

QFL0341 - Estrutura e Propriedades de Compostos Orgânicos - Noturno (2019)

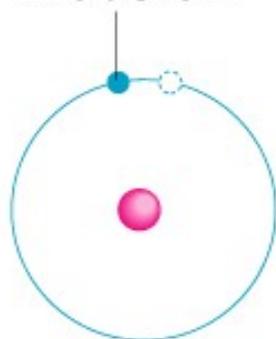
27/agosto/2019

Estruturas, nomenclatura e caracterização de compostos nitrogenados.

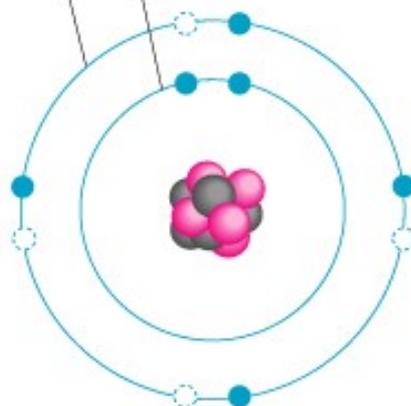
Outermost electron shell (can hold 8 electrons)

First electron shell (can hold 2 electrons)

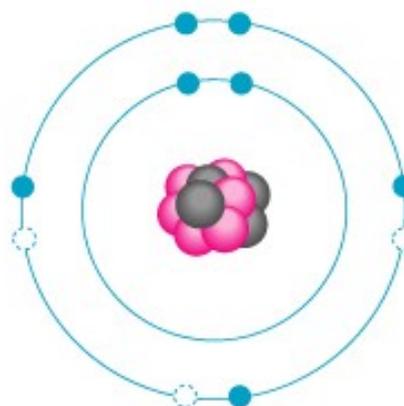
Electron



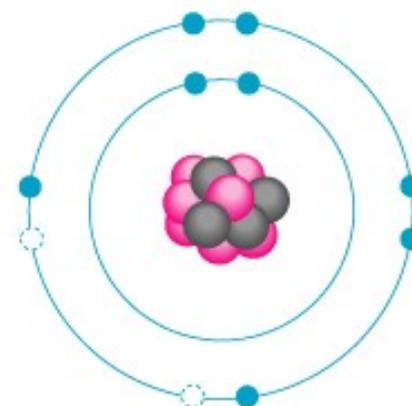
HYDROGEN (H)
Atomic number
= 1



CARBON (C)
Atomic number
= 6



NITROGEN (N)
Atomic number
= 7

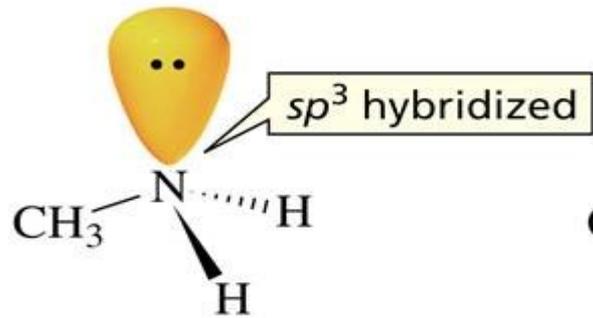


OXYGEN (O)
Atomic number
= 8

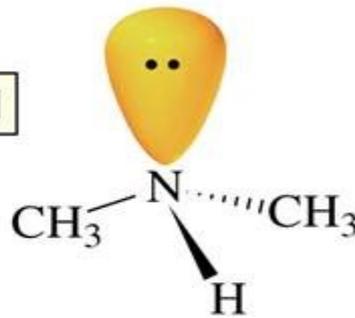
©Addison Wesley Longman, Inc.

Octet Rule = atoms tend to gain, lose or share electrons so as to have 8 electrons

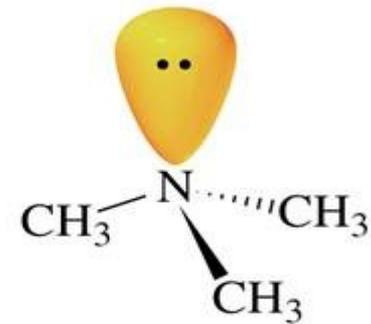
Estruturas de Aminas



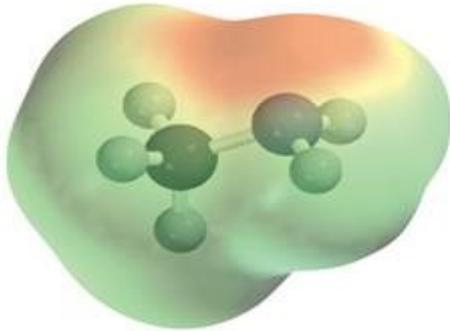
methylamine
a primary amine



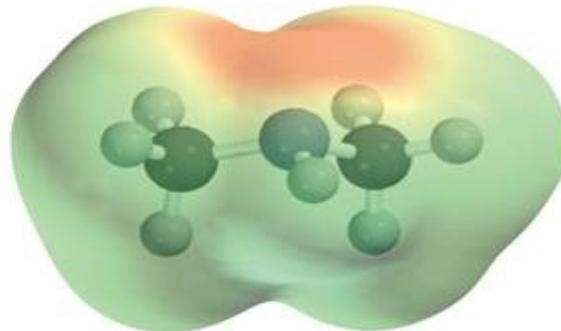
dimethylamine
a secondary amine



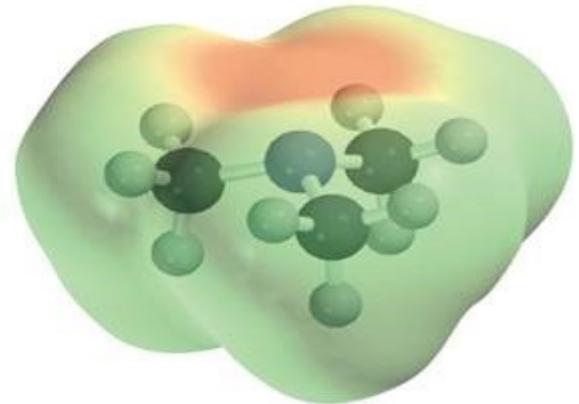
trimethylamine
a tertiary amine



methylamine



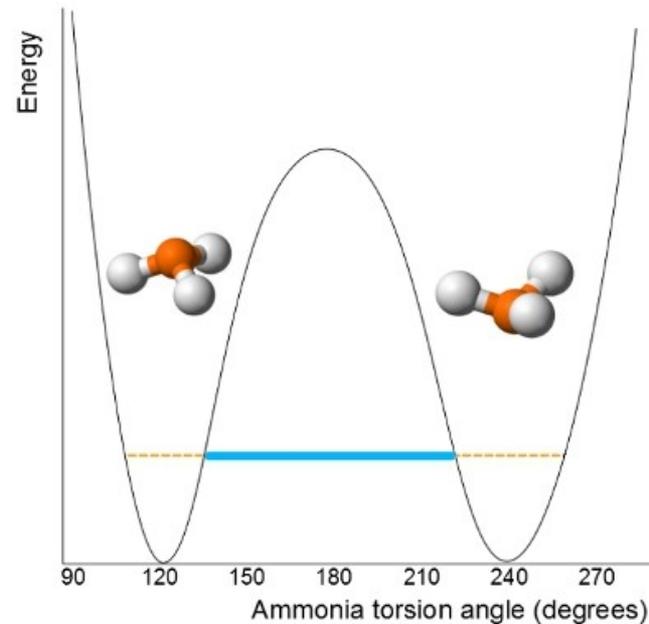
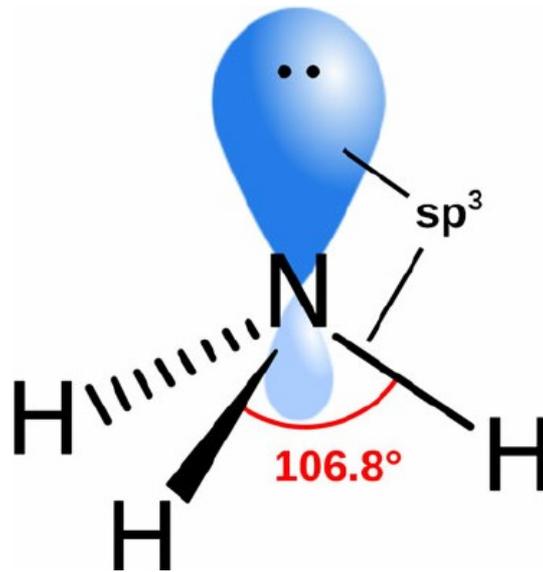
dimethylamine



trimethylamine

electrostatic potential maps for

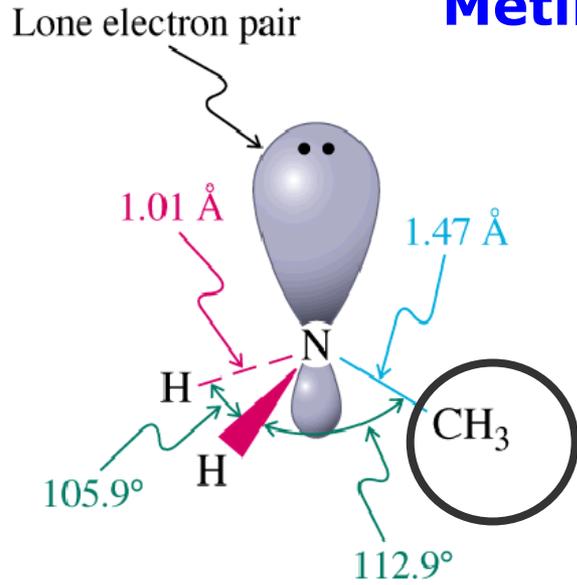
Aminas (estrutura com geometria piramidal)



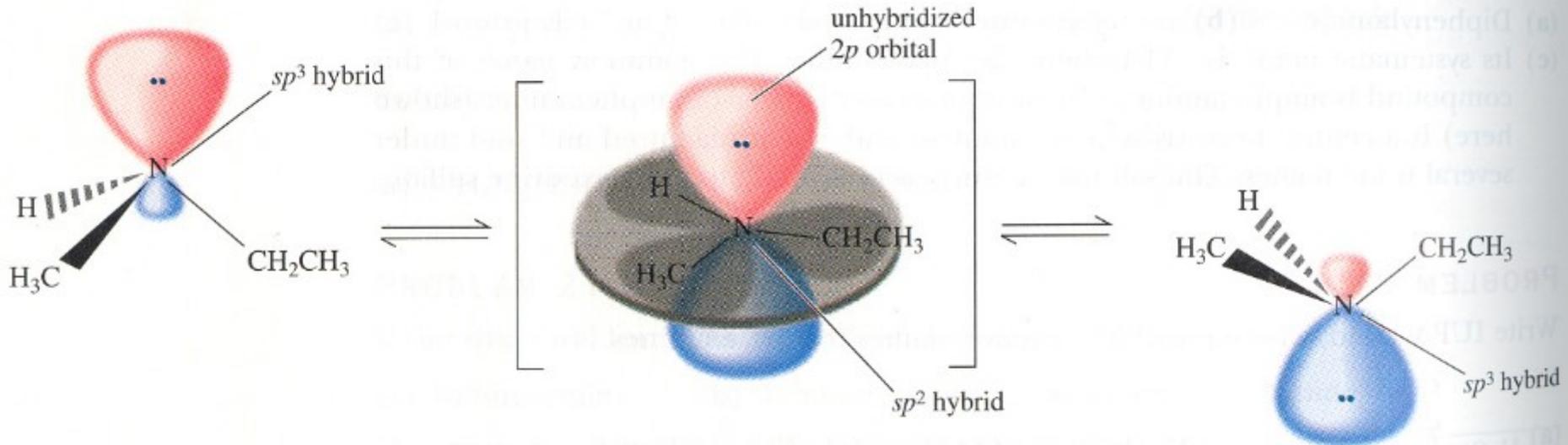
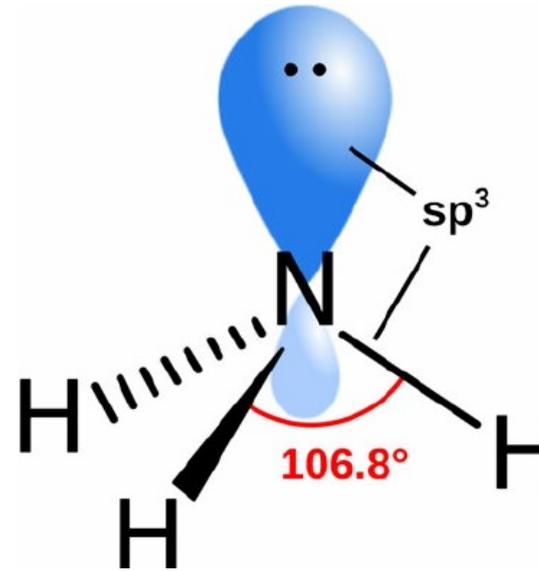
- ✓ Para a amônia ocorrem $2 \cdot 10^{11}$ inversões por segundo!
- ✓ Inversão de uma amina:

<http://www.youtube.com/watch?v=13MBKYHI7mQ>

Metilamina



Amônia



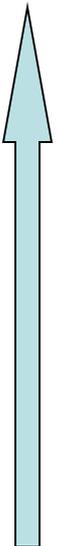
- **Eletronegatividade**: medida da “força” com que um átomo atrai os elétrons compartilhados numa ligação química com outro átomo

Escala de Pauling

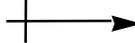
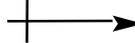
H 2,1	
Li 1,0	Be 1,5
Na 1,0	Mg 1,2
K 0,9	Ca 1,0



B 2,0	C 2,5	N 3,0	O 3,5	F 4,0
Al 1,5	Si 1,8	P 2,1	S 2,5	Cl 3,0
				Br 2,8
				I 2,5



Dipolos médios de algumas ligações

Ligação	Dipolo (D)	Ligação	Dipolo (D)	Ligação	Dipolo (D)
					
H-C	0.4	C-F	1.4	C-O	0.7
H-N	1.3	C-Cl	1.5	C=O	2.3
H-O	1.5	C-Br	1.4	C-N	0.2
H-S	0.7	C-I	1.2	C=N	3.5

menor que 0.5

covalente apolar

0.5 a 1.9

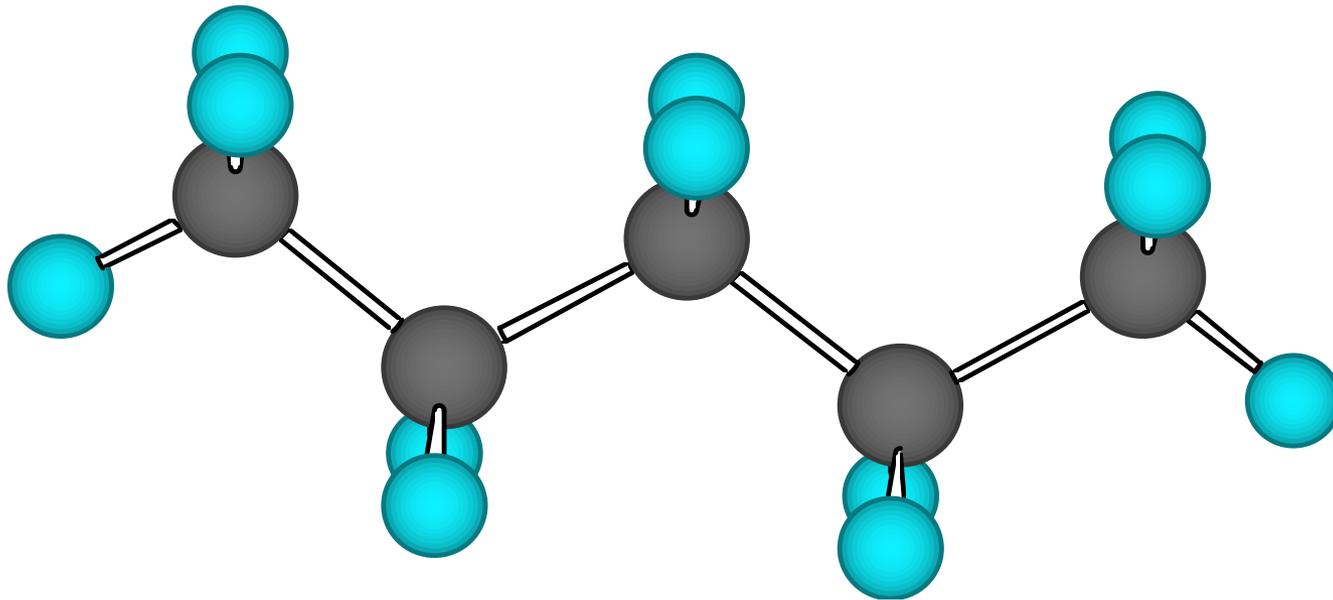
covalente polar

maior que 1.9

iônica

Moléculas apolares

Hidrocarbonetos (alcanos)



n-butano

A polaridade de uma molécula depende:

das ligações individuais dos átomos;

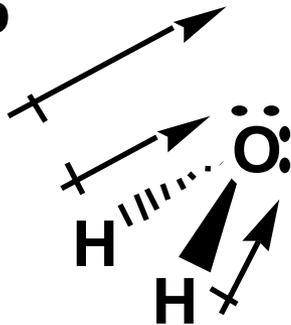
do arranjo espacial dessas ligações

A medida da polaridade e momento de
Dipolo (μ) (vetor somatório dos dipolos
individuais de cada ligação na molécula)

Moléculas Polares

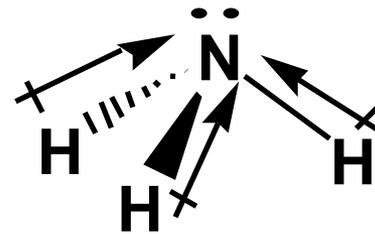
- Moléculas com ligações polares, e um momento de dipolo maior que zero

direção do
momento
de dipolo
da água



Água

$$\mu = 1.85\text{D}$$

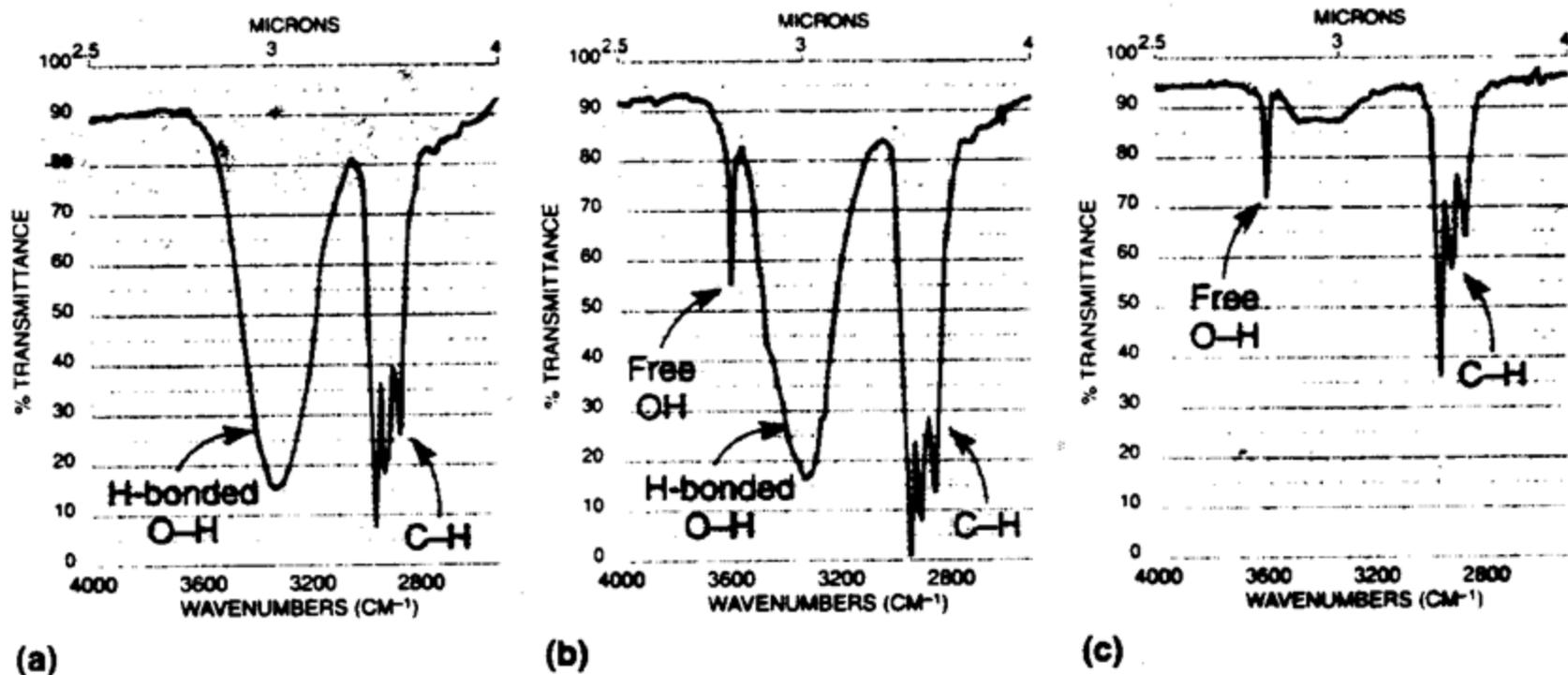


Amônia

$$\mu = 1.47\text{D}$$

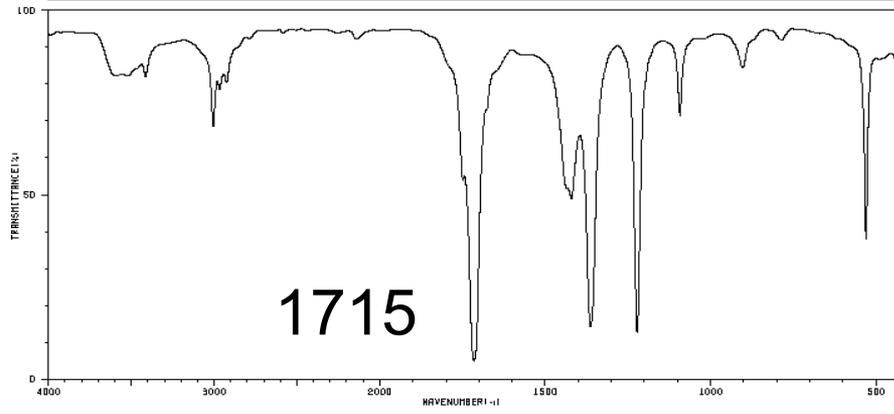
direção do
momento
de dipolo
da amônia

Free OH and Hydrogen bonded OH

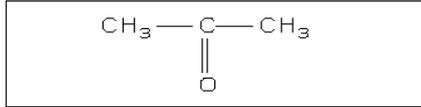


- **FIGURE 2.32** The O—H stretch region. (a) Hydrogen-bonded O—H only (neat liquid). (b) Free and hydrogen-bonded O—H (dilute solution). (c) Free and hydrogen-bonded O—H (very dilute solution).

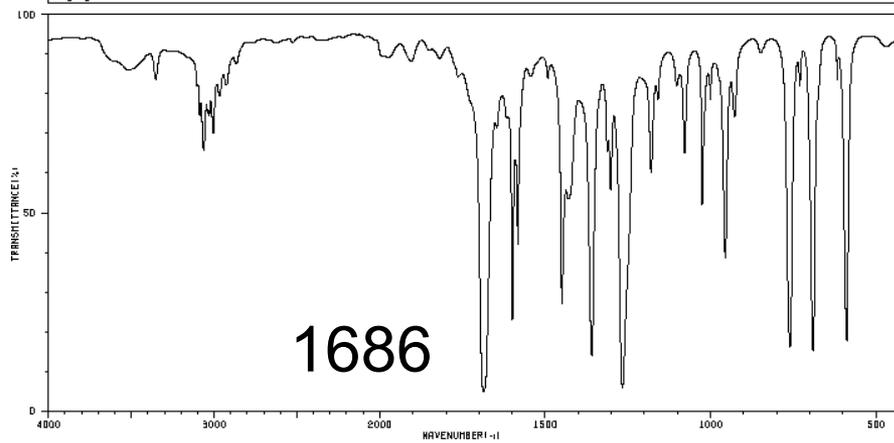
HIT-NO=960 SCORE= () SDBS-NO=319 IR-NIDA-63533 : LIQUID FILM
 ACETONE
 C_3H_6O



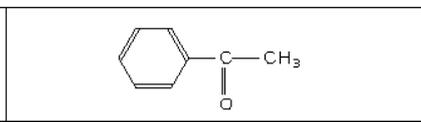
3414	79	1421	47
3005	86	1363	19
2966	74	1223	12
2925	77	1093	68
1749	52	903	81
1715	4	531	96
1434	49		



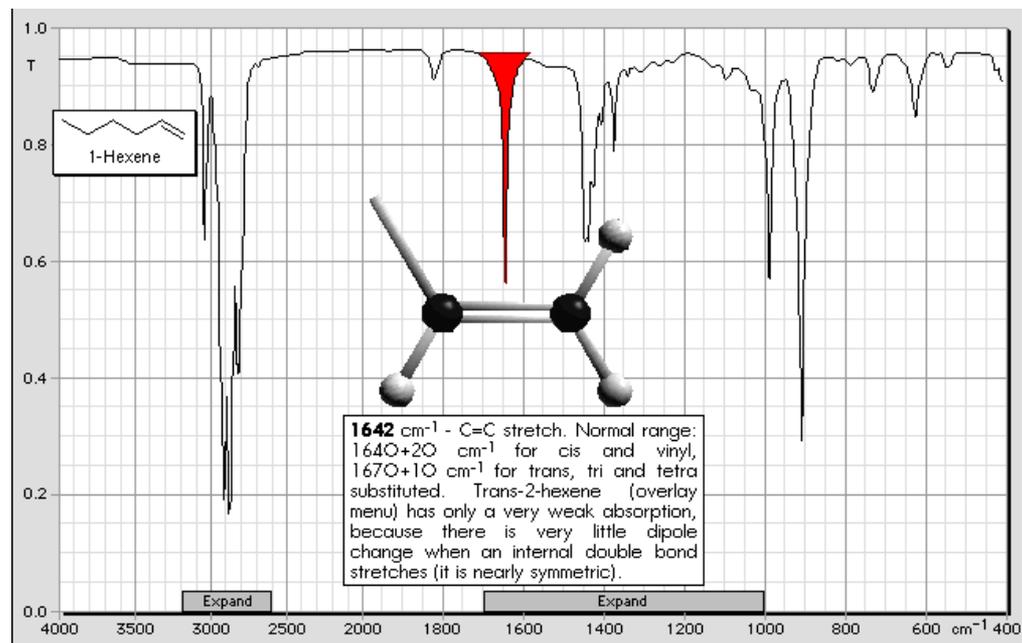
HIT-NO=1153 SCORE= () SDBS-NO=722 IR-NIDA-05227 : LIQUID FILM
 ACETOPHENONE
 C_8H_8O



3604	84	2967	77	1646	81	1257	5	956	37
3352	81	2925	79	1492	81	1181	58	928	72
3087	72	2867	84	1450	26	1160	74	761	15
3063	64	1686	4	1430	62	1103	79	731	79
3040	72	1646	68	1360	13	1079	62	691	14
3029	72	1599	21	1313	82	1025	50	618	61
3005	68	1683	41	1303	63	1001	74	588	17

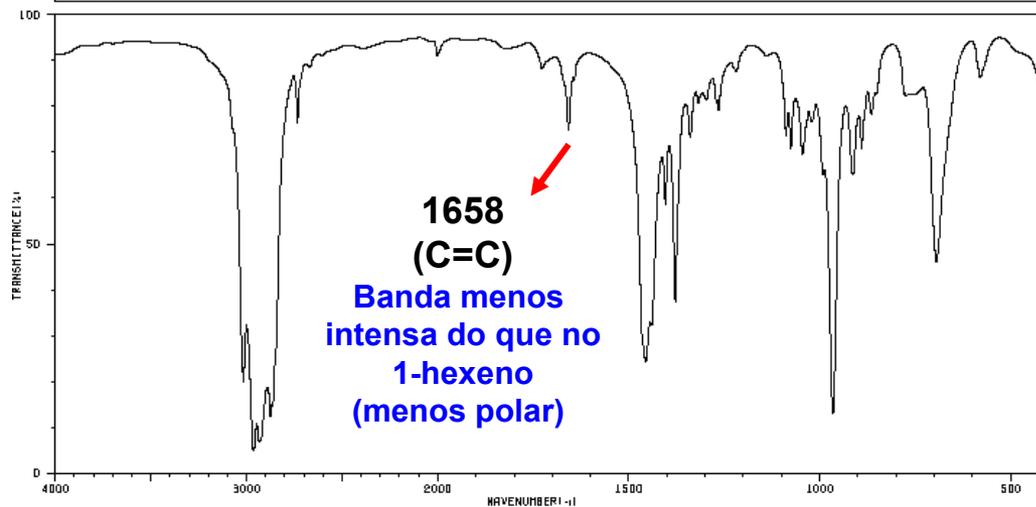


Infrared spectrum for 1-hexene

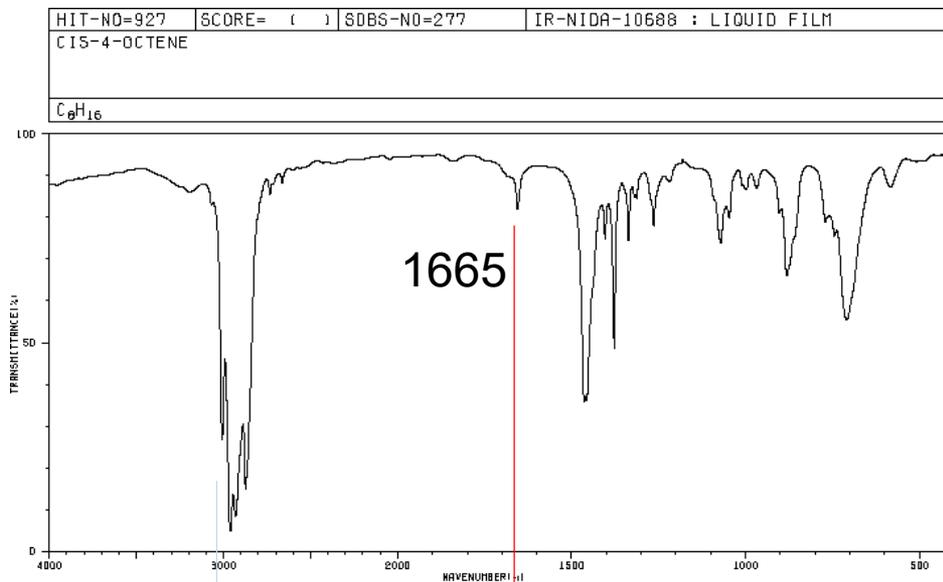
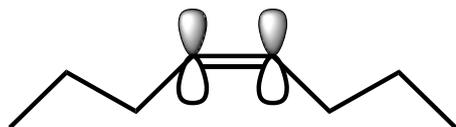


HIT-NO=2748	SCORE= ()	SBS-NO=4717	IR-NIDA-05742 ; LIQUID FILM
2-HEXENE			
C_6H_{12}			

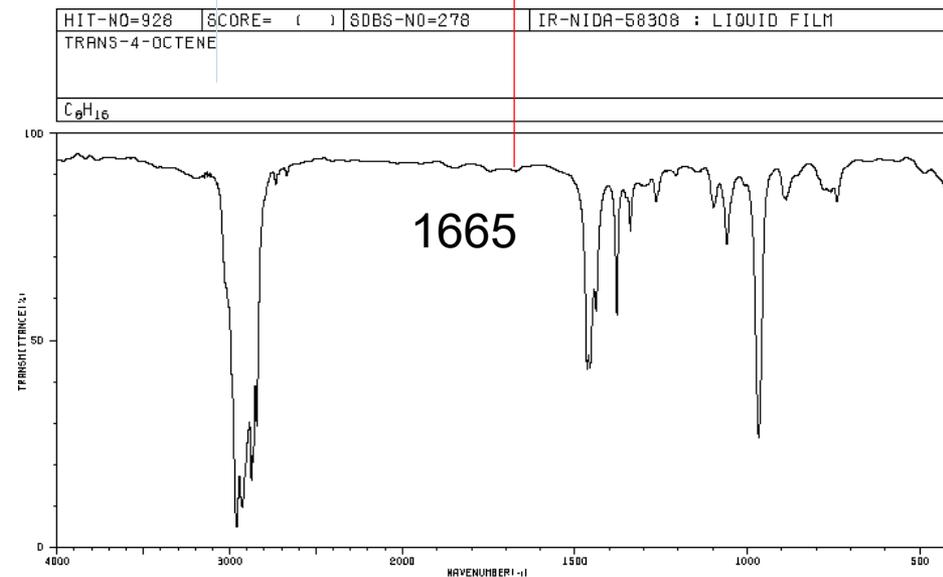
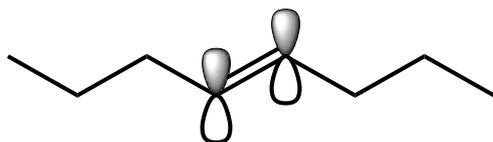
2-hexene



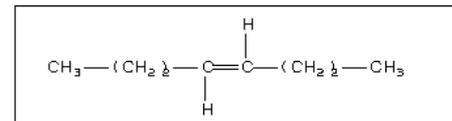
cis-4-octene (mais polarizada)



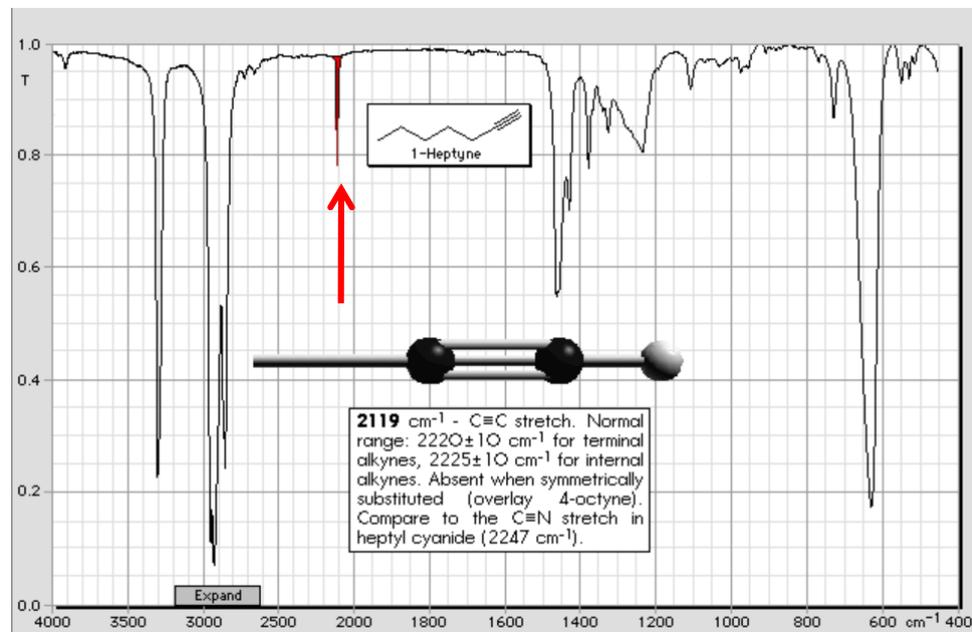
trans-4-octene (menos polarizada)



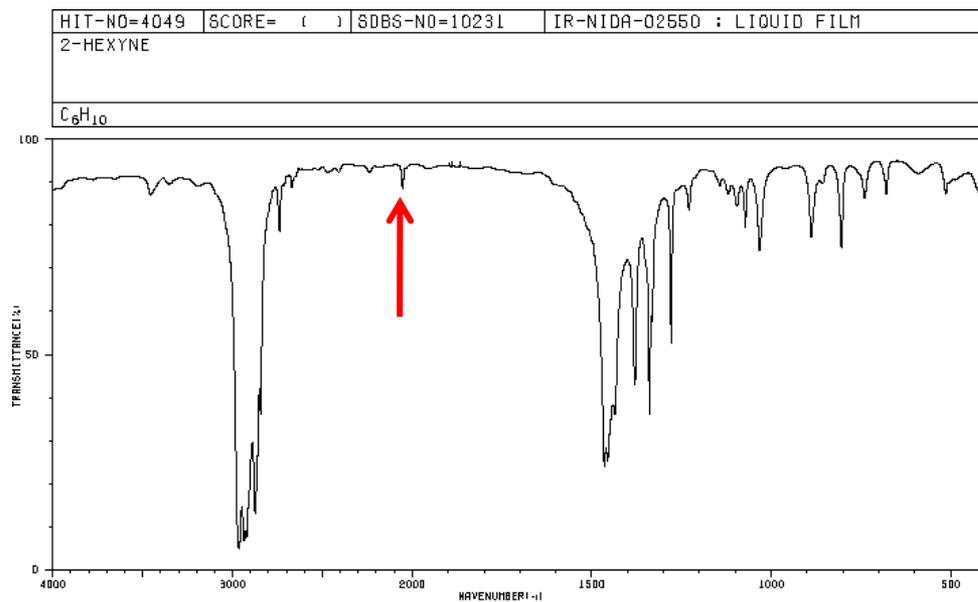
3193	86	2733	84	1266	81	768	81
2959	4	2670	86	1207	86	740	81
2941	14	1466	42	1098	79		
2926	9	1466	42	1060	70		
2875	15	1439	55	967	25		
2864	20	1379	59	892	81		
2844	28	1340	74	886	81		



Infrared spectrum of 1-heptyne



Infrared spectrum of 2-hexyne

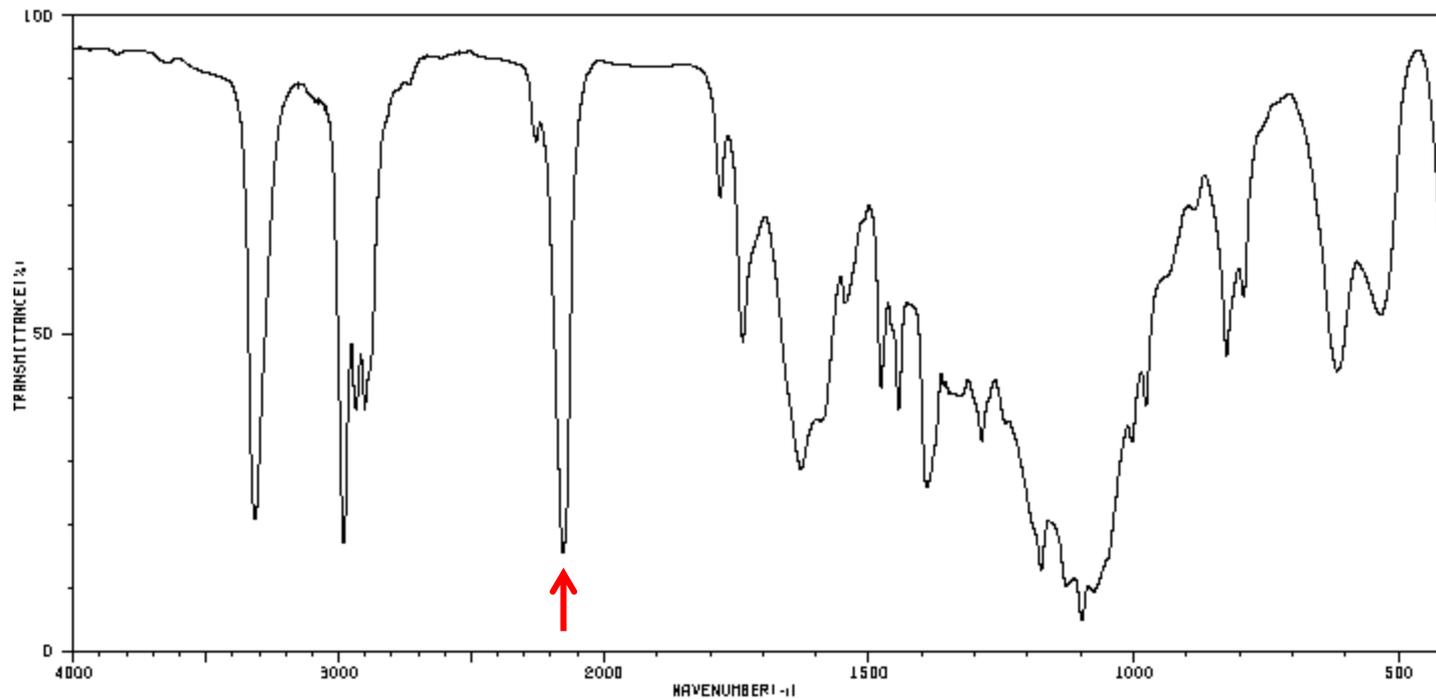


3456	84	2739	77	1340	35	1073	77	505	86
3354	86	2671	86	1333	55	1033	72		
2964	4	2054	84	1279	50	889	74		
2936	6	1466	23	1229	81	806	72		
2922	7	1458	24	1144	86	740	84		
2875	12	1438	34	1120	84	679	84		
2844	36	1380	41	1096	81	614	84		

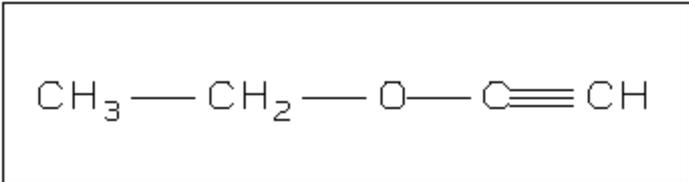
CC#CCCC

IR spectrum of ethoxyacetylene

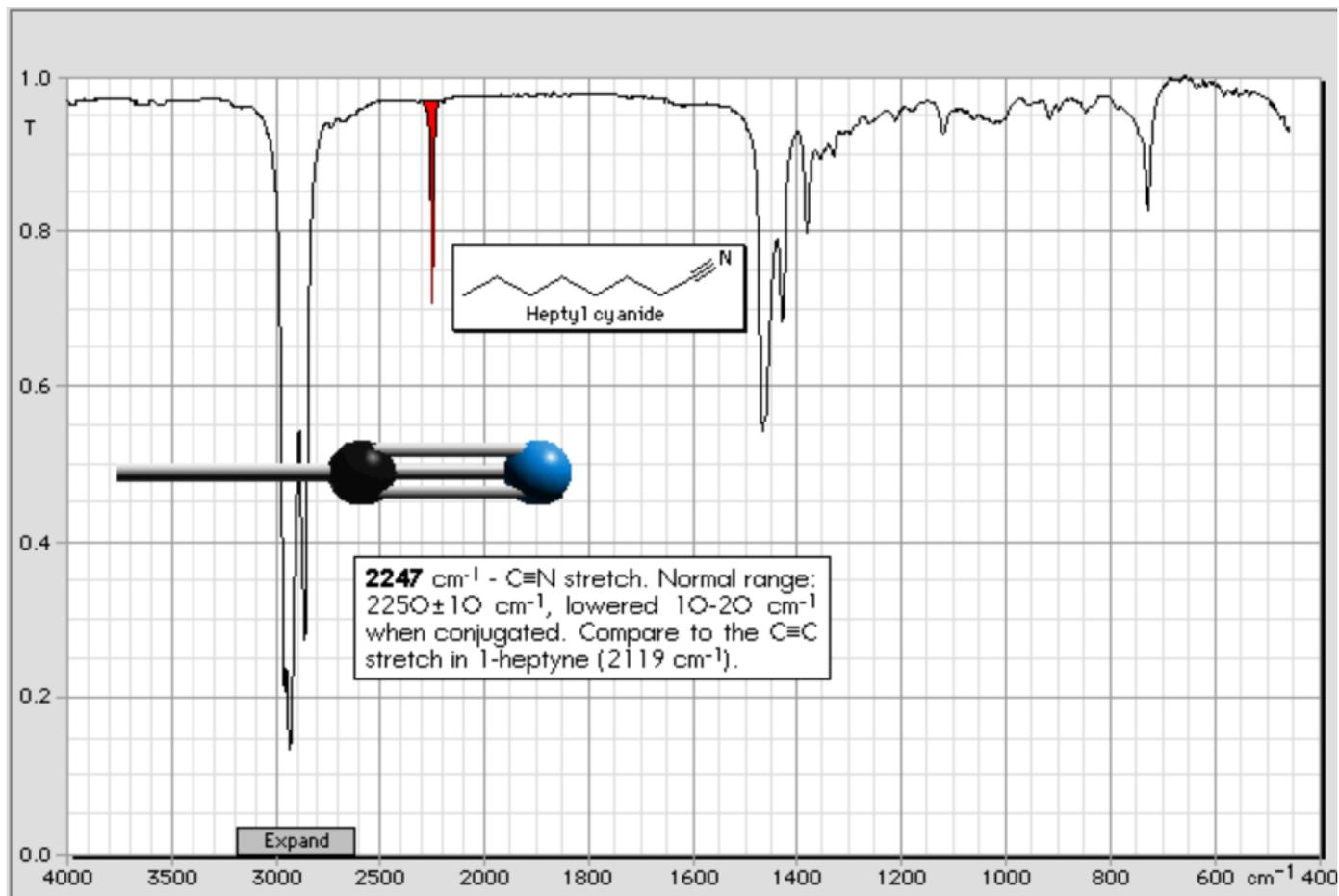
HIT-NO=4547	SCORE= ()	SDBS-NO=12491	IR-NIDA-15173 : LIQUID FILM (5
ETHOXYACETYLENE			
C ₄ H ₆ O			



3316	20	1781	68	1339	38	1003	31
2981	16	1738	46	1334	38	977	37
2960	42	1628	27	1329	36	825	44
2939	36	1644	62	1287	31	793	69
2901	36	1477	39	1176	12	616	42
2256	77	1444	36	1128	10	535	50
2153	14	1391	24	1098	4		



Infrared spectra for heptyl cyanide



Higher frequency (2247 cm^{-1}) than triple bond C-C (2120 cm^{-1})

Glicosídeos cianogênicos da mandioca-brava



Maniçoba

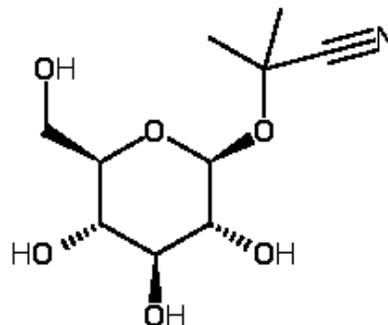
(prato paraense feito com as folhas da mandioca)

(3 dias de cozimento para eliminar o cianeto)



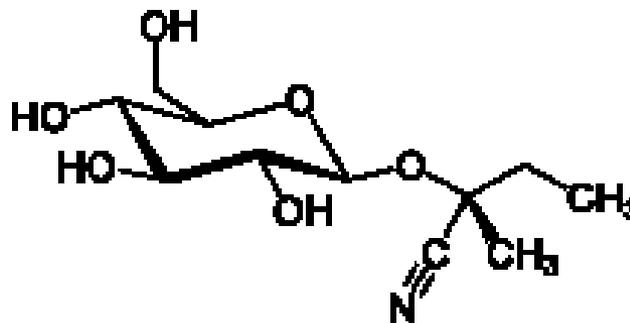
Tucupi

(tempero paraense e amazonense)



linamarina

2-methyl-2-[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxy-propanenitrile

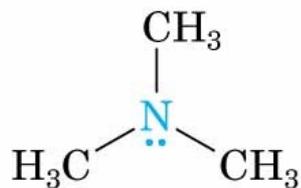


lotaustralina

(2*R*)-2-methyl-2-[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl]oxy}butanenitrile

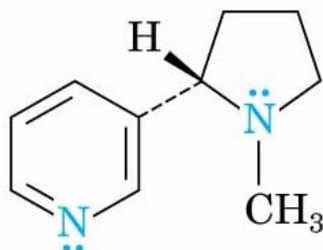
Amines – Organic Nitrogen Compounds

- Organic derivatives of ammonia, NH_3 ,
- Nitrogen atom with a lone pair of electrons, making amines both basic and nucleophilic
- Occur in plants and animals

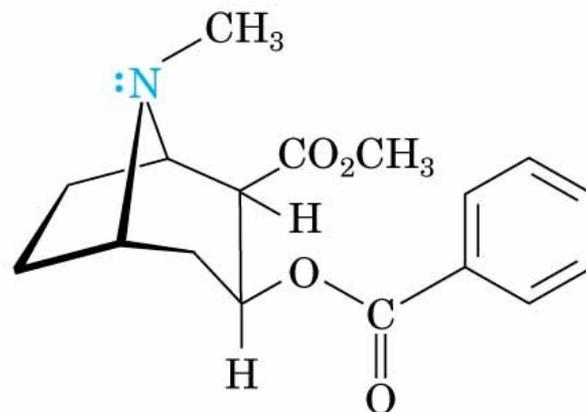


Trimethylamine

© 2004 Thomson/Brooks Cole



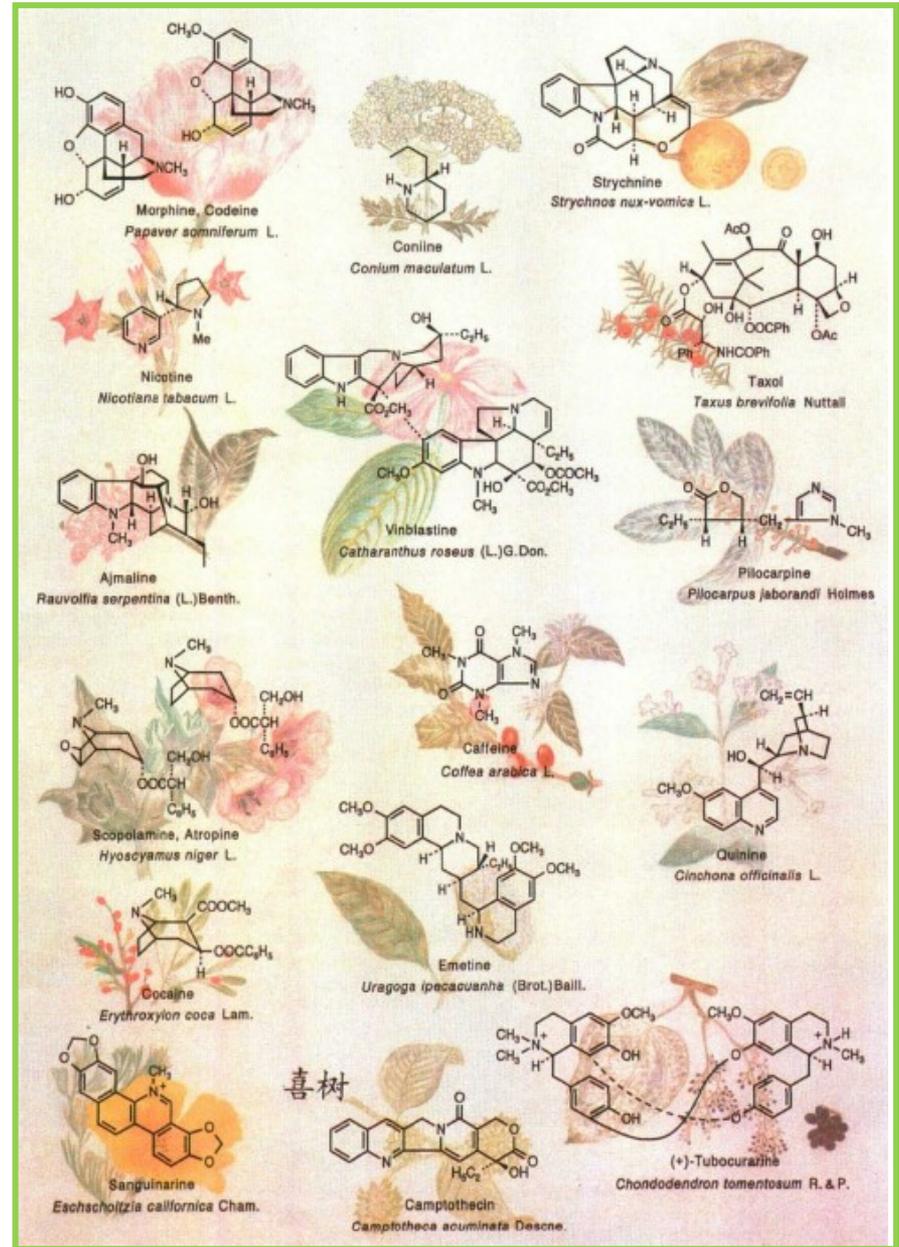
Nicotine



Cocaine

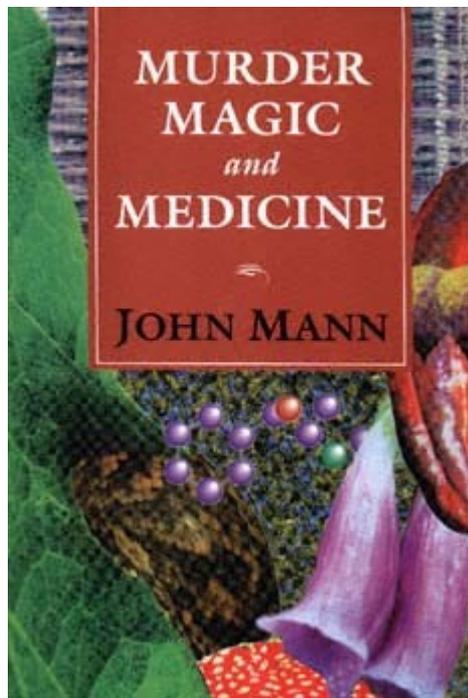
alcaloides!!!

ALCALOIDES (Meissner, 1819)



Alcaloides fisiologicamente ativos utilizados na medicina Moderna

Alkaloid	Plant source	Use
Ajmaline	<i>Rauwolfia serpentina</i>	Antiarrhythmic that functions by inhibiting glucose uptake by heart tissue mitochondria
Atropine, -(±)-hyoscyamine	<i>Hyoscyamus niger</i>	Anticholinergic, antidote to nerve gas poisoning
Caffeine	<i>Coffea arabica</i>	Widely used central nervous system stimulant
Camptothecin	<i>Camptotheca acuminata</i>	Potent anticancer agent
Cocaine	<i>Erythroxylon coca</i>	Topical anaesthetic, potent central nervous system stimulant, and adrenergic blocking agent; drug of abuse
Codeine	<i>Papaver somniferum</i>	Relatively nonaddictive analgesic and antitussive
Coniine	<i>Conium maculatum</i>	First alkaloid to be synthesized; extremely toxic, causes paralysis of motor nerve endings, used in homeopathy in small doses
Emetine	<i>Uragoga ipecacuanha</i>	Orally active emetic, amoebicide
Morphine	<i>P. somniferum</i>	Powerful narcotic analgesic, addictive drug of abuse
Nicotine	<i>Nicotiana tabacum</i>	Highly toxic, causes respiratory paralysis, horticultural insecticide; drug of abuse
Pilocarpine	<i>Pilocarpus jaborandi</i>	Peripheral stimulant of the parasympathetic system, used to treat glaucoma
Quinine	<i>Cinchona officinalis</i>	Traditional antimalarial, important in treating <i>Plasmodium falciparum</i> strains that are resistant to other antimalarials
Sanguinarine	<i>Eschscholzia californica</i>	Antibacterial showing antiplaque activity, used in toothpastes and oral rinses
Scopolamine	<i>H. niger</i>	Powerful narcotic, used as a sedative for motion sickness
Strychnine	<i>Strychnos nux-vomica</i>	Violent tetanic poison, rat poison, used in homeopathy
(+)-Tubocurarine	<i>Chondrodendron tomentosm</i>	Nondepolarizing muscle relaxant producing paralysis, used as an adjuvant to anaesthesia
Vinblastine	<i>Catharanthus roseus</i>	Antineoplastic used to treat Hodgkin's disease and other lymphomas.



Murder:

Arrow poisons

Classical poisons (tropane alkaloids, aconite, hemlock)

Amphibians toxins

Magic:

stimulants

Psychotomimetics

Inebriants

Medicine:

Antibacterial

Anti-inflammatory

Drugs affecting CNS

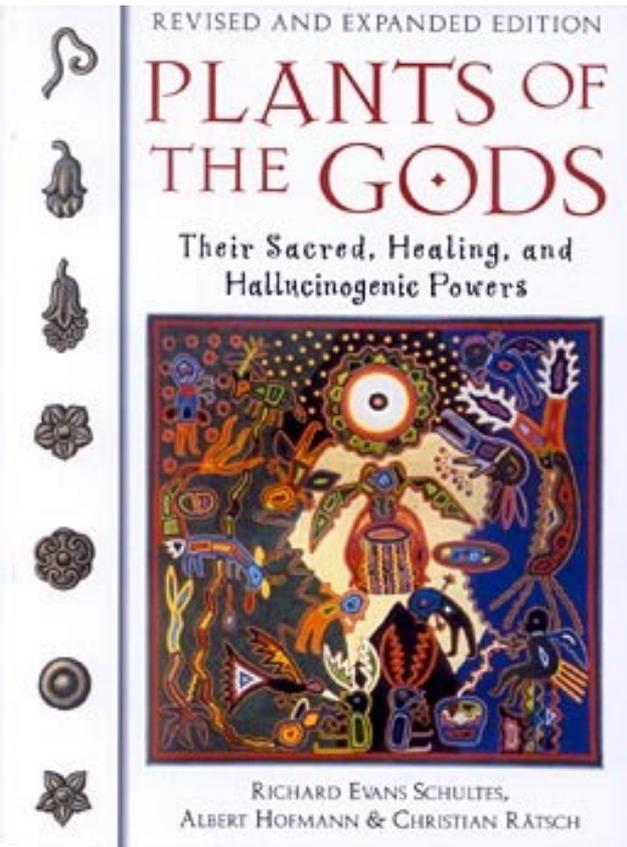
Heart and circulation

Anti-asthma drugs

Drugs affecting gastrointestinal tract

Antiparasitic agents

Anticancer



Richard Evans Schultes



(outros livros)

Potions, Poisons, & Panaceas (1997)

Ethnobotany: Evolution of a Discipline (1995)

Plants of the Gods (1992)

Vine of the Soul (1992)

The Glass Flowers at Harvard (1992)

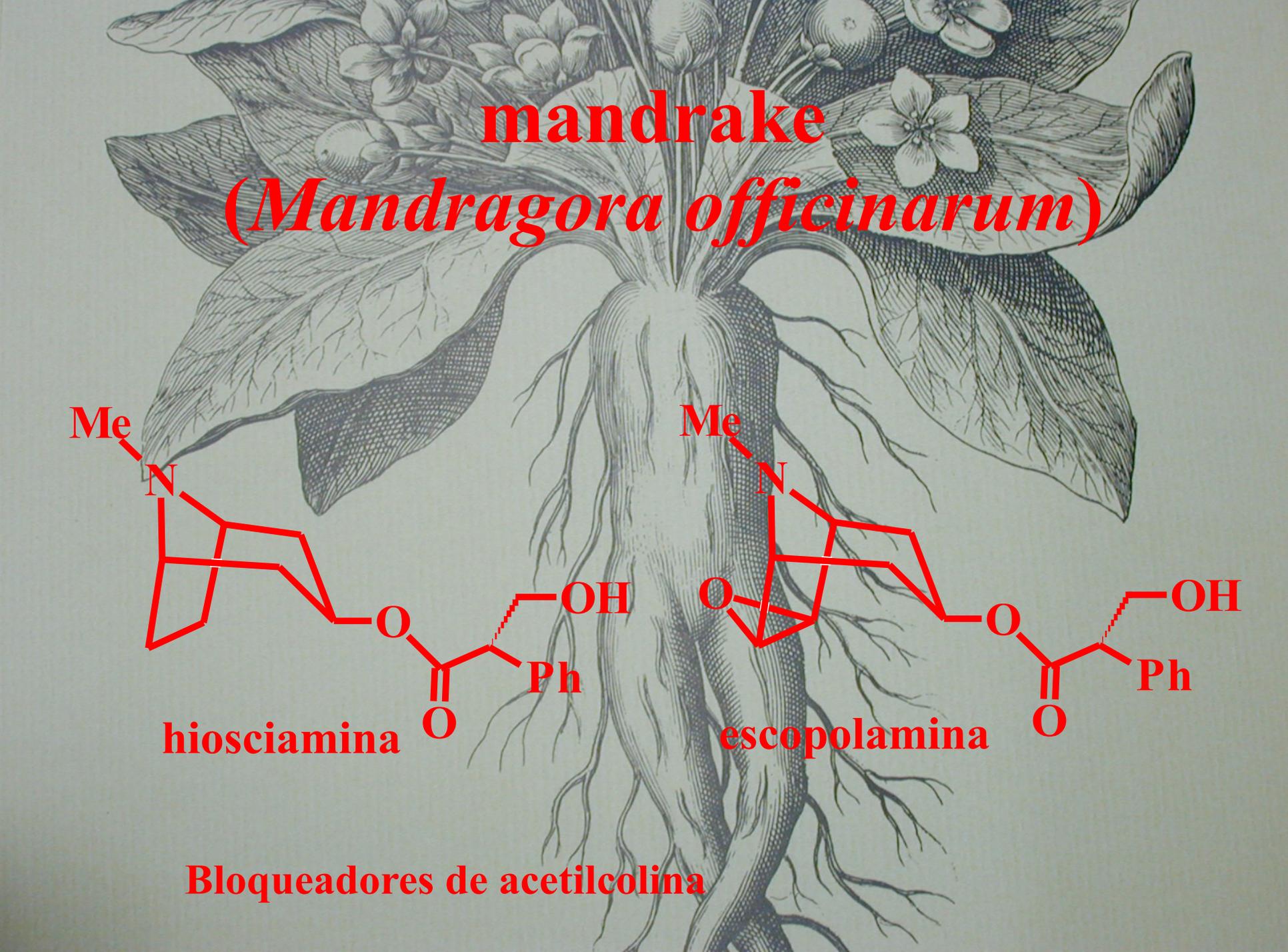
The Healing Forest (1990)

Where the Gods Reign (1988)

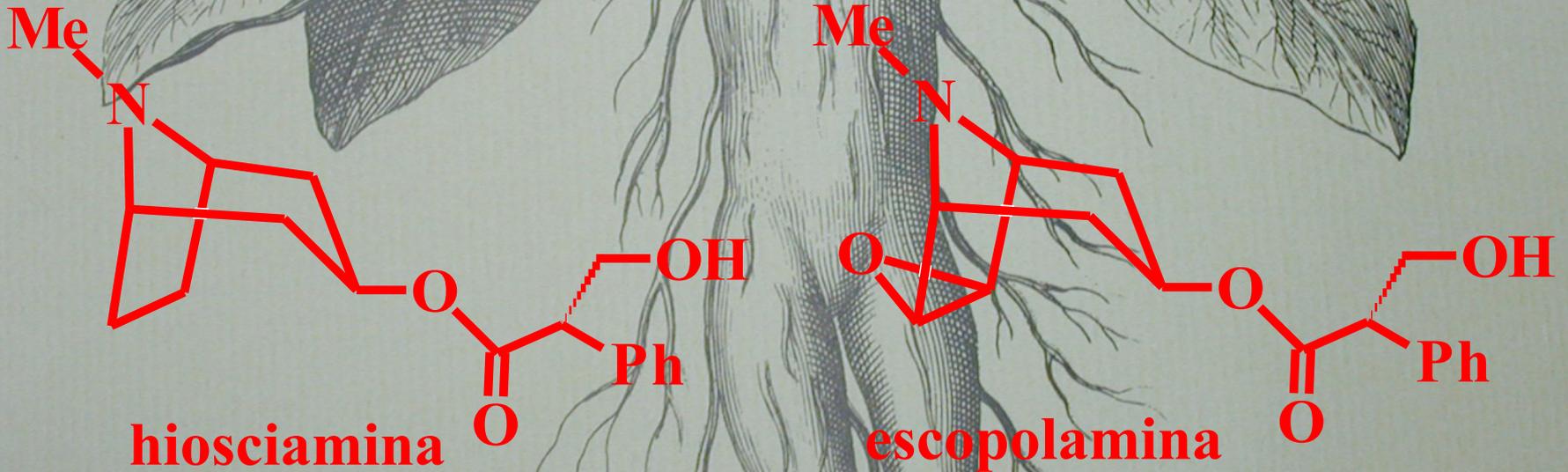
The Botany and Chemistry of Hallucinogens (1980)

Hallucinogenic Plants (1976)

Flesh of the Gods (1972)

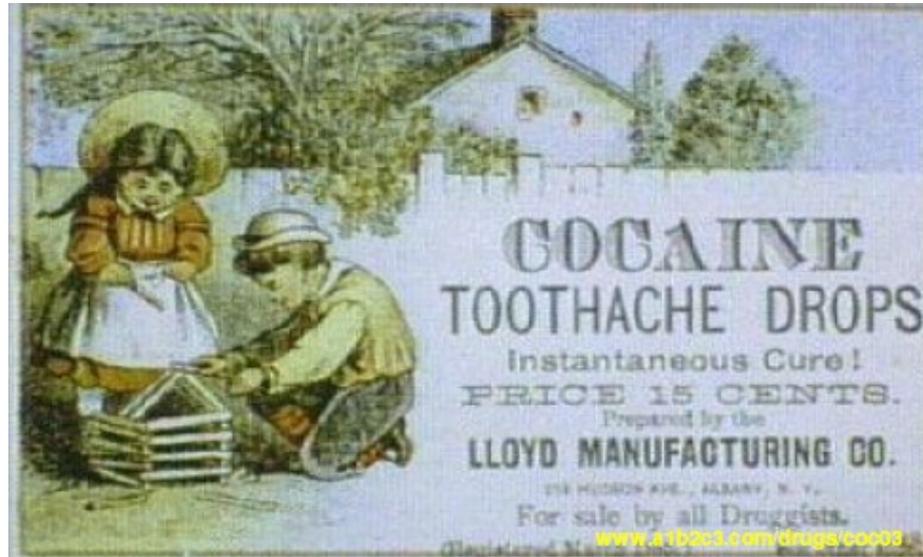


mandrake
(Mandragora officinarum)

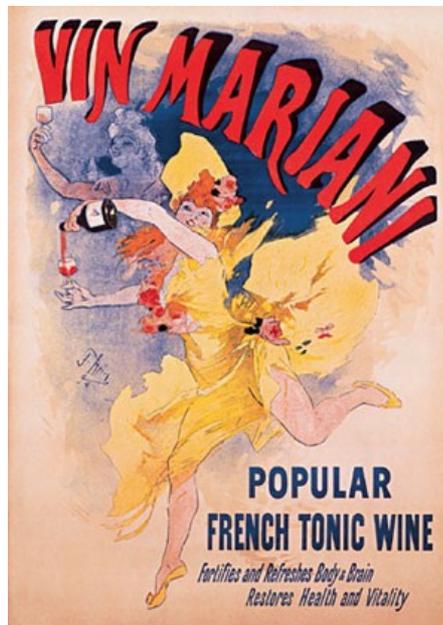


Bloqueadores de acetilcolina

Em 1886



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Instantaneous Cure!
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VIN MARIAN!
POPULAR
FRENCH TONIC WINE
*Fortifies and Refreshes Body • Drain
Restores Health and Vitality*

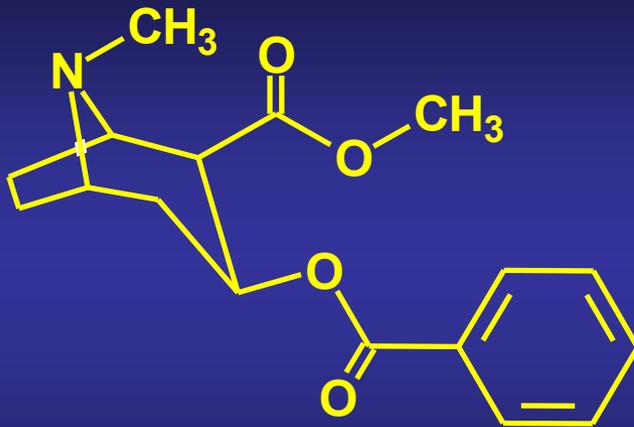


Revised Retail Prices of
COCA WINE.
ARMBRECHT'S
FOR FATIGUE OF MIND AND BODY.
And Chronic Affections, as
NEURALGIA,
SLEEPLESSNESS,
DESPONDENCY,
etc., etc.
TWELVE BOTTLES, 48s. TWENTY-FOUR BOTTLES, 94s.
*(Change Post England and Wales, and 2/6 for Ireland and Scotland. Postage and 1/6 for
Professional Price: 40s. per dozen; 21s. half-dozen.
(Change Post in steam.)*
ARMBRECHT, NELSON & CO.,
Trafalgar Square, 2, Duke St., Grosvenor Square, London, W.
Telegraphic Address: "ARMBRECHT, LONDON."
A Sample Bottle free to Medical Men and Chemists on receipt of professional card.
ANÚNCIO DA SEARS EM 1900 www.historyhouse.com

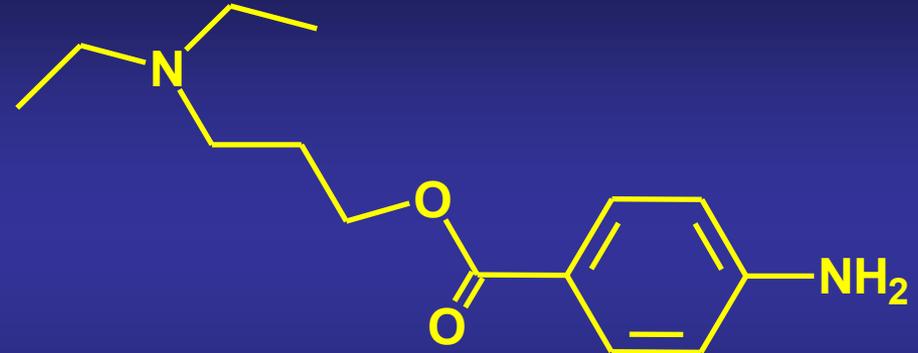


DELICIOUS AND REFRESHING
DRINK
Coca-Cola
5 AT FOUNTAINS IN BOTTLES 5

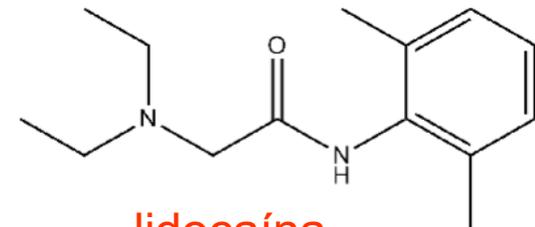
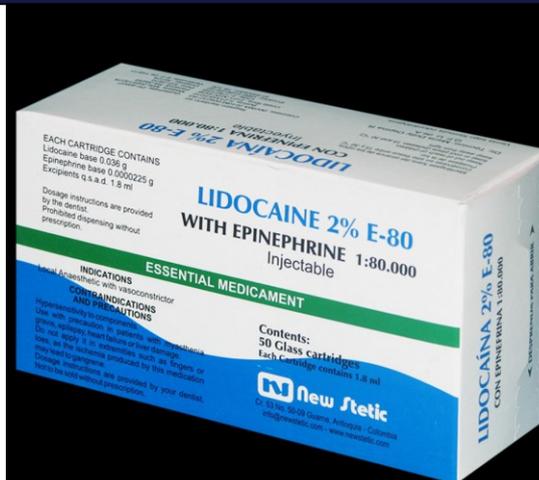
Desenvolvimento de um anestésico com base na estrutura da cocaína



cocaína
(*Erythroxylum coca*)

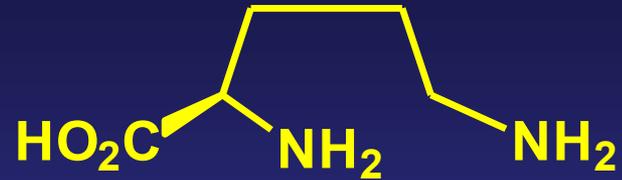


procaina
(sintético)



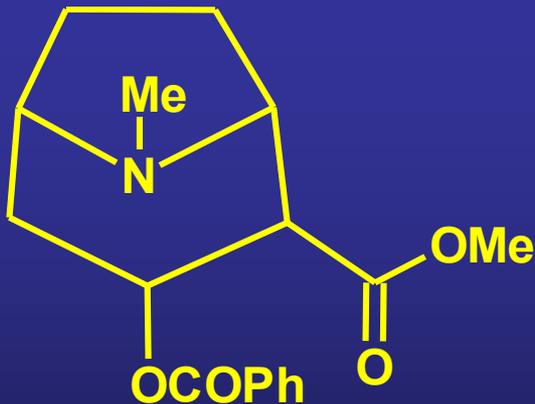
lidocaína

Aminoácido precursor

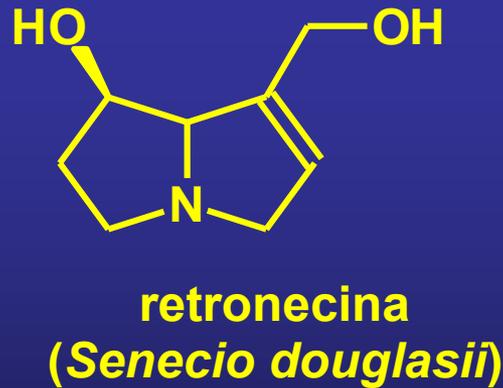


L-ornitina

Alcaloides



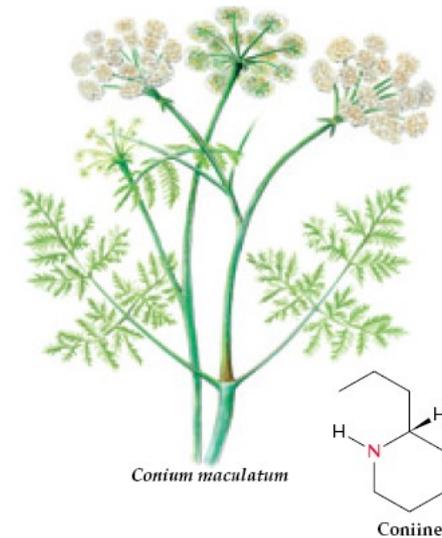
cocaína
(*Erhthroxyllum coca*)



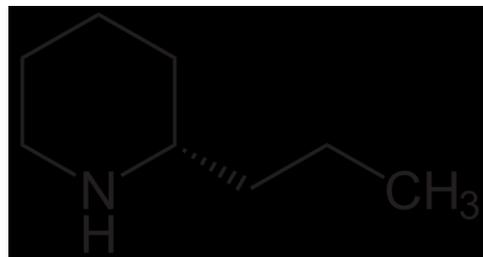
retronecina
(*Senecio douglasii*)



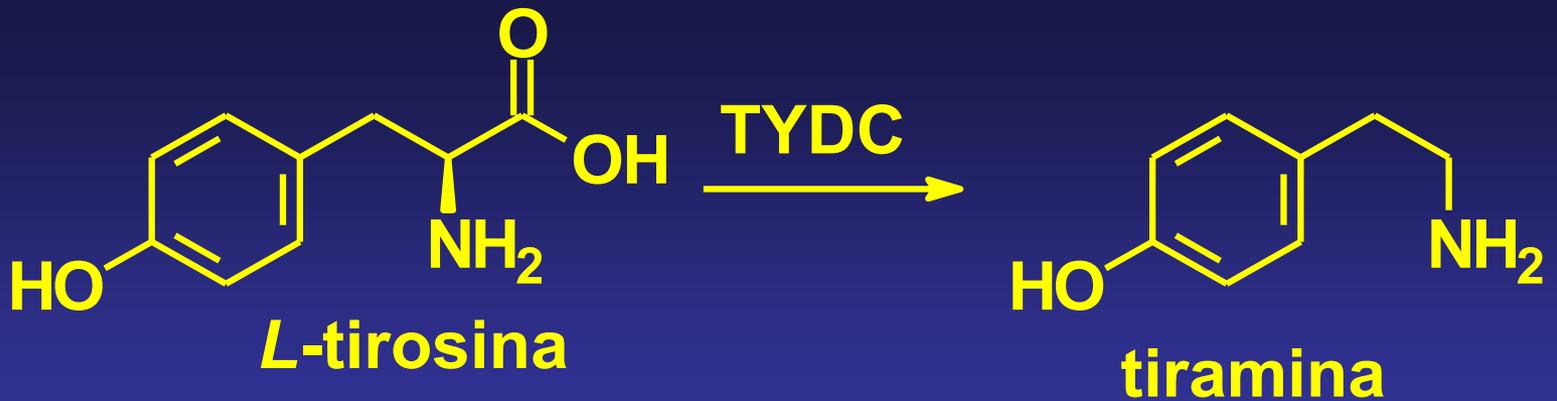
nicotina
(*Nicotiana tabacum*)



399 B.C., the philosopher Socrates drank an extract of coniine containing hemlock (*Conium maculatum*)



coniina

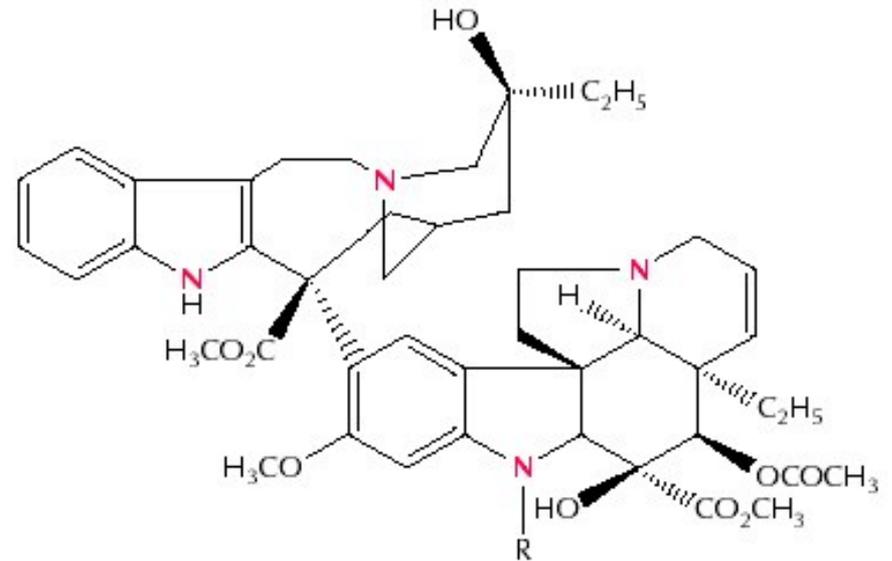


L-DOPA: precursor metabólico da dopamina, para o tratamento de Parkinson.

Alcaloides Indólicos



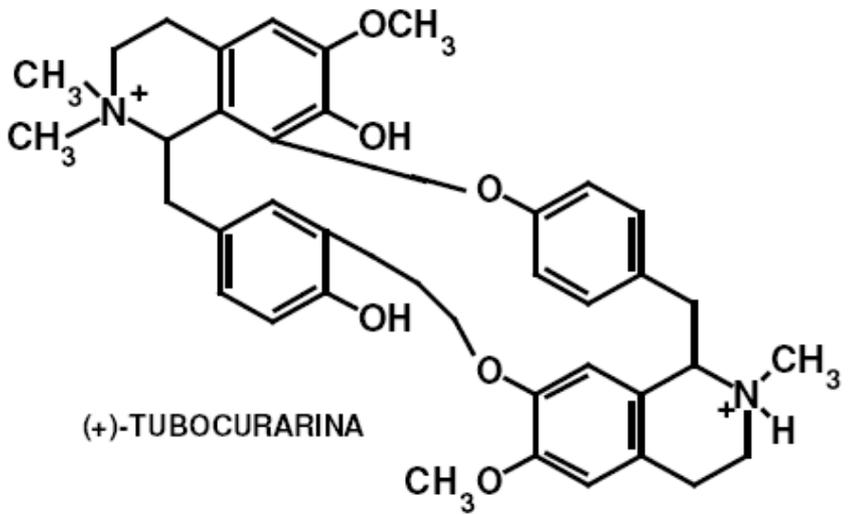
Catharanthus roseus



R = CH₃ R = CHO
Vinblastine Vincristine

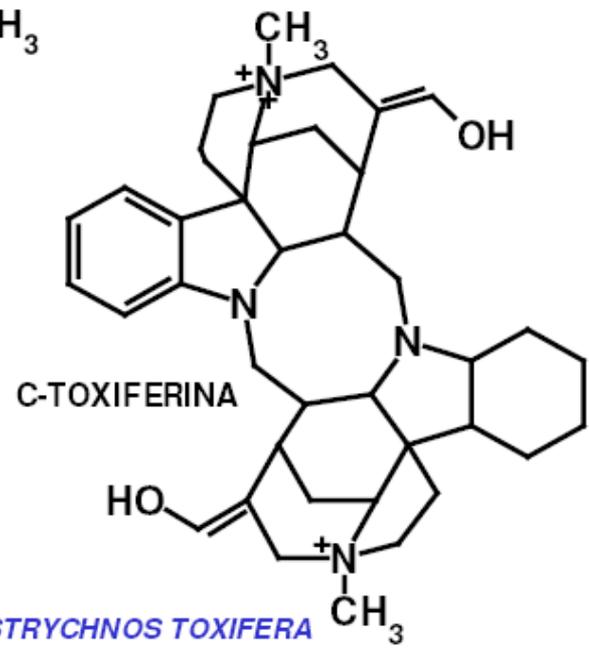


Utilizado no tratamento de câncer de ovário, mal de Hodgkin, leucemia linfática aguda e tumores de testículos.



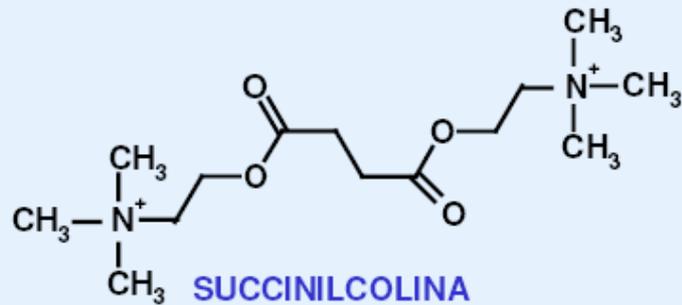
(+)-TUBOCURARINA

METABÓLITO DE *CHONDODENDRON TOMENTOSUM* (MENISPERMACEAE)

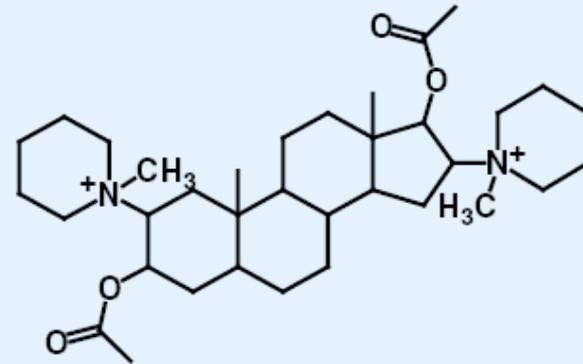


C-TOXIFERINA

METABÓLITO DE *STRYCHNOS TOXIFERA* (LOGANIACEAE)



**O PRIMEIRO CURARE
ARTIFICIAL SINTETIZADO
(1935)**

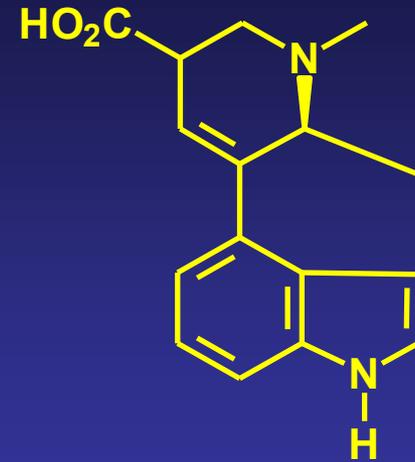


UM CURARE SINTÉTICO RECENTE

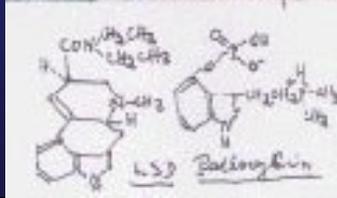
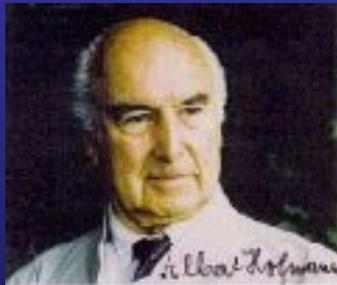
**ATUALMENTE, NÃO SE USAM MAIS OS CURARES
NATURAIS.**

**ELES FORAM FUNDAMENTAIS COMO *MODELOS*
ESTRUTURAIS PARA A PRODUÇÃO DE CURARES
SINTÉTICOS.**

Claviceps purpurea



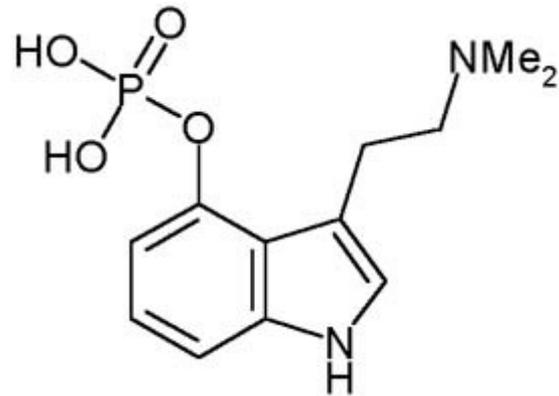
ácido lisérgico - LSD
(fungo, *Claviceps purpurea*)
(*Ipomeae* sp)



Dr. Albert Hofmann sintetizou LSD em 1938 e 1943. Foi o primeiro a experimentar seus efeitos. Posteriormente ele isolou e sintetizou a psilocyбина, O princípio ativo da *Psilocybe mexicana*, Sagrada aos Huichol.



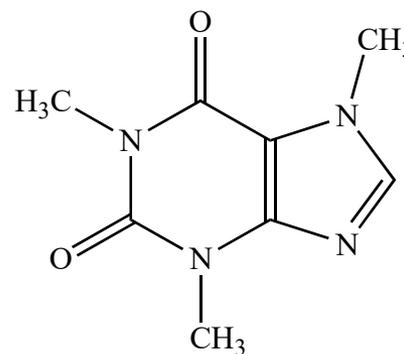
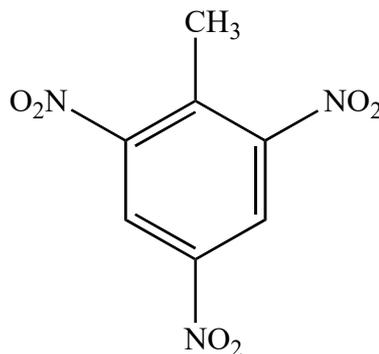
Psilocybe mexicana



psilocybin



Caracterização de compostos nitrogenados: Espectrometria de massas



Formula:



m/z (M):

17

32

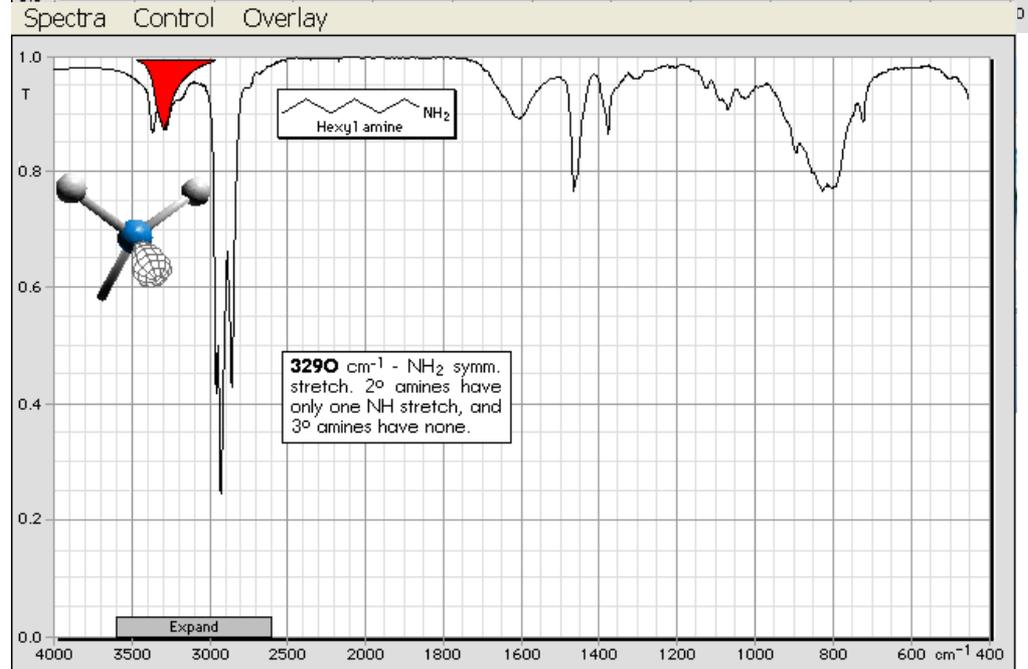
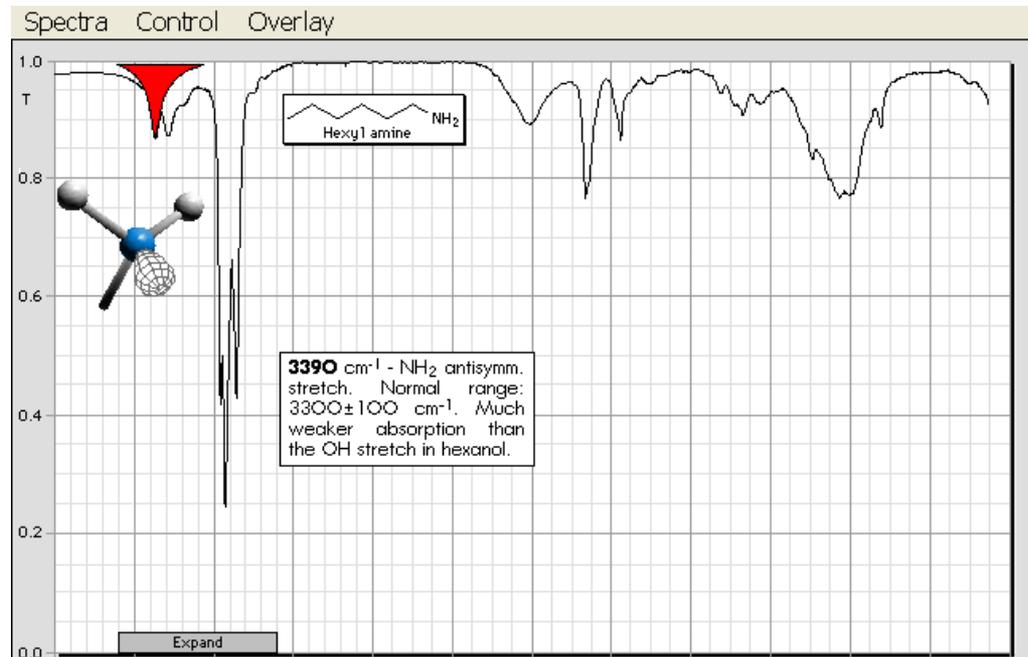
227

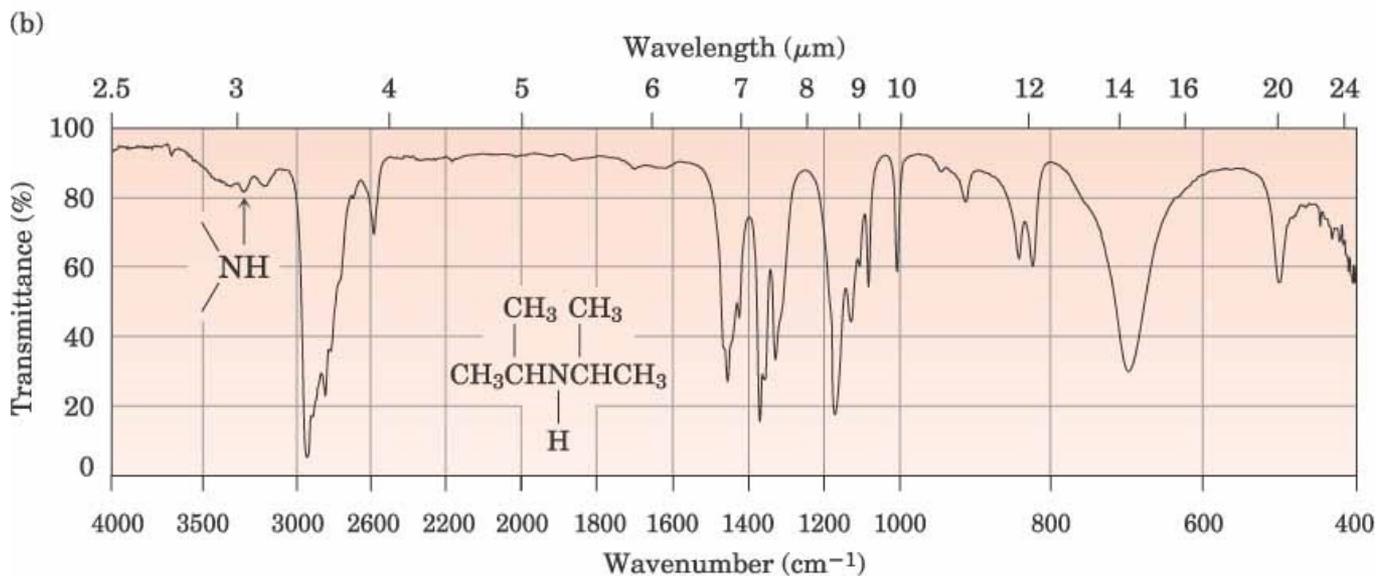
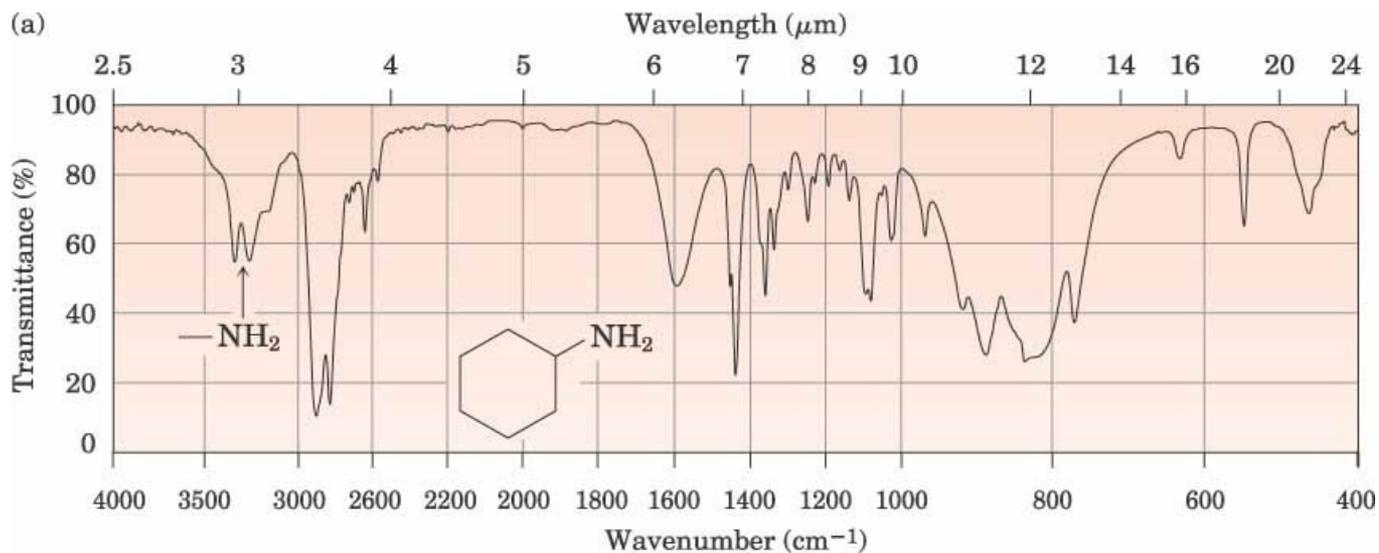
194

- When m/z (M) = **even**, number of N in formula is **even**
 - When m/z (M) = **odd**, number of N in formula is **odd**
- } **The Nitrogen Rule**

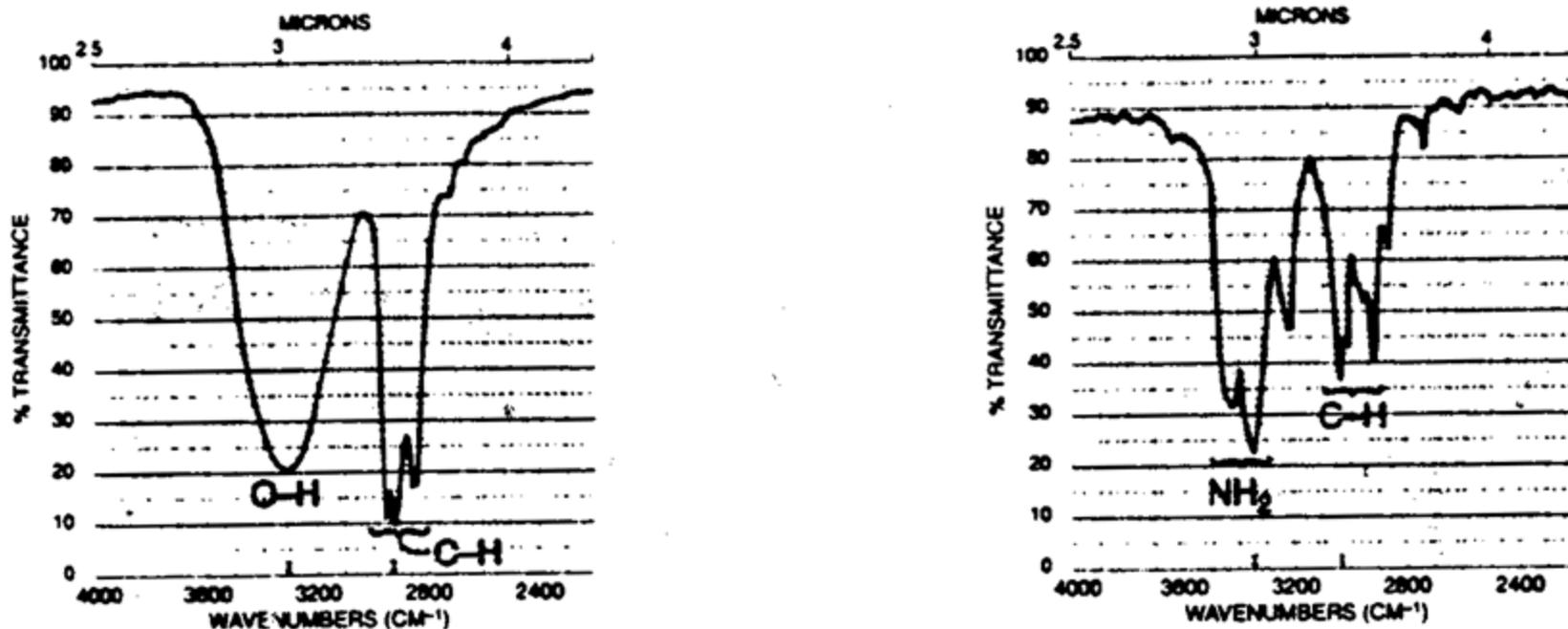
Caracterização de compostos Nitrogenados

Espectros no Infravermelho de aminas





Band Shape: OH vs NH₂ vs CH



► **FIGURE 2.6** A comparison of the shapes of the absorption bands for the O—H and N—H groups.

Physical Properties of Some Organic Compounds

Formula	IUPAC Name	Molecular Weight	Boiling Point	Water Solubility
CH₃(CH₂)₂CO₂H	butanoic acid	88	164 °C	very soluble
CH ₃ (CH ₂) ₄ OH	1-pentanol	88	138 °C	slightly soluble
CH ₃ (CH ₂) ₃ CHO	pentanal	86	103 °C	slightly soluble
CH ₃ CO ₂ C ₂ H ₅	ethyl ethanoate	88	77 °C	moderately soluble
CH ₃ CH ₂ CO ₂ CH ₃	methyl propanoate	88	80 °C	slightly soluble
CH₃(CH₂)₂CONH₂	butanamide	87	216 °C	soluble
CH ₃ CON(CH ₃) ₂	N,N-dimethylethanamide	87	165 °C	very soluble
CH ₃ (CH ₂) ₄ NH ₂	1-aminobutane	87	103 °C	very soluble
CH ₃ (CH ₂) ₃ CN	pentanenitrile	83	140 °C	slightly soluble
CH₃(CH₂)₄CH₃	hexane	86	69 °C	insoluble

Dielectric Solvent Constants¹

Solvent	Dielectric Constant
Formamide (HCONH ₂)	109
Water	80
Methanol (CH ₃ OH)	33
Ethanol (CH ₃ CH ₂ OH)	25
1-Propanol (CH ₃ CH ₂ CH ₂ OH)	20
1-Butanol (CH ₃ CH ₂ CH ₂ CH ₂ OH)	18
Benzene (C ₆ H ₆)	2

¹Dielectric solvent constant is a measure of the ability of a solvent to diminish electrostatic attraction between dissolved ions

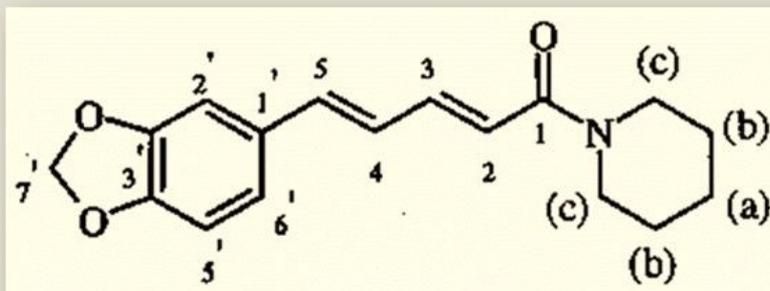
PIPERINE



◦ **PIPERINE**, $C_{17}H_{19}NO_3$, m.p. 128-129.5 °C

◦ **UV:** $\lambda_{\text{max}}^{\text{EtOH}}$ 245 nm (log ϵ 4.4).

IR (KBr): ν_{max} 3000 (aromatic C-H stretching), 1635, 1608 (sym and asym C = C stretching of diene) 1608, 1580, 1495 (C = C stretching of phenyl ring), 1635 (amide carbonyl stretching), 2925, 2840 (CH₂ asym and sym stretching), 1450 (CH₂ bending), 995 (C-H bending of trans CH = CH-), 850, 830, 805 (out of plane C-H bending 1,2,4-trisubstituted phenyl group) cm^{-1} .

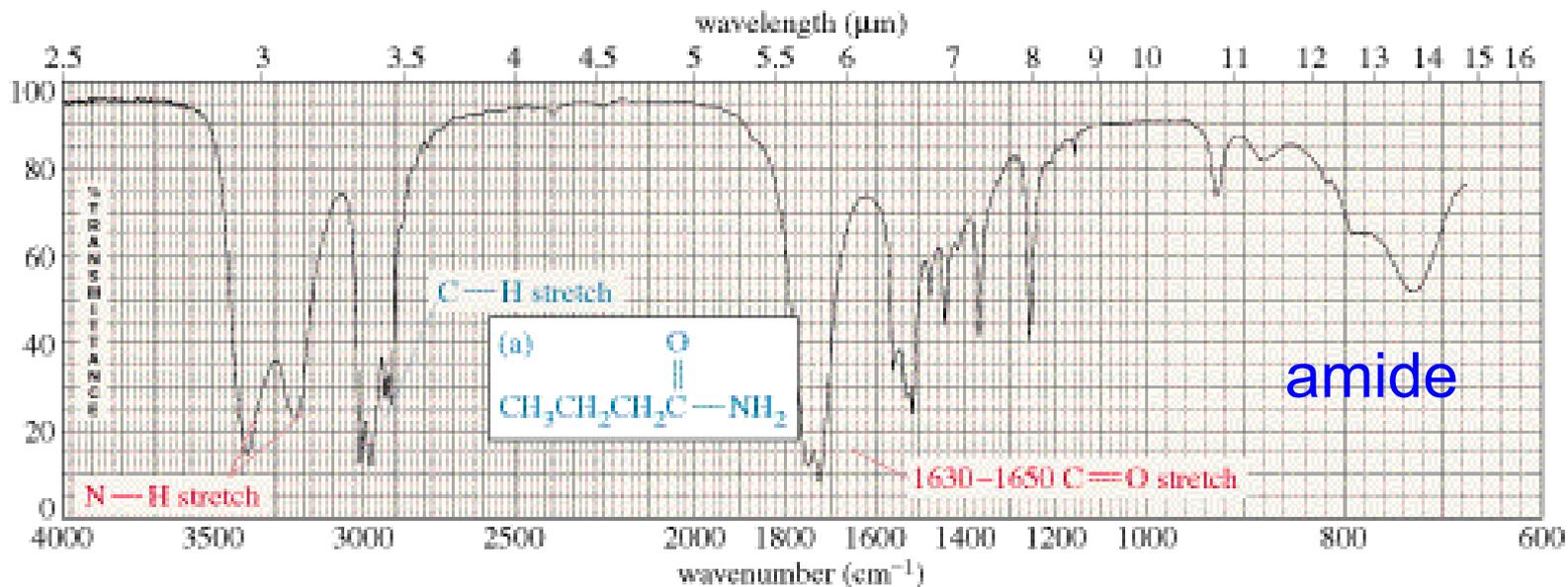
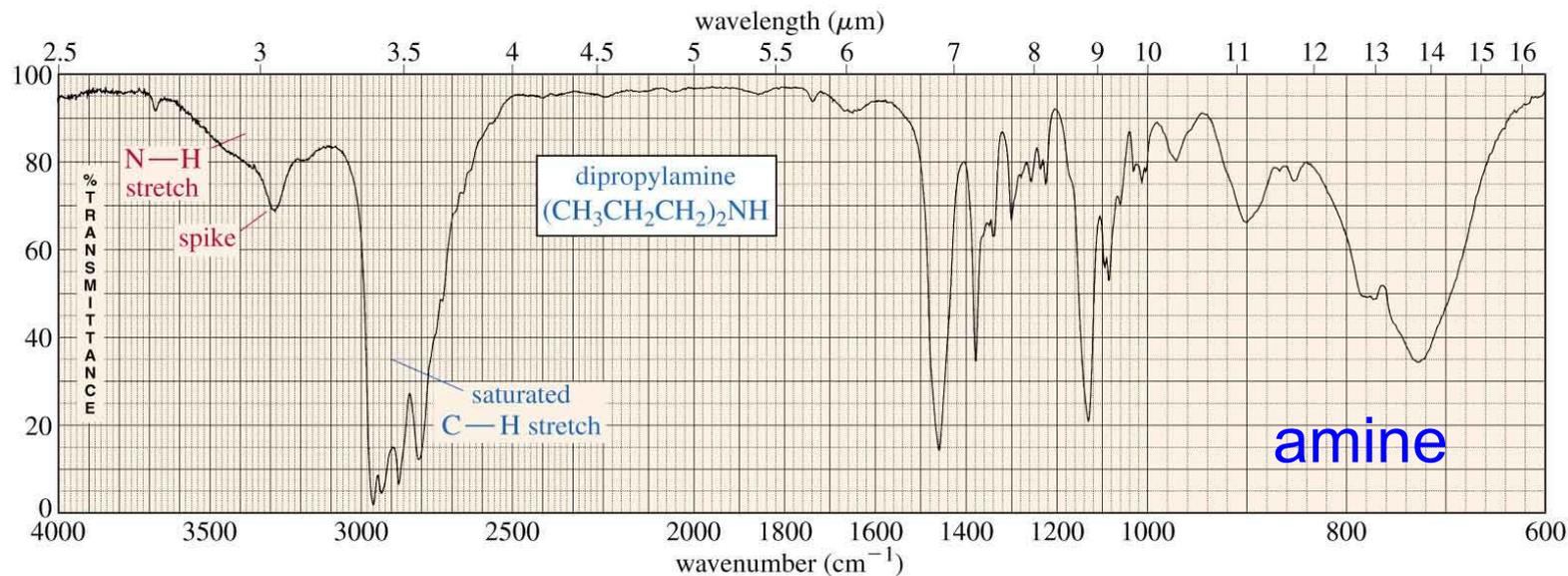


◦ **¹H NMR:** δ 5.93 (2H, H-7), 7.40(1H, H-3), 6.43(1H, H-2), 3.57(4H, H-c), 1.62 (4H,H-b), 1.62 (2H,H-a).

◦ **¹³C NMR:** δ 164.5 (C-1), 119.4 (C-2), 141.6 (C-3), 124.6 (C-4), 137.3 (C-5), 132.2 (C-1'), 104.9 (C-2'), 147.6 (C-3'), 147.4 (C-4'), 107.6 (C-5'), 121.7 (C-6') and 100.6 (C-7').

MS: m/z 285 (M^+ , 65%), 202 (29%), 201 (100%), 174 (25%), 173 (42%), 171 (26%), 143 (32%), 115 (92%). ³⁶

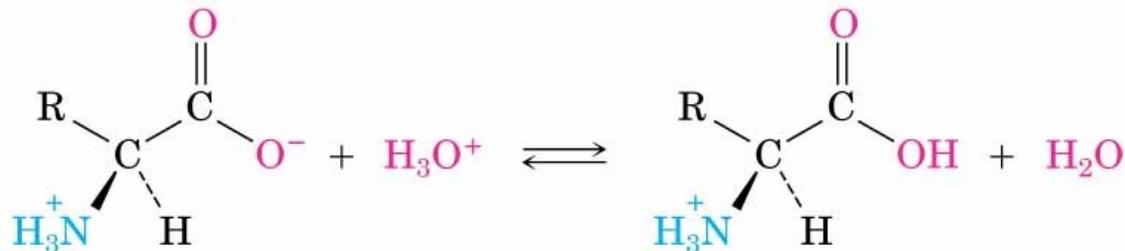
IR Spectra of amines and amides



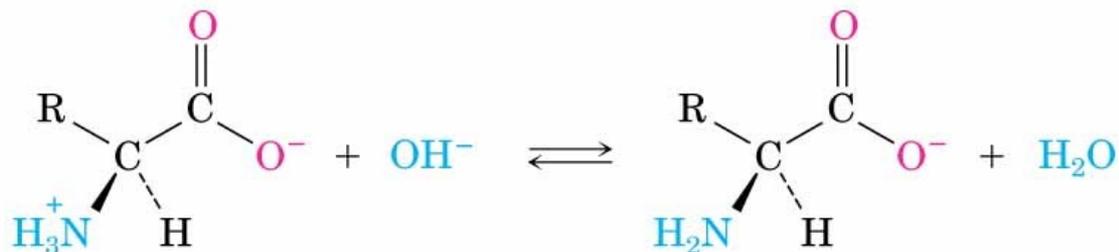
Structures of Amino Acids

- In neutral solution, the COOH is ionized and the NH₂ is protonated
- The resulting structures have “+” and “-” charges (a *dipolar ion*, or *zwitterion*)
- They are like ionic salts in solution

In acid solution

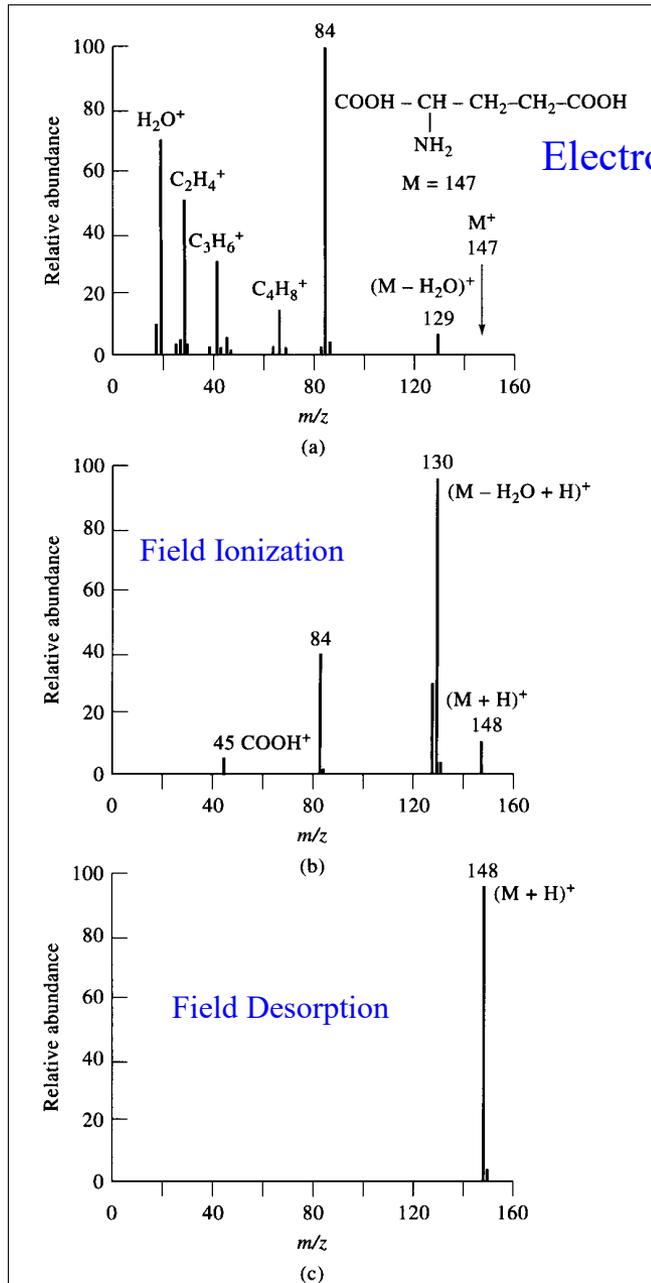


In base solution

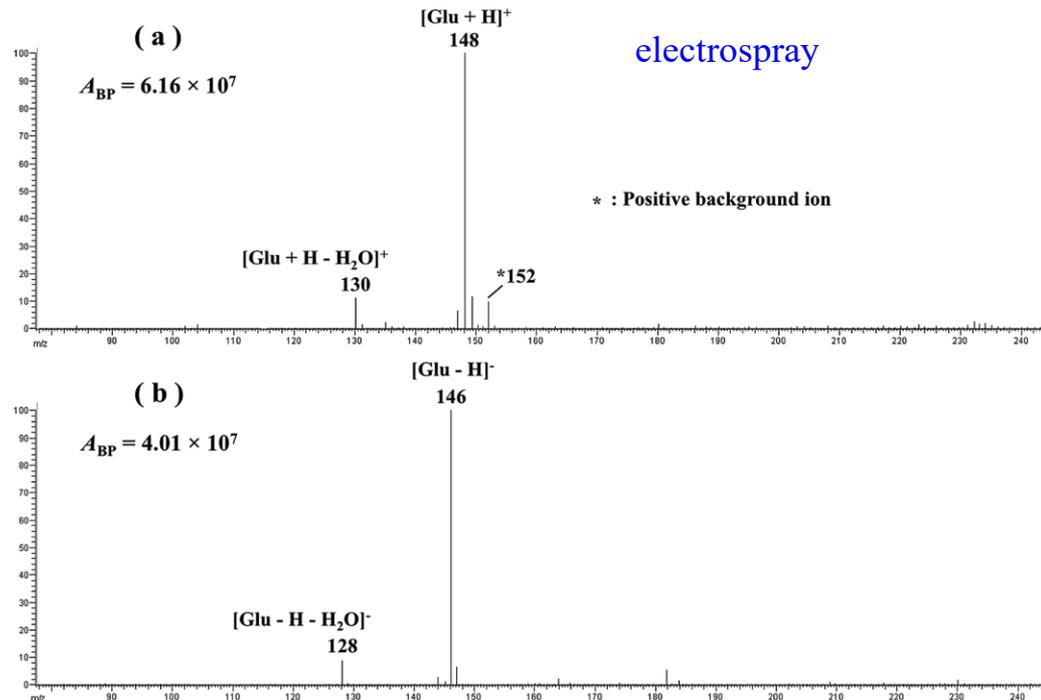
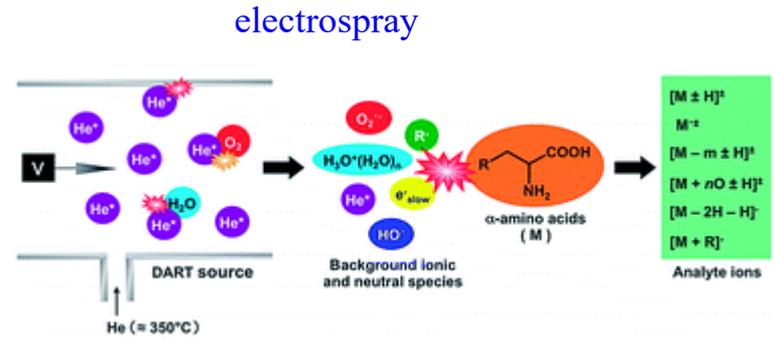


© 2004 Thomson/Brooks Cole

Mass spectra of Glutamic Acid



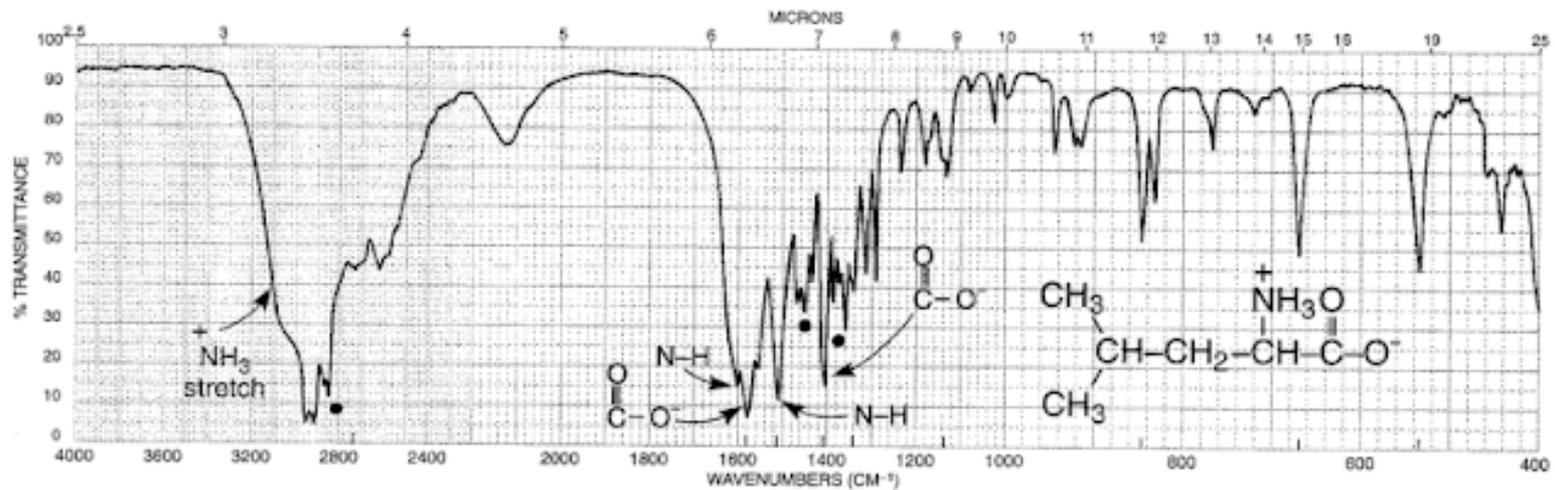
Electron Impact (EI)



electrospray

* : Positive background ion

IR spectrum of aminoacids



Abbreviations and Codes

Alanine **A, Ala**

Arginine **R, Arg**

Asparagine **N, Asn**

Aspartic acid **D, Asp**

Cysteine **C, Cys**

Glutamine **Q, Gln**

Glutamic Acid **E, Glu**

Glycine **G, Gly**

Histidine **H, His**

Isoleucine **I, Ile**

Leucine **L, Leu**

Lysine **K, Lys**

Methionine **M, Met**

Phenylalanine **F, Phe**

Proline **P, Pro**

Serine **S, Ser**

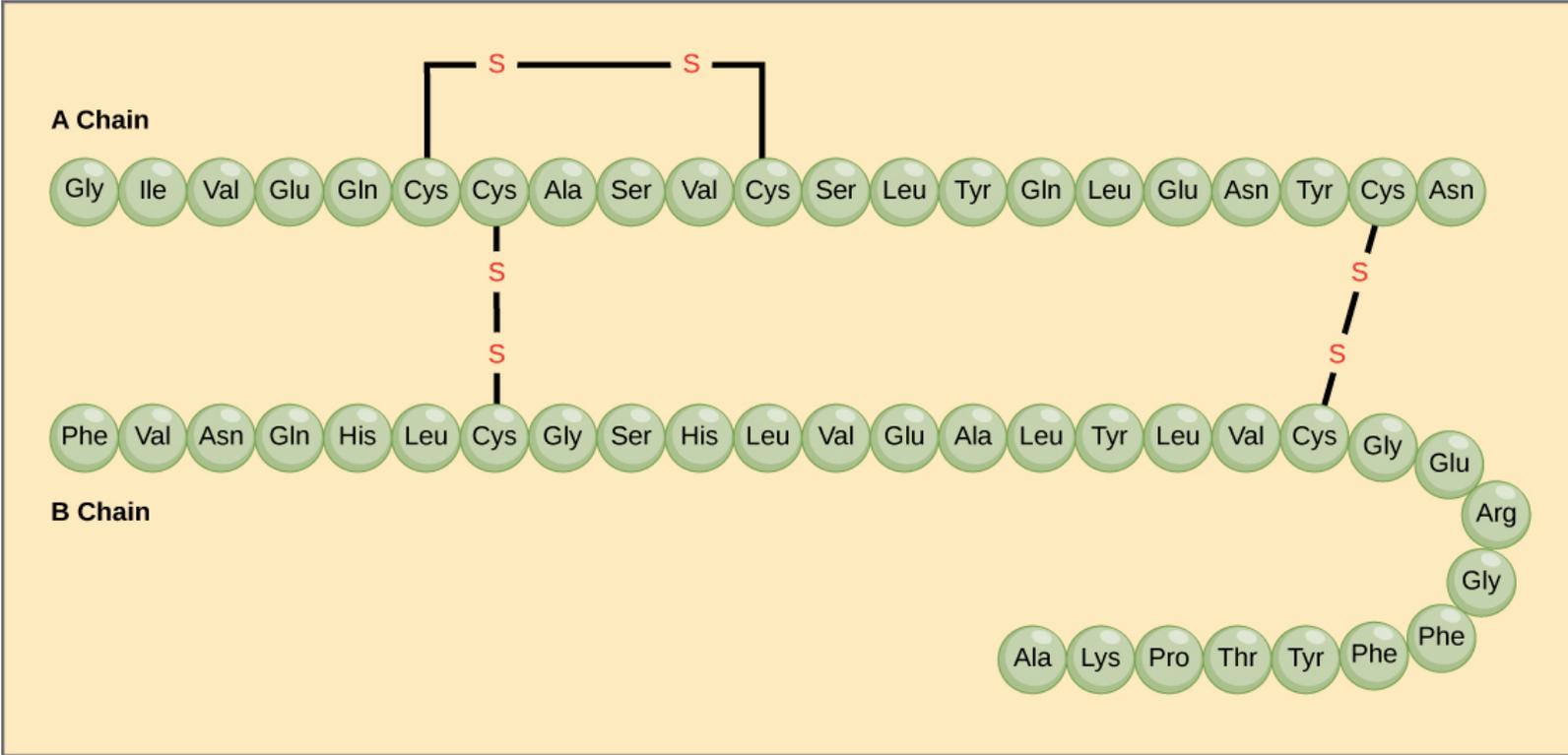
Threonine **T, Thr**

Tryptophan **W, Trp**

Tyrosine **Y, Tyr**

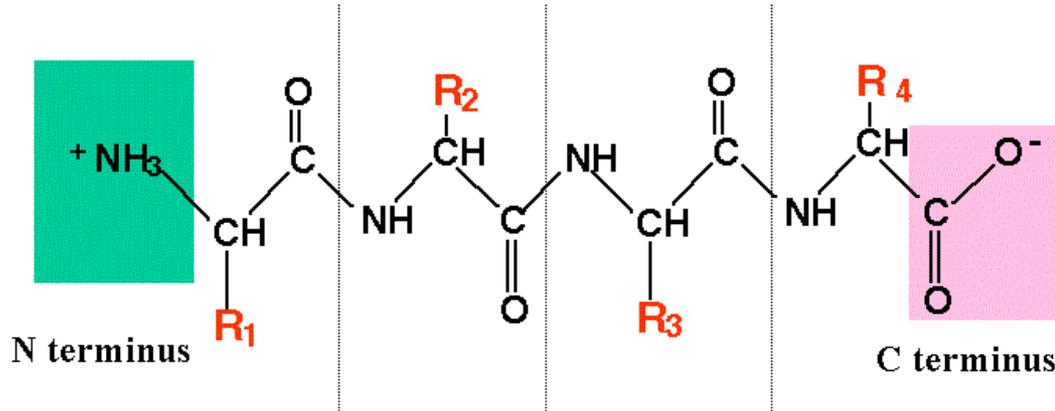
Valine **V, Val**

Estrutura primária: uma sequência de aminoácidos em uma cadeia polipeptídica.



Estrutura primária: sequencia de aminoácidos

Peptide = chain of amino acids



polypeptide chain

Vegan Protein Sources

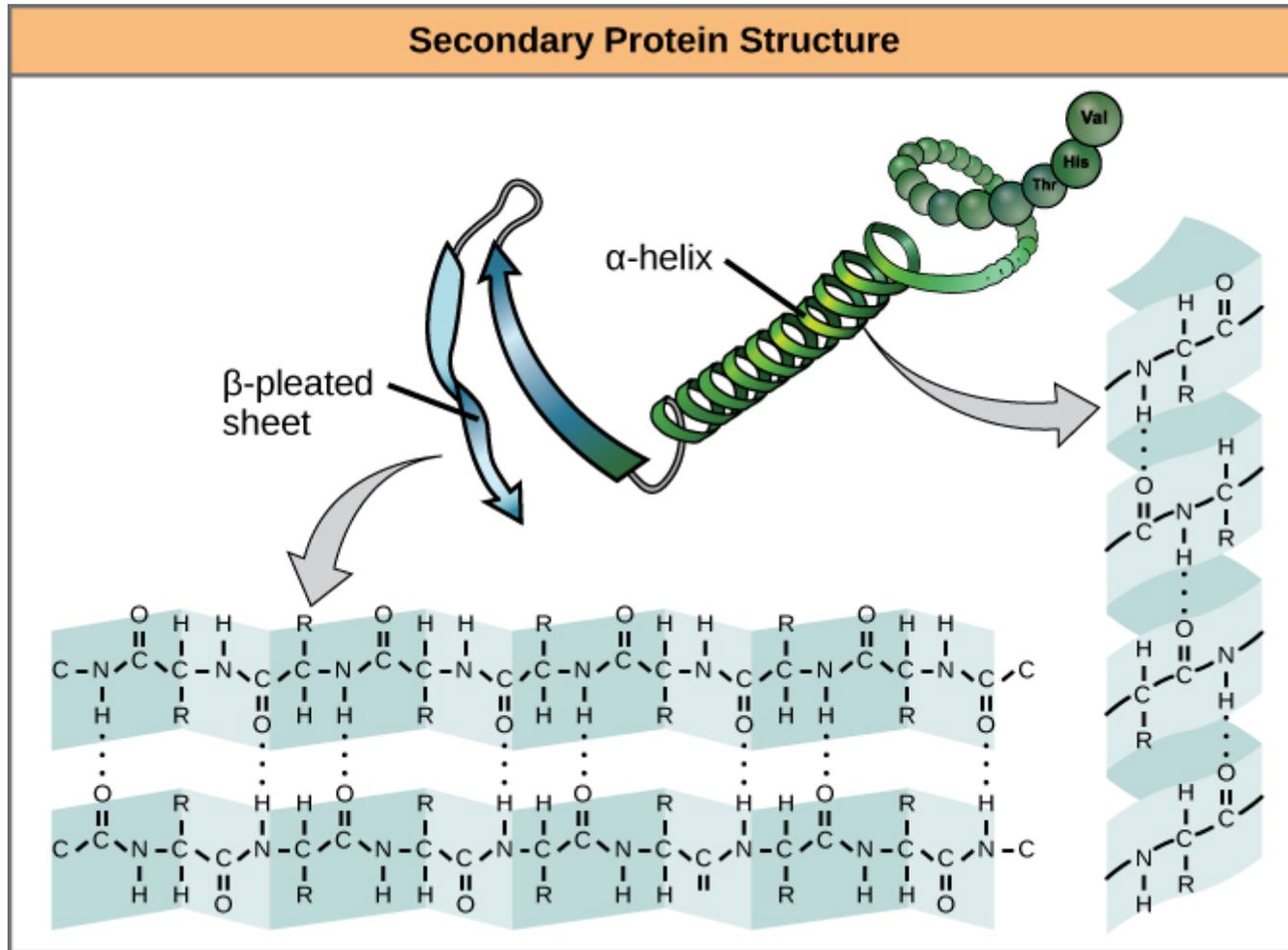
By VEGANS OF INSTAGRAM

Tempeh 41g (1 cup)	Wheat Germ 33g (1 cup)	Seitan 31g (3 oz)	Soy Beans 29g (1 cup)
Beckweat 24g (1 cup)	Lentils 18g (1 cup)	Beans Black 15g (1 cup) Kidney 13g (1 cup) Pinto 12g (1 cup) Garbanzo 12g (1 cup)	Quinoa 9g (1 cup)
Peas 9g (1 cup)	Wild Rice 7g (1 cup)	Tofu 11g (1 cup)	Seeds Pumpkin 8g (1 oz) Sunflower 5g (1 oz)
Nuts Peanuts 7g (1 oz) Almonds 6g (1 oz) Pistachios 6g (1 oz) Cashew 5g (1 oz) Brazilian 4g (1 oz) Walnuts 4g (1 oz)	Raisins 5g (1 cup)	Avocado 4g (1 med)	Spinach 5g (1 cup)
	Artichoke 4g (1 cup)	Sprouts 4g (1 cup)	

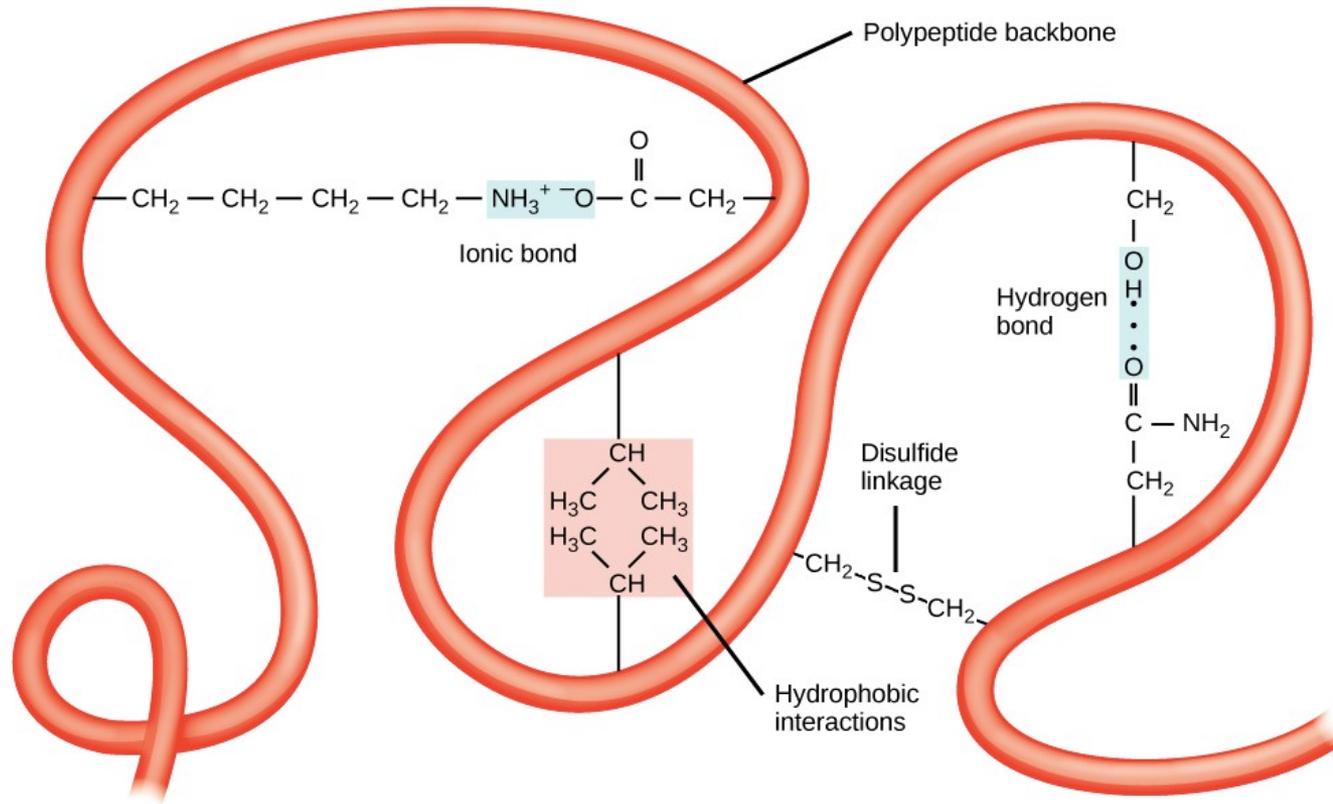
*Peanuts are technically a legume



Estrutura secundária: estruturas de um polipeptídeo dobradas de sobre si mesmas resultantes das às interações entre os átomos da estrutura primária. Exemplos: α -hélice e a folha- β pregueada.



Estrutura terciária: A estrutura geral tridimensional de um polipeptídeo

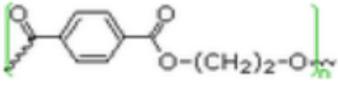
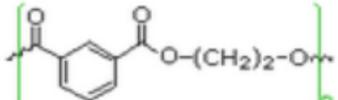
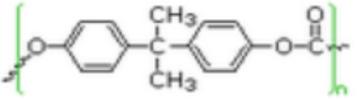
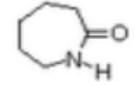
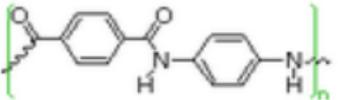
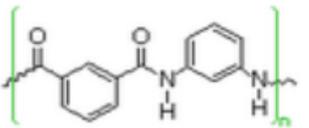
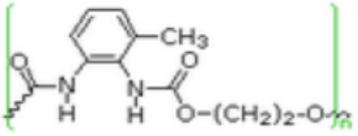
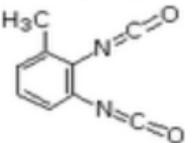


Interações envolvidas nos grupos R: todas as ligações não-covalentes como ligações de hidrogênio, ligações iônicas, interações dipolo-dipolo, ligação iônica e forças de dispersão London.

Tg: glass transition temperature; Tm: melting temperature

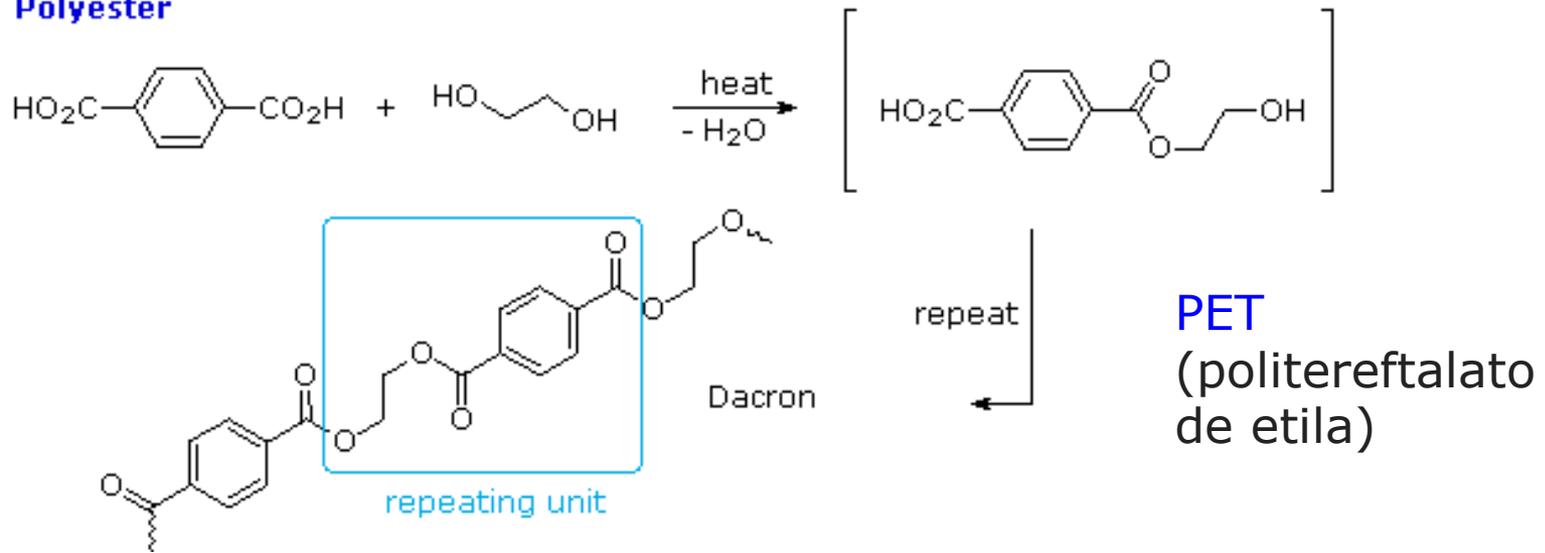
poliésteres

poliamidas

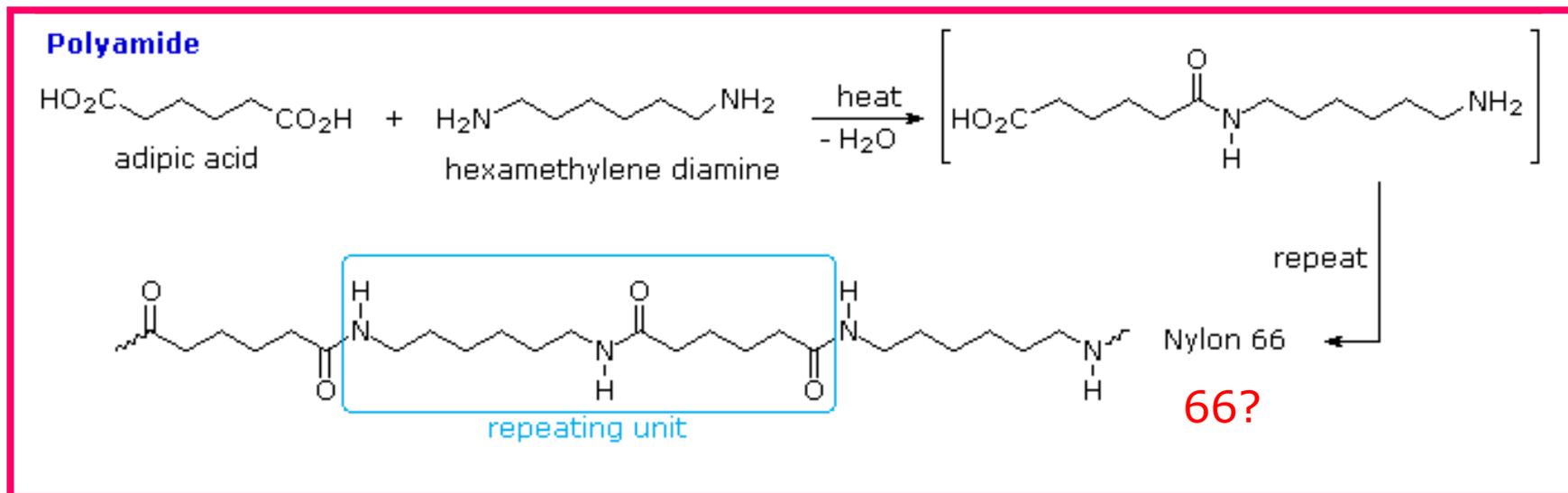
Formula	Type	Components	T _g °C	T _m °C
$\sim[\text{CO}(\text{CH}_2)_4\text{CO}-\text{OCH}_2\text{CH}_2\text{O}]_n\sim$	polyester	HO ₂ C-(CH ₂) ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH	< 0	50
	polyester Dacron Mylar	para HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH	70	265
	polyester	meta HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH	50	240
	polycarbonate Lexan	(HO-C ₆ H ₄ -) ₂ C(CH ₃) ₂ (Bisphenol A) X ₂ C=O (X = OCH ₃ or Cl)	150	267
$\sim[\text{CO}(\text{CH}_2)_4\text{CO}-\text{NH}(\text{CH}_2)_6\text{NH}]_n\sim$	polyamide Nylon 66	HO ₂ C-(CH ₂) ₄ -CO ₂ H H ₂ N-(CH ₂) ₆ -NH ₂	45	265
$\sim[\text{CO}(\text{CH}_2)_5\text{NH}]_n\sim$	polyamide Nylon 6 Perlon		53	223
	polyamide Kevlar	para HO ₂ C-C ₆ H ₄ -CO ₂ H para H ₂ N-C ₆ H ₄ -NH ₂	---	500
	polyamide Nomex	meta HO ₂ C-C ₆ H ₄ -CO ₂ H meta H ₂ N-C ₆ H ₄ -NH ₂	273	390
	polyurethane Spandex	HOCH ₂ CH ₂ OH 	52	---

Condensation (Step) Polymerization

Polyester

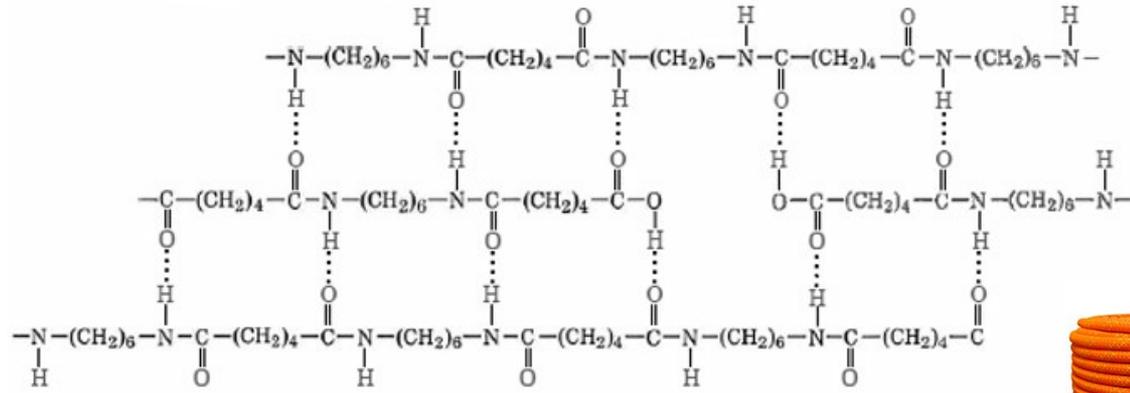


Condensation (Step) Polymerization

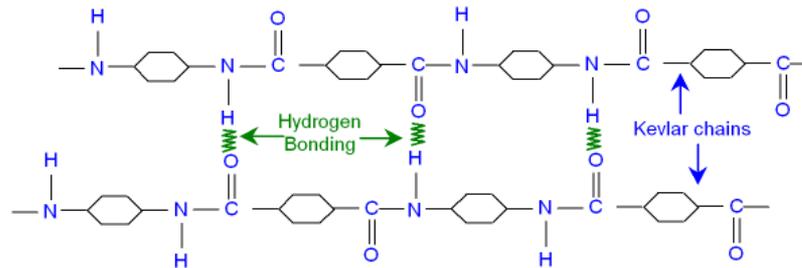


Polyamides

KIT 4 LEGGINGS
ESTAMPADAS SUPLEX
POWER
POLIAMIDA
POR APENAS
R\$ 100,00



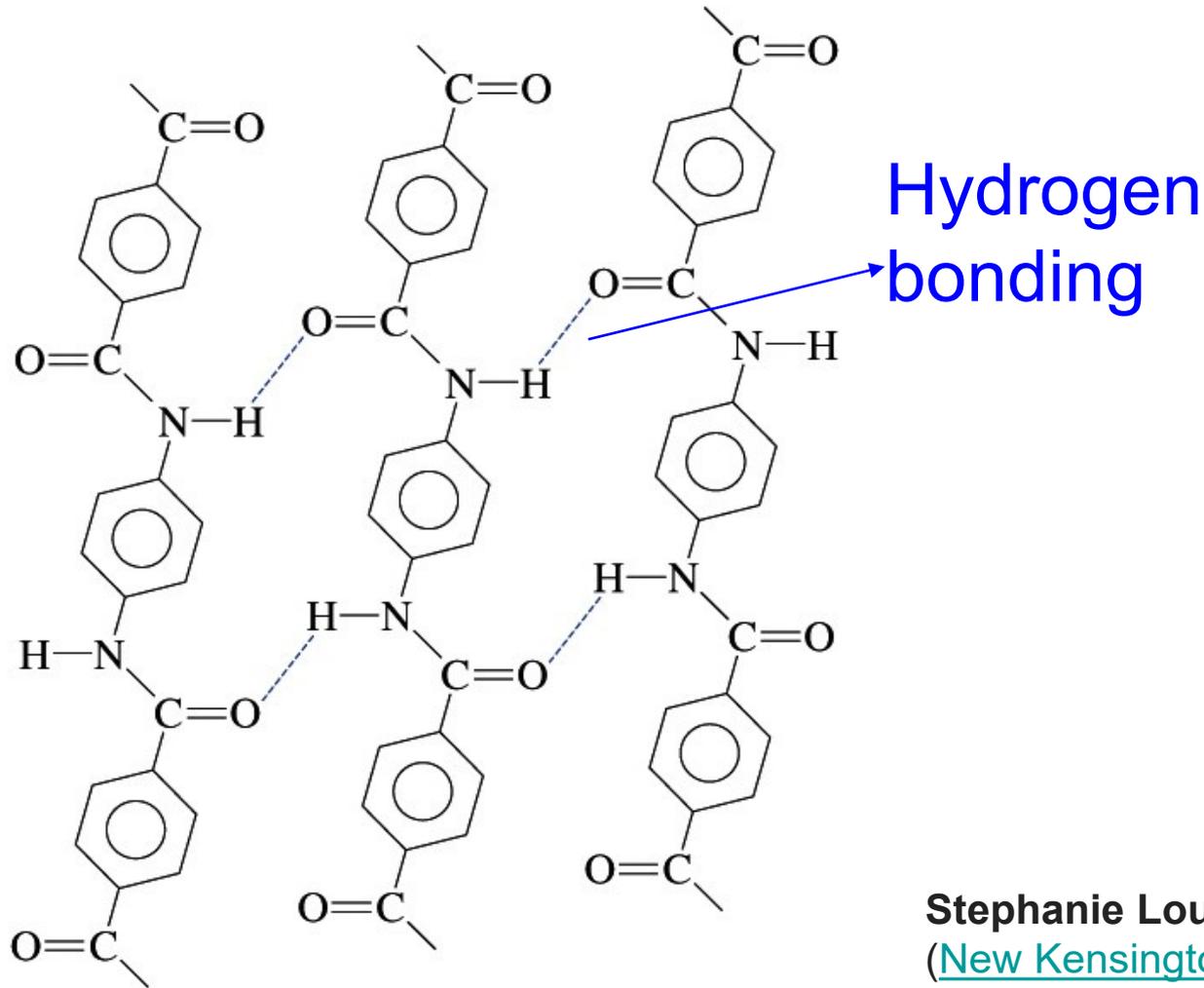
Nylon 66



Kevlar



Partial structure of Kevlar

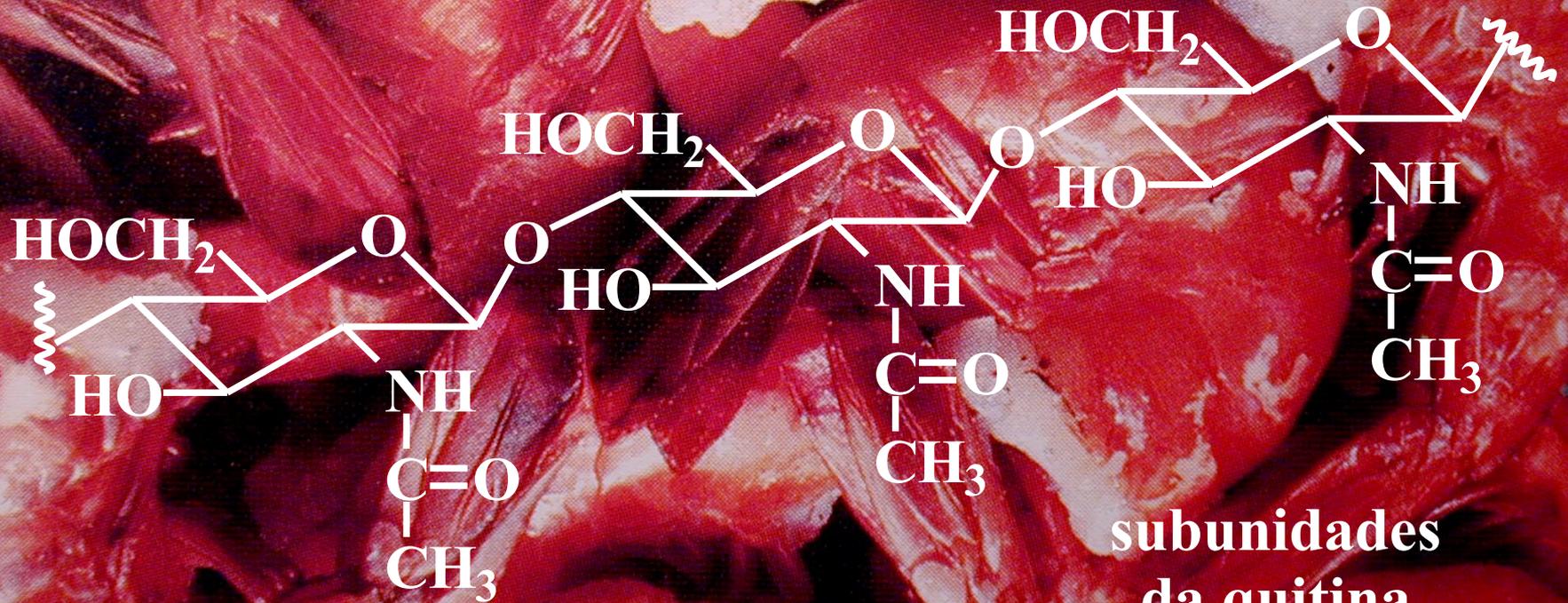


Stephanie Louise Kwolek

([New Kensington](#), [31 de julho](#) de [1923](#) — [18 de junho](#) de [2014](#))
[Inventora do Kevlar](#)

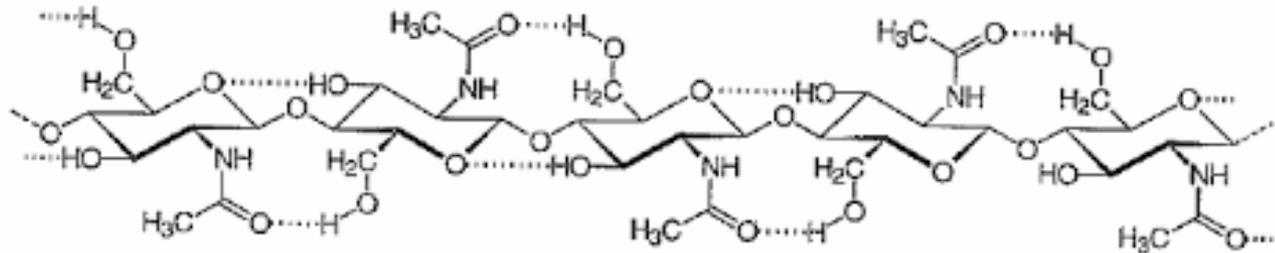
QUITINA:

(crustáceos e exoesqueleto de insetos)



subunidades
da quitina

Structure of chitin



Why these hydrogen bonding is so effective?

1811 Chitin was discovered by Henri Braconnot, who isolated it from mushrooms and named it “fungine”

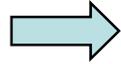
1823 – Antoine Odier found a chitin while studying beetle cuticles and named it “chitin” (from Greek chiton (tunic, envelop)

1859 – Rouget discovered chitosan, a desacetylchitin

1950 – Structures of chitin and chitosan were identified by X-ray diffraction, Infrared spectra and enzymatic analysis

Componentes de um espectrômetro de massas

**Geração de íons
(ionização)**



**Separação de
íons**



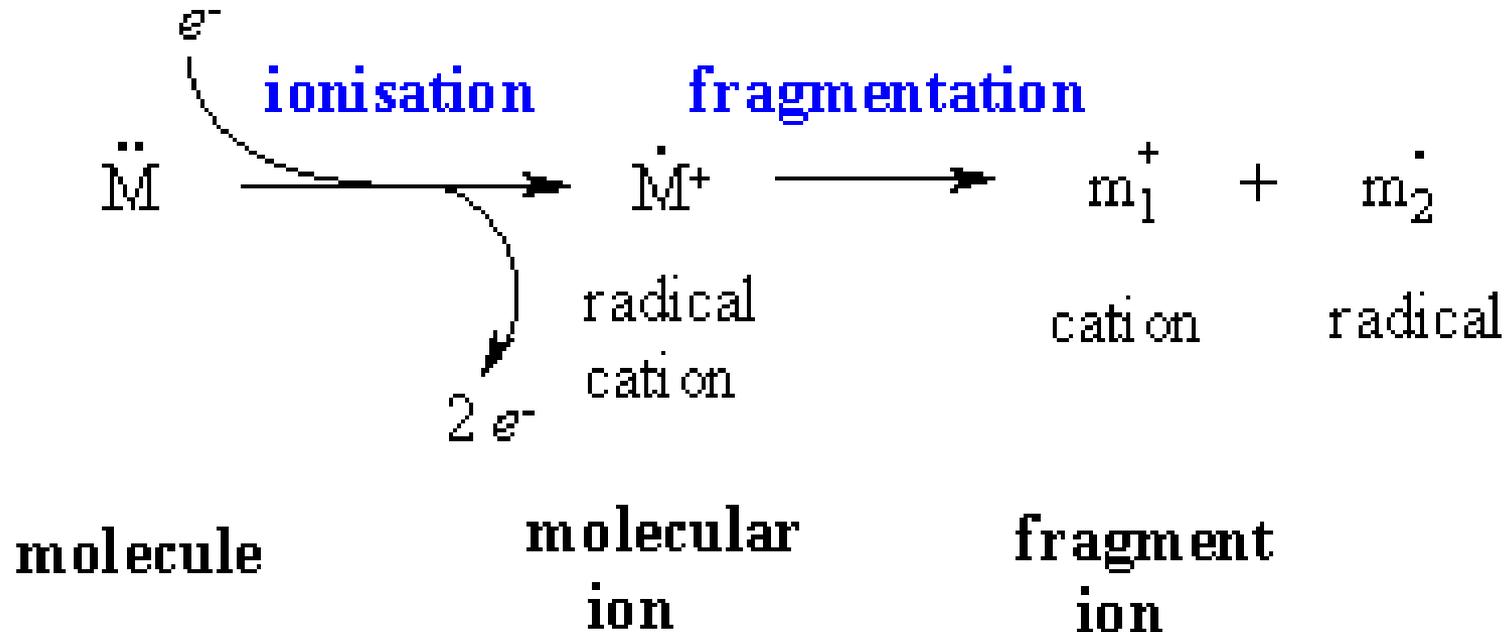
Detecção

- **Impacto de elétrons**
- **Ionização química**
- **Electrospray**
- **MALDI**

- **quadrupolo**
- **Ion trap**
- **TOF**

Ionização por Impacto de Elétrons (IE)

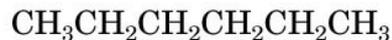
Bombardeamento de alta energia (70 eV) na amostra gasosa



Homolytic dissociation energy for chemical bond

Bond	DH°		Bond	DH°	
	kcal/mol	kJ/mol		kcal/mol	kJ/mol
CH ₃ -H	105	439	H-H	104	435
CH ₃ CH ₂ -H	101	423	F-F	38	159
CH ₃ CH ₂ CH ₂ -H	101	423	Cl-Cl	58	242
(CH ₃) ₂ CH-H	99	414	Br-Br	46	192
(CH ₃) ₃ C-H	97	406	I-I	36	150
CH ₃ -CH ₃	88	368	H-F	138	568
CH ₃ CH ₂ -CH ₃	85	355	H-Cl	103	431
(CH ₃) ₂ CH-CH ₃	84	351	H-Br	88	366
(CH ₃) ₃ C-CH ₃	80	334	H-I	71	297
H ₂ C=CH ₂	152	635	CH ₃ -F	108	451
HC≡CH	200	836	CH ₃ -Cl	84	349
HO-H	119	497	CH ₃ CH ₂ -Cl	82	343
CH ₃ O-H	102	426	(CH ₃) ₂ CH-Cl	81	338
CH ₃ -OH	91	380	(CH ₃) ₃ C-Cl	79	330
			CH ₃ -Br	70	293
			CH ₃ CH ₂ -Br	69	289
			(CH ₃) ₂ CH-Br	68	285
			(CH ₃) ₃ C-Br	63	264
			CH ₃ -I	56	234
			CH ₃ CH ₂ -I	55	230

PhCOO-OCOPh (30 kcal/mol)



Hexane



Molecular ion, M^+

($m/z = 86$)



m/z : 71

57

43

29

Relative
abundance (%): 10

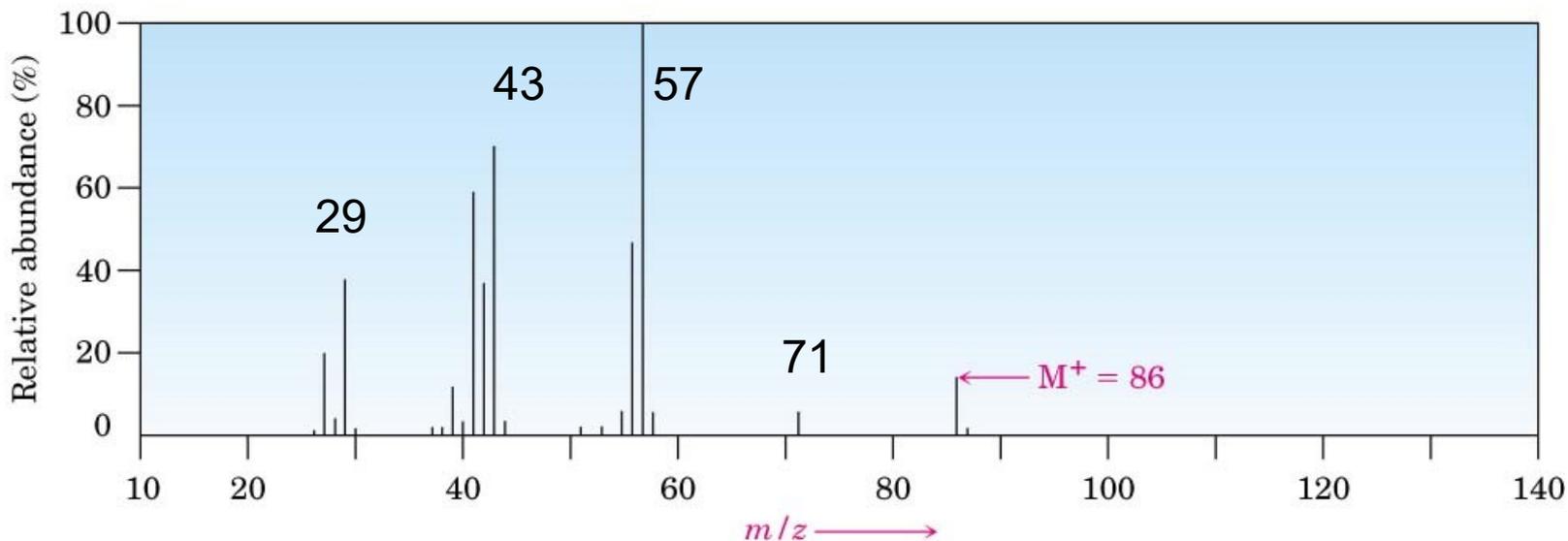
100 (base peak)

75

40

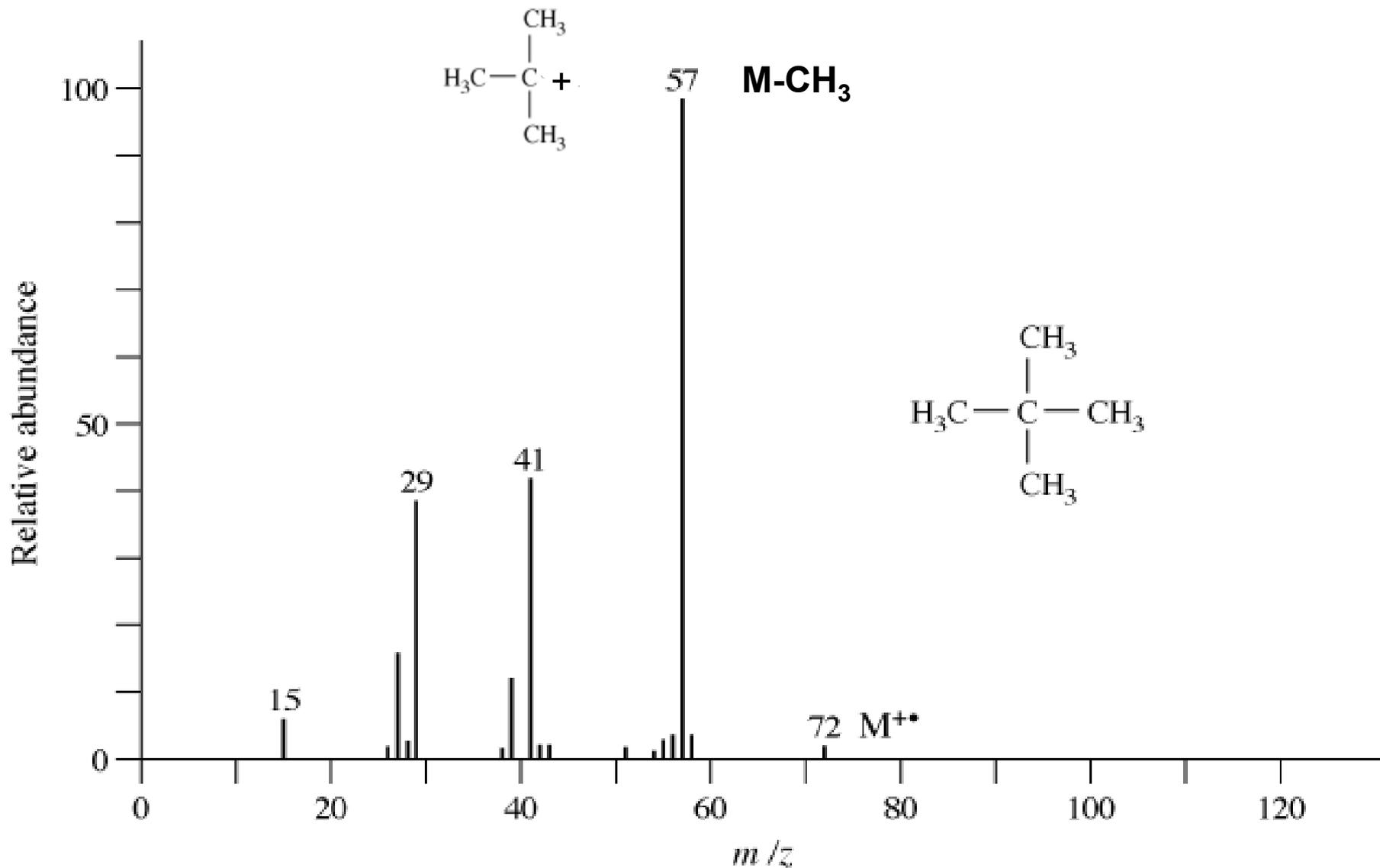
© Thomson - Brooks Cole

Mass Spectrum of Hexane

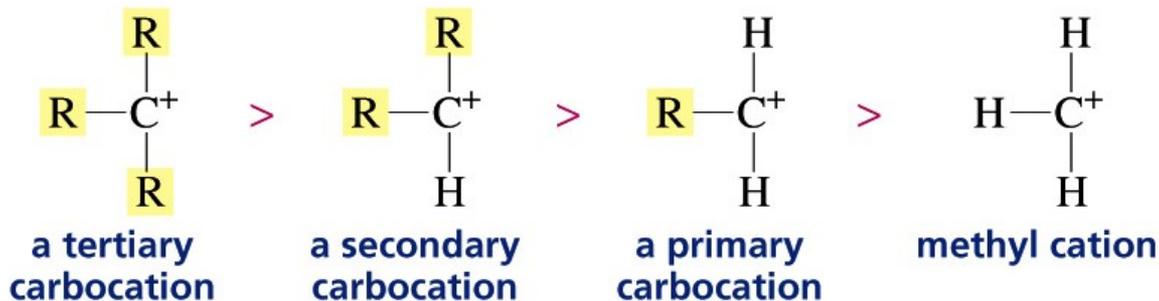


© Thomson - Brooks Cole

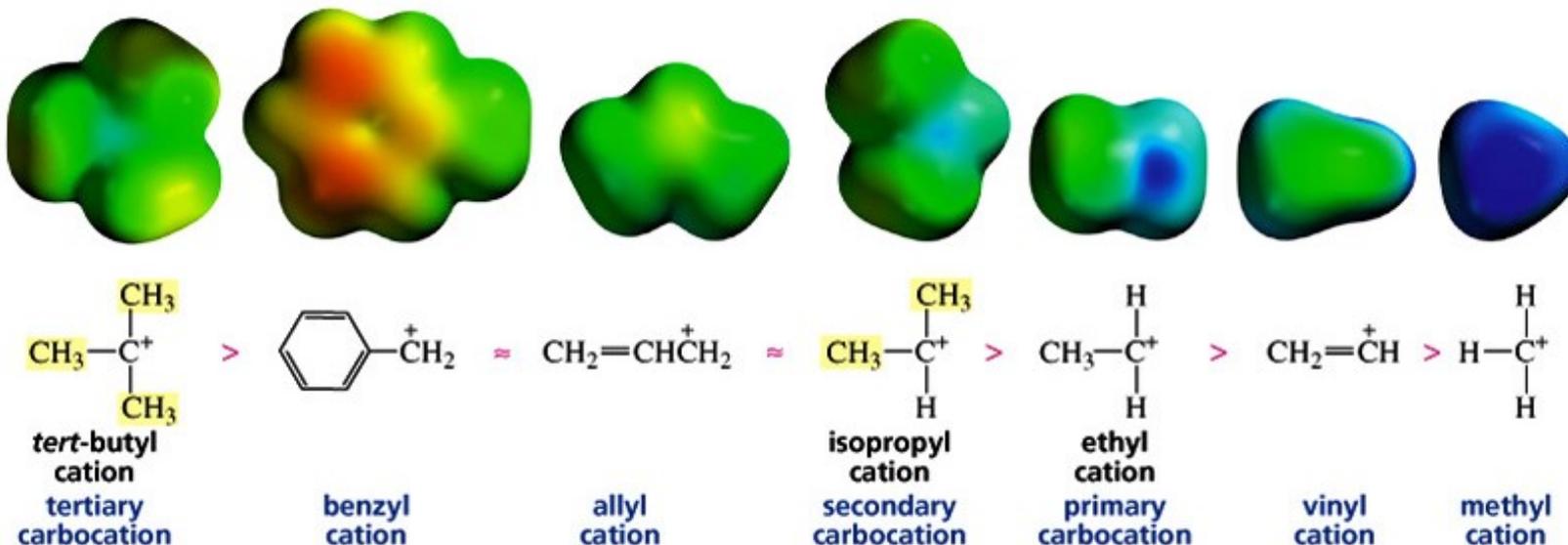
Espectro de massas do 2,2-dimetil-propano



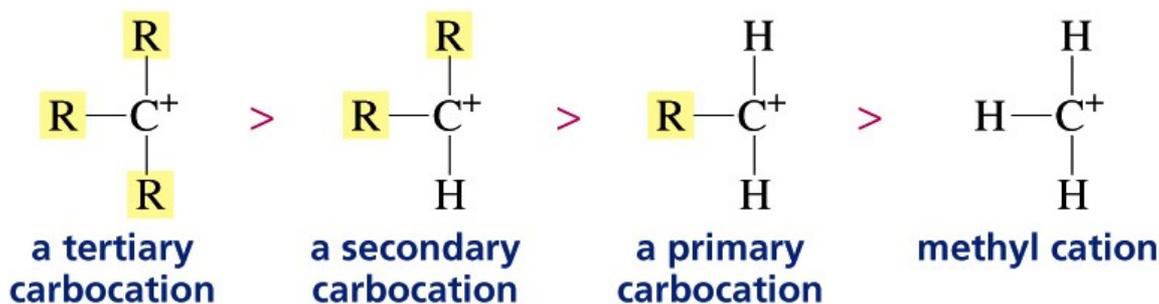
Estabilidades Relativas de Carbocátions



relative stabilities of carbocations



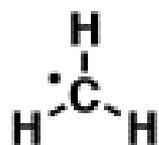
Estabilidade Relativa de carbocátions e Radicais Alquílicos seguem a mesma ordem



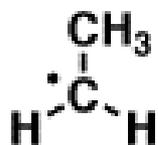
Fatores contribuem para a estabilização de radicais livres:

1) Número de grupos alquílicos

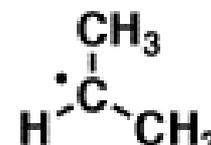
Para a série alquílica saturada:



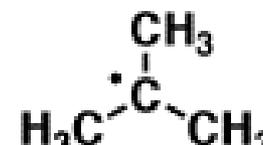
<



<



<



Methyl radical

Primary radical

Secondary radical

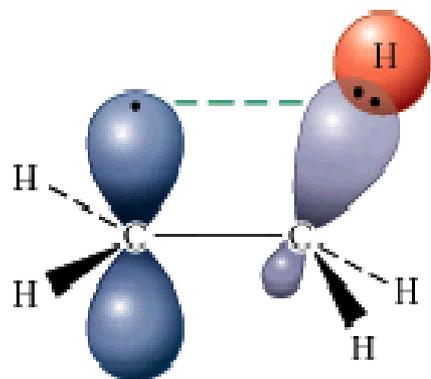
Tertiary radical

Least stable

Most stable

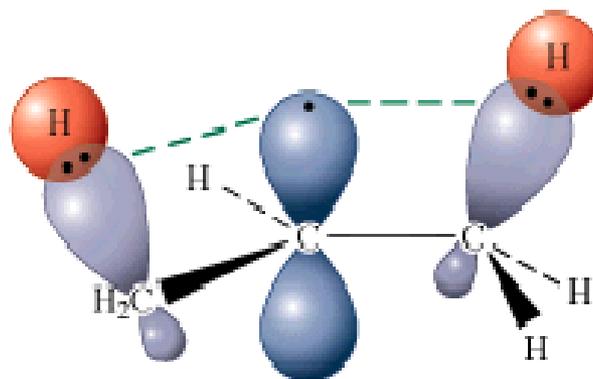
Estabilidade Relativa dos Radicais

- ✓ Um grupo alquila doa elétrons, estabilizando o radical.
- ✓ Quanto mais grupos alquila estiverem ligados, mais estável será o radical.
- ✓ Doação de elétrons do grupo alquila para o radical ocorre por **hiperconjugação**.
- ✓ **Hiperconjugação** é a sobreposição com orbitais de ligações sigma.

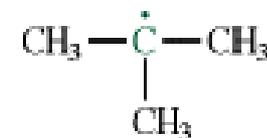
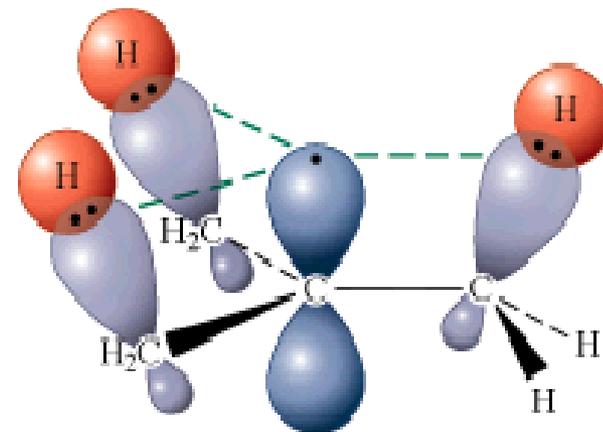


Ethyl radical

A



1-Methylethyl radical
(Isopropyl)

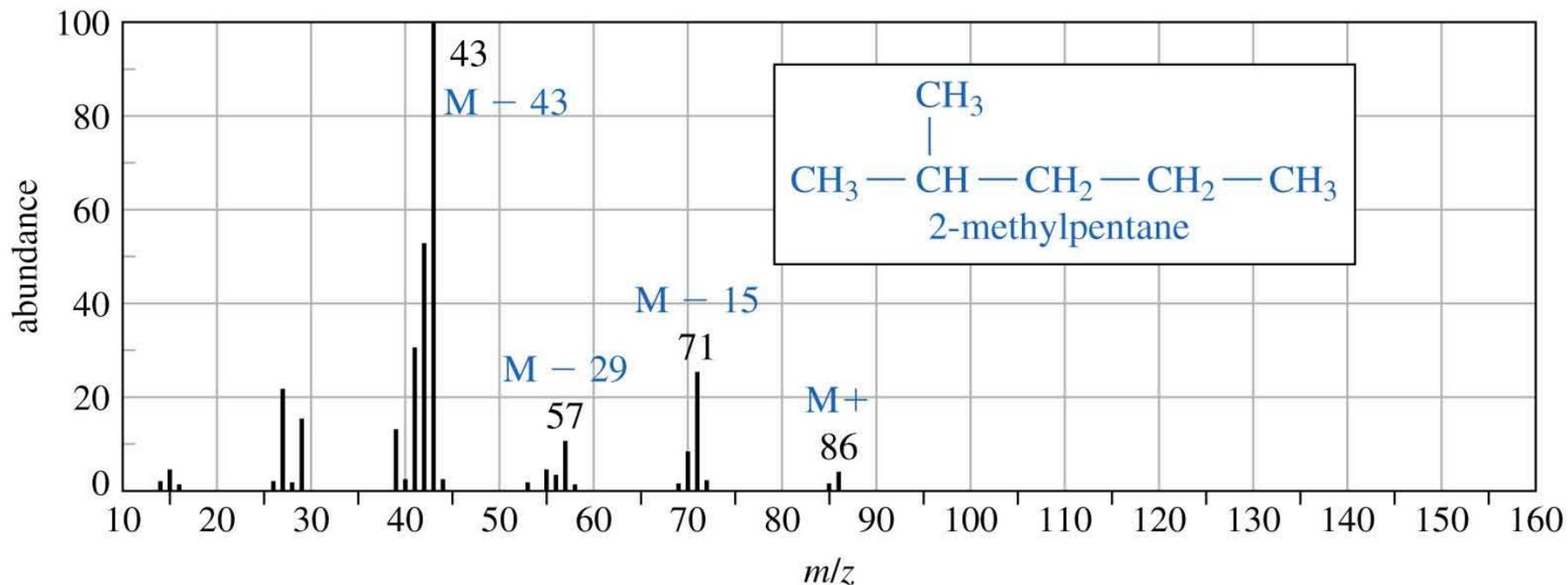


1, 1-Dimethylethyl radical
(*tert*-Butyl)

B

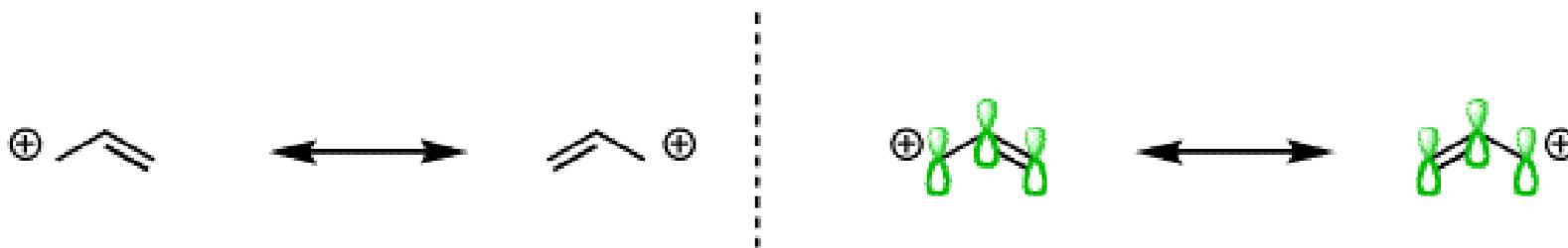
Mass Spectra of Alkanes

More stable carbocations will be more abundant!

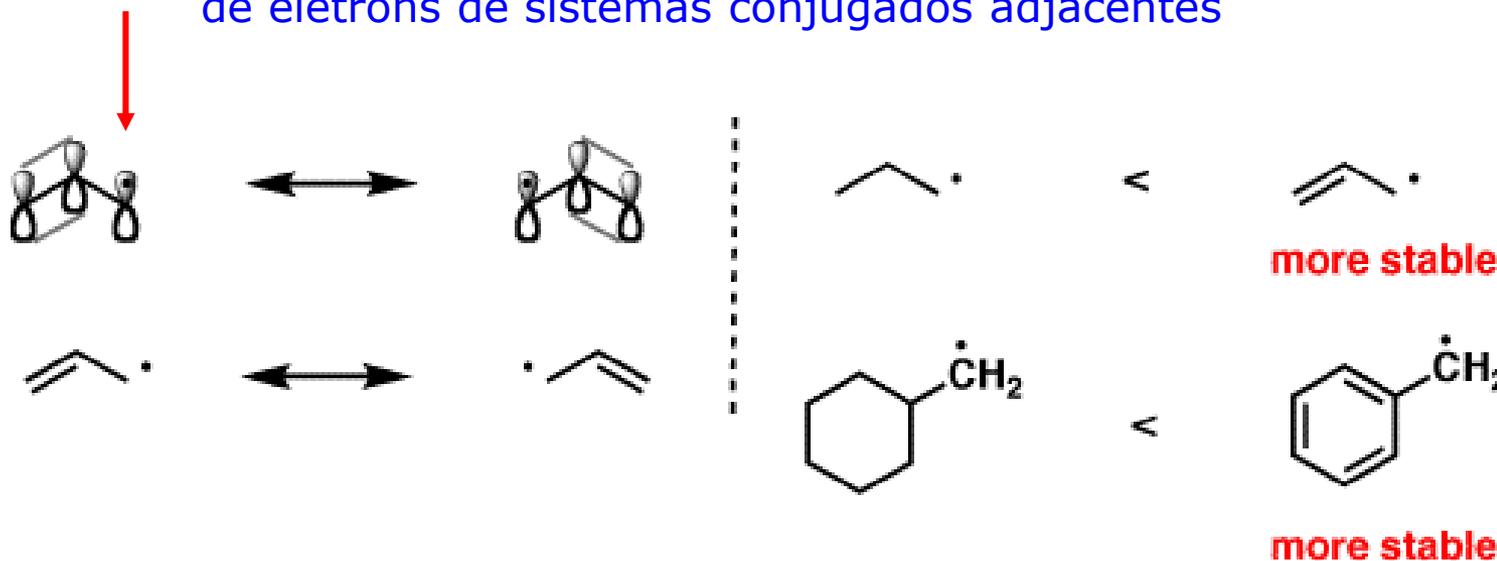


Fatores contribuem para a estabilização de radicais livres:

Deslocalização por ressonância (tal qual carbocátions conjugados)

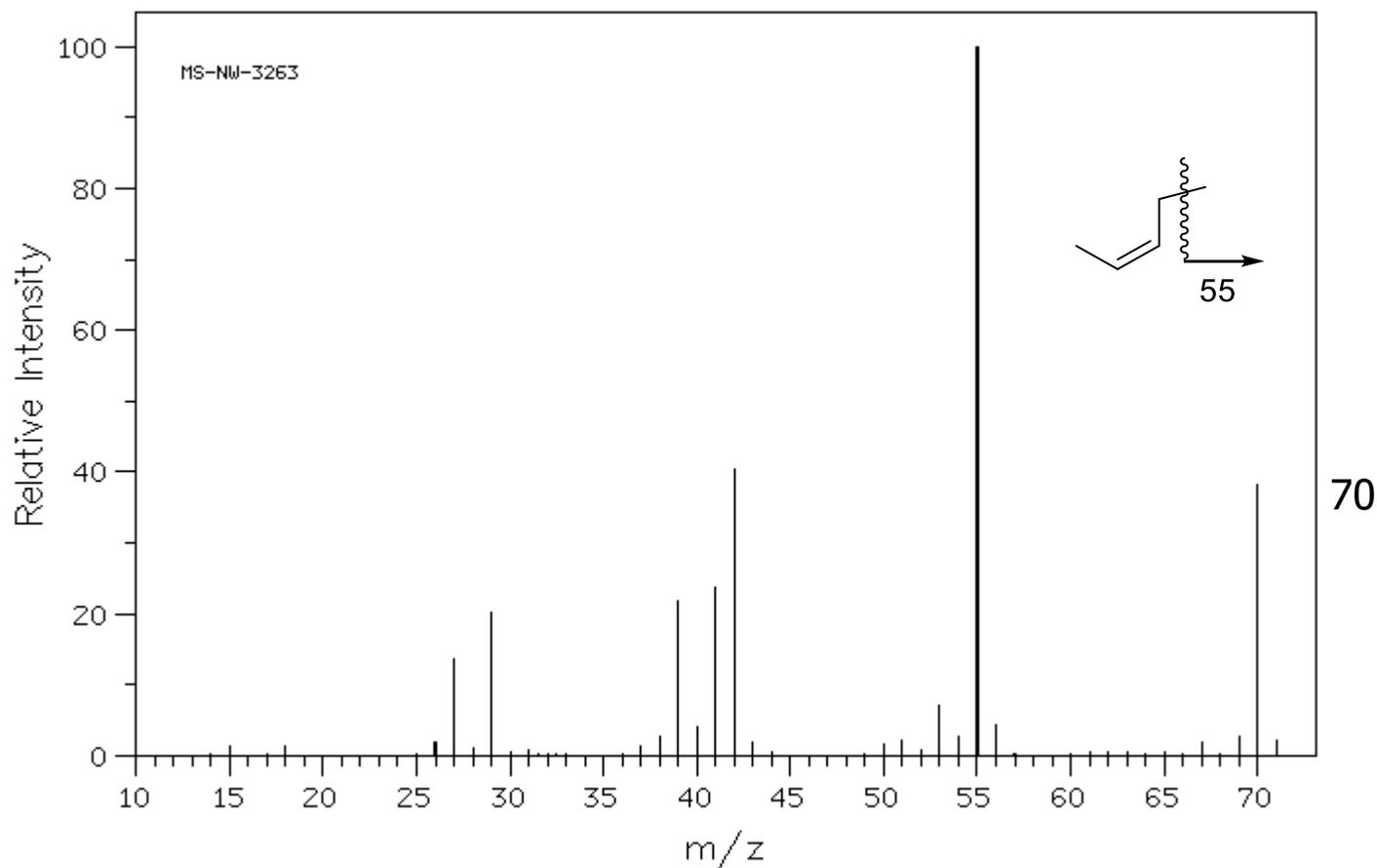


Orbitais p parcialmente preenchidos como em radicais podem aceitar o par de elétrons de sistemas conjugados adjacentes



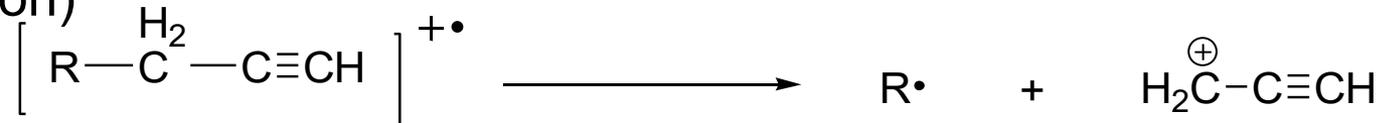
Como um carbon radicalar possui geometria “piramidal achatada” ele comporta-se como um carbono hibridizado “sp²” possibilitando uma extensão de conjugação!!!

The Mass Spectrum of Alkenes (*cis*-2-pentene)



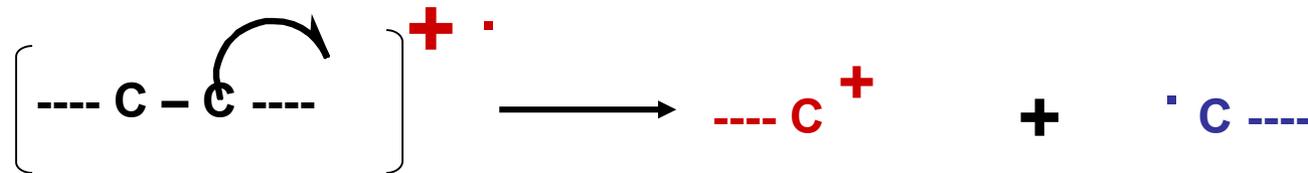
Fragmentation Patterns of Alkynes – Fragment Ions

- The π -bond of an alkyne can also absorb substantial energy – molecular ions are commonly observed
- For terminal alkynes, the loss of terminal hydrogen is observed (M-1) – this may occur at such intensity to be the base peak or eliminate the presence of M^+
- Terminal alkynes form the propargyl cation, m/z 39 (lower intensity than the allyl cation)

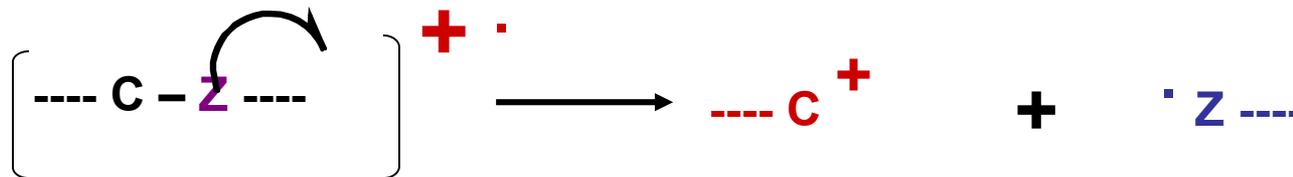


Regras comuns de fragmentação em espectrometria de massas

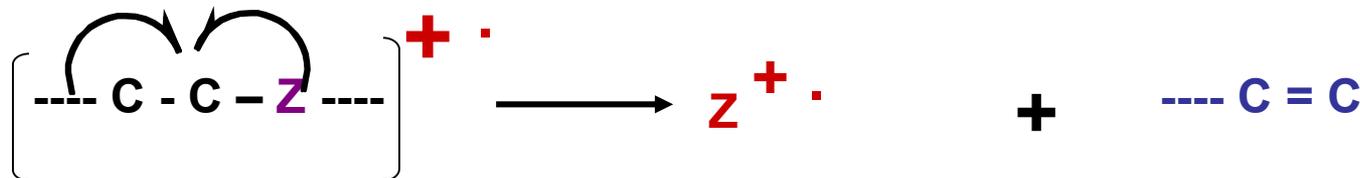
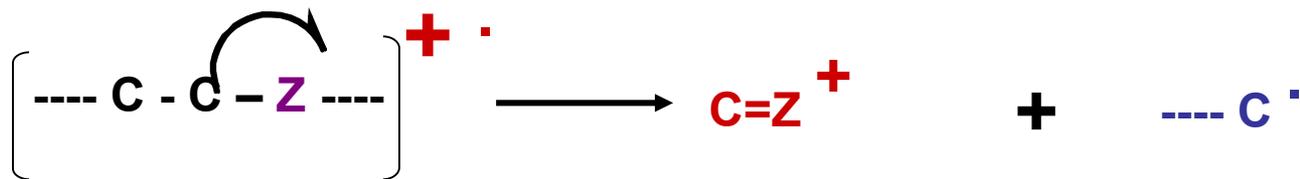
1) Quebra de ligações σ resultando em cations mais estáveis



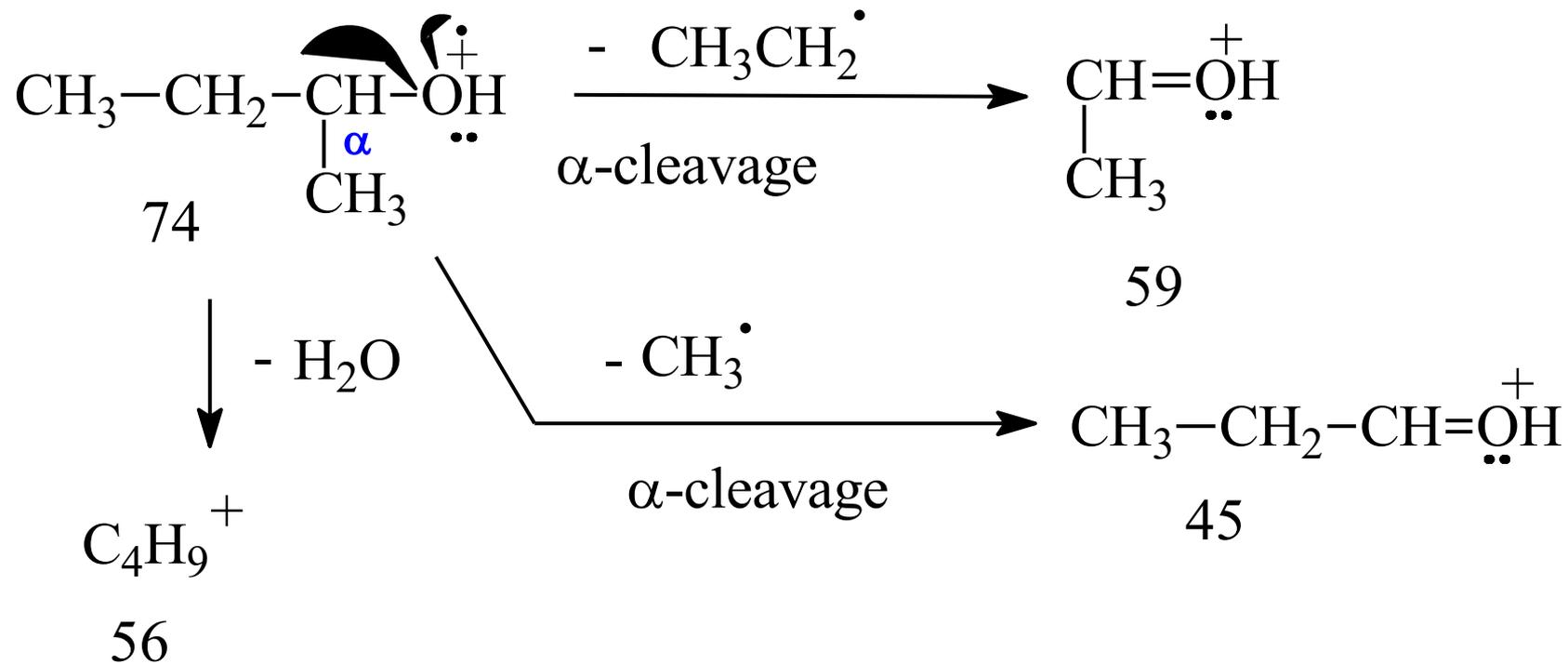
Quebra do heteroátomo



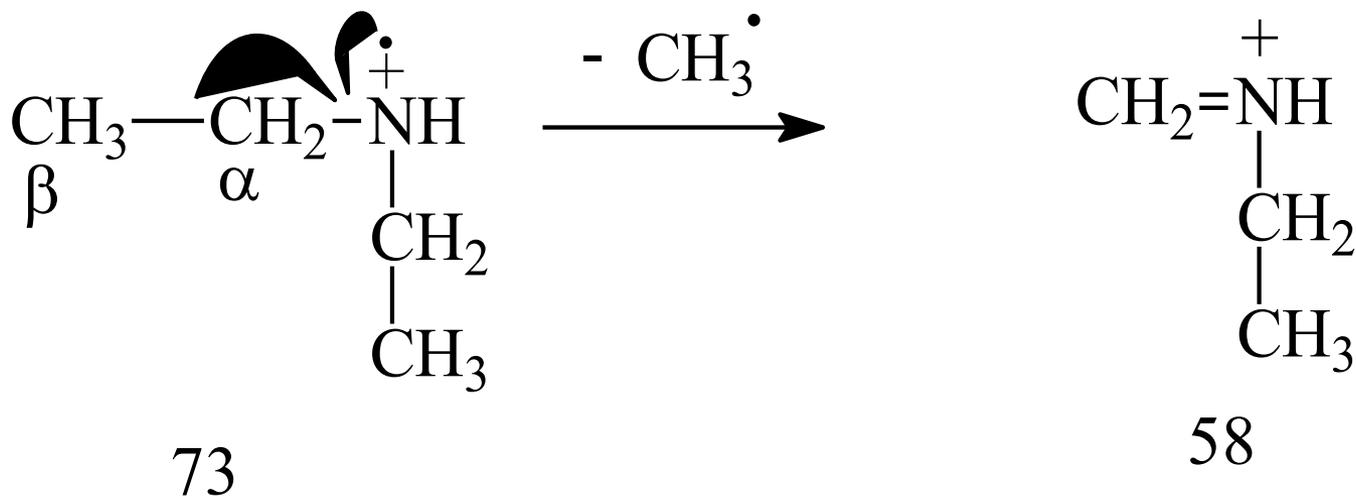
Quebra na posição α a um heteroátomo (O, N, C=O) ou em posição alílica
Ou benzílica (estabilização por ressonância)



α -Fragmentation in alcohols

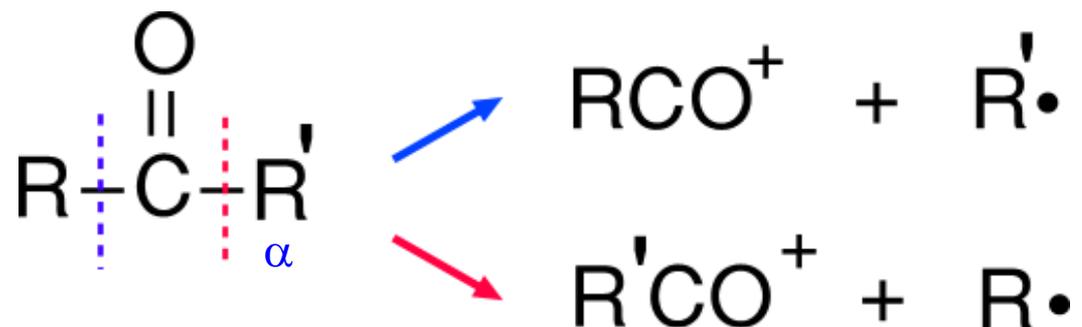


α -Fragmentation in amines



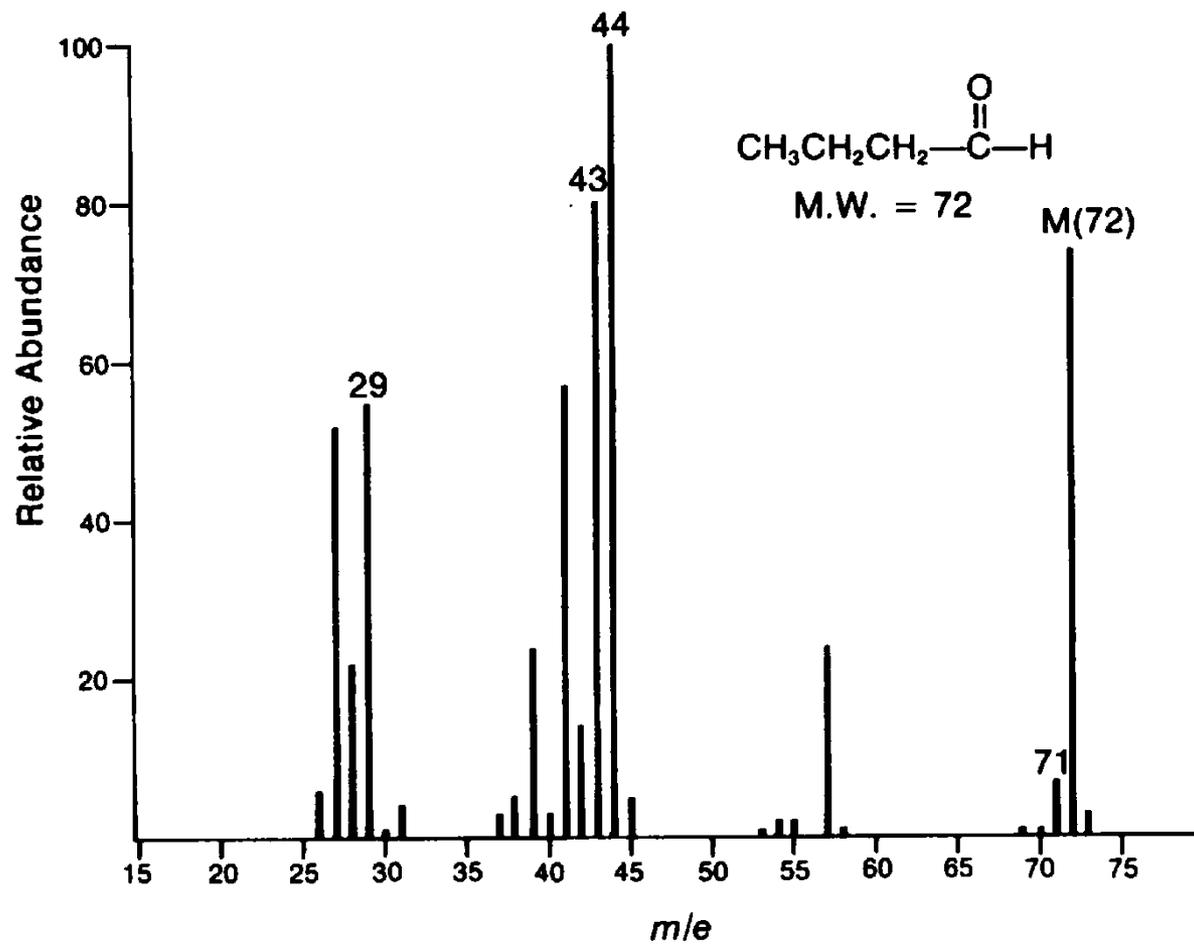
FRAGMENTATION PATTERNS in ALDEHYDES AND KETONES

A fragmentação pode ocorrer em ambos os lados do carbono carbonílico.
Ocorre ainda uma eliminação de CO (28 unidades)

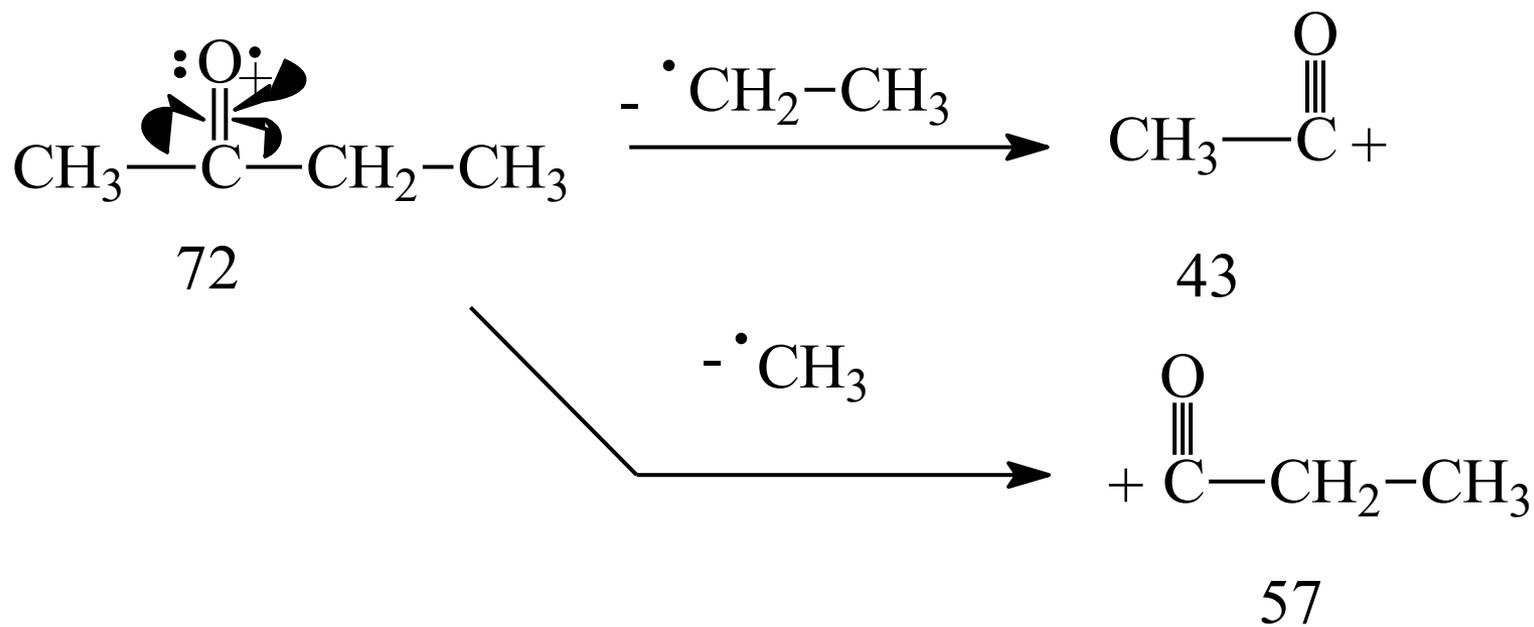


Para compostos carbonílicos, por definição o carbono alfa é o primeiro ligado ao carbono carbonílico, mas para fins de espectrometria de massas, a quebra ocorre Entre o carbono carbonílico e o carbono alfa (e não depois).

butyraldehyde



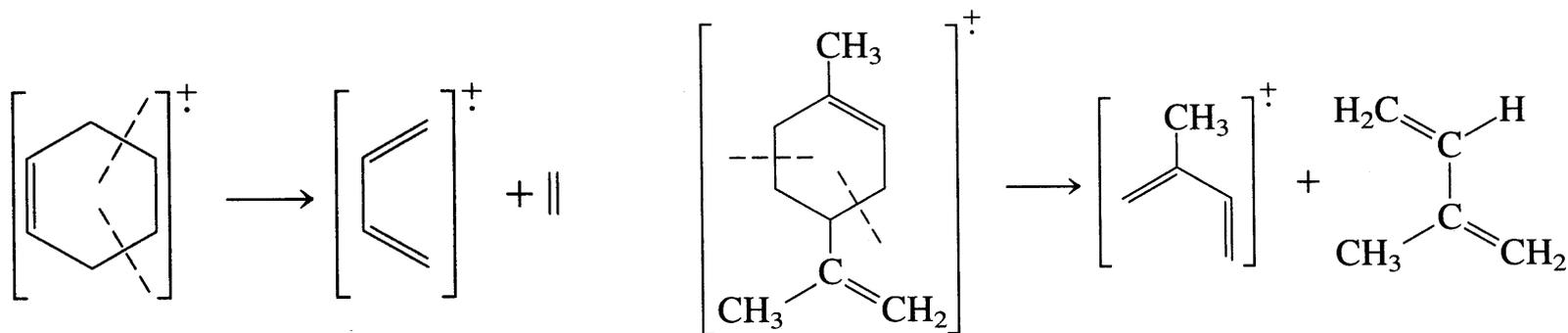
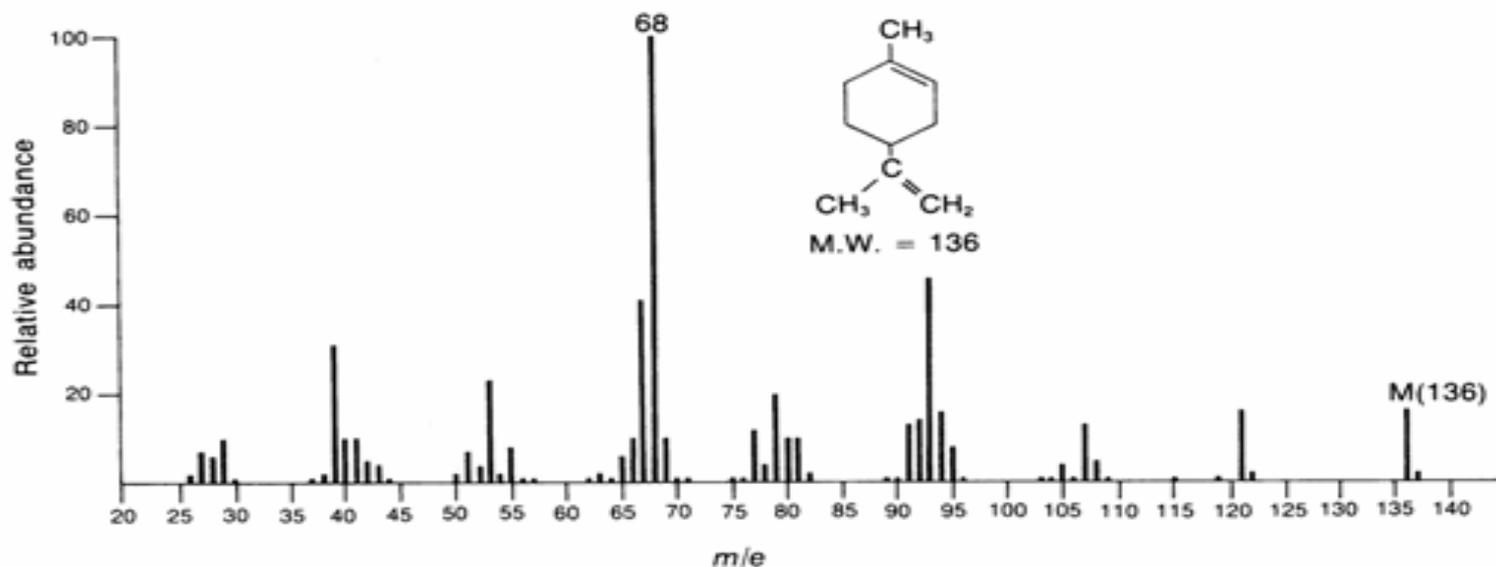
α -cleavage



favor loss of larger radical

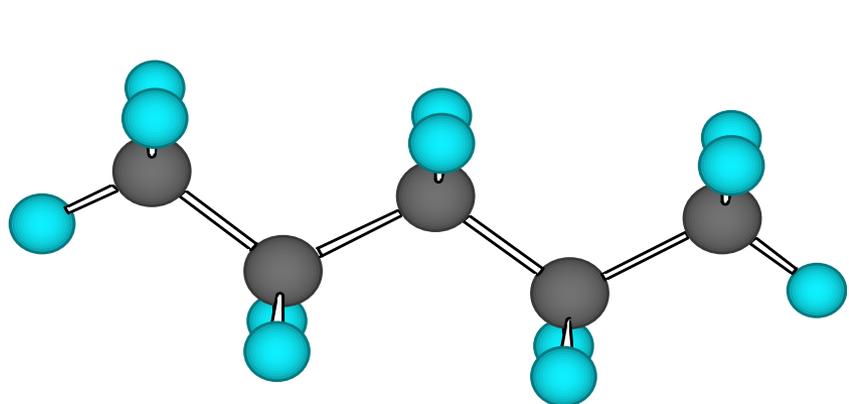
Espectro de massas do limoneno

Qual a estrutura do cátion radicalar em 68 ?

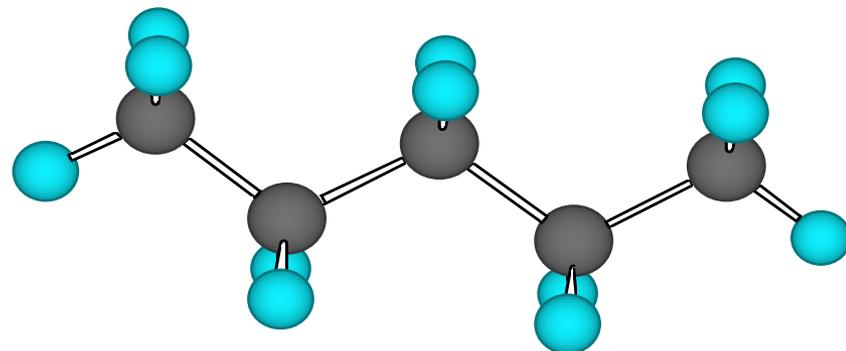


Reação retro Diels-Alder
(uma reação pericíclica)

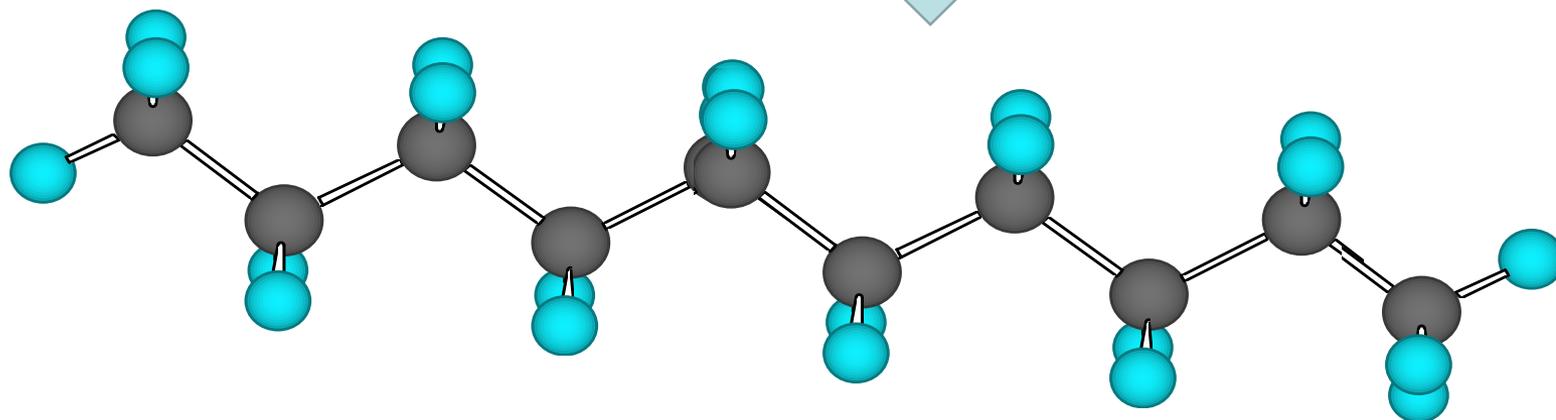
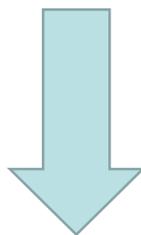
Como fazer a reação?



n-pentano

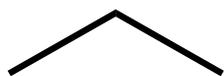
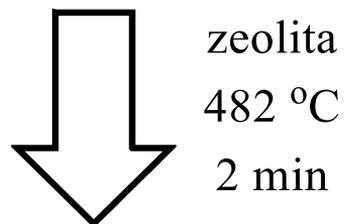
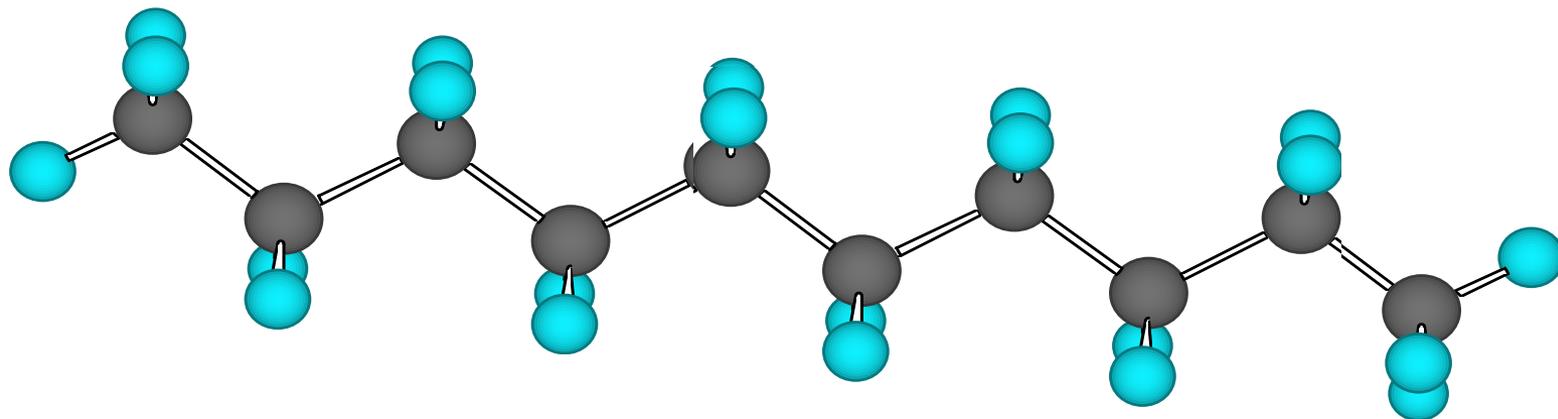


n-pentano



n-decano

Craking de hidrocarbonetos



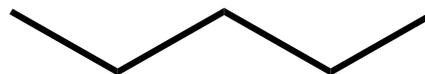
17%

+



31%

+



23%

+



18%

+

outros

11%

Condições para ocorrer reações químicas entre compostos orgânicos:

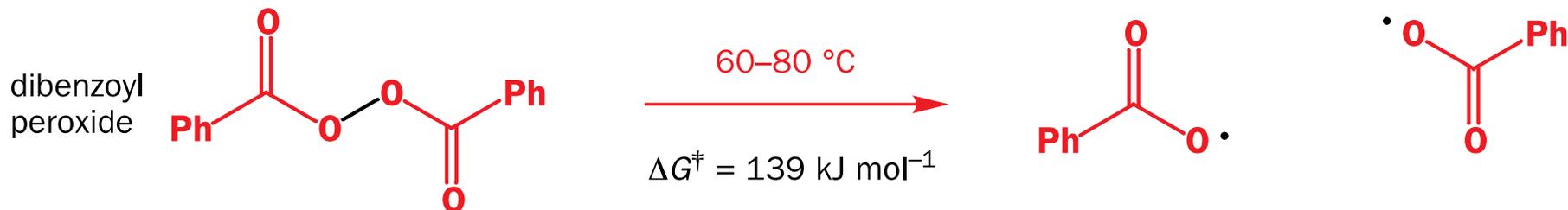
- Quando do fornecimento de energia suficiente para quebrar e formar novas ligações (aleatórias em compostos saturados e direcionadas para **reações pericíclicas**): por aquecimento ou por luz UV
- Quando da presença de espécies reativas como **radicais** (R^\bullet), **eletrófilos** (carbocátions R^+ ; $C=O$; NO^+ , etc), **nucleófilos** (C^- ; X^- ; $N:$, etc) e combinação adequada de alguns ($R^\bullet + R^\bullet = R-R$; eletrófilo + nucleófilos) desses podem resultar na formação de novas ligações (C-C; C-N e etc).

Formação de Radicais

✓ Halogênios:



✓ Peróxidos (bons iniciadores de reações radicalares)



Clivagens homolíticas

(solventes não polares, fase gasosa)

Clivagens heterolíticas

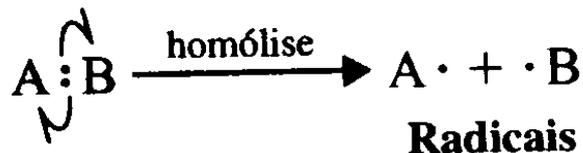
(solventes polares – estabilizam;

Presença de átomos eletronegativos e estruturas

Que contribuem para a estabilização de cargas)

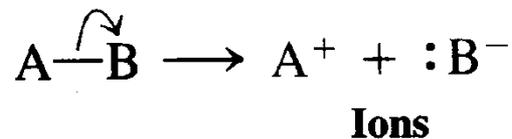
Estrutura, Formação e Estabilidade de Radicais

- ✓ Clivagem Homolítica: em uma homólise cada átomo fica com um elétron da ligação covalente



- ✓ Clivagem Heterolítica: resulta na formação de íons

Heterolytic Cleavage



1. Setas \curvearrowright ou \curvearrowleft sempre mostram a direção do movimento dos elétrons.
2. A seta com uma só farpa \curvearrowright mostra o ataque (ou o movimento) de um elétron não-emparelhado.
3. Setas com duas farpas \curvearrowright mostram o ataque (ou movimento) de um par de elétrons.