Hybridization, Molecular Geometry, and Polarity — Study Guide

Why is methane a tetrahedron, ethylene flat, and acetylene a straight line? Why is water polar but carbon dioxide not? Why is the C–H bond of acetylene acidic enough to remove with $NaNH_2$ while ethane's is not? All three questions are answered by the same small set of ideas: how atomic orbitals combine into bonds, how electron domains arrange themselves in space, and how unequal sharing of electrons creates polarity.

Builds on Atomic Structure, Lewis Structures, and Formal Charge. Drawing on Klein, Clayden, Wade, McMurry, Pauling's electronegativity work, and the CRC Handbook.

Section	Topic
1	How Covalent Bonds Form: σ and π Bonds
2	Hybridization: sp^3, sp^2, and sp
3	VSEPR: Predicting Molecular Shape
4	Bond Length, Bond Strength, and s-Character
5	Electronegativity and Bond Polarity
6	Molecular Dipole Moments
7	A First Look at Molecular Orbitals

1. How Covalent Bonds Form: σ and π Bonds

Valence bond theory describes a covalent bond as the overlap of two atomic orbitals, each holding one electron, so that the shared pair sits between both nuclei. The greater the overlap, the stronger the bond. Two geometries of overlap give the two kinds of bond in organic chemistry.

Feature	σ (sigma) bond	π (pi) bond
Overlap	Head-on, along the internuclear axis	Side-by-side, of parallel p orbitals
Electron density	Concentrated between the nuclei, cylindrically symmetric	Above and below the internuclear axis; node along the axis
Rotation about the bond	Free (only ~3 kcal/mol barrier in ethane)	Restricted; rotation breaks the overlap
Where found	Every single bond; one of the bonds in every double and triple bond	Second bond of a double bond; second and third of a triple bond
Relative strength (C–C)	~83 kcal/mol	~63–65 kcal/mol (weaker, more reactive)

> *Single bond = 1 σ. Double bond = 1 σ + 1 π. Triple bond = 1 σ + 2 π. Every bond between two atoms contains exactly one σ bond.*

The simplest case is H_2: two hydrogen 1s orbitals overlap head-on, the bond length is 0.74 Å, and breaking it costs 104 kcal/mol (436 kJ/mol). Carbon is more complicated, because its ground-state configuration has only two unpaired electrons (see the companion guide, Figure 1), yet it forms four equivalent bonds in methane. Hybridization explains this.

2. Hybridization: sp^3, sp^2, and sp

Hybridization is a model in which an atom's valence s and p orbitals mix to form new, equivalent hybrid orbitals pointed toward its bonding partners. Linus Pauling introduced the idea in 1931 to explain the tetrahedral geometry of methane. The number of hybrid orbitals always equals the number of atomic orbitals mixed.

Determining Hybridization: Count Electron Domains

Count the steric number: the number of atoms bonded to the atom (σ bonds) plus its lone pairs. Multiple bonds count once, because only one of their bonds is σ.

Steric number	Hybridization	Hybrid orbitals	Unhybridized p	Ideal angle	Electron geometry
4	sp^3	4 (s + 3p)	0	109.5°	Tetrahedral
3	sp^2	3 (s + 2p)	1	120°	Trigonal planar
2	sp	2 (s + p)	2	180°	Linear

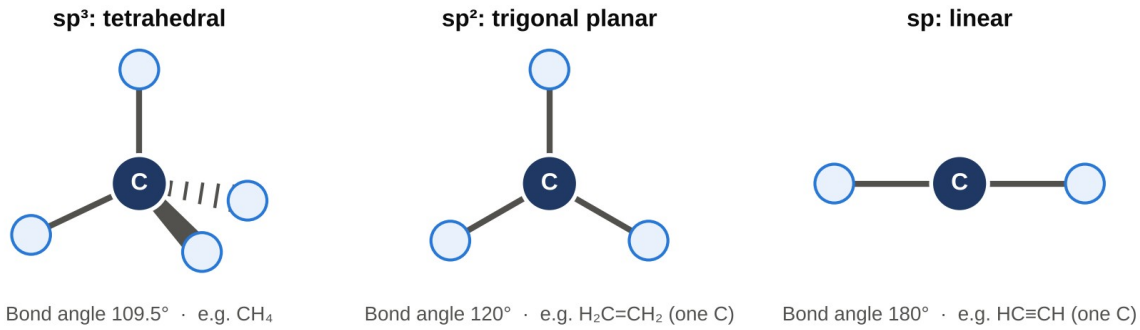


Figure 1. The three carbon geometries. In the sp^3 drawing the wedge points toward the viewer and the dashes away; the sp^2 and sp carbons are drawn with all bonds in the page. The unhybridized p orbitals of sp^2 and sp carbon (not shown) sit perpendicular to these bonds and form the π bonds.
Source: Geometries per VSEPR and valence bond theory; Klein, Ch. 1; Clayden, Ch. 4.

sp^3 Carbon (Four σ Bonds)

Mixing one 2s and three 2p orbitals gives four sp^3 orbitals, each 25% s and 75% p, pointed to the corners of a tetrahedron. All four bonds in methane are identical, 1.09 Å long, with 109.5° angles. Every carbon with four single bonds is sp^3.

sp^2 Carbon (Double Bonds)

Mixing one 2s and two 2p orbitals gives three sp^2 orbitals (33% s) in a plane at 120°. The leftover p orbital stands perpendicular to that plane. In ethylene, sp^2–sp^2 overlap forms the C–C σ bond and the two leftover p orbitals overlap sideways to form the π bond. This is why all six atoms of ethylene are coplanar.

sp Carbon (Triple Bonds and Allenes)

Mixing one 2s and one 2p orbital gives two sp orbitals (50% s) pointing 180° apart. The two remaining p orbitals are perpendicular to the axis and to each other, and in acetylene they form two π bonds. Nitriles (C≡N) and the central carbon of an allene (C=C=C) are also sp.

Hybridization of Nitrogen and Oxygen

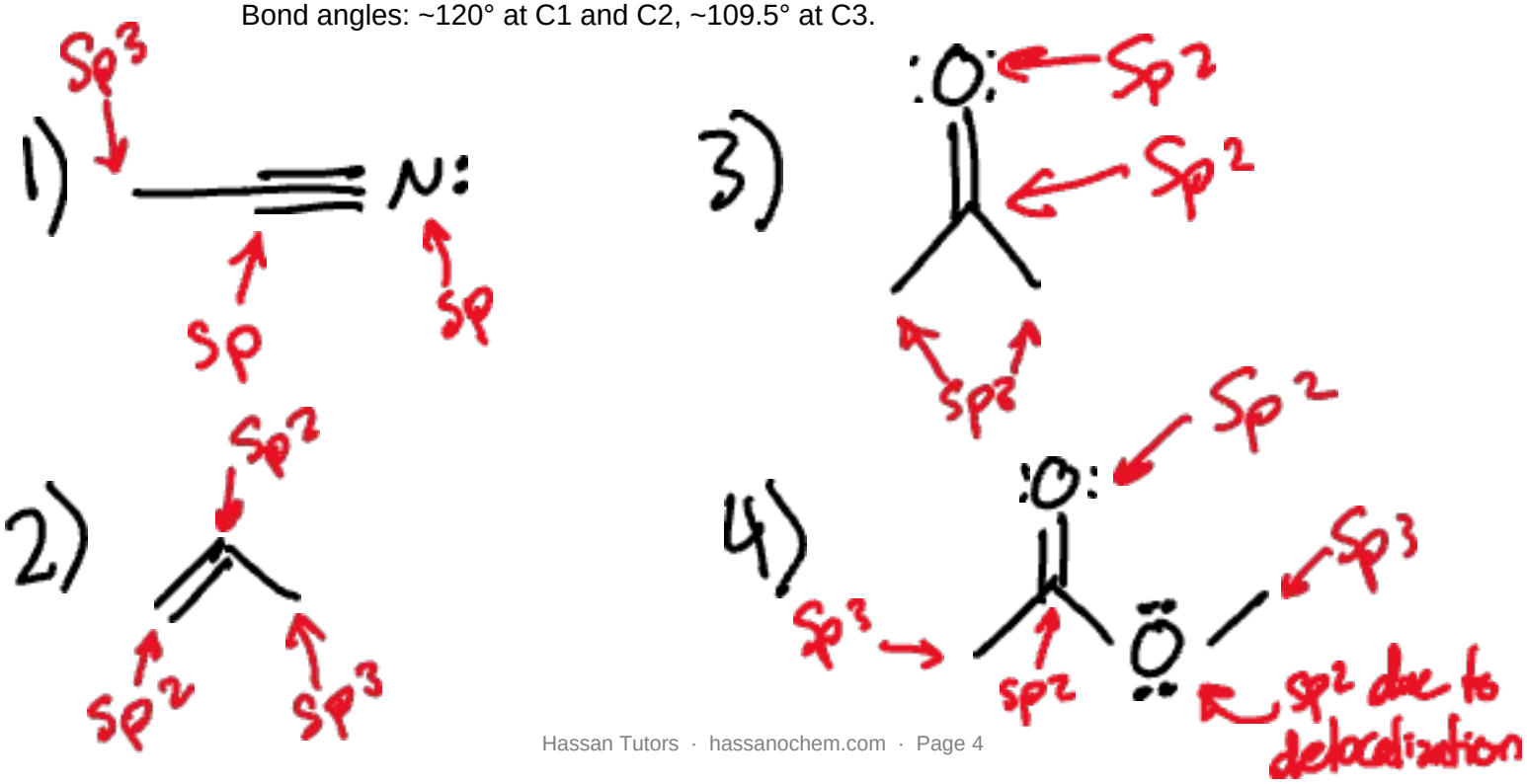
The same counting rule applies to heteroatoms, with lone pairs counted as domains.

Example	Atom	σ bonds + lone pairs	Hybridization	Shape around that atom
Ammonia, NH_3	N	3 + 1 = 4	sp^3	Trigonal pyramidal
Water, H_2O	O	2 + 2 = 4	sp^3	Bent
Imine, $R_2C{=}NR$	N	2 + 1 = 3	sp^2	Bent
Carbonyl, $R_2C{=}O$	O	1 + 2 = 3	sp^2	Terminal (one neighbour)
Nitrile, RC≡N	N	1 + 1 = 2	sp	Linear

> Important exception: a lone pair next to a π bond is usually delocalised by resonance, and the atom becomes sp^2 so its lone pair can sit in a p orbital. The nitrogen of an amide ($RCONH_2$) and of aniline are sp^2 and nearly planar, even though counting domains gives 4. See the Resonance companion guide.

Worked Example — Hybridization in Acetonitrile and Propene

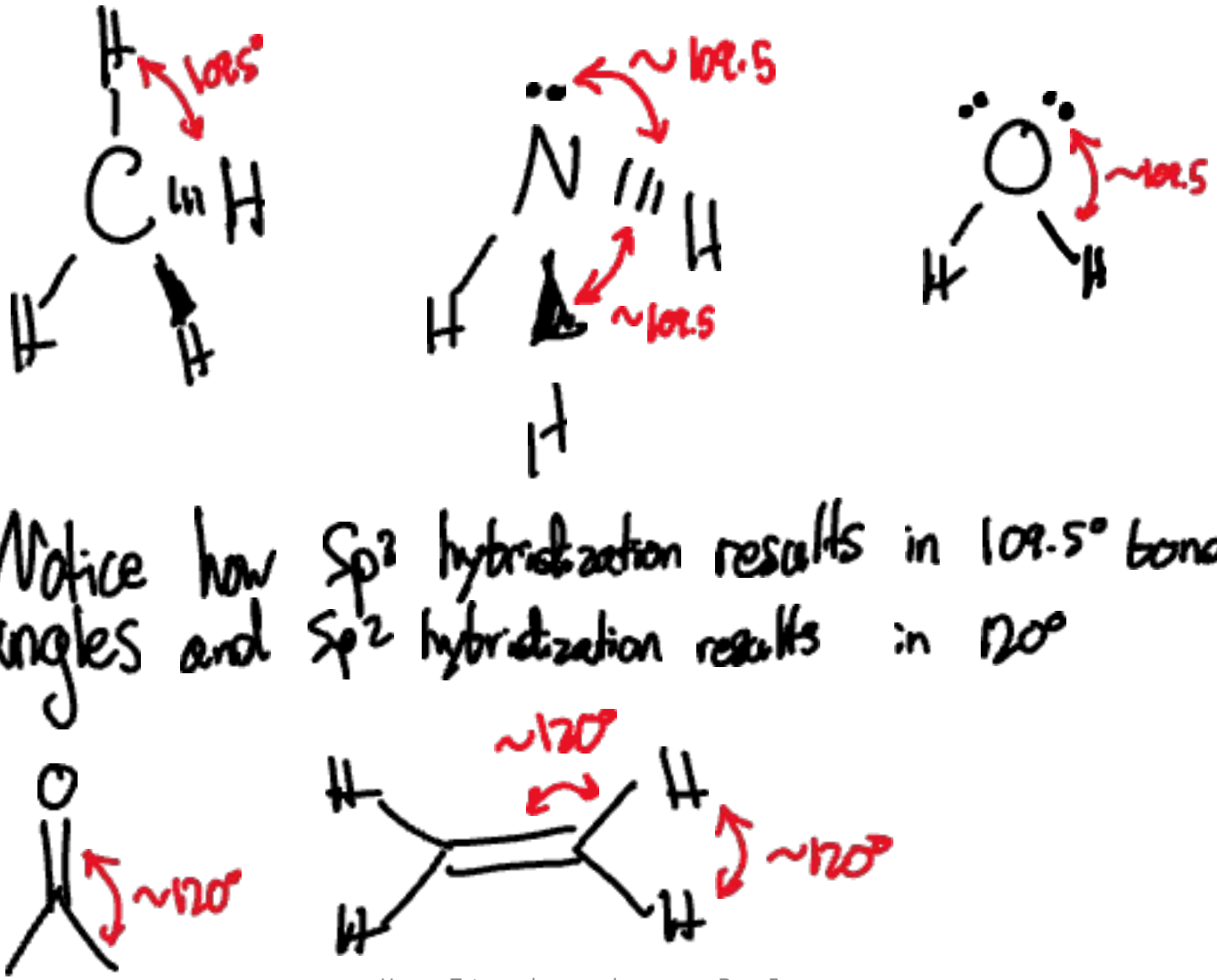
1. Acetonitrile, $CH_3–C{\equiv}N$: the CH_3 carbon has 4 σ bonds (sp^3); the nitrile carbon has 2 σ bonds (sp); nitrogen has 1 σ bond + 1 lone pair (sp).
2. Propene, $CH_2{=}CH–CH_3$: C1 and C2 each have 3 σ bonds (sp^2); C3 has 4 σ bonds (sp^3). Bond angles: ~120° at C1 and C2, ~109.5° at C3.



3. VSEPR: Predicting Molecular Shape

Valence Shell Electron Pair Repulsion (VSEPR) theory says that electron domains around an atom repel one another and spread as far apart as possible. The arrangement of all domains is the electron geometry. The shape we name for the molecule (the molecular geometry) describes only the positions of atoms, so lone pairs are invisible in the name even though they shape the molecule.

Molecule	Bonded atoms	Lone pairs	Electron geometry	Molecular shape	Bond angle
CH_4	4	0	Tetrahedral	Tetrahedral	109.5°
NH_3	3	1	Tetrahedral	Trigonal pyramidal	107°
H_2O	2	2	Tetrahedral	Bent	104.5°
BF_3	3	0	Trigonal planar	Trigonal planar	120°
$H_2C{=}O$	3	0 (on C)	Trigonal planar	Trigonal planar	~120°
CO_2	2	0 (on C)	Linear	Linear	180°



Why Lone Pairs Squeeze Bond Angles

A lone pair is held by only one nucleus, so its electron cloud is fatter and closer to the central atom than a bonding pair. It pushes the bonding pairs together. This is why the H–N–H angle in ammonia (one lone pair) is 107° and the H–O–H angle in water (two lone pairs) is 104.5°, both smaller than the ideal 109.5°.

> *Repulsion strength: lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair.*

> Exam habit: when asked for the shape of an atom, first count domains to get the electron geometry, then name the shape using only the atoms. "Water is tetrahedral" is the electron geometry; the correct molecular shape is bent.

4. Bond Length, Bond Strength, and s-Character

Two trends run through every bond comparison in organic chemistry. First, more bonds between the same two atoms make a shorter, stronger connection. Second, hybrid orbitals with more s-character hold electrons closer to the nucleus, which shortens and strengthens bonds and stabilises lone pairs.

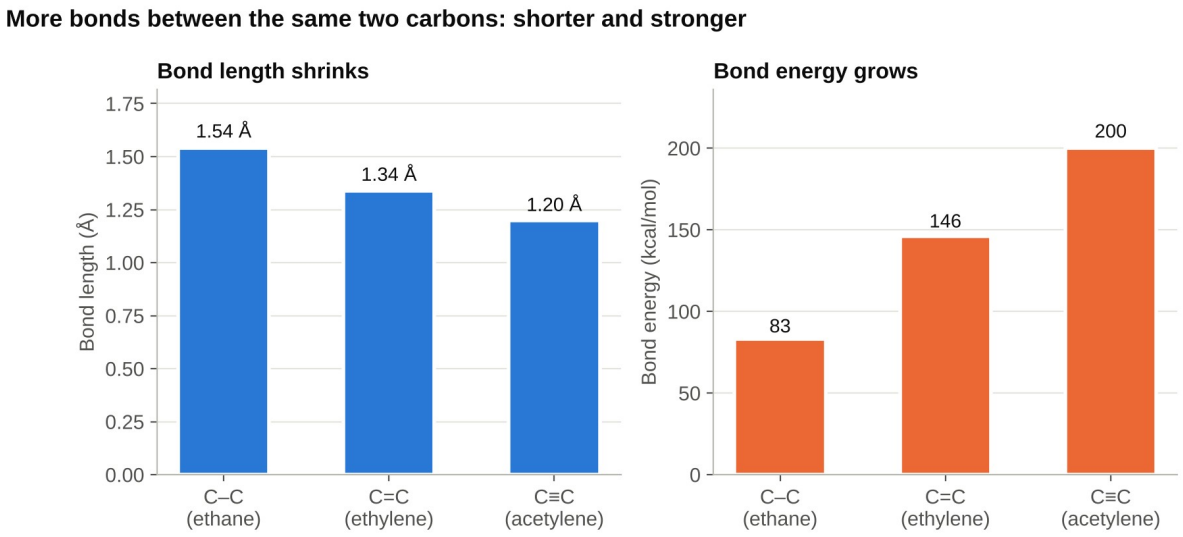


Figure 2. Carbon–carbon bond length and bond energy for single, double, and triple bonds. Each extra π bond pulls the carbons closer together, but adds less energy than the σ bond: the double bond is 146 kcal/mol, not 2 × 83. Source: Bond lengths from Allen et al., J. Chem. Soc. Perkin Trans. 2, 1987, S1–S19; average bond energies as tabulated in Klein, Ch. 1, and Wade, Ch. 2.

s-Character and the C–H Bond

C–H bond in	Carbon hybridization	% s	C–H length (Å)	C–H bond dissociation energy (kcal/mol)
Ethane	sp^3	25	1.09	101
Ethylene	sp^2	33	1.08	111
Acetylene	sp	50	1.06	133

The same s-character effect controls acidity. When a C–H bond is broken heterolytically, the lone pair left behind sits in the hybrid orbital. An sp orbital holds that lone pair closest to the nucleus, so the acetylide anion is the most stable carbanion and acetylene is by far the most acidic hydrocarbon.

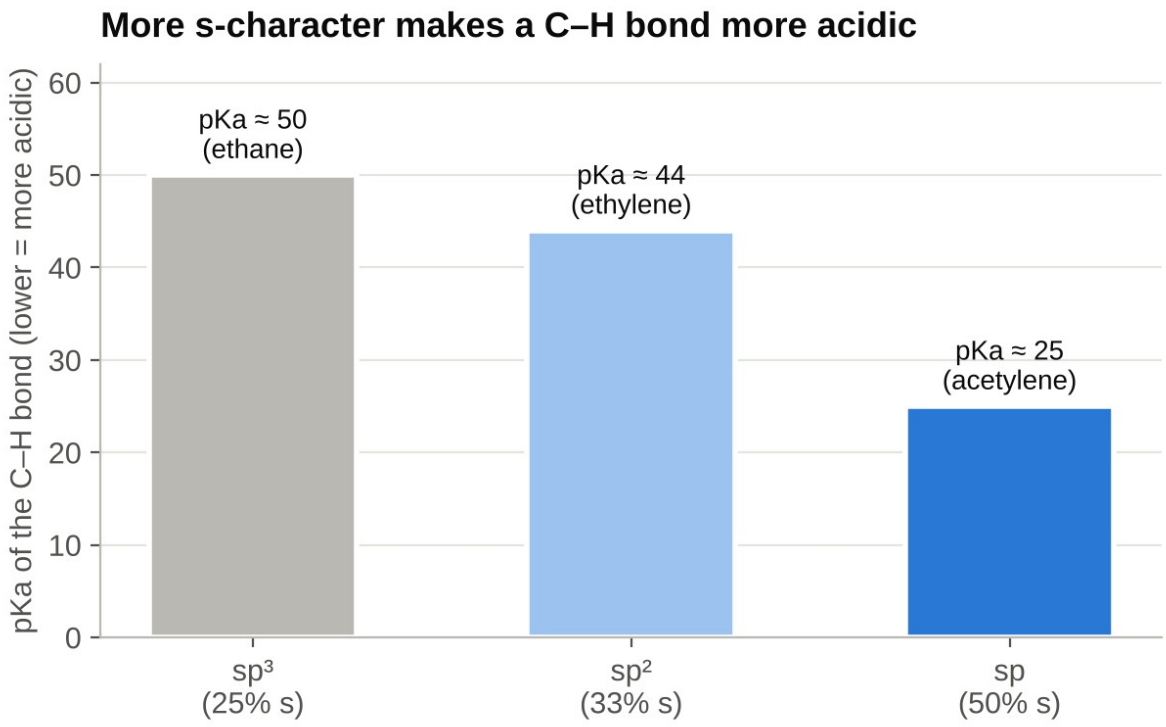


Figure 3. pKa of hydrocarbon C–H bonds by hybridization. Each step from sp³ to sp² to sp makes the C–H bond more acidic; acetylene (pKa ≈ 25) is about 10^{25} times more acidic than ethane (pKa ≈ 50).
Source: Approximate pKa values from the Evans pKa table and Klein, Ch. 3.

This is why $NaNH_2$ (conjugate acid NH_3, pKa ≈ 38) deprotonates a terminal alkyne but NaOH (conjugate acid H_2O, pKa 15.7) does not. You will use this in acetylide chemistry and again with enolates.

5. Electronegativity and Bond Polarity

Electronegativity (EN) is an atom's ability to attract the shared electrons of a bond toward itself. Linus Pauling defined the first quantitative scale in 1932 from bond energies; the values used in textbooks today are A. L. Allred's 1961 revision of Pauling's scale. Fluorine is the most electronegative element (3.98).

Pauling electronegativity of the main-group elements organic chemists use

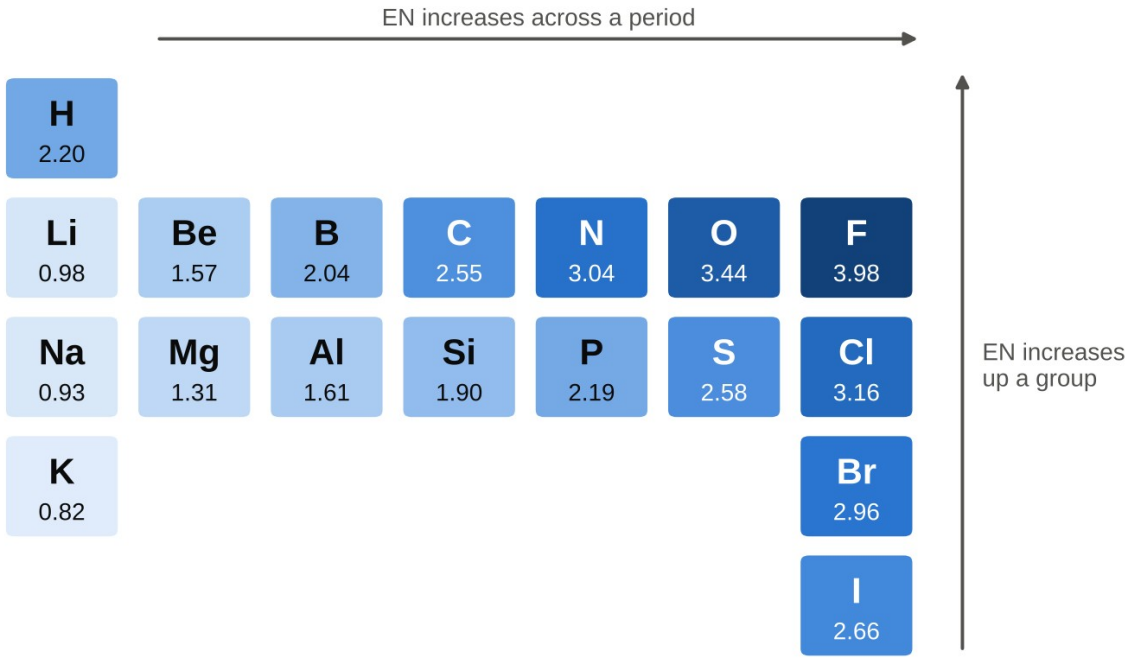
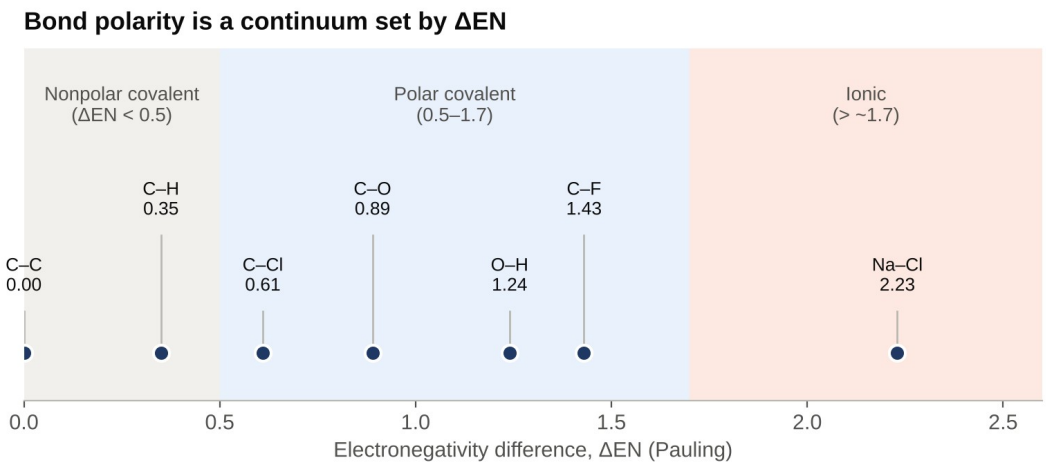


Figure 4. Pauling electronegativities of the main-group elements most common in organic molecules. Darker blue = more electronegative. EN rises left to right across a period and from bottom to top in a group. Carbon (2.55) and hydrogen (2.20) are close, which is why C–H bonds are nearly nonpolar. Source: Pauling, J. Am. Chem. Soc. 1932, 54, 3570; values as revised by Allred, J. Inorg. Nucl. Chem. 1961, 17, 215.

From Electronegativity Difference to Bond Polarity

When two bonded atoms differ in EN, the shared electrons spend more time near the more electronegative atom. That atom gains a partial negative charge (δ−) and its partner a partial positive charge (δ+). The larger the difference (ΔEN), the more polar the bond.



Boundaries are conventions, not sharp cutoffs; C–H is treated as nonpolar in organic chemistry.

Figure 5. Selected bonds placed on the ΔEN scale. The labelled zones follow the common textbook convention (nonpolar below 0.5, polar covalent 0.5–1.7, ionic above about 1.7). Note that C–N (ΔEN 0.49) sits at the boundary but behaves as a polar bond in practice. Source: Differences computed from the Allred–Pauling values in Figure 4; zone boundaries per Klein, Ch. 1.

Why Polarity Matters for Reactivity

Bond polarity tells you which atom is electron-poor (an electrophile, attacked by nucleophiles) and which is electron-rich. This single idea predicts the starting point of most mechanisms.

Bond	δ+ atom	δ− atom	Consequence
C–Br, C–Cl	C	Halogen	Carbon is attacked by nucleophiles (SN2, SN1)
C=O	C	O	Carbonyl carbon is electrophilic (nucleophilic addition)
O–H	H	O	H is acidic; O is a hydrogen-bond acceptor
C–Li, C–Mg	Li, Mg	C	Carbon becomes nucleophilic (Grignard reagents)

The Inductive Effect

Polarisation is transmitted through σ bonds. An electronegative atom pulls electron density not only from the atom it is bonded to but, more weakly, from atoms two and three bonds away. This through-bond pull is the inductive effect, and it falls off quickly with distance. Trifluoroacetic acid (pKa ≈ 0.5) is about 10^4 times more acidic than acetic acid (pKa 4.76) because three fluorines inductively stabilise the carboxylate anion.

> Electronegativity and formal charge answer different questions. Formal charge tells you where to draw a + or − symbol; electronegativity tells you where electron density actually sits. In H_3O^+ the formal charge is on O, but the electron-poor atoms are the hydrogens.

6. Molecular Dipole Moments

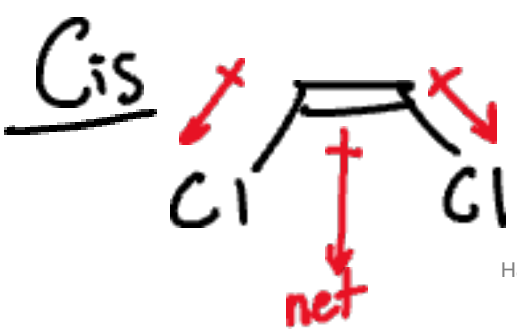
A molecule can contain polar bonds and still be nonpolar overall. Each polar bond has a bond dipole, a vector pointing toward its δ− end. The molecular dipole moment is the vector sum of all bond dipoles and lone-pair contributions, measured in debyes (D). Geometry decides whether the bond dipoles cancel.

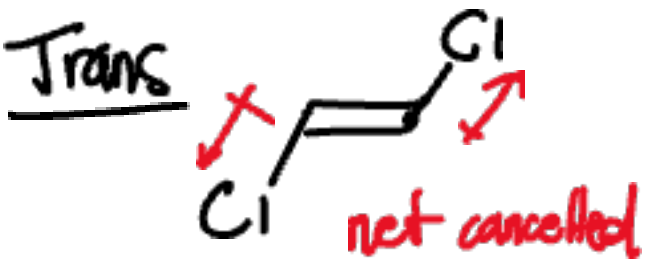
Molecule	Shape	Polar bonds?	Dipole moment (D)	Why
CO_2	Linear	Yes (2 C=O)	0	Two equal dipoles point in opposite directions and cancel
H_2O	Bent	Yes (2 O–H)	1.85	Bent shape: dipoles add; lone pairs add more
NH_3	Trigonal pyramidal	Yes (3 N–H)	1.47	Dipoles add toward N and its lone pair
CCl_4	Tetrahedral	Yes (4 C–Cl)	0	Four equal dipoles cancel in a symmetric tetrahedron
$CHCl_3$	Tetrahedral	Yes	1.04	One C–H replaces a C–Cl: symmetry broken
CH_2Cl_2	Tetrahedral	Yes	1.60	Dipoles add on one side
CH_3Cl	Tetrahedral	Yes	1.87	One strong C–Cl dipole dominates
Acetone, $(CH_3)_2C{=}O$	Trigonal planar at C	Yes (C=O)	2.88	Large C=O dipole, uncancelled

Worked Example — cis- vs trans-1,2-Dichloroethene

1. Both isomers have the formula $C_2H_2Cl_2$ and two identical C–Cl bond dipoles.
2. In the cis isomer both chlorines are on the same side of the C=C, so their dipoles add: μ = 1.90 D.
3. In the trans isomer the chlorines are on opposite sides, the dipoles point in opposite directions, and they cancel: μ = 0 D.
4. Consequence: the cis isomer is more polar and has the higher boiling point (60 °C vs 48 °C).

> Rule of thumb: a molecule is nonpolar if it has no polar bonds, or if its polar bonds are arranged symmetrically (linear with identical ends, trigonal planar with three identical groups, tetrahedral with four identical groups). Any lone pair on the central atom almost always makes the molecule polar.





7. A First Look at Molecular Orbitals

Hybridization is the model you will use most, but molecular orbital (MO) theory explains reactivity more directly, and you have already met its vocabulary (π* orbitals, HOMO, LUMO). In MO theory, atomic orbitals combine to form orbitals that belong to the whole molecule.

Bonding and Antibonding Orbitals

- Two atomic orbitals combine to give two molecular orbitals: a lower-energy **bonding** orbital (electron density between the nuclei) and a higher-energy **antibonding** orbital (a node between the nuclei), marked with an asterisk.
- Two s or hybrid orbitals overlapping head-on give σ and σ*. Two parallel p orbitals give π and π*.
- Electrons fill the bonding orbital first. A stable bond has its bonding orbital filled and its antibonding orbital empty.

HOMO and LUMO: The Orbitals That React

The highest occupied molecular orbital (HOMO) holds the most available electrons; the lowest unoccupied molecular orbital (LUMO) is the most accessible empty orbital. In a polar reaction, electrons flow from the HOMO of the nucleophile into the LUMO of the electrophile. Every curved arrow you draw is a picture of this flow.

Reaction you know	Nucleophile HOMO	Electrophile LUMO
HBr adding to an alkene	Alkene π	H–Br σ*
SN2 on an alkyl bromide	Nucleophile lone pair	C–Br σ* (explains backside attack)
Nucleophilic addition to C=O	Nucleophile lone pair	C=O π*
Hydroboration	Alkene π	Empty p orbital on boron

> The C–Br σ* orbital has its large lobe on the side of carbon opposite the bromine. A nucleophile must attack that lobe, which is why SN2 occurs with backside attack and inversion of configuration.

Quick Recap

Concept	Key fact
σ vs π	Every bond has one σ; extra bonds are π, weaker and above/below the axis
Hybridization	Steric number 4 = sp^3 (109.5°), 3 = sp^2 (120°), 2 = sp (180°)
VSEPR	Lone pairs shape the molecule but are not named: NH_3 pyramidal (107°), H_2O bent (104.5°)
Bond order	Triple < double < single in length; triple > double > single in strength
s-character	More s = shorter, stronger C–H and more acidic: sp (pKa 25) > sp^2 (44) > sp^3 (50)
Electronegativity	F 3.98 > O 3.44 > N 3.04 ≈ Cl 3.16 > C 2.55 > H 2.20
Molecular dipole	Vector sum of bond dipoles; symmetric shapes cancel (CO_2, CCl_4 = 0 D)
HOMO → LUMO	Nucleophile HOMO donates into electrophile LUMO; curved arrows trace this flow

- ✓ Count σ bonds + lone pairs to get hybridization; multiple bonds count once
- ✓ Name the molecular shape from atoms only, after finding the electron geometry
- ✓ Use s-character to explain bond strength and C–H acidity
- ✓ Use ΔEN to find δ+ (electrophilic) and δ− (nucleophilic) atoms
- ✓ Check symmetry before calling a molecule polar
- × Do not forget that amide and aniline nitrogens are sp^2 because of resonance
- × Do not confuse formal charge with real charge density
- × Do not call CO_2 or CCl_4 polar molecules; their bonds are polar but the dipoles cancel

References & Further Reading

- Pauling, L. The Nature of the Chemical Bond. Application of Results Obtained from the Quantum Mechanics and from a Theory of Paramagnetic Susceptibility to the Structure of Molecules. J. Am. Chem. Soc. 1931, 53 (4), 1367–1400. DOI: 10.1021/ja01355a027 (hybridization)
- Pauling, L. The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms. J. Am. Chem. Soc. 1932, 54 (9), 3570–3582. DOI: 10.1021/ja01348a011
- Allred, A. L. Electronegativity Values from Thermochemical Data. J. Inorg. Nucl. Chem. 1961, 17 (3–4), 215–221. DOI: 10.1016/0022-1902(61)80142-5 (source of the values in Figure 4)
- Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of Bond Lengths Determined by X-Ray and Neutron Diffraction. J. Chem. Soc., Perkin Trans. 2 1987, S1–S19. DOI: 10.1039/P298700000S1
- Blanksby, S. J.; Ellison, G. B. Bond Dissociation Energies of Organic Molecules. Acc. Chem. Res. 2003, 36 (4), 255–263. DOI: 10.1021/ar020230d (C–H bond energies)

- Rumble, J. R., Ed. CRC Handbook of Chemistry and Physics, 104th ed.; CRC Press, 2023. (dipole moments, boiling points)
- Klein, D. R. Organic Chemistry, 4th ed.; Wiley, 2021. Chapter 1.
- Clayden, J.; Greeves, N.; Warren, S. Organic Chemistry, 2nd ed.; Oxford University Press, 2012. Chapter 4 (Structure of Molecules).
- Wade, L. G.; Simek, J. W. Organic Chemistry, 9th ed.; Pearson, 2017. Chapter 2.
- Ripin, D. H.; Evans, D. A. pKa Table. Harvard University, 2005 (widely reproduced compilation of aqueous and DMSO pKa values).
- Chemistry LibreTexts: Hybrid Orbitals; VSEPR; Dipole Moments. https://chem.libretexts.org