Organic Chemistry 1

A review of general chemistry

Chapter 1

Electrons, Bonds, and Molecular Properties

25 original problems with step-by-step solutions

Easy	8 problems. One idea at a time: a warm-up that builds the basic skill.
Exam	10 problems. The kind of multi-step question you can expect on a test.
Challenge	7 problems. Harder, combines several ideas; go slowly and show your work.

How to use this set

1. Open **Part A** and try each problem on paper first, before you look at any solution.
2. Then open **Part B**, check your answer in the yellow box, and read the numbered steps. If your answer differs, find the step where your reasoning and the solution part ways.
3. Redo any problem you missed a few days later, without looking.

USOrgo

Original practice problems written for Orgo 1 students. Not affiliated with any textbook publisher, university or exam body.

Part A Problems

Try each one first. No answers here.

Easy One idea at a time

1 Easy

For each species, give the formal charge on the central atom (shown in bold in the name) and the number of lone pairs on it.

(a) hydronium ion, $H_3\mathbf{O}^+$

(b) borohydride ion, $\mathbf{B}H_4^-$

(c) methyl anion, $\mathbf{C}H_3^-$

(d) ammonium ion, $\mathbf{N}H_4^+$

2 Easy

Use these Pauling electronegativities: H 2.20, C 2.55, N 3.04, O 3.44, F 3.98, Cl 3.16.

(a) Rank the bonds C-H, C-N, C-O, C-F, C-Cl from most polar to least polar.

(b) For the C-O and C-H bonds, state which atom carries the partial negative charge.

3 Easy

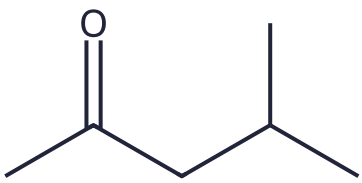
Consider 4-methylpentan-2-one drawn in bond-line form.

(a) What is its molecular formula?

(b) How many hydrogen atoms are on each carbon, starting from the methyl group next to the carbonyl and moving along the chain?

(c) How many lone pairs does the molecule have in total?

(d) How many carbons are sp^2 hybridized?



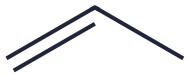
4-methylpentan-2-one

4 Easy

Propene and acetonitrile are both small molecules with multiple bonds.

(a) Give the hybridization of every carbon and the nitrogen.

(b) Count the sigma bonds and pi bonds in each molecule.



propene



acetonitrile

5 Easy

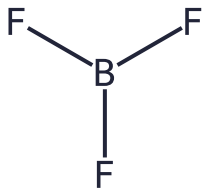
For each molecule give the electron-pair geometry, the molecular shape and the approximate bond angle.

(a) ammonia, NH_3

(b) boron trifluoride, BF_3

(c) water, H_2O

(d) carbon dioxide, CO_2



(b) boron trifluoride, BF_3

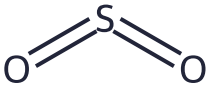


(d) carbon dioxide, CO_2

6 Easy

Which of the following have a nonzero net dipole moment? Explain each in one sentence.

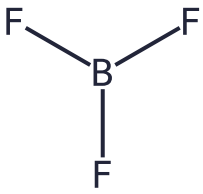
sulfur dioxide, SO_2; carbon dioxide, CO_2; boron trifluoride, BF_3; ammonia, NH_3.



sulfur dioxide, SO_2



carbon dioxide, CO_2



boron trifluoride, BF_3

7 Easy

Name the strongest intermolecular attraction between molecules of each pure substance (or in the solution), and justify briefly.

(a) hexane

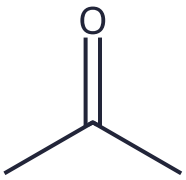
(b) acetone

(c) ethanol

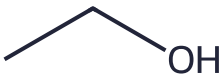
(d) sodium chloride dissolved in water, in



(a) hexane



(b) acetone



(c) ethanol





(d) water

8 Easy

How many constitutional isomers have the molecular formula $C_4H_{10}O$? Draw the bond-line structure of each and group them by functional group.

Exam *Test-level, multi-step*

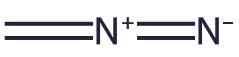
9 Exam

Diazomethane, CH_2N_2, has two important Lewis structures: and.

(a) Compute the formal charge on each non-hydrogen atom in both structures.

(b) Which structure is the better contributor to the resonance hybrid, and why?

(c) Show that each structure accounts for all 16 valence electrons.





10 Exam

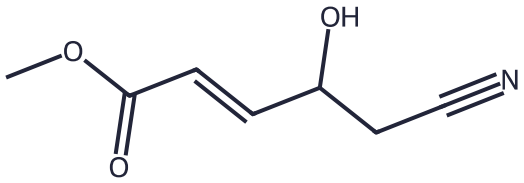
Methyl 5-cyano-4-hydroxypent-2-enoate (E/Z not specified) is shown as a bond-line structure.

(a) Give its molecular formula.

(b) Give the total number of lone pairs.

(c) How many carbons are sp^3, sp^2 and sp?

(d) Which atoms are sp hybridized?



methyl 5-cyano-4-hydroxypent-2-enoate (E/Z not specified)

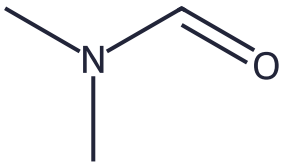
11 Exam

N,N-Dimethylformamide and trimethylamine each have a nitrogen bonded to three carbons.

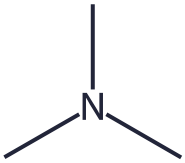
(a) State the hybridization and local geometry at nitrogen in each molecule.

(b) Explain the difference.

(c) Which has the larger C-N-C bond angle?



N,N-Dimethylformamide



trimethylamine

12 Exam

(a) Rank ethane, ethene and ethyne by increasing carbon-carbon bond length and by increasing carbon-hydrogen bond length.

(b) Rank the CH_3-C single bond in propane, propene and propyne from longest to shortest.

(c) Explain both trends in terms of orbitals.

(a) ethene



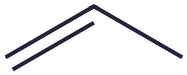
ethene



ethyne



(b) propane



propene



propyne

13 Exam

The three isomers of dichloroethene are cis-1,2-dichloroethene, trans-1,2-dichloroethene and 1,1-dichloroethene.

(a) Predict which has no dipole moment.

(b) Rank the other two by dipole moment, using vector addition of the C-Cl bond dipoles (ignore the small C-H dipoles).

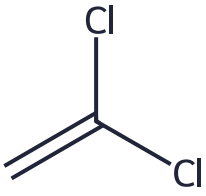
(c) What angle apart are the two C-Cl bond vectors in each isomer?



cis-1,2-dichloroethene



trans-1,2-dichloroethene



1,1-dichloroethene

14 Exam

The four compounds below have similar molar masses (72-74 g/mol). Rank them from highest to lowest boiling point and justify.

butan-1-ol; butanal; pentane; 2,2-dimethylpropane.



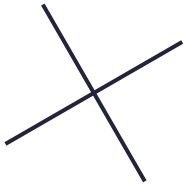
butan-1-ol



butanal



pentane



2,2-dimethylpropane

15 Exam

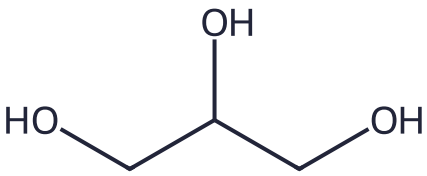
Equal volumes of water and hexane are shaken together in a separatory funnel, and a different solute is added to each trial. In which layer does each solute mainly end up? State the main interaction responsible.

(a) glycerol (propane-1,2,3-triol)

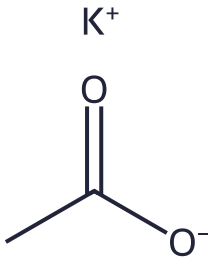
(b) potassium acetate

(c) dodecan-1-ol

(d) heptane



(a) glycerol (propane-1,2,3-triol)



(b) potassium acetate



(c) dodecan-1-ol



(d) heptane

Also, which layer is the top layer (density of water 1.00 g/mL, hexane 0.66 g/mL)?

16 Exam

Pent-1-en-3-yne contains three different carbon hybridization states.

(a) Number the carbons C1 (CH_2=) through C5 (CH_3) and give the hybridization of each.

(b) Which carbons lie on one straight line?

(c) Give the approximate bond angles at C2 (C1-C2-C3), C3 and C4.

(d) How many sigma and pi bonds are in the molecule?

(e) The skeleton has two C-C single bonds, C2-C3 and C4-C5. Which is shorter?



pent-1-en-3-yne

17 Exam

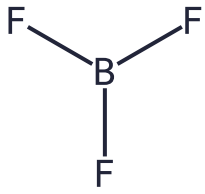
Boron trifluoride reacts with ammonia to form the adduct H_3N-BF_3.

(a) Draw the Lewis structure of BF_3 and of the adduct, and give formal charges.

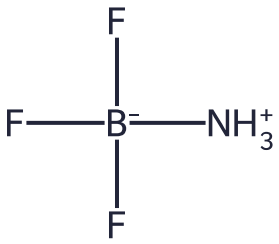
(b) Give the hybridization and geometry of boron before and after.

(c) Predict the F-B-F angle before and after.

(d) Why does BF_3 react with NH_3 at all?



boron trifluoride



adduct H_3N-BF_3

18 Exam

Draw all constitutional isomers of C_4H_8, and classify each as an alkene or a cycloalkane. How many are there? Are cis-but-2-ene and trans-but-2-ene counted separately?

19 Challenge

Ozone, O3, and the nitrite ion, NO_2^-, each have 18 valence electrons.

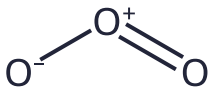
(a) Show that both have 18 valence electrons.

(b) Draw the Lewis structures with formal charges, including both resonance forms.

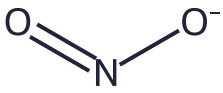
(c) Give the hybridization of the central atom, the shape, and a reasonable bond-angle prediction.

(d) Compare the two terminal bond lengths and say whether they are single, double or in between.

(e) Why is CO_2 (16 valence electrons) linear but these two are bent?



ozone, O3



nitrite ion, NO_2^-

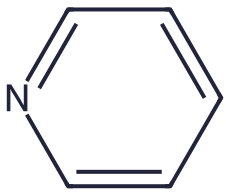
20 Challenge

Consider pyridine, pyrrole, piperidine, and imidazole.

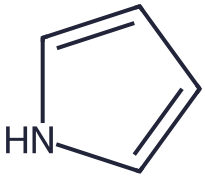
(a) Give the hybridization of every nitrogen atom.

(b) For each nitrogen, state whether its lone pair lies in the plane of the ring (an sp^2 or sp^3 orbital) or in a p orbital perpendicular to the ring and part of the pi system.

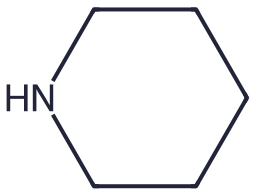
(c) How many pi electrons are in the pi system of pyridine, pyrrole and imidazole?



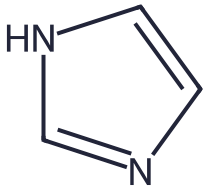
pyridine



pyrrole



piperidine



imidazole

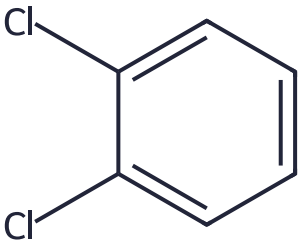
21 Challenge

Assume each C-Cl bond on an aromatic ring contributes a bond dipole of 1.6 D along the bond direction, and ignore all other contributions. The three dichlorobenzene isomers are 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene.

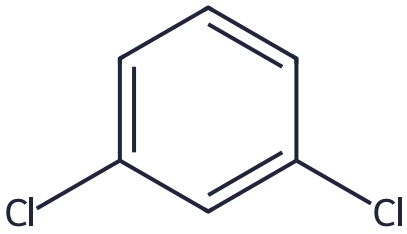
(a) Calculate the predicted net dipole of each.

(b) Rank them.

(c) Why are the real values (about 2.5 D, 1.7 D, 0 D) only approximately equal to your calculation?



1,2-dichlorobenzene



1,3-dichlorobenzene



1,4-dichlorobenzene

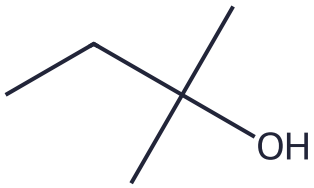
22 Challenge

Rank these four compounds from highest to lowest boiling point and justify in terms of intermolecular forces and shape.

pentan-1-ol; 2-methylbutan-2-ol; 1-methoxybutane; pentane.



pentan-1-ol



2-methylbutan-2-ol



1-methoxybutane



pentane

23 Challenge

4-Ethynylcyclohex-1-ene-1-carbaldehyde is given.

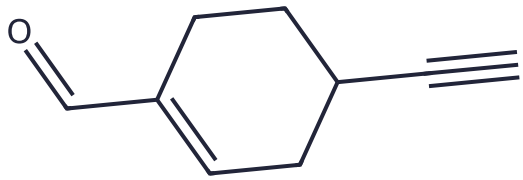
(a) Give its molecular formula.

(b) How many sigma bonds and how many pi bonds does it have?

(c) How many carbons are sp, sp^2, sp^3?

(d) How many C-H bonds use an sp^3 carbon, an sp^2 carbon and an sp carbon?

(e) How many lone pairs are on the molecule?



4-ethynylcyclohex-1-ene-1-carbaldehyde

24 Challenge

Propadiene (allene) is an isomer of propyne.

(a) Give the hybridization of each carbon and the C=C=C bond angle.

(b) Describe how the two pi bonds are oriented relative to each other and the consequence for the two CH_2 groups.

(c) Is the molecule planar? Does it have a net dipole moment?

(d) How does this differ from buta-1,3-diene?



propadiene (allene)



(d) buta-1,3-diene

25 Challenge

The measured dipole moments of propane, propene and propyne are about 0.08 D, 0.36 D and 0.78 D respectively.

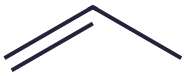
(a) Explain why the dipole moment increases in this order, even though all three are hydrocarbons.

(b) In propyne, which end of the molecule is partially positive?

(c) Is the hydrogen of the C-H bond in ethyne (HC#CH) more or less delta-plus than a hydrogen in ethane? Explain.



propane



propene



propyne

Part B Worked solutions

Check your answer in the yellow box, then read the steps.

Easy One idea at a time

1 Easy

FC, Lewis

Answer (a) O +1, 1 lone pair. (b) B −1, 0 lone pairs. (c) C −1, 1 lone pair. (d) N +1, 0 lone pairs.

Solution

1. Formal charge = (valence electrons of the free atom) - (nonbonding electrons) - (number of bonds).
2. (a) O: 6 - 2 - 3 = +1. The 8 electrons around O are 3 bonds plus 1 lone pair.
3. (b) B: 3 - 0 - 4 = −1. Boron forms four bonds and has no lone pair.
4. (c) C: 4 - 2 - 3 = −1. Three C-H bonds and one lone pair.
5. (d) N: 5 - 0 - 4 = +1. Four bonds, no lone pair.
6. Common mistake: assuming the charge on the ion must sit on the atom that "looks" more electronegative, or forgetting the lone pair when counting the nonbonding electrons. Always do the arithmetic; it is the only reliable method.

2 Easy

EN, bond polarity

Answer (a) C-F > C-O > C-Cl > C-N > C-H. (b) In C-O the oxygen is delta-minus (carbon delta-plus); in C-H the carbon is delta-minus (hydrogen delta-plus), but only very slightly: C-H is usually treated as essentially nonpolar.

Solution

1. Bond polarity increases with the electronegativity difference (the larger the difference, the more polar the bond).
2. Differences: C-F 1.43, C-O 0.89, C-Cl 0.61, C-N 0.49, C-H 0.35. Ranking them gives the order above.
3. The more electronegative atom pulls the bonding electrons toward itself and carries the partial negative charge: O in C-O (3.44 vs 2.55).
4. In C-H the carbon (2.55) is slightly more electronegative than hydrogen (2.20), so carbon is the delta-minus end, though the bond is only weakly polar.
5. Common mistake: assuming every C-halogen bond is more polar than C-O (compare the electronegativity differences, not the group in the periodic table), or reversing the direction in C-H.

3 Easy

BondLine, count H and lone pairs

Answer (a) $C_6H_{12}O$. (b) 3, 0, 2, 1, 3, 3 (the CH_3 next to C=O, the C=O carbon, CH_2, CH, and two terminal CH_3 groups). (c) 2 lone pairs (both on the carbonyl oxygen). (d) 1.

Solution

1. A corner or line end in a bond-line structure is a carbon; each carbon has enough hydrogens to make four bonds in total.
2. The carbonyl carbon has a double bond to O and single bonds to two carbons: that is 4 bonds, so no H. The CH_2 has two C neighbors, so 2 H; the branch carbon has three C neighbors, so 1 H; each methyl has 3 H.
3. Total H = 3 + 0 + 2 + 1 + 3 + 3 = 12; carbons = 6; one oxygen: $C_6H_{12}O$.
4. Lone pairs are not drawn but must be counted: a neutral oxygen with a double bond has two lone pairs. There are no other heteroatoms.
5. Only the carbonyl carbon (trigonal planar) is sp^2.
6. Common mistake: counting two hydrogens on the carbonyl carbon or forgetting that oxygen's lone pairs exist when none are drawn.

4 Easy

Hybrid, SigmaPi

Answer (a) Propene: CH_2 sp^2, CH sp^2, CH_3 sp^3. Acetonitrile: CH_3 sp^3, nitrile carbon sp, N sp. (b) Propene: 8 sigma, 1 pi. Acetonitrile: 5 sigma, 2 pi.

Solution

1. Count the electron domains (sigma bonds plus lone pairs) on each atom: 4 = sp^3, 3 = sp^2, 2 = sp.
2. Propene: the two alkene carbons each have three sigma bonds (domains) so they are sp^2; the methyl carbon has four, so sp^3.
3. Acetonitrile: the nitrile carbon has one sigma bond to CH_3 and one to N, i.e., 2 domains: sp. Nitrogen has one sigma bond and one lone pair: 2 domains, sp.
4. Every single bond is one sigma bond; a double bond is 1 sigma + 1 pi; a triple bond is 1 sigma + 2 pi. Propene: 6 C-H + 2 C-C sigma = 8 sigma, 1 pi. Acetonitrile: 3 C-H + C-C + C-N sigma = 5 sigma, 2 pi.
5. Common mistake: counting a multiple bond as "one bond" when counting sigma bonds, or giving the nitrile nitrogen sp^3 because it has a lone pair.

5 Easy

VSEPR, geometry and bond angles

Answer (a) tetrahedral electron geometry, trigonal pyramidal shape, about 107 degrees. (b) trigonal planar, trigonal planar, 120 degrees. (c) tetrahedral, bent, about 104.5 degrees. (d) linear, linear, 180 degrees.

Solution

1. Count electron domains around the central atom (a double bond counts as one domain).
2. NH_3: three bonds + one lone pair = 4 domains, tetrahedral arrangement; the lone pair is invisible in the shape, so the molecule is pyramidal. The lone pair repels more than a bond pair, so the angle is compressed below 109.5 degrees.
3. BF_3: three domains, trigonal planar, 120 degrees.
4. H_2O: two bonds + two lone pairs = 4 domains; shape is bent, with an angle compressed further (about 104.5 degrees) by two lone pairs.
5. CO_2: two domains (two double bonds), linear.
6. Common mistake: giving the electron-pair geometry (tetrahedral) when the question asks for the molecular shape (pyramidal or bent).

6 Easy

Dipole, molecular polarity

Answer SO_2 and NH_3 are polar; CO_2 and BF_3 are nonpolar.

Solution

1. A molecule is polar only if its bond dipoles do not cancel; this depends on shape as well as bond polarity.
2. CO_2 is linear: the two C=O dipoles point in opposite directions and cancel.
3. BF_3 is trigonal planar and symmetric: the three B-F dipoles at 120 degrees sum to zero.
4. SO_2 is bent (a lone pair on S), so the two S=O dipoles do not oppose each other and there is a net dipole.
5. NH_3 is pyramidal, so the three N-H dipoles and the lone pair give a net dipole pointing toward nitrogen's lone pair.
6. Common mistake: saying "CO_2 has polar bonds, so it is polar." Polar bonds do not guarantee a polar molecule.

7 Easy

IMF

Answer (a) London dispersion forces. (b) Dipole-dipole forces (plus dispersion). (c) Hydrogen bonding. (d) Ion-dipole forces.

Solution

1. Hexane is a nonpolar hydrocarbon with only C-C and C-H bonds, so only London dispersion forces act.
2. Acetone has a polar C=O bond and a net dipole, so dipole-dipole attractions dominate. It has no O-H or N-H bond, so molecules of acetone cannot hydrogen-bond to each other.
3. Ethanol has an O-H bond: the hydrogen is bonded to oxygen and can hydrogen-bond to the oxygen lone pair on a neighbor.
4. In aqueous NaCl, Na^+ is attracted to the oxygen end of water and Cl^- to the hydrogen end of water: ion-dipole interactions.
5. Common mistake: saying acetone molecules hydrogen-bond to each other. Acetone can accept hydrogen bonds from water or an alcohol, but pure acetone has no hydrogen bond donors.

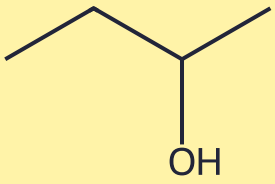
8 Easy

Isomers (constitutional)

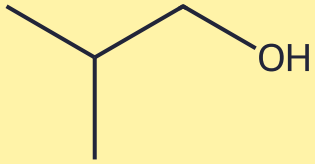
Answer 7: four alcohols and three ethers. Alcohols: butan-1-ol; butan-2-ol; 2-methylpropan-1-ol; 2-methylpropan-2-ol. Ethers: 1-methoxypropane; 2-methoxypropane; ethoxyethane.



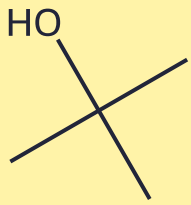
butan-1-ol



butan-2-ol



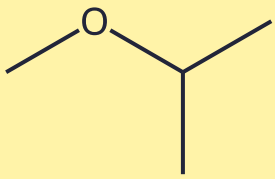
2-methylpropan-1-ol



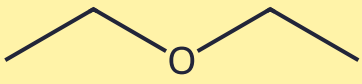
2-methylpropan-2-ol



1-methoxypropane



2-methoxypropane



ethoxyethane

Solution

1. $C_4H_{10}O$ has no rings or pi bonds (it is fully saturated), so the oxygen is either in an O-H group (alcohol) or between two carbons (ether).

2. Alcohols: attach OH to a four-carbon skeleton. Straight chain: OH on C1 or C2 (two isomers). Branched (isobutane skeleton): OH on a primary carbon or on the tertiary carbon (two isomers).
3. Ethers: split the four carbons between two sides of the oxygen as 1 + 3 (propyl or isopropyl: two isomers) or 2 + 2 (one isomer).
4. Total: 4 + 3 = 7.
5. Common mistake: counting both enantiomers of butan-2-ol as separate constitutional isomers (that would give 8). Enantiomers have the same connectivity, so they are stereoisomers, not constitutional isomers.

Exam *Test-level, multi-step*

9 Exam *FC, Lewis, resonance*

Answer (a) Structure 1: C 0, central N +1, terminal N −1. Structure 2: C −1, central N +1, terminal N 0. (b) Structure 1 puts the negative charge on the more electronegative atom (nitrogen rather than carbon), which favors it, but both structures matter: diazomethane has a short, nearly triple N-N bond, so structure 2 is a major contributor too. (c) Both use 16 electrons (4 + 2 x 1 + 5 + 5 = 16).

Solution

1. Structure 1: C has 4 bonds (2 C-H, double bond to N) and no lone pair, so 4 - 0 - 4 = 0. Central N has 4 bonds, no lone pair: 5 - 0 - 4 = +1. Terminal N has a double bond and two lone pairs: 5 - 4 - 2 = −1.
2. Structure 2: carbon has 3 bonds (2 H, 1 N) and one lone pair: 4 - 2 - 3 = −1. Central N has a triple bond: 4 bonds, no lone pair: +1. Terminal N has a triple bond and one lone pair: 5 - 2 - 3 = 0.
3. Both have the same net charge (zero) and full octets, so choose by where the negative charge sits: nitrogen (3.04) accommodates negative charge better than carbon (2.55). This favors structure 1, although the nearly triple N-N bond measured for diazomethane shows structure 2 contributes substantially as well.
4. Electron count: structure 1 has 2 C-H bonds (4 e) + C=N (4 e) + N=N (4 e) + two lone pairs on the terminal N (4 e) = 16. Structure 2 has 2 C-H (4 e) + C-N (2 e) + N#N (6 e) + a lone pair on C (2 e) + a lone pair on the terminal N (2 e) = 16. Both account for every valence electron.
5. Common mistake: drawing C=N=N with no charges. The central N would then have four bonds and no lone pair, so its formal charge is +1, not 0.

10 Exam

BondLine, formula, lone pairs, hybridization

Answer (a) $C_7H_9NO_3$. (b) 7. (c) 3 sp^3, 3 sp^2, 1 sp. (d) The nitrile carbon and the nitrile nitrogen.

Solution

1. Carbons: OCH_3 (3 H), ester C=O (0 H), =CH (1 H), =CH (1 H), CH(OH) (1 H), CH_2 (2 H), C of C#N (0 H). Add 1 H for the OH: 3 + 1 + 1 + 1 + 1 + 2 = 9 H. Atoms: $C_7H_9NO_3$.
2. Lone pairs: nitrile N, 1; carbonyl O, 2; ester (methoxy) O, 2; hydroxyl O, 2. Total 7.
3. sp^3: OCH_3, CH(OH), CH_2 = 3. sp^2: ester carbonyl, the two alkene carbons = 3. sp: nitrile carbon = 1. (3 + 3 + 1 = 7 carbons.)
4. The nitrile carbon (two domains) and the nitrile nitrogen (one sigma bond and one lone pair: two domains) are sp.
5. Common mistake: forgetting the hydrogen on the OH group and on the CH carrying it, which gives a wrong formula, or classifying the carbon next to the nitrile as sp.

11 Exam

Hybrid, VSEPR (amide nitrogen)

Answer (a) Trimethylamine: N is sp^3, trigonal pyramidal. DMF: N is sp^2, trigonal planar. (b) The nitrogen lone pair in DMF is delocalized into the C=O pi system and sits in a p orbital. (c) DMF (about 120 degrees vs about 110 degrees in trimethylamine).

Solution

1. Trimethylamine: three sigma bonds plus one lone pair give four domains, tetrahedral arrangement, pyramidal shape, sp^3 nitrogen.
2. DMF: the carbonyl group is next to nitrogen, so the lone pair on N can overlap with the pi system of C=O (resonance: N^+=C-O^-). A lone pair in conjugation must occupy a p orbital that is parallel to the pi system.
3. A nitrogen with a p-orbital lone pair uses its three remaining orbitals as sp^2 hybrids to form its three sigma bonds, giving a planar nitrogen with angles near 120 degrees.
4. The pyramidal amine angle is about 110 degrees, close to tetrahedral; the lone pair makes it pyramidal rather than flat.
5. Common mistake: assigning hybridization from the atom type alone ("all neutral amine nitrogens are sp^3"). Hybridization depends on whether the lone pair is delocalized.

12 Exam

Length, hybridization and s character

Answer (a) C-C length: ethyne (1.20 A) < ethene (1.34 A) < ethane (1.54 A). C-H length: ethyne (1.06 A) < ethene (1.08 A) < ethane (1.09 A). (b) Propane (about 1.53 A) > propene (about 1.50 A) > propyne (about 1.46 A).

Solution

1. For C-C multiple bonds, the more bonds between the carbons, the shorter and stronger the connection: triple < double < single.
2. For the C-H bonds, compare the hybrid orbital on carbon: sp (50% s), sp^2 (33% s), sp^3 (25% s).
3. An orbital with more s character is held closer to the nucleus (s electrons are lower in energy and closer to the nucleus), so the bond made from it is shorter and stronger.
4. For (b), the same hybridization argument applies to a single bond: CH_3-C(sp^3) is longest, CH_3-C(sp^2) is shorter, CH_3-C(sp) is shortest.
5. Common mistake: attributing the shorter C-H bond in ethyne only to the triple bond. The triple bond is between the carbons; the shorter C-H is due to the carbon's sp hybrid orbital.

13 Exam

Dipole, vector addition (dichloroethenes)

Answer (a) trans-1,2-dichloroethene (zero). (b) cis > 1,1 > trans. (c) cis: 60 degrees; 1,1: 120 degrees; trans: 180 degrees.

Solution

1. Each carbon is sp^2, so the substituents are about 120 degrees apart around each carbon, and the molecule is planar.
2. Trans isomer: the two C-Cl bonds are antiparallel (180 degrees); the dipoles cancel and the net dipole is zero.
3. Cis isomer: the two C-Cl vectors are 60 degrees apart, so the net is 2 x cos(30 degrees) = 1.73 times a single bond dipole.
4. 1,1-Isomer: both Cl are on the same carbon, 120 degrees apart, net = 2 x cos(60 degrees) = 1.0 times a single bond dipole.
5. So cis (1.73) > 1,1 (1.0) > trans (0), consistent with measured values of about 1.9 D, 1.3 D and 0 D.
6. Common mistake: concluding that the isomer with both Cl atoms on the same carbon must be the most polar. The angle between the vectors matters, not which carbon holds them.

14 Exam

IMF, boiling point ranking

Answer butan-1-ol (about 118 degrees C) > butanal (about 75 degrees C) > pentane (about 36 degrees C) > 2,2-dimethylpropane (about 9.5 degrees C).

Solution

1. With molar masses similar, the intermolecular forces differ in type and strength.
2. Butan-1-ol has an O-H group that is both a hydrogen-bond donor and acceptor: the strongest attraction.
3. Butanal has a polar C=O bond, so it has dipole-dipole attractions, but it has no O-H, so it cannot hydrogen-bond to itself.
4. Pentane and 2,2-dimethylpropane are nonpolar and have only London dispersion forces.
5. Of these two, the straight-chain isomer has more surface area in contact with neighbors; the compact, nearly spherical branched isomer has a smaller contact area and weaker dispersion forces, so it boils lower.
6. Common mistake: ranking by molar mass, which is nearly the same here. Another is thinking butanal can hydrogen-bond with itself; its C-H hydrogens are not hydrogen-bond donors.

15 Exam

Solub

Answer (a) water (hydrogen bonding). (b) water (ion-dipole). (c) hexane (dispersion forces with the long hydrocarbon chain). (d) hexane (dispersion). Top layer: hexane.

Solution

1. Use "like dissolves like": polar and ionic solutes dissolve in polar water; nonpolar solutes dissolve in nonpolar hexane.
2. Glycerol has three OH groups, each a hydrogen-bond donor and acceptor, so it is extremely water-soluble.
3. Potassium acetate is an ionic salt: water solvates K^+ and acetate with ion-dipole interactions and hydrogen bonds; hexane cannot.
4. Dodecan-1-ol has a polar OH head, but the 12-carbon chain is a large hydrophobic region; one OH cannot pull that much hydrocarbon into water, so it prefers hexane.
5. Heptane is nonpolar and goes to hexane.
6. Hexane is less dense than water, so it forms the top layer.
7. Common mistake: concluding that every alcohol is water soluble. Water solubility drops quickly as the nonpolar chain grows (around 5 or more carbons per OH group).

16 Exam

Hybrid, VSEPR, SigmaPi (multi-center)

Answer (a) C1 sp^2, C2 sp^2, C3 sp, C4 sp, C5 sp^3. (b) C2, C3, C4 and C5. (c) About 120 degrees at C2, 180 degrees at C3 and at C4. (d) 10 sigma, 3 pi. (e) C2-C3 (sp^2-sp) is shorter than C4-C5 (sp-sp^3).

Solution

1. Count domains: C1 and C2 are alkene carbons with 3 domains (sp^2). C3 and C4 are alkyne carbons with 2 domains (sp). C5 has 4 domains (sp^3).
2. An sp carbon has a 180 degrees bond angle. C3 is bonded to C2 and C4; C4 is bonded to C3 and C5. So C2-C3-C4 and C3-C4-C5 are both linear, and C2, C3, C4, C5 are all on one line.
3. C2 is sp^2, so C1=C2-C3 is about 120 degrees.
4. There are 11 atoms (5 C and 6 H); a molecule with no rings has 10 sigma bonds (one fewer than the number of atoms), and the double and triple bonds contribute 1 + 2 = 3 pi bonds.
5. A single bond is shorter when its carbons have more s character: C2-C3 joins sp^2 to sp (average about 42% s), C4-C5 joins sp to sp^3 (average 37.5% s), so C2-C3 is the shorter one.
6. Common mistake: counting only three carbons as collinear, forgetting that the methyl carbon attached to an sp carbon sits on the same line, and also the alkene carbon C2.

17 Exam

Lewis, FC, VSEPR (change in hybridization)

Answer (a) BF_3: B has 3 single bonds and 6 electrons, all formal charges zero. Adduct: N +1, B −1. (b) BF_3: B is sp^2 and trigonal planar; adduct: B is sp^3 and tetrahedral. (c) 120 degrees before, about 109.5 degrees after. (d) BF_3 is electron-deficient (6 electrons around B, an empty p orbital) and accepts the nitrogen lone pair.

Solution

1. In BF_3, boron (3 valence electrons) forms 3 single bonds, so formal charge 3 - 0 - 3 = 0. It has only 6 electrons, an incomplete octet.
2. Three electron domains: sp^2, trigonal planar, with an empty p orbital perpendicular to the plane.
3. Ammonia's lone pair forms a new N-B bond using the empty p orbital. Nitrogen now has 4 bonds: 5 - 0 - 4 = +1. Boron now has 4 bonds: 3 - 0 - 4 = −1. The adduct is neutral overall.
4. Boron now has four domains: sp^3, tetrahedral, F-B-F angle near 109.5 degrees.
5. The octet at boron is completed, which is the driving force.
6. Common mistake: keeping the 120 degrees angle or the sp^2 label after the lone pair has been donated, or forgetting that formal charges appear when both electrons of the new bond come from nitrogen.

18 Exam

Isomers (constitutional), unsaturation

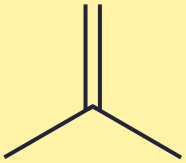
Answer 5 constitutional isomers. Alkenes: but-1-ene, but-2-ene, 2-methylpropene. Cycloalkanes: cyclobutane, methylcyclopropane. cis- and trans-but-2-ene are one constitution (stereoisomers), so they are not counted separately.



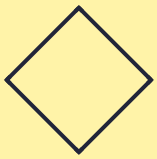
but-1-ene



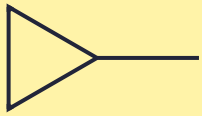
but-2-ene



2-methylpropene



cyclobutane



methylcyclopropane

Solution

1. Degrees of unsaturation for C_4H_8: (2 x 4 + 2 - 8) / 2 = 1, so each isomer has either one ring or one double bond.
2. One double bond, four carbons: the double bond can be terminal (but-1-ene) or internal (but-2-ene) in a straight chain, or in a branched skeleton (2-methylpropene). That gives three.
3. One ring: a four-membered ring (cyclobutane) or a three-membered ring with a methyl group (methylcyclopropane). That gives two.
4. Total: 3 + 2 = 5.
5. Common mistake: counting cis- and trans-but-2-ene as two constitutional isomers (giving 6). They have the same connectivity and differ only in spatial arrangement.

19 Challenge

Lewis, FC, VSEPR, Hybrid (isoelectronic species)

Answer (a) O3: 3 x 6 = 18. NO_2^-: 5 + 6 + 6 + 1 = 18. (b) O3: central O +1, one terminal O −1 (single bond) and one terminal O 0 (double bond); the two forms differ by swapping which terminal oxygen is double-bonded. NO_2^-: N 0, single-bonded O −1, double-bonded O 0; again two equivalent forms. (c) Central atom sp^2, bent, a bit less than 120 degrees (about 117 degrees in O3, about 115 degrees in NO_2^-). (d) The two terminal bonds are identical, with bond order 1.5. (e) CO_2 has no lone pair on the central atom; O3 and NO_2^- have one.

Solution

1. Count: O3 has 18 e-; NO_2^- has 5 + 12 + 1 (negative charge) = 18 e-.
2. Ozone: central O makes one single and one double bond and has one lone pair: 6 - 2 - 3 = +1. Terminal O with a double bond has two lone pairs: 6 - 4 - 2 = 0. Terminal O with a single bond has three lone pairs: 6 - 6 - 1 = −1.
3. Nitrite: N has one single, one double bond and one lone pair: 5 - 2 - 3 = 0. Singly bonded O: −1; doubly bonded O: 0.
4. Both resonance forms are equally good, so the real structure is an average: both terminal bonds are identical, intermediate between single and double (bond order 1.5, and the negative charge is shared).
5. The central atom has three domains (two bonded atoms and one lone pair), so sp^2 and trigonal planar electron geometry; the lone pair makes the shape bent and slightly compresses the angle below 120 degrees.
6. CO_2 has 16 electrons and the central carbon has only two domains and no lone pair, so linear.
7. Common mistake: drawing one single and one double bond and claiming the two O-O (or N-O) bonds have different lengths. Resonance structures are not real equilibrating species; the hybrid has equal bonds.

20 Challenge

Hybrid, lone pairs (nitrogen heterocycles)

Answer (a) Pyridine N: sp^2. Pyrrole N: sp^2. Piperidine N: sp^3. Imidazole: both N atoms are sp^2. (b) Pyridine N: lone pair in an in-plane sp^2 orbital, not in the pi system. Pyrrole N (N-H): lone pair in a p orbital, part of the pi system. Piperidine N: lone pair in an sp^3 orbital. Imidazole: N-H nitrogen has its lone pair in the pi system; the other nitrogen has an in-plane lone pair. (c) 6 pi electrons in each.

Solution

1. Pyridine: nitrogen is part of the planar ring and double bonded to a carbon (one sigma + one pi). Its domains: two sigma bonds + one lone pair = 3, sp^2. The pi bond uses a p orbital; the lone pair sits in an sp^2 orbital pointing outward in the plane, so it does not belong to the pi system. Pi electrons: three C=C/C=N double bonds = 6.
2. Pyrrole: the N-H nitrogen has two ring bonds and one N-H bond (three sigma bonds) so it is sp^2 and planar. Its lone pair occupies the p orbital and overlaps with the four ring carbon p orbitals: pi electrons = 4 (from two C=C) + 2 (lone pair) = 6.
3. Piperidine: all bonds are single; nitrogen has three sigma bonds and one lone pair: sp^3, pyramidal.
4. Imidazole has one "pyrrole-type" nitrogen (N-H, lone pair in the pi system) and one "pyridine-type" nitrogen (C=N, in-plane lone pair). Pi electrons: 4 (two C=C/C=N pi bonds) + 2 (lone pair from N-H) = 6.
5. Common mistake: assigning sp^3 to pyrrole's nitrogen because it carries H and a lone pair. In a conjugated planar ring a lone pair that participates in the pi system forces sp^2.

21 Challenge

Dipole, vector addition (dichlorobenzenes)

Answer (a) ortho (1,2): 2.77 D; meta (1,3): 1.6 D; para (1,4): 0 D. (b) ortho > meta > para. (c) Substituents interact (induced dipoles in the ring, repulsion between adjacent Cl), so simple vector addition is only an approximation.

Solution

1. The C-Cl bonds point radially outward from the ring center. Substituents on adjacent ring atoms (ortho) are 60 degrees apart, meta substituents are 120 degrees apart and para substituents are 180 degrees apart.
2. Net dipole for two equal vectors of size m at angle theta: 2m cos(theta/2).
3. Ortho: 2 x 1.6 x cos(30 degrees) = 2 x 1.6 x 0.866 = 2.77 D.
4. Meta: 2 x 1.6 x cos(60 degrees) = 2 x 1.6 x 0.5 = 1.6 D.
5. Para: 2 x 1.6 x cos(90 degrees) = 0; the two vectors are antiparallel.
6. Real measurements are close to, but not equal to, the vector-sum prediction because bond dipoles are not perfectly additive.
7. Common mistake: writing 120 degrees for ortho (the interior ring angle) rather than the 60 degrees between the outward-pointing C-Cl bonds.

22 Challenge

IMF, boiling point ranking (isomers)

Answer pentan-1-ol (about 138 degrees C) > 2-methylbutan-2-ol (about 102 degrees C) > 1-methoxybutane (about 70 degrees C) > pentane (about 36 degrees C).

Solution

1. The first three are constitutional isomers ($C_5H_{12}O$); pentane (C_5H_{12}) has lower molar mass and is nonpolar.
2. Only the two alcohols can donate and accept hydrogen bonds, which are stronger than dipole-dipole forces; so they boil higher than the ether and pentane.
3. Between the alcohols: pentan-1-ol is a straight chain with an unhindered OH group and a large surface area for dispersion forces. In 2-methylbutan-2-ol the OH is on a tertiary carbon, crowded by three alkyl groups, and the molecule is more compact; hydrogen bonding and dispersion contacts are both reduced.
4. The ether has a polar C-O-C unit and dipole-dipole attractions but no O-H, so it cannot donate hydrogen bonds to its own kind; it boils well below both alcohols.
5. Pentane has only dispersion forces and the lowest boiling point.
6. Common mistake: ranking all isomers equal because they share the same formula, or assuming the tertiary alcohol, being more branched, boils lower than the ether (hydrogen bonding outweighs the shape effect here).

23 Challenge

SigmaPi, Hybrid, BondLine

Answer (a) $C_9H_{10}O$. (b) 20 sigma, 4 pi. (c) 2 sp, 3 sp^2, 4 sp^3. (d) 7 C(sp^3)-H, 2 C(sp^2)-H, 1 C(sp)-H. (e) 2.

Solution

1. Carbons: CHO (1), ring (6), ethynyl (2) = 9. Hydrogens: CHO 1; ring: =CH 1, CH_2 2, CH 1, CH_2 2, CH_2 2 = 8; ethynyl CH 1. Total 10 H. Formula $C_9H_{10}O$.
2. Atoms: 9 C + 10 H + 1 O = 20. A structure with one ring has as many sigma bonds as atoms: 20 sigma bonds. (A tree would have 19; the ring adds one.)
3. Pi bonds: C=O (1), ring C=C (1), C#C (2) = 4.
4. Hybridization: alkyne carbons sp (2); aldehyde carbon and the two alkene ring carbons sp^2 (3); the other four ring carbons (CH_2, CH, CH_2, CH_2) sp^3 (4). Total 9.
5. C-H bonds: sp^3 carbons have 2 + 1 + 2 + 2 = 7 H; sp^2 carbons have 1 (CHO) + 1 (=CH) = 2 H; sp has 1 H. Total 10.
6. Lone pairs: only oxygen has any, 2.
7. Common mistake: treating the ring as acyclic and getting 19 sigma bonds, or assigning the ring carbon bearing the alkyne as sp.

24 Challenge

Hybrid, VSEPR, orbitals (allene)

Answer (a) Terminal carbons sp^2, central carbon sp; C=C=C is 180 degrees. (b) The two pi bonds are perpendicular, so the two CH_2 planes are twisted 90 degrees relative to each other. (c) No, not planar (the two CH_2 groups lie in perpendicular planes); no net dipole, by symmetry. (d) In butadiene the p orbitals on all four carbons are parallel and the molecule can be planar.

Solution

1. The central carbon forms two sigma bonds (one to each neighbor) and no lone pair: two domains, sp; it has two unhybridized p orbitals at right angles to each other, both perpendicular to the molecular axis.
2. Each terminal carbon has three sigma bonds: sp^2, with one unhybridized p orbital.
3. The pi bond C1=C2 uses the p orbital on C2 that lies in one plane (say y); the pi bond C2=C3 must use the other p orbital on C2 (z). Pi bonds need parallel p orbitals, so the p orbitals on C1 and C3 are also perpendicular to each other.
4. Each CH_2 group's plane is perpendicular to the p orbital of its carbon, so the two CH_2 planes are perpendicular to each other: the molecule is nonplanar.
5. The molecule has D2d symmetry: the dipoles of the two CH_2 groups lie along the molecular axis, point in opposite directions and cancel, so the net dipole is zero.
6. In 1,3-butadiene, the four p orbitals are all parallel (perpendicular to the molecular plane), so they can overlap in a continuous row and the carbon skeleton can be planar.
7. Common mistake: drawing allene as a planar molecule with all hydrogens in one plane.

25 Challenge

Dipole, EN, hybridization effect

Answer (a) Carbon becomes more electronegative as its s character increases (sp > sp^2 > sp^3). The methyl-to-unsaturated-carbon bond is polarized toward the more electronegative sp^2 or sp carbon, and the effect is larger for sp. (b) The methyl end is delta-plus (the alkyne end is delta-minus). (c) More delta-plus: the sp carbon pulls electron density from hydrogen more strongly than an sp^3 carbon does.

Solution

1. Propane is almost symmetric and has essentially no bond polarity (C-C and C-H differences are small), so its dipole is close to zero.
2. In propene and propyne, one carbon of the C-C bond to the methyl group is sp^2 or sp. An orbital with more s character holds its electrons closer to the nucleus, so the sp or sp^2 carbon is more electronegative than an sp^3 carbon.
3. This polarizes the CH_3-C single bond with the methyl group at the delta-plus end. The greater the s character, the larger the polarity: 50% (sp) > 33% (sp^2) > 25% (sp^3).
4. The net dipole points from the CH_3 end toward the unsaturated end, which explains the order 0.78 > 0.36 > 0.08 D.
5. For the C-H bond itself, the more electronegative sp carbon polarizes it more, which means the H on an sp carbon is more delta-plus. (This is the same effect that makes alkyne C-H bonds more acidic than alkene or alkane C-H bonds.)
6. Common mistake: thinking that an overall dipole needs a heteroatom. Differences in carbon hybridization alone can produce a measurable (though small) dipole.