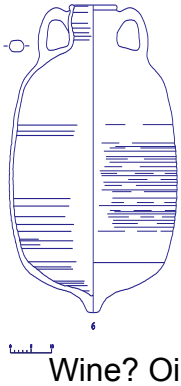


Acido linolenico ($C_{18:3}$)

Omega-6 , **Omega-9**

Organic acids in archaeology

- What did this amphora really transport?



Wine? Oil?

- What was cooked in medieval jars?

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J. Mass Spectrom. 2008; **43**: 108–115
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(www.interscience.wiley.com) DOI: 10.1002/jms.1283

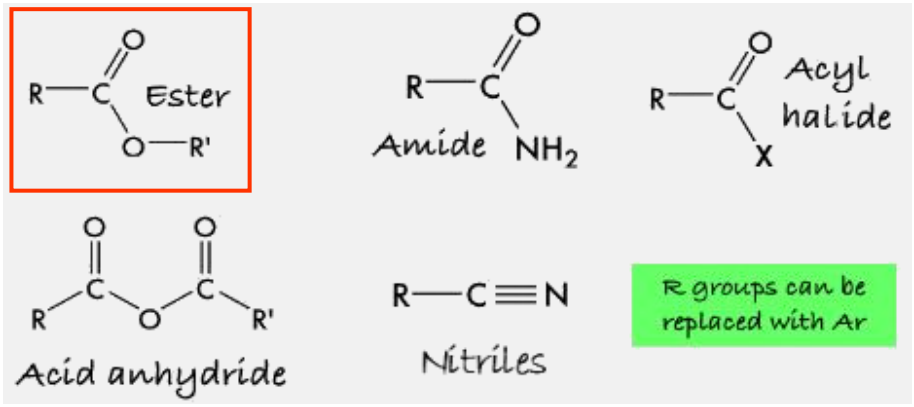
JMS

Cooking activities during the Middle Ages: organic residues in ceramic vessels from the Sant'Antimo Church (Piombino–Central Italy)†

Laura Salvini,[1] Alessandra Pecci[2] and Gianluca Giorgi[3]*

#	Compound	Retention time (min)
1	2-Hydroxypropanoic acid (Lactic acid) - 2TMS	15:77
2	2-Hydroxyacetic acid -2TMS	16:44
3	Oxalic acid 2TMS	19:30
4	β-Hydroxybutyric acid -2TMS	20:41
5	Benzoic acid TMS	23:92
6	Octanoic acid (Caprylic acid) –TMS	24:87
7	Glycerol -3TMS	25:92
8	α,ω-Butanedioic acid (Succinic acid) - 2TMS	27:30
9	Nonanoic acid (Pelargonic acid) –TMS	29:07
10	2-Hydroxyheptanoic acid - 2TMS	29:63
11	α,ω-Pentandioic (Glutaric acid) - 2TMS	31:17
12	Decanoic acid (Vapric acid) – TMS	33:08
13	α,ω-Hexanedioic (Adipic acid) - 2TMS	35:30
14	α,ω-Heptanedioic (Pimelic acid) - 2TMS	39:02
15	α,ω-Octanedioic (Suberic acid) - 2TMS	42:47
16	α,ω-Nonanedioic (Azelaic acid) - 2TMS	45:92
17	Tetradecanoic (Myristic acid) - 2TMS	47:40

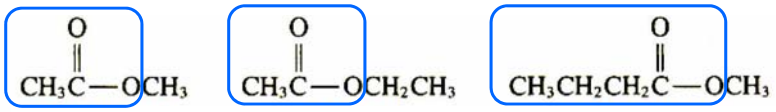
Derivati degli acidi carbossilici

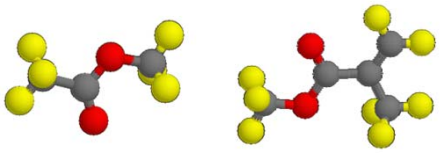


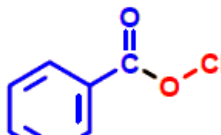
Esteri

Derivano dagli acidi per sostituzione del gruppo OH con un gruppo **OR**.

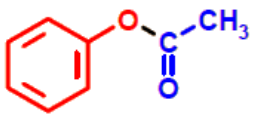
Nomenclatura: prima si mette il nome della componente acida, con la desinenza *-ico* cambiata in *-ato*, poi quello del radicale R del gruppo –OR con la desinenza **–ile**.





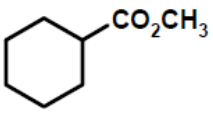


benzoato di metile

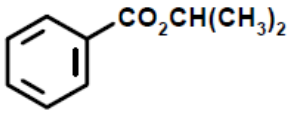


acetato di fenile

Se il gruppo -CO_2R' (-CO_2Ar') è legato ad un anello, si indica con la desinenza "-carbossilato" di alchile (arile).



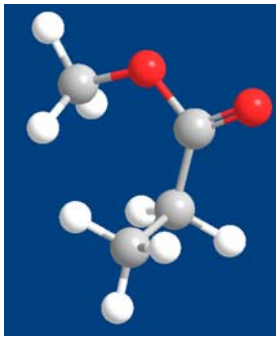
cicloesan**carbossilato** *di* metile



benzen**carbossilato** *di* isopropile

benzoato di isopropile

Esteri

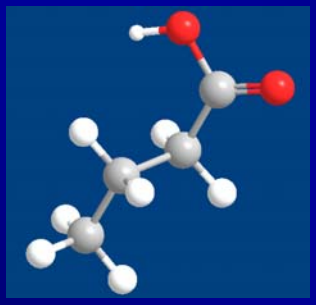


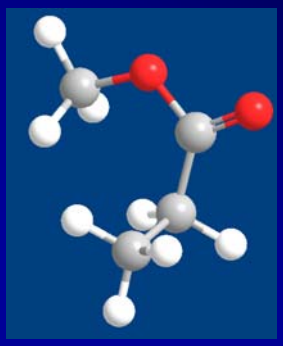
Non possono dare legami a idrogeno

↓

Punti di ebollizione minori degli acidi carbossilici e degli alcoli

Acido $\xrightarrow{ROH}$ Estere





Composto	Punto Ebolliz. (°C)
$CH_3CH_2CH_2COOH$	162
$CH_3CH_2COOCH_3$	78

Esteri in natura …

$CH_3CH_2CH_2COSCH_3$

methylthiobutanoate

$CH_3CH_2CH_2COCH_2CH_3$

ethylbutanoate

$CH_3CH_2CH_2CO(CH_2)_4CH_3$

pentylbutanoate

Il metil butirrato e il propil acetato, molecole di aromi e fragranze organiche trovate, rispettivamente, nelle mele e nelle pere

$CH_3CH_2CH_2COCH_3$

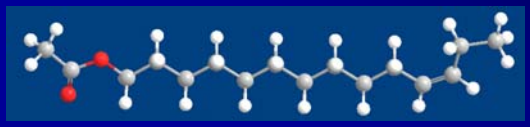
$CH_3COCH_2CH_2CH_3$

Esteri in natura …

Pheromones - chemicals secreated by animals alter the behavior of other members of the same species.

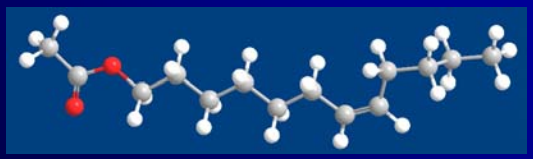
$CH_3CH(CH_3)CH_2CH_2OCCH_3$

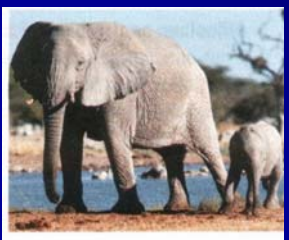
isoamyl acetate
(honey bee alarm)



acetato di (Z)-11-tetradecenile

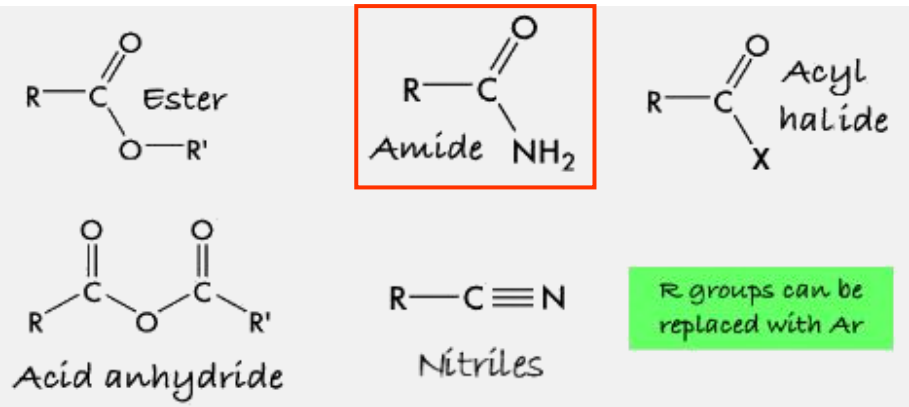
Ormone sessuale della *Piralide del mais*



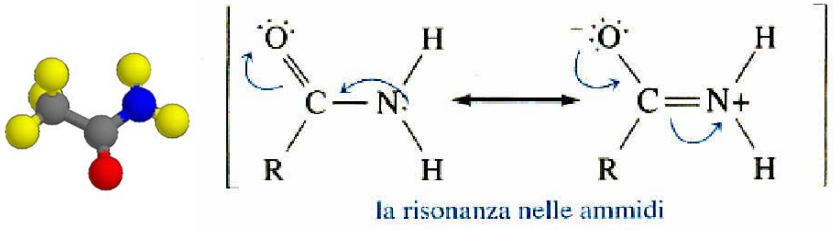


Le elefantesse rilasciano un estere, l'acetato di (*Z*)-7-dodecenile per attirare i maschi.

Derivati degli acidi carbossilici



Sebbene il legame carbonio-azoto venga scritto come legame semplice, la risonanza mostra che si comporta anche come un doppio legame. Infatti la lunghezza di legame è di 1.32Å, più corta di un legame semplice C—N che è di 1.47Å.



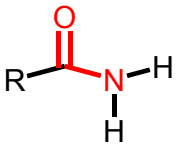
la risonanza nelle ammidi

Ne consegue che:

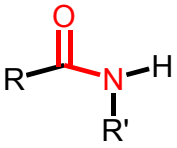
1. la rotazione attorno al legame C-N risulta parzialmente impedita
2. le ammidi hanno geometria piana e di conseguenza, l'azoto, il carbonio carbonilico e gli atomi ad essi legati giacciono sullo stesso piano.

Acidi carbossilici e derivati
Ammidi

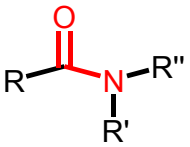
Le ammidi possono essere *primarie*, *secondarie* o *terziarie* a seconda di quanti gruppi sono legati all'atomo di azoto.



Ammide primaria



Ammide secondaria



Ammide terziaria

Acidi carbossilici e derivati
Ammidi

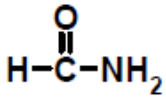
- Nomenclatura

- Il nome è quello del composto che contiene il gruppo acilico, eliminando il termine "acido" e la desinenza "-oico" e sostituendola con "ammide".

- Qualora all'azoto siano legati gruppi alchilici/ arilici, il nome è preceduto da "*N-alchil-/aril-*".

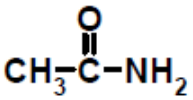
- Se il gruppo -$CONH_2$ è legato ad un anello, si indica con la desinenza "-carbossiammide".

Acidi carbossilici e derivati
Ammidi



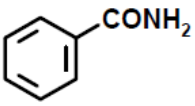
metanammide

formammide

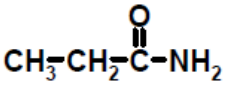


etanammide

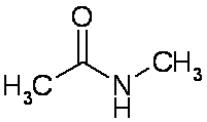
acetammide



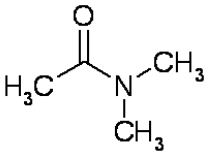
benzencarbossiammide
benzammide



propanammide
(Propionammide)

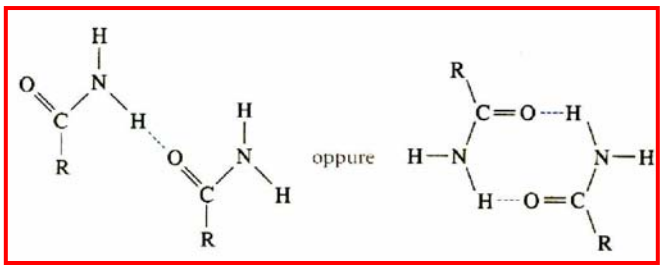


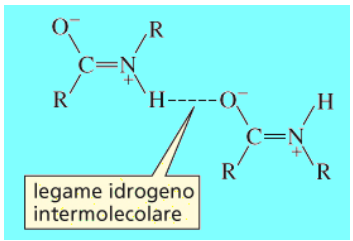
N-metiletanammide
(*N*-metilacetammide)

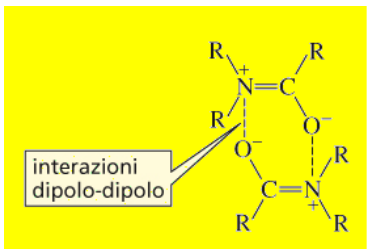


N,N-dimetiletanammide
(*N,N*-dimetilacetammide)

Le ammidi sono composti polari e quelle primarie e secondarie formano legami a idrogeno e forti interazioni dipolo-dipolo







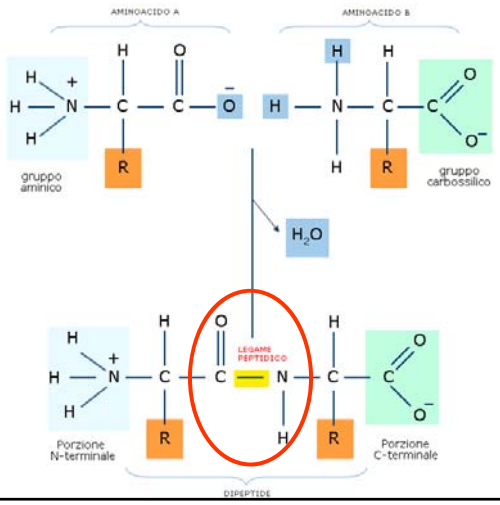
Nome		p.e. °C	p.f. °C	Solubilità, g/100 g di H_2O a 25 °C
Formammide	PM=45	210	2	solubile
Acetammide	PM=59	222	81	solubile
Propanammide	PM=73	213	80	solubile
N-metilformam.	PM=59	200	3	solubile
N,N-dimet.form.	PM=73	153	-61	solubile

Acidi	formico	PM=46 PM=60	101	8	completamente miscibili (∞)
	acetico		118	17	
	propanoico		141	− 22	
	butanoico		164	− 8	
	esanoico		205	− 1,5	1,0
	ottanoico		240	17	0,06
	decanoico		270	31	0,01
	benzoico		249	122	0,4 (ma 6,8 a 95 °C)

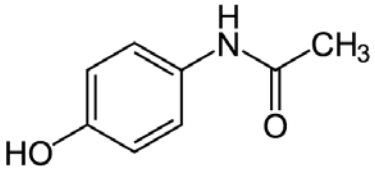
Acidi carbossilici e derivati
Ammidi

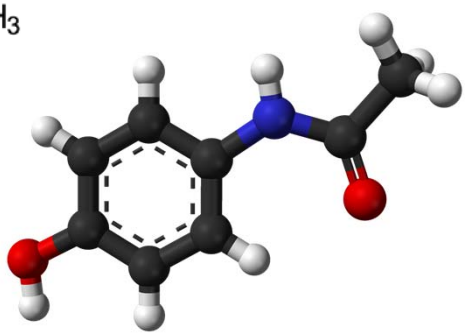
Sono estremamente diffuse in natura e sono, tra i derivati degli acidi carbossilici, i composti meno reattivi.

Le ammidi più importanti sono le proteine.



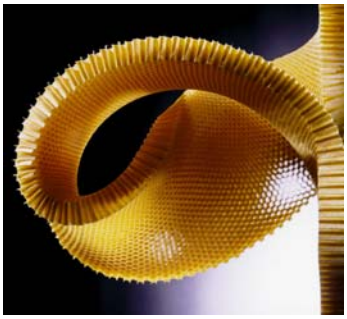
PARACETAMOLO

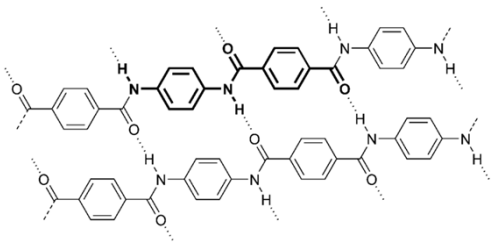


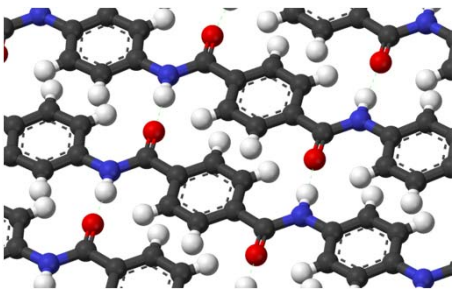


N-acetil-*p*-amminofenolo
N-(4-idrossifenil)acetammide

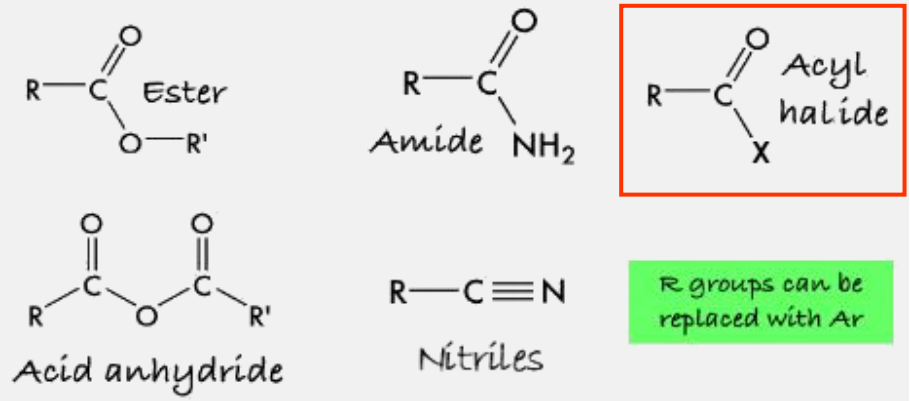
DUPONT
Kevlar.







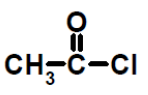
Derivati degli acidi carbossilici



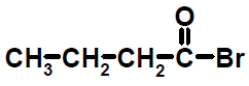
Acidi carbossilici e derivati

Alogenuri acilici

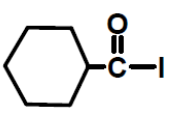
- Nomenclatura
- Nel nome dell'acido da cui derivano, si sostituisce il termine "acido" con "alogenuro di" e la desinenza "-oico"con "-oile".
- Se il gruppo -C(O)X è legato ad un anello, si indica con la desinenza " -carbonile"



cloruro di etanoile
cloruro di acetile



bromuro di butanoile



ioduro di
cicloesancarbonile

Proprietà chimico-fisiche

Gli alogenuri acilici, come del resto gli esteri e le anidridi, sono molecole polari che danno luogo a interazioni intermolecolari dipolo-dipolo e di van der Waals.

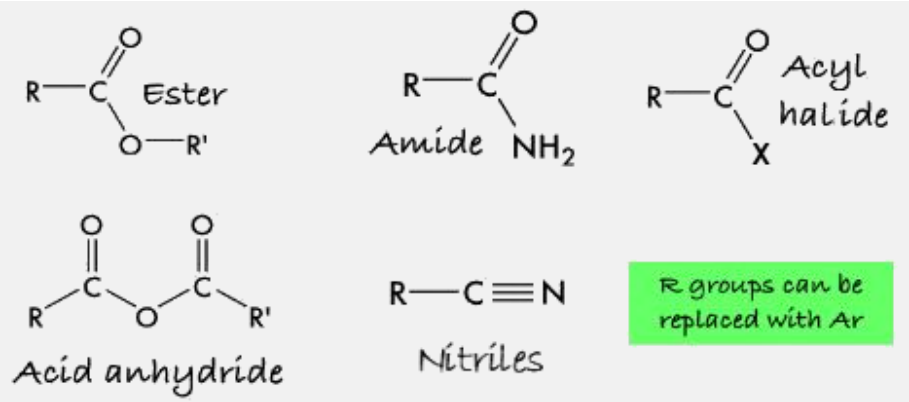
Per l'assenza di legami a idrogeno, i punti di ebollizione dei derivati acilici sono simili a quelli di aldeidi e chetoni con lo stesso peso molecolare, ma inferiori a quelli degli acidi carbossilici di peso molecolare comparabile.

Ad esempio, il cloruro di etanoile (PM 78) ha punto di ebollizione 51°C. L'acido propionico (PM 74) ha punto di ebollizione 141°C.

Il cloruro di etanoile è un liquido incolore fumante con un forte odore a metà tra quello di aceto (acido acetico) e quello acre di acido cloridrico.

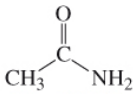
I cloruri acilici reagiscono, spesso violentemente, con l'acqua e ciò impedisce di ottenere una soluzione acquosa di un cloruro acilico.

Derivati degli acidi carbossilici

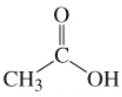


Punti di ebollizione relativi

Ammide > acido carbossilico > alcol > estere ~ alogenuro acilico ~ aldeide ~ chetone

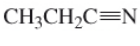


p.e. = 221 °C



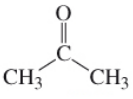
p.e. = 118 °C

p.e. = 97.4 °C

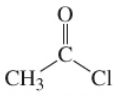


p.e. = 97 °C

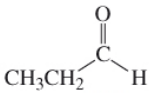
PM	59	58	60	55



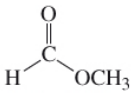
p.e. = 56 °C



p.e. = 51 °C



p.e. = 49 °C



p.e. = 32 °C

p.e. = 10.8 °C

PM	58	88	58	60	60