



OLLI AT ILLINOIS



Molecular Literacy for All

making sense of the “monstrous and boundless thicket” of everyday chemistry

The covalency model will help us understand
“Why Nature Chose...”

I ILLINOIS

Beckman Institute for Advanced
Science & Technology

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Today's Outline

transferability

Covalent bonding descriptions ✓

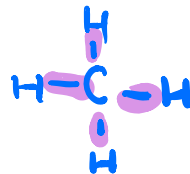
Oxidation state

Connectedness and the functional groups

Implied hydrogen atoms

Bonding in phosphorus and sulfur

The universe of organic molecules



val = 4

- Octet Rule $8e^-$ sharing

- Formal Chg

- Oxidation

Concepts to describe bonding in molecules

Table 1. Simple Definitions of Common Terms

Term	Definition
Valence	Number of electrons that an atom uses in bonding.
Oxidation number	The charge remaining on an atom when all ligands are removed heterolytically in their closed form, with the electrons being transferred to the more electronegative partner; homonuclear bonds do not contribute to the oxidation number.
Formal charge	The charge remaining on an atom when all ligands are removed homolytically .
Coordination number	The number of atoms bonded to the atom of interest.

move e^- within a mol.

J. Chem. Educ. 2006, 83, 5, 791

Publication Date: May 1, 2006

<https://doi.org/10.1021/ed083p791>

Assigning oxidation number

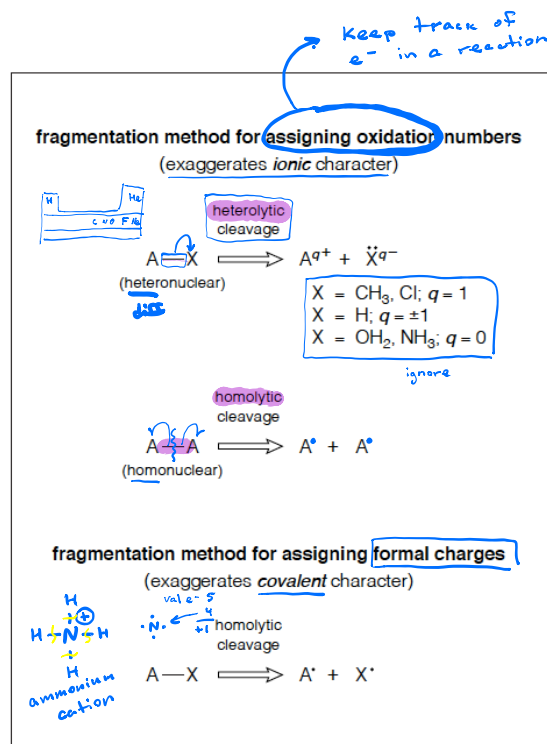


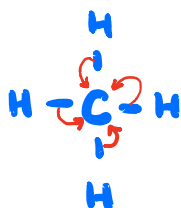
Figure 2. Fragmentation methods for assigning oxidation number and formal charge.

Table 2. Comparison of the Valence, Oxidation Number, Number of Bonds, and Coordination Number for Some Simple Molecules

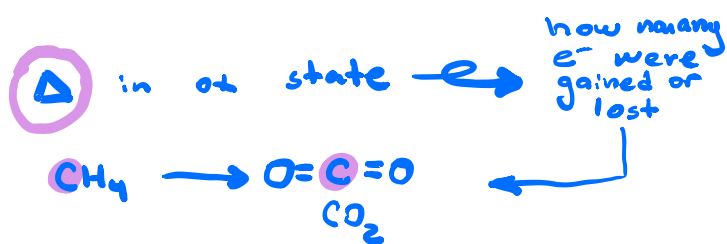
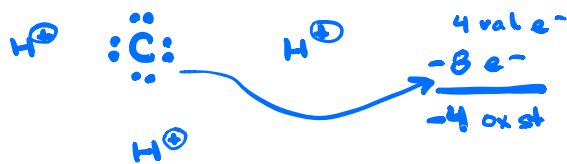
Molecule	No. of Electrons in Valence Shell of Free Atom (N)	No. of Nonbonding Electrons on Atom in Molecule	Valence	Oxidation Number	No. of Bonds	Coordination Number
<i>AH_n: Examples Where Valence = Oxidation Number = No. of Bonds = Coordination Number</i>						
BH ₃	3	0	3	+3	3	3
CH ₄	4	0	4	-4	4	4
NH ₃	5	2	3	-3	3	3
H ₂ O	6	4	2	-2	2	2
FH	7	6	1	-1	1	1
<i>Examples Where Valence ≠ Oxidation Number </i>						
H ₃ C-CH ₃	4	0	4	-3	4	4
CMe ₄	4	0	4	0	4	4
CH ₂ Cl ₂	4	0	4	0	4	4
[NH ₄] ⁺	5	0	5	-3	4	4
[OH ₃] ⁺	6	2	4	-2	3	3
<i>Examples Where Valence ≠ Number of 2-Center, 2-Electron Bonds</i>						
[BH ₄] ⁻	3	0	3	+3	4	4
[NH ₄] ⁺	5	0	5	-3	4	4
<i>Examples Where Valence ≠ Coordination Number</i>						
H ₂ C=CH ₂	4	0	4	-2	4	3
HC≡CH	4	0	4	-1	4	2
H ₃ NBH ₃	3	0	3	+3	4	4

Bonding
descriptions
in practice

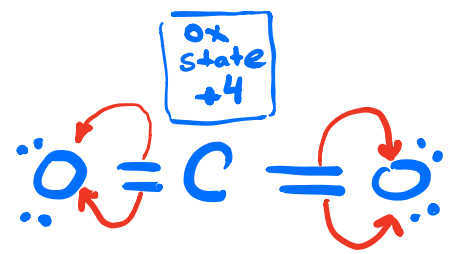
What is ox state of C in methane?



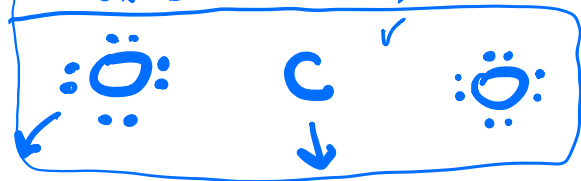
heteroat.



What is ox state of C in CO_2 ?

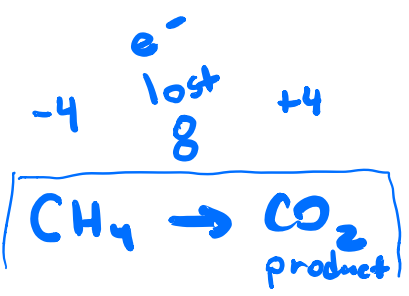


ox state calc (hypothetical)



$\frac{6 \text{ val } e^-}{-8 \text{ in } \text{CO}_2}$
 -2 ox st

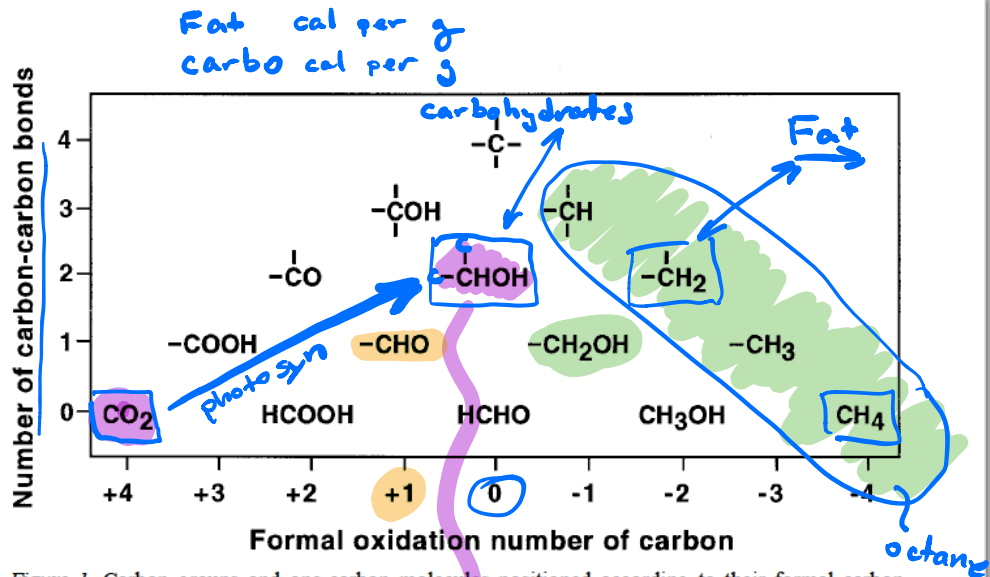
$\frac{4 \text{ val } e^-}{-0}$
 $+4 \text{ ox st}$



$\Delta \text{ ox } \text{C} = +4 - (-4) = 8 \text{ e}^-$
 (product) starting mol.

Tracking Oxidation State

gain of e^- → reduction
 ← loss of e^- oxidation



From: "Sugars as the Optimal Biosynthetic Carbon Substrate of Aqueous Life Throughout the Universe"
Origins of Life and Evolution of the Biosphere 30: 33–43, 2000

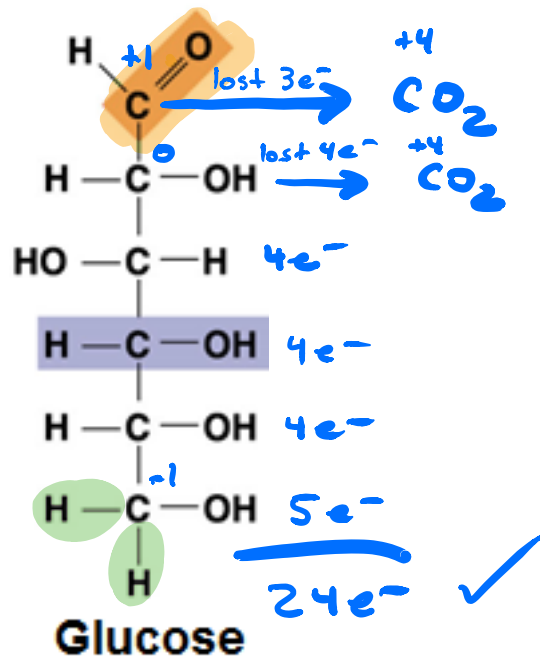
Why nature chose carbohydrates

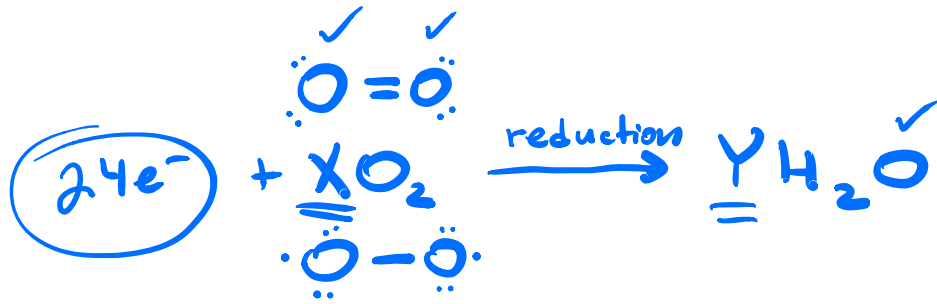
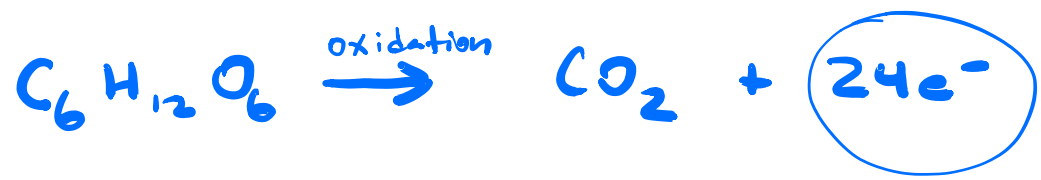
to facilitate biochemical transformations

the carbonyl group ($>C=O$) strongly facilitates the reversible making and breaking of carbon-carbon bonds necessary for the synthesis of intermediates of varying size

the number of high energy electrons per carbon

alcohols – both internal alcohol groups ($>CHOH$ and $>COH-$) and terminal alcohol groups ($-CH_2OH$) – are the best biosynthetic substrates, because they have the largest number of biosynthetically useful high energy electron pairs/carbon





EPDs vs. Connectedness

EPDs are useful for predicting geometry

Connectivity map is experimentally determined by X-ray diffraction

Connectedness is useful to efficiently draw molecular structures, assign charges and lone pairs

Show amine – 4 EPDs but 3-connected

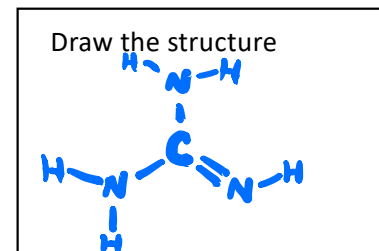
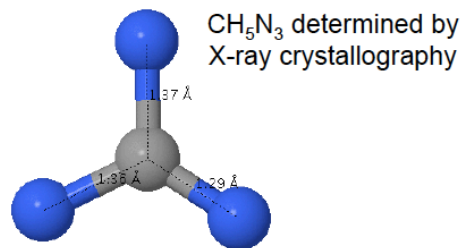
Building blocks by connectedness (i.e., coordination number)

charge	connectedness			
	1	2	3	4
hydrogen				
neutral	-H			
carbon				
neutral		-C≡ =C=	$\begin{array}{c} \diagdown \\ \text{C} \\ \diagup \\ \parallel \end{array}$	$\begin{array}{c} \\ -\text{C}- \\ \end{array}$
+1		-C ⁺ =	$\begin{array}{c} \diagdown \\ \text{C}^+ \\ \diagup \end{array}$	
-1	:C [⊖] ≡	$\begin{array}{c} \ominus \\ \text{C} \\ \parallel \end{array}$	$\begin{array}{c} \ominus \\ \text{C} \\ \diagup \\ \diagdown \end{array}$	

charge	connectedness			
	1	2	3	4
nitrogen				
neutral	$\text{:N}\equiv$	$\begin{array}{c} \cdot \\ \text{N} \\ \parallel \end{array}$	$\begin{array}{c} \cdot \\ \text{N} \\ \cdot \end{array}$	
+1		$\begin{array}{c} \oplus \\ \text{N} \\ \equiv \end{array}$ $\begin{array}{c} \oplus \\ \text{N} \\ = \end{array}$	$\begin{array}{c} \cdot \\ \text{N} \\ \parallel \\ \oplus \end{array}$	$\begin{array}{c} \oplus \\ \text{N} \\ \oplus \end{array}$
-1	$\begin{array}{c} \cdot \\ \text{N} \\ \cdot \\ \ominus \end{array}$	$\begin{array}{c} \cdot \\ \text{N} \\ \cdot \\ \ominus \end{array}$		
oxygen				
neutral	$\begin{array}{c} \cdot \\ \text{O} \\ \cdot \\ \parallel \end{array}$	$\begin{array}{c} \cdot \\ \text{O} \\ \cdot \end{array}$		
+1	$\begin{array}{c} \oplus \\ \text{O} \\ \equiv \end{array}$	$\begin{array}{c} \cdot \\ \text{O} \\ \cdot \\ \parallel \\ \oplus \end{array}$	$\begin{array}{c} \oplus \\ \text{O} \\ \oplus \end{array}$	
-1	$\begin{array}{c} \cdot \\ \text{O} \\ \cdot \\ \ominus \end{array}$			
fluorine				
neutral	$\begin{array}{c} \cdot \\ \text{F} \\ \cdot \end{array}$			
+1	$\begin{array}{c} \cdot \\ \text{F} \\ \cdot \\ \parallel \\ \oplus \end{array}$	$\begin{array}{c} \oplus \\ \text{F} \\ \oplus \end{array}$		

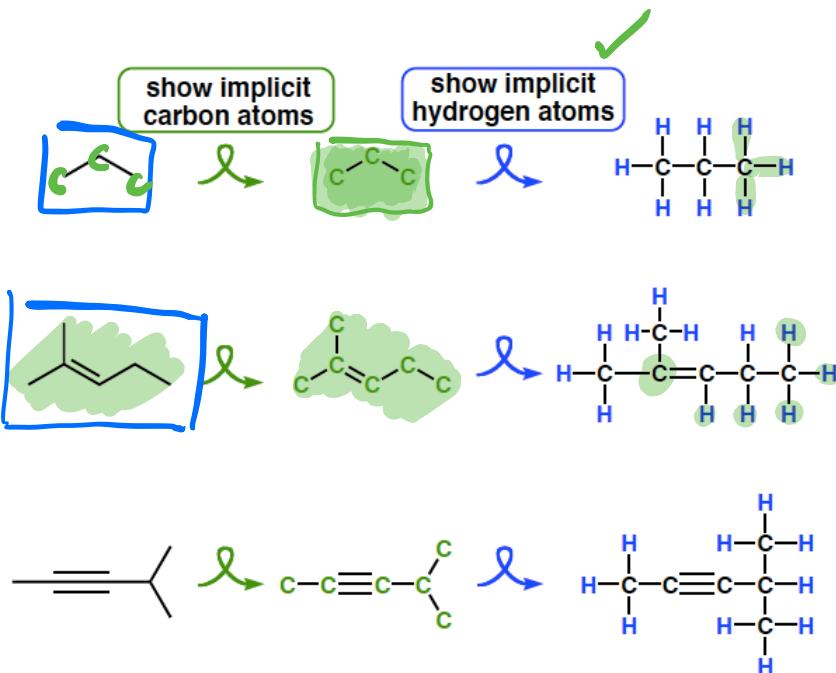
Connectivity maps are experimentally determined by X- ray crystallography

Experimental structural data, such as that obtained from X-ray crystallography, provides chemists with a molecule's "connectivity map" for all atoms that are heavier than hydrogen. This powerful technique even provides the Cartesian coordinates for each non-hydrogen, so bond distances and angles can be determined. However, it is up to the chemist to determine the electron configuration of each atom and the location of the hydrogen atoms. The connectivity map for CH_5N_3 is shown below. You are told that the structure is neutral, i.e., it has a net charge of zero. Your task is to draw a satisfactory structure.

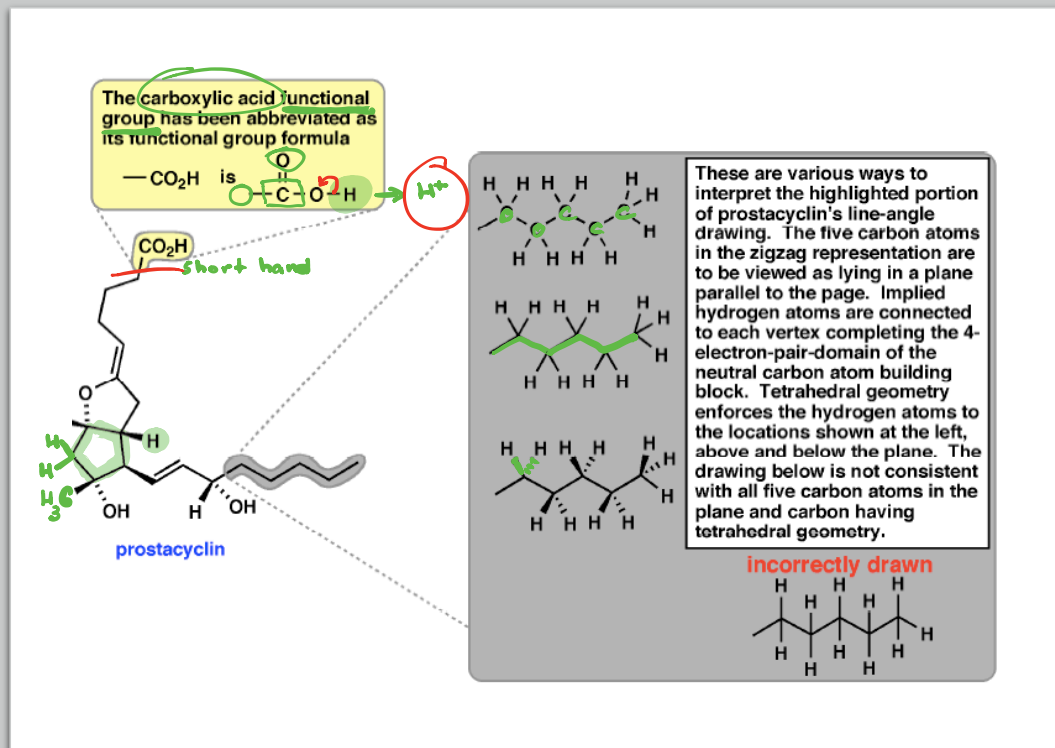


REFERENCE: *Chem. Commun.*, 2007, 3180-3182, DOI: 10.1039/b705100j

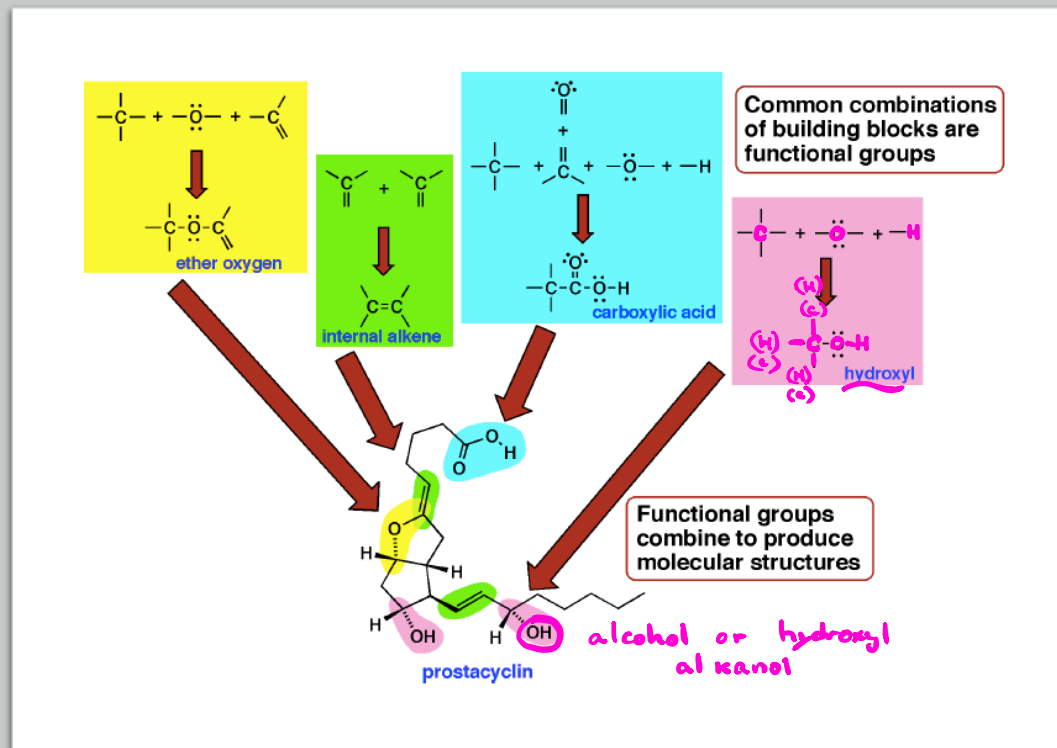
Implied atoms in molecular structure drawings

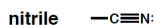
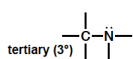
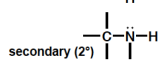
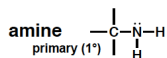
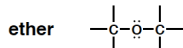
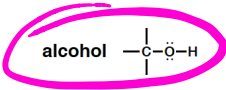
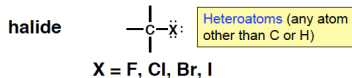
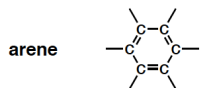
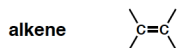
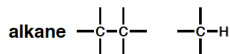
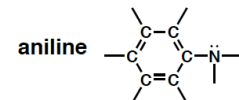
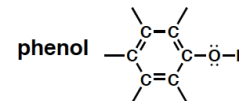
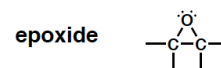
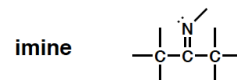
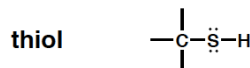
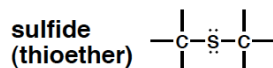
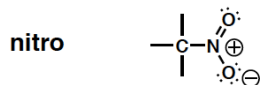
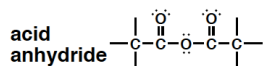
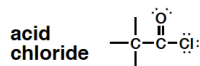
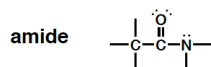
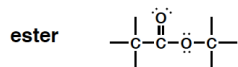
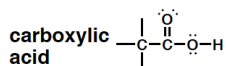
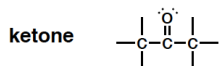
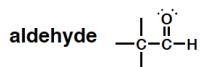
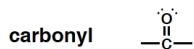


Interpreting molecular structures



Functional groups are the common combinations of the building blocks



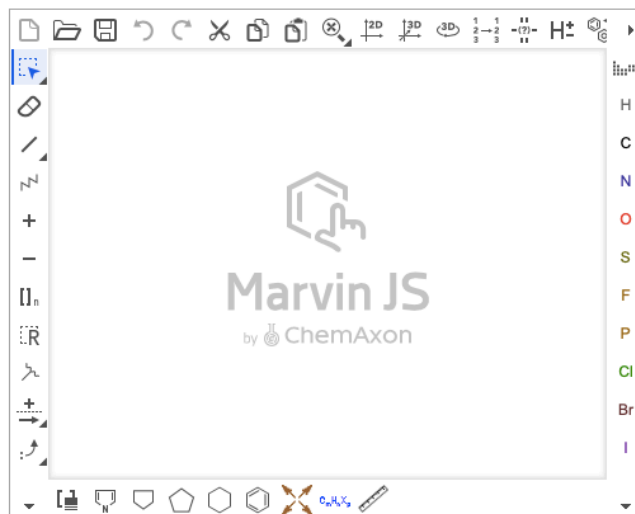


Common functional groups

Functional Group Finder

ACE functional group finder

Draw a compound, and press the button to find which functional groups it contains.



<https://epoch.uky.edu/ace/public/fnalGroups.jsp>

Check for functional groups

9:17 AM Fri Sep 11

en.wikipedia.org

onlineibrary.wiley.com/doi/pdfdirect... Google Calendar - Week of Septemb... Acridine - Wikipedia Functional-group finder Cinnamaldehyde - Wikipedia

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Article Talk

Cinnamaldehyde

From Wikipedia, the free encyclopedia

Cinnamaldehyde is an organic compound with the formula C₉H₈CH=CHCHO. Occurring naturally as predominantly the *trans* (E) isomer, it gives cinnamon its flavor and odor. [1] It is a phenylpropene that is naturally synthesized by the shikimate pathway.[2] This pale yellow, viscous liquid occurs in the bark of cinnamon trees and other species of the genus *Cinnamomum*. The essential oil of cinnamon bark is about 90% cinnamaldehyde.[3]

Contents [hide]

- Structure and synthesis
 - Biosynthesis
 - Synthesis
 - Metabolism
- Applications
 - As a flavorant
 - As an agricultural
 - Miscellaneous uses
- Derivatives
- Toxicology
- References
- External links

Structure and synthesis [edit]

Cinnamaldehyde was isolated from cinnamon essential oil in 1834 by Jean-Baptiste Dumas and Eugène-Melchior Péligot[4] and synthesized in the laboratory by the Italian chemist Luigi Chiozza in 1854.[5]

The natural product is *trans*-cinnamaldehyde. The molecule consists of a benzene ring attached to an unsaturated aldehyde. As such, the molecule can be viewed as a derivative of acrolein. Its color is due to the π → π* transition: increased conjugation in comparison with acrolein shifts this band towards the visible.[6]

Biosynthesis [edit]

The biosynthesis of cinnamaldehyde begins with deamination of L-phenylalanine into cinnamic acid by the action of phenylalanine ammonia-lyase (PAL).[7][8] PAL catalyzes this reaction by a non-oxidative deamination. This deamination relies on the MDG prosthetic group of PAL.[9] PAL gives rise to *trans*-cinnamic acid.

Pathway for the biosynthesis of *trans*-cinnamaldehyde.

Copy Look Up Share

Integrated IUPAC name: E)-3-Phenylprop-2-enal

Other names: Cinnamaldehyde, Cinnamic aldehyde, *trans*-Cinnamaldehyde

Identifiers

CAS Number: 14371-10-9

3D model (JSmol): Interactive image

SDMI: 000138

Beilstein Reference: 1071571

CHEBI: CHEBI:16731

CHEMBL: CHEMBL203492

ACE functional group finder

Draw a compound, and press the button to find which functional groups it contains.

Paste

Marvin JS by ChemAxon

Check for functional groups

Back to public ACE pages.

Draw a compound, and press the button to find which functional groups it contains.

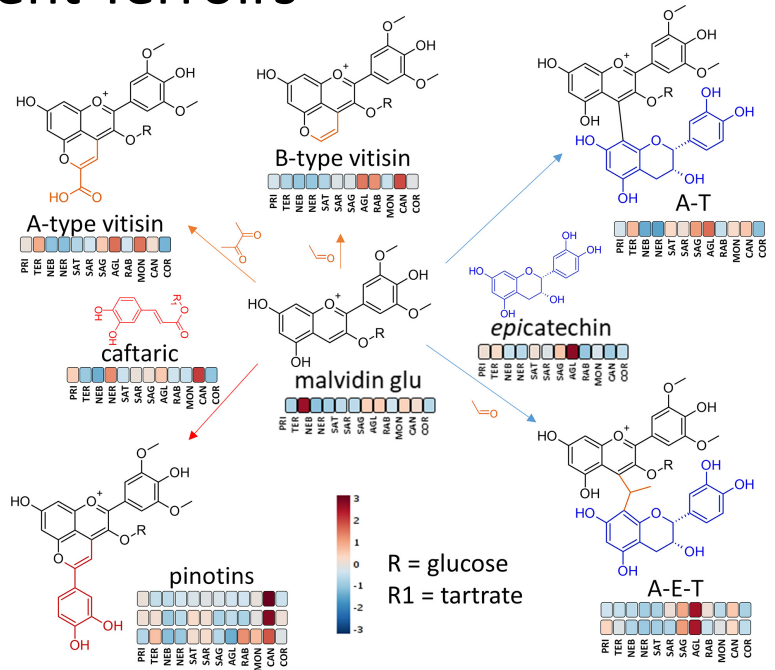
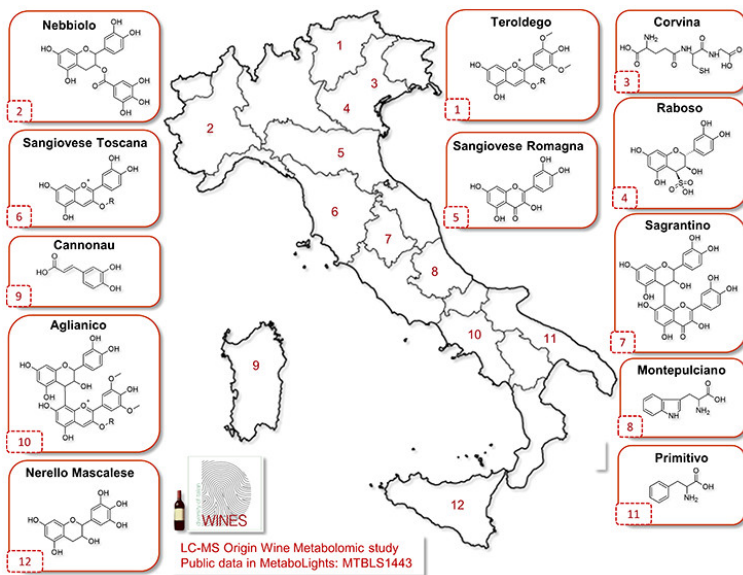
Check for functional groups

after pasting

check for functional group

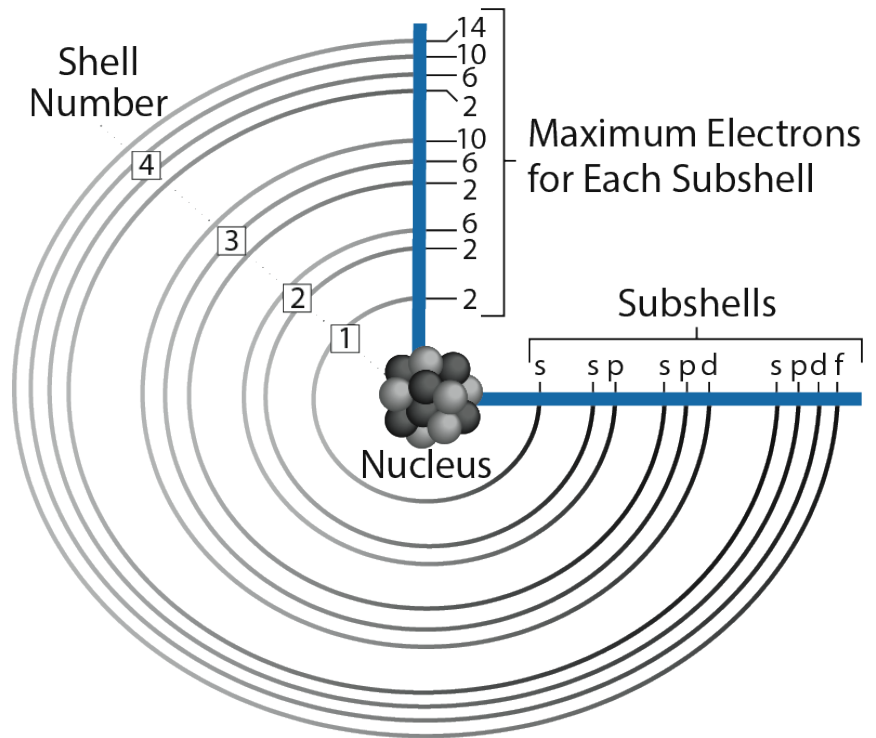
No.	Category	Functional group	ID number	Present?
1	Aromatics	aldehyde	25	
2	Aromatics	alkene	48	YES
3	Aromatics	aromaticity	133	no
4	Aromatics	carbonyl oxide	132	no
5	Aromatics	benzene ring	70	YES
6	Aromatics	hydrocarbon	69	no
7	Aromatics	phenol	56	no
8	CH only	alkene	46	YES
9	CH only	aldehyde	47	no
10	CH only	aromaticity	211	no
11	CH only	alkene	48	no
12	CH only	carbanion	190	no
13	CHN-containing	nitric oxide	138	no
14	CHN-containing	nitride	12	no
15	CHN-containing	aminal	28	no
16	CHN-containing	aldehyde	23	no

Discriminating Italian Monovarietal Red Wines from Different Terroirs



<https://doi.org/10.1021/acs.jafc.0c00879>

Bonding in Phosphorus and Sulfur



Bonding in Phosphorus

Phosphorus Oxidation States in Organic Compounds

-3	-1	0	+1	+3	+5
<p style="text-align: center;">PH_3 phosphine</p> <p style="text-align: center;">R_3P trialkyl phosphines</p> <p style="text-align: center;"> $\begin{array}{c} \text{R} \\ \\ \text{R}-\text{P}^{\oplus}-\text{R} \\ \\ \text{R} \end{array}$ tetraalkyl phosphonium </p>	<p style="text-align: center;"> $\begin{array}{c} \text{R} \\ \\ \text{R}-\text{P}=\text{O} \\ \\ \text{R} \end{array}$ phosphine oxides </p>	<p style="text-align: center;">P elemental</p>	<p style="text-align: center;"> $\begin{array}{c} \text{O} \\ \\ \text{R}-\text{P}-\text{OH} \\ \\ \text{R} \end{array}$ phosphenic acids </p>	<p style="text-align: center;"> $\begin{array}{c} \text{O} \\ \\ \text{R}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$ phosphonic acids </p> <p style="text-align: center;"> $\begin{array}{c} \text{OR} \\ \\ \text{RO}-\text{P} \\ \\ \text{OR} \end{array}$ phosphite esters </p>	<p style="text-align: center;">P_2O_5</p> <p style="text-align: center;"> $\begin{array}{c} \text{O} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}-\text{R} \\ \\ \text{O}-\text{R} \end{array}$ phosphate esters </p>

Why nature chose phosphates

Phosphate esters and anhydrides dominate the living world but are seldom used as intermediates by organic chemists. Phosphoric acid is specially adapted for its role in nucleic acids because it can link two nucleotides and still ionize; the resulting negative charge serves both to stabilize the diesters against hydrolysis and to retain the molecules within a lipid membrane. A similar explanation for stability and retention also holds for phosphates that are intermediary metabolites and for phosphates that serve as energy sources. Phosphates with multiple negative charges can react by way of the monomeric metaphosphate ion PO_3^- as an intermediate. No other residue appears to fulfill the multiple roles of phosphate in biochemistry. Stable, negatively charged phosphates react under catalysis by enzymes; organic chemists, who can only rarely use enzymatic catalysis for their reactions, need more highly reactive intermediates than phosphates.

Science 06 Mar 1987: Vol. 235, pp. 1173-1178
DOI: 10.1126/science.2434996

Table 1. Examples of phosphates in biochemistry.

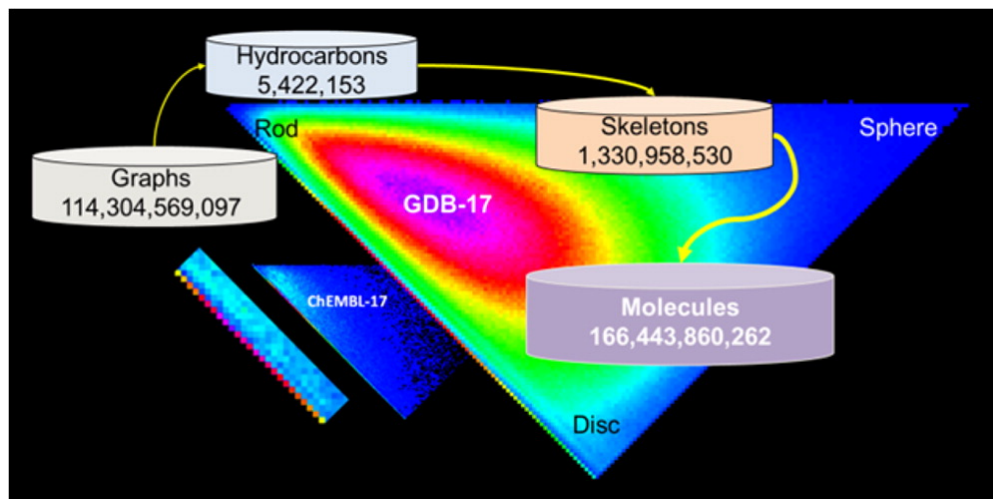
Phosphate	Acid derivative
DNA	Diester of phosphoric acid
RNA	Diester of phosphoric acid
ATP	Anhydride of phosphoric acid
Creatine phosphate	Amide of phosphoric acid
Phosphoenolpyruvate	Enol ester of phosphoric acid
Pyridoxal phosphate	Phenol ester of phosphoric acid
Nicotine adenine dinucleotide	Ester and anhydride of phosphoric acid
Fructose 1,6-diphosphate	Ester of phosphoric acid
Glucose-6-phosphate	Ester of phosphoric acid
Isopentenyl pyrophosphate	Ester of pyrophosphoric acid
Ribose-6-phosphate-1-pyrophosphate	Ester of phosphoric and pyrophosphoric acids

Bonding in Sulfur

Sulfur Oxidation States in Organic Compounds

-2	-1	0	+2	+4	+6
<p>H_2S</p> <p>$\text{R}-\ddot{\text{S}}-\text{H}$ thiols</p> <p>$\text{R}-\ddot{\text{S}}-\text{R}$ sulfides</p> <p>$\text{R}-\overset{\oplus}{\text{S}}-\text{R}$ R sulfonium ions</p>	<p>$\text{R}-\ddot{\text{S}}-\ddot{\text{S}}-\text{R}$ disulfides</p>	<p>S elemental</p> <p>$\text{R}-\overset{\text{O}}{\parallel}{\text{S}}-\text{R}$ sulfoxides</p> <p>$\text{R}-\ddot{\text{S}}-\text{OH}$ sulfenic acids</p>	<p>$\text{R}-\overset{\text{O}}{\parallel}{\text{S}}-\text{R}$ sulfones</p> <p>$\text{R}-\overset{\text{O}}{\parallel}{\text{S}}-\text{OH}$ sulfinic acids</p>	<p>SO_2</p> <p>$\text{R}-\overset{\text{O}}{\parallel}{\text{S}}-\text{OH}$ sulfonic acids</p> <p>$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{S}}-\text{O}-\text{R}$ sulfite esters</p>	<p>SO_3</p> <p>$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{S}}-\text{O}-\text{R}$ sulfate esters</p>

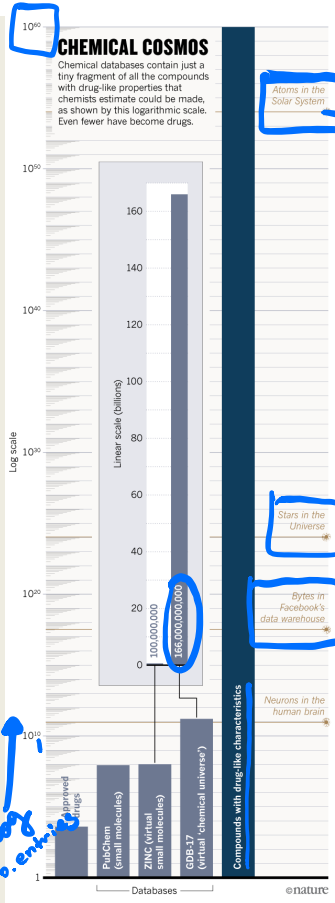
The universe of organic molecules



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Modular is a good word to describe the structure of organic molecules. The parts are interchangeable and come together in many different ways. The building blocks are combined to construct functional groups. The functional groups, in turn, are combined to construct molecules. Given the large number of building blocks and functional groups and their various combinations, it is no wonder that the “Universe of Organic Molecules” – the subset of molecules containing up to 30 C, N, O and S atoms – is estimated[†] to be something like 1×10^{60} . That’s a really big number! It should be obvious that if we are to make sense of this complexity, we need to develop good skills in recognizing the functional groups in organic molecules. With just a little practice you will be able to instantly look at a new molecule and see it for the functional groups that it contains.

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How machine learning and big data are helping chemists search the vast chemical universe for better medicines

