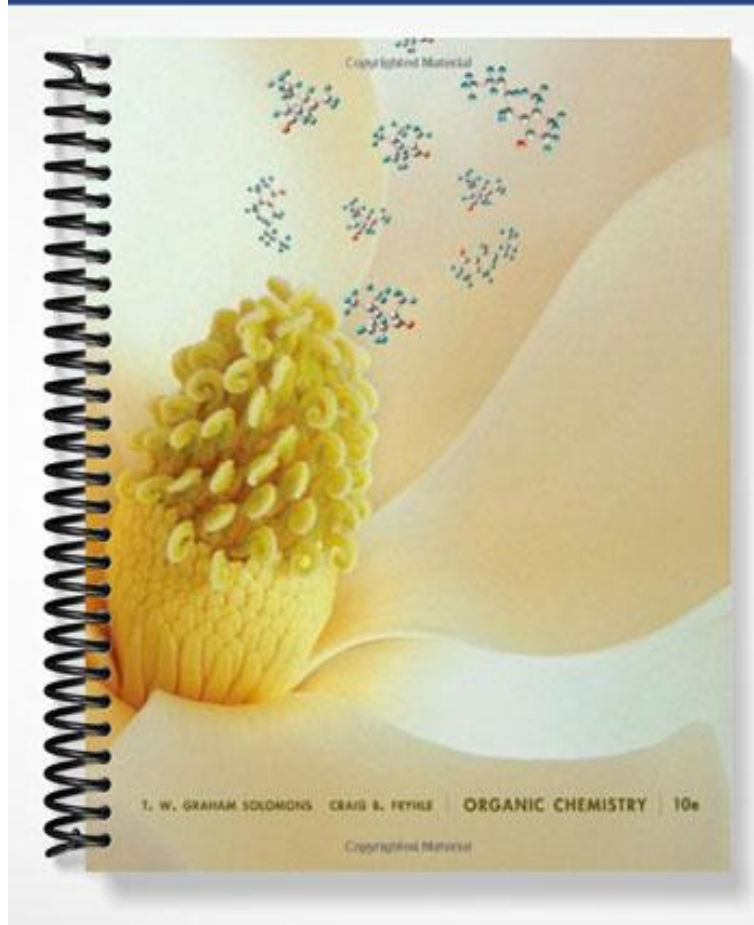


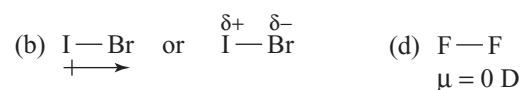
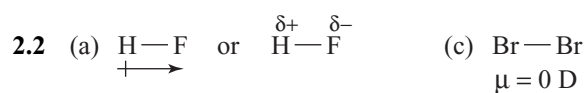
SOLUTIONS MANUAL



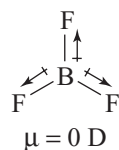
2 FAMILIES OF CARBON COMPOUNDS: FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY

SOLUTIONS TO PROBLEMS

2.1 The four carbon atoms occupy different positions in the two representations (cf. rule 2, Sec. 1.8A).

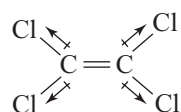


2.3 VSEPR theory predicts a planar structure for BF_3 .

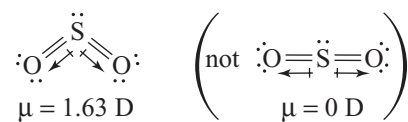


The vector sum of the bond moments of a trigonal planar structure would be zero, resulting in a prediction of $\mu = 0 \text{ D}$ for BF_3 . This correlates with the experimental observation and confirms the prediction of VSEPR theory.

2.4 The shape of $\text{CCl}_2=\text{CCl}_2$ (below) is such that the vector sum of all of the C—Cl bond moments is zero.



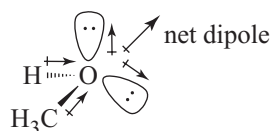
2.5 The fact that SO_2 has a dipole moment indicates that the molecule is angular, not linear.



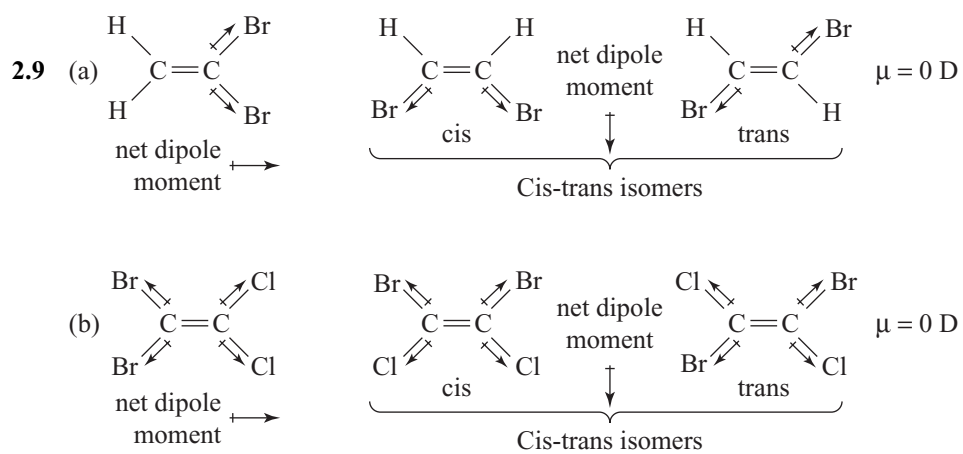
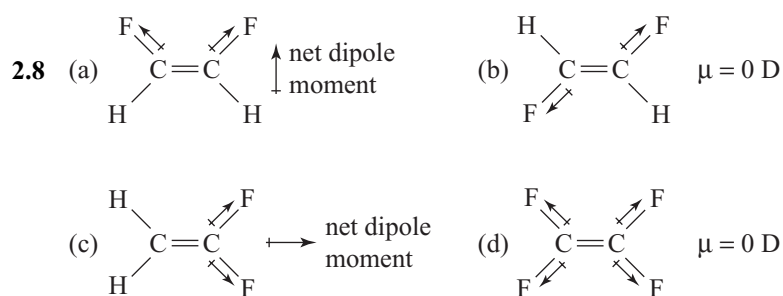
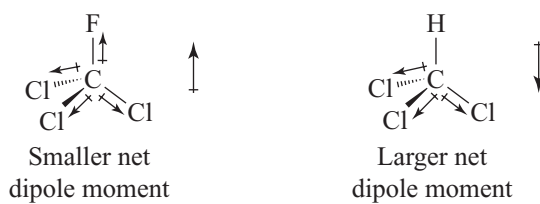
An angular shape is what we would expect from VSEPR theory, too.

FAMILIES OF CARBON COMPOUNDS 21

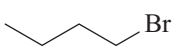
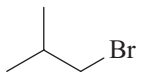
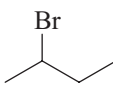
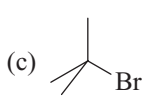

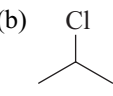
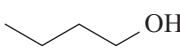
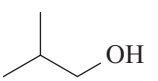
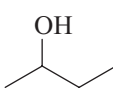
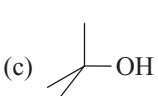
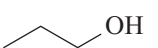
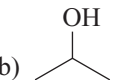
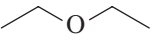
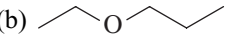
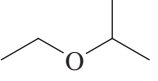
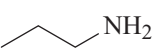
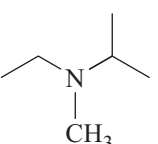
2.6 Again, this is what VSEPR theory predicts.



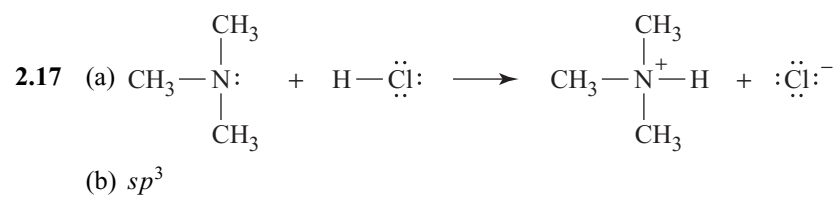
2.7 In CFCl_3 the large $\text{C}-\text{F}$ bond moment opposes the $\text{C}-\text{Cl}$ moments, leading to a net dipole moment in the direction of the fluorine. Because hydrogen is much less electronegative than fluorine, no such opposing effect occurs in CHCl_3 ; therefore, it has a net dipole moment that is larger and in the direction of the chlorine atoms.



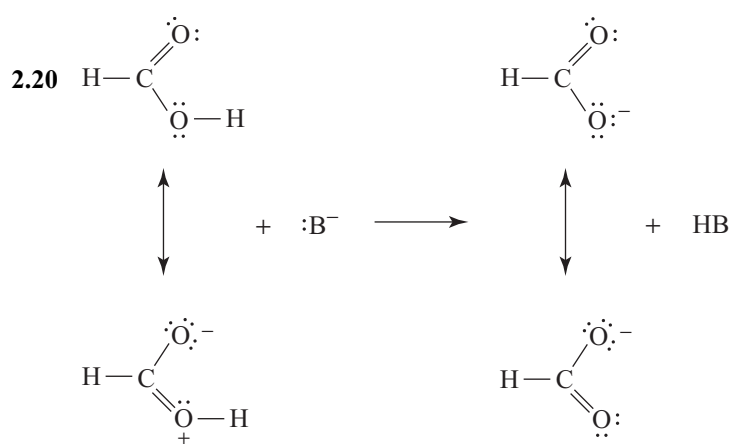
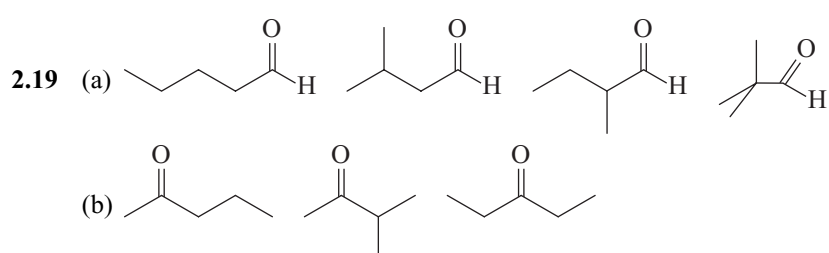
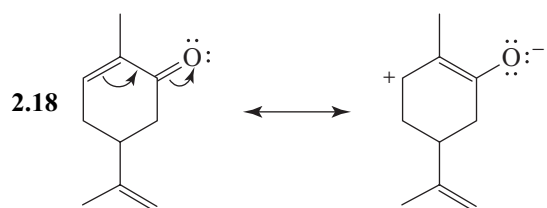
22 FAMILIES OF CARBON COMPOUNDS

- 2.10 (a)  and 
- (b)  (c) 
- 2.11 (a)  (b) 
- (c) Propyl bromide (d) Isopropyl fluoride
 (e) Phenyl iodide
- 2.12 (a)  and 
- (b)  (c) 
- 2.13 (a)  (b) 
- 2.14 (a)  (b) 
- (c)  (d) Methyl propyl ether
 (e) Diisopropyl ether (f) Methyl phenyl ether
- 2.15 (a) Isopropylpropylamine (b) Tripropylamine
 (c) Methylphenylamine (d) Dimethylphenylamine
 (e)  (f) $\text{CH}_3-\text{N}(\text{CH}_3)_2$ or $(\text{CH}_3)_3\text{N}$
- (g) 

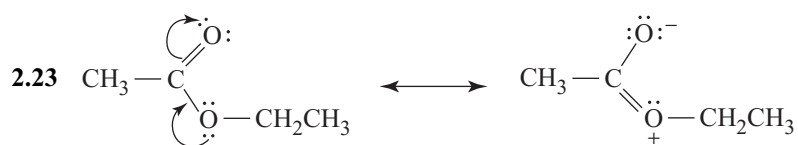
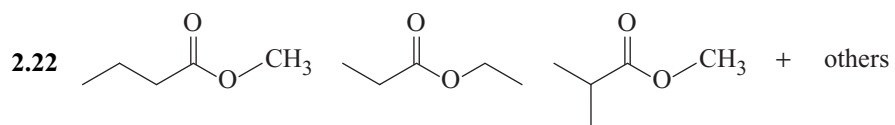
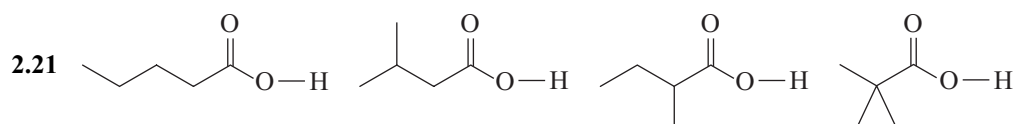
- 2.16 (a) (e) only (b) (a, c) (c) (b, d, f, g)



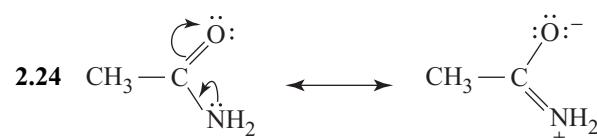
FAMILIES OF CARBON COMPOUNDS 23

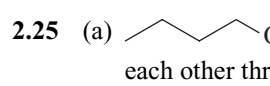


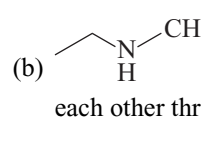
The formate ion is more stabilized by resonance because its two resonance structures are equivalent (Rule 4, Sec. 1.8A).

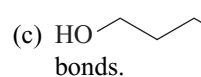


24 FAMILIES OF CARBON COMPOUNDS



2.25 (a)  would boil higher because its molecules can form hydrogen bonds to each other through the $\text{—}\ddot{\text{O}}\text{—H}$ group.

(b)  would boil higher because its molecules can form hydrogen bonds to each other through the $\text{—}\ddot{\text{N}}\text{—H}$ group.

(c)  because by having two $\text{—}\ddot{\text{O}}\text{—H}$ groups, it can form more hydrogen bonds.

2.26 Cyclopropane would have the higher melting point because its cyclic structure gives it a rigid compact shape that would permit stronger crystal lattice forces.

2.27 $d < a < b < c$

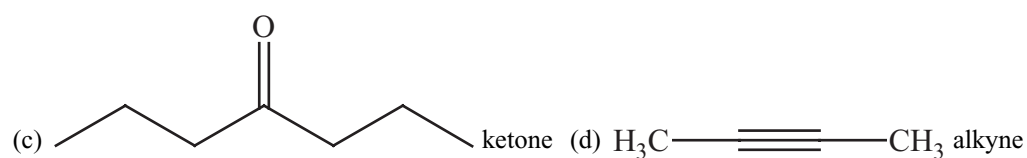
(c) has the highest boiling point due to hydrogen bonding involving its O—H group.

(b) is a polar molecule due to its C=O group, hence higher boiling than the essentially non-polar (a) and (d).

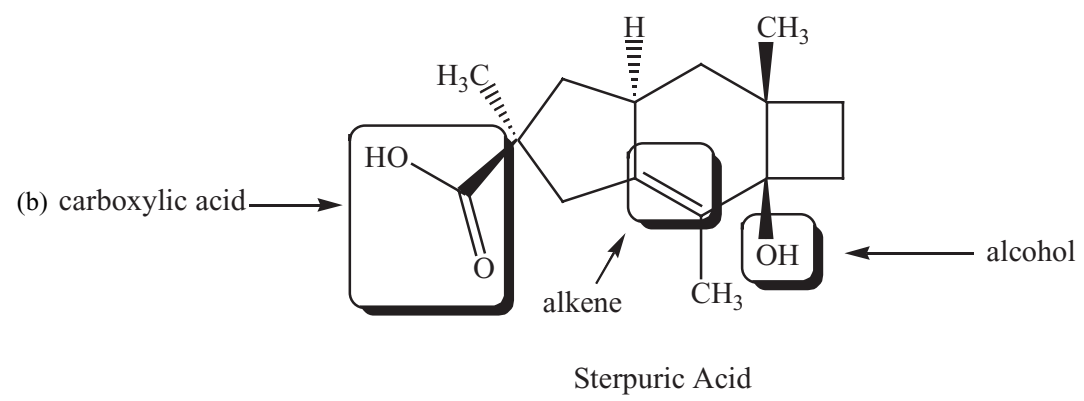
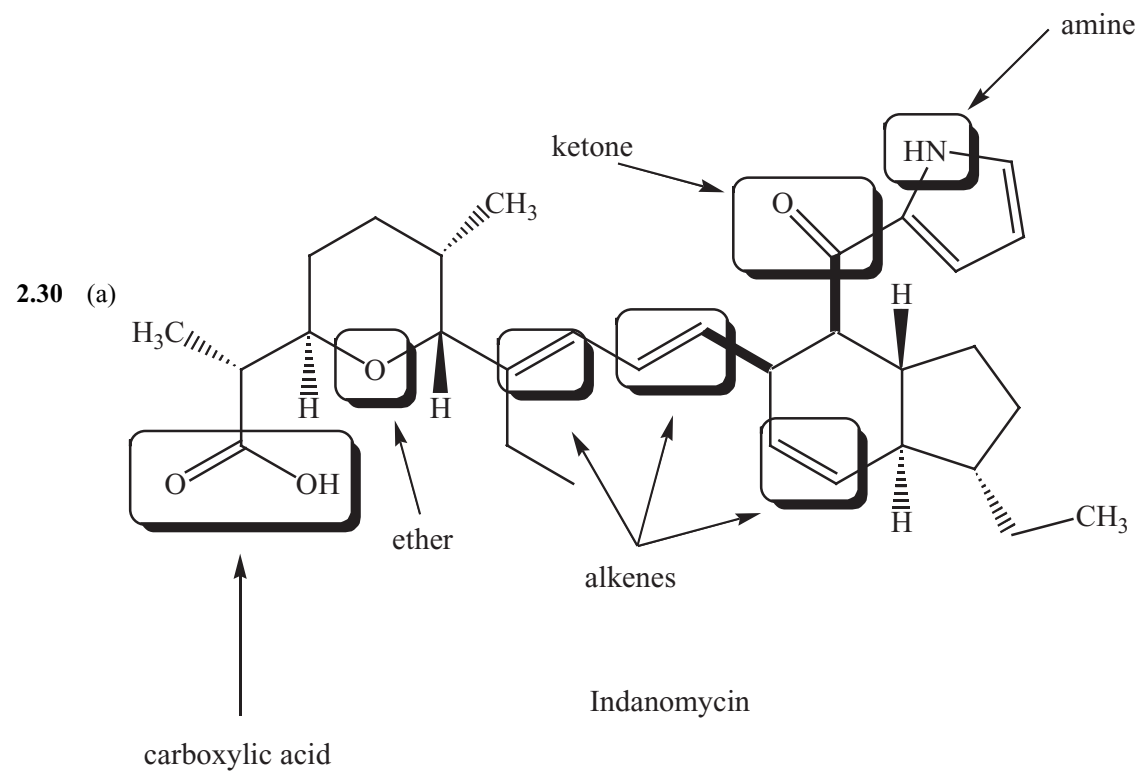
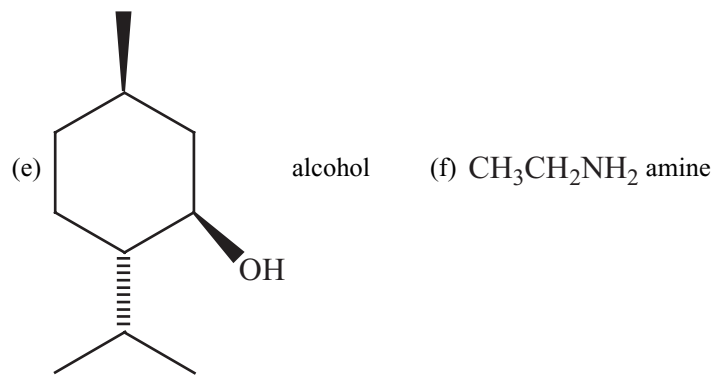
(a) has a higher boiling point than (d) because its unbranched structure permits more van der Waals attractions.

2.28 If we consider the range for carbon-oxygen double bond stretching in an aldehyde or ketone to be typical of an unsubstituted carbonyl group, we find that carbonyl groups with an oxygen or other strongly electronegative atom bonded to the carbonyl group, as in carboxylic acids and esters, absorb at somewhat higher frequencies. On the other hand, if a nitrogen atom is bonded to the carbonyl group, as in an amide, then the carbonyl stretching frequency is lower than that of a comparable aldehyde or ketone. The reason for this trend is that strongly electronegative atoms increase the double bond character of the carbonyl, while the unshared electron pair of an amide nitrogen atom contributes to the carbonyl resonance hybrid to give it less double bond character.

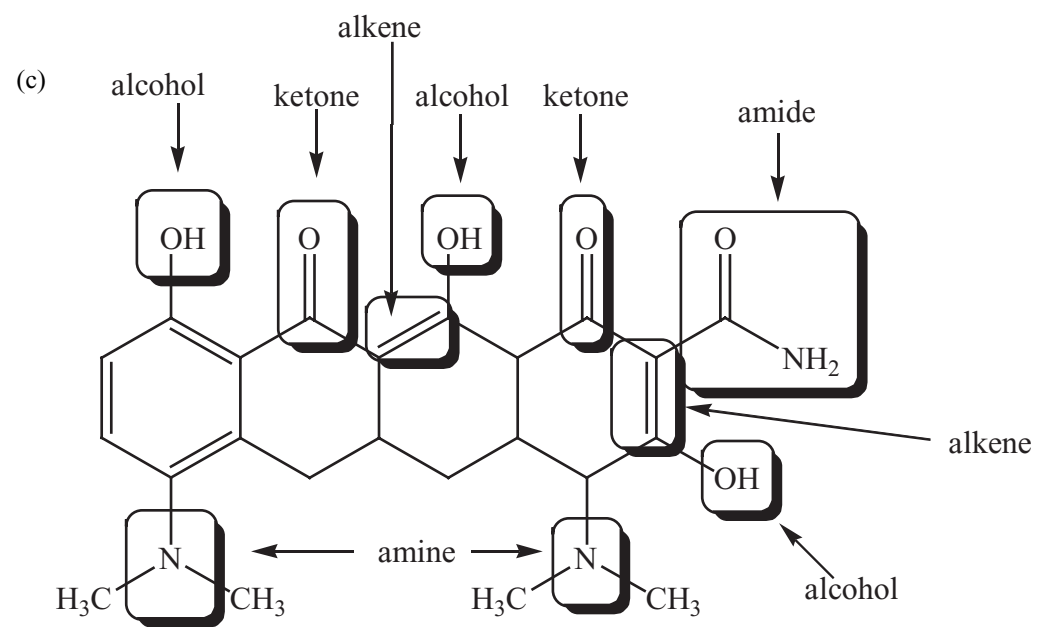
Functional Groups and Structural Formulas



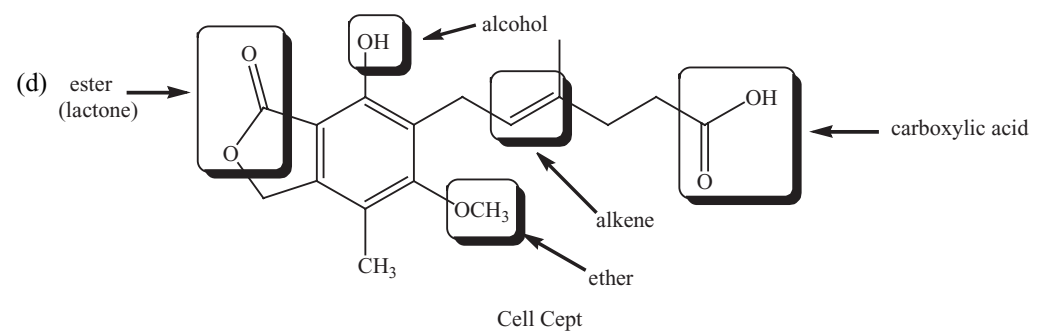
FAMILIES OF CARBON COMPOUNDS 25



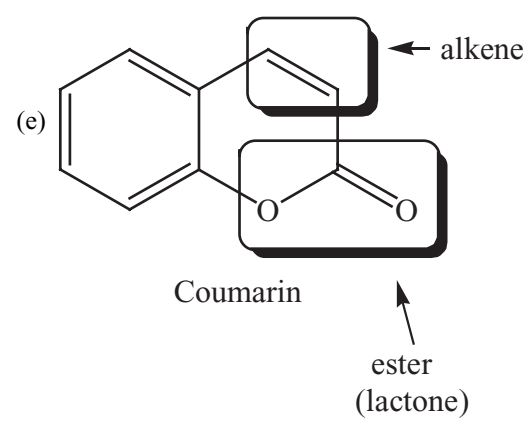
26 FAMILIES OF CARBON COMPOUNDS



Solodyn

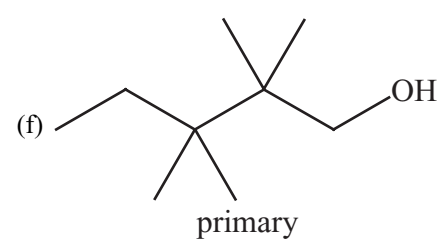
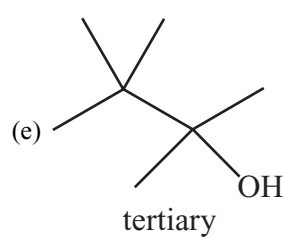
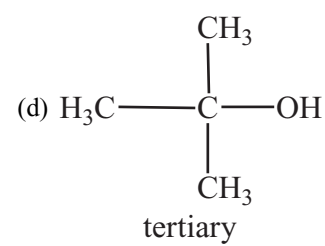
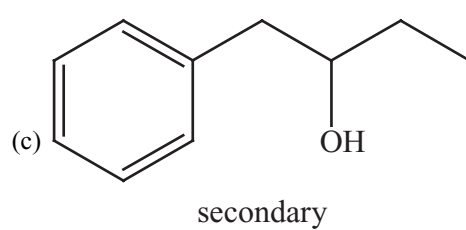
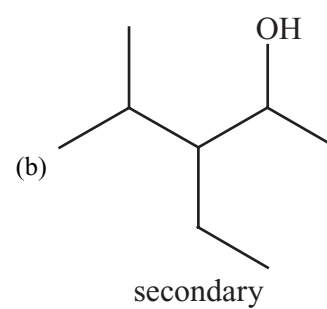
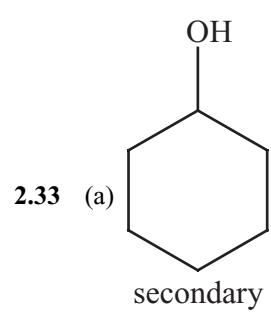
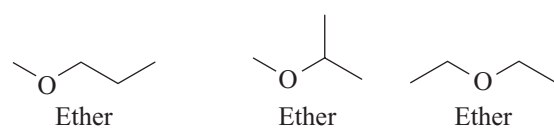
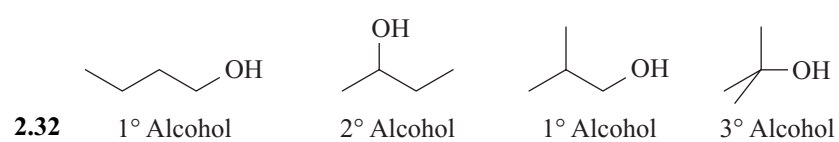
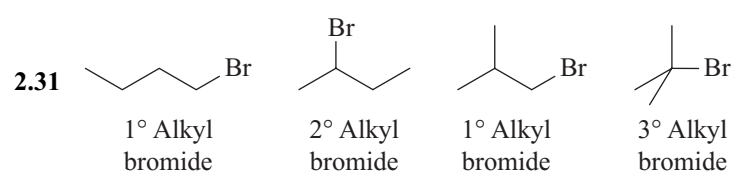


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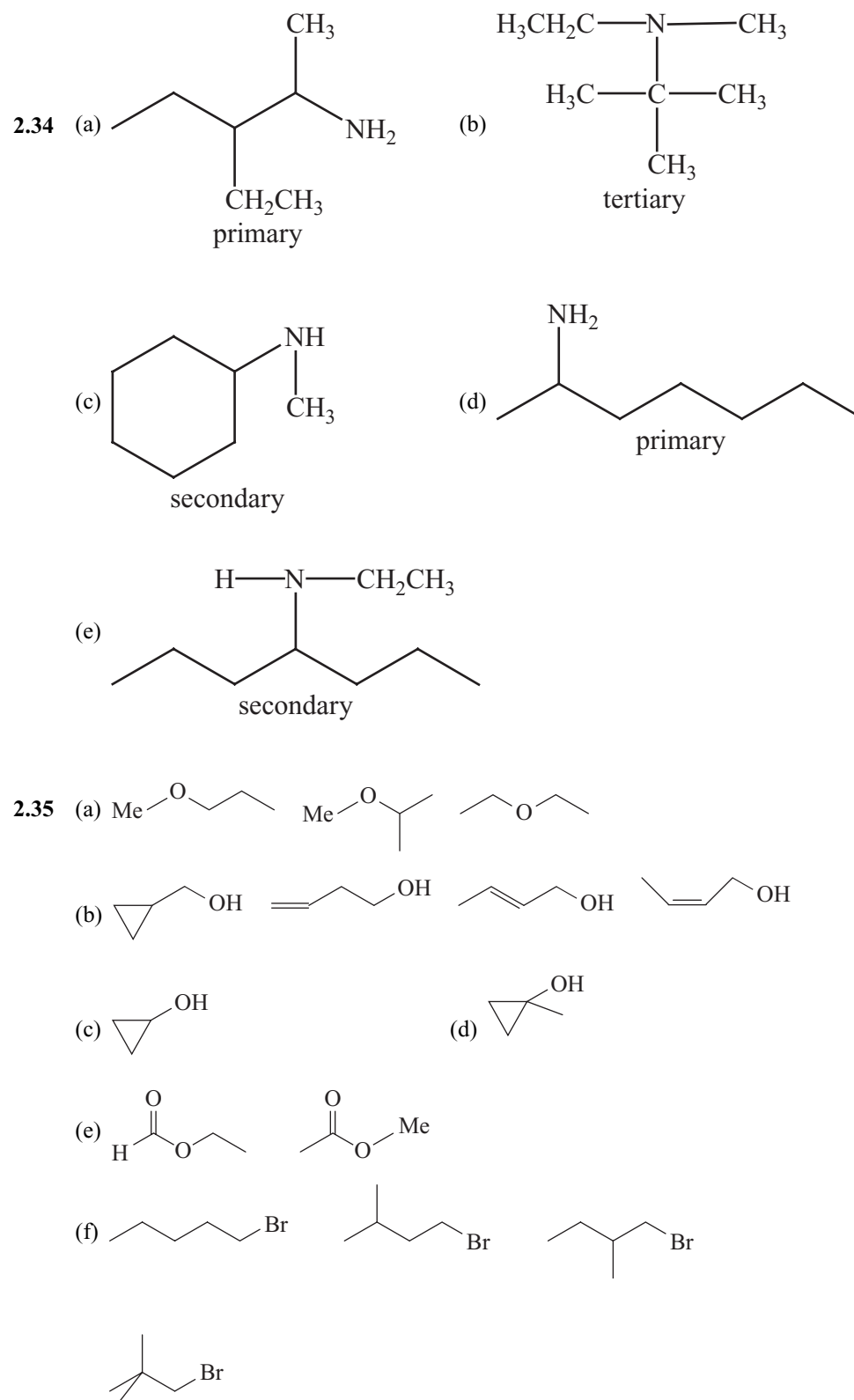


Coumarin

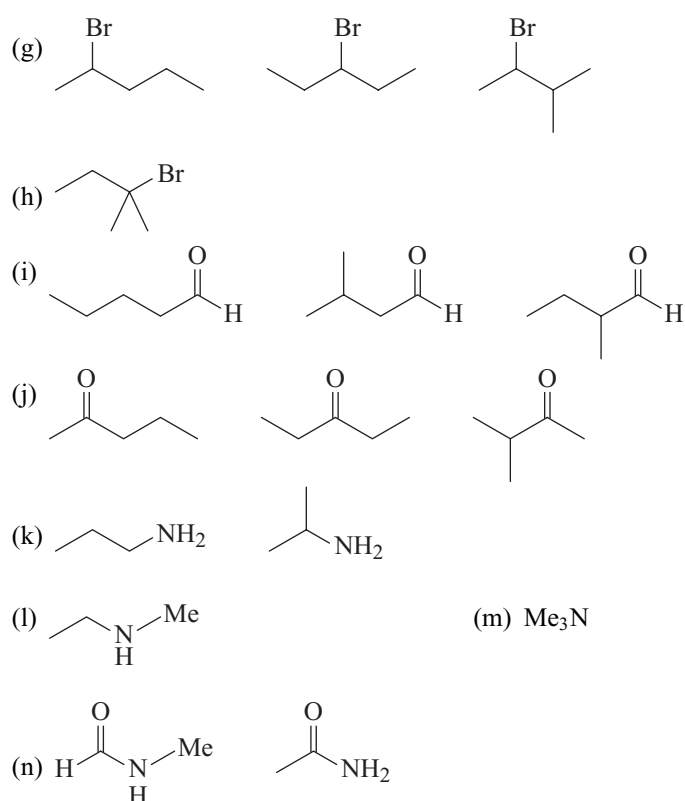
FAMILIES OF CARBON COMPOUNDS 27



28 FAMILIES OF CARBON COMPOUNDS



FAMILIES OF CARBON COMPOUNDS 29



Physical Properties

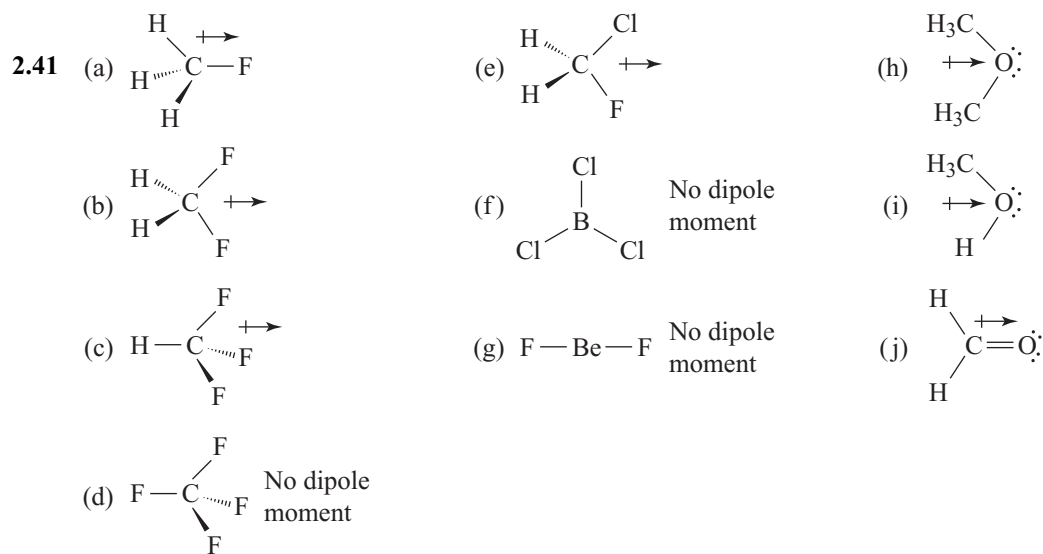
- 2.36** Explain why 1-pentanol has a solubility of 2.7 grams per 100 mL of water whereas methanol is completely miscible in water.
1-pentanol contains five (5) carbons while methanol has only one (1) carbon. The —OH group in 1-pentanol does confer some water solubility (like-dissolves-like) however, with the hydrocarbon portion of the molecule being rather large (C_5H_{11} —) the molecule looks mostly like “grease”, mostly like an alkane, which would have no water solubility. Methanol does not look as much like an alkane; half alkane and half water. In methanol the —OH group (aids water solubility) is a larger contributor to the overall structure.
- 2.37** The attractive forces between hydrogen fluoride molecules are the very strong dipole-dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of an ethyl fluoride molecule is buried in the ethyl group and is shielded by the surrounding electrons. Thus the positive end of one hydrogen fluoride molecule can approach the negative end of another hydrogen fluoride molecule much more closely, with the result that the attractive force between them is much stronger.)
- 2.38** The cis isomer is polar while the trans isomer is nonpolar ($\mu = 0$ D). The intermolecular attractive forces are therefore greater in the case of the cis isomer, and thus its boiling point should be the higher of the two.

30 FAMILIES OF CARBON COMPOUNDS

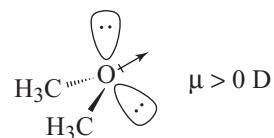
2.39 Explain why the boiling point of 2,2-dimethylbutane (49.7°C) is lower than the boiling point of hexane (69°C) despite the fact that they have the same molecular formula, C₆H₁₄.

Hexane is a linear, unbranched alkane. Because of the lack of branching, the hexane chains can get close to one another. The intermolecular attractive forces, although rather weak, can reinforce each other resulting in the chains being held together more closely. As energy is supplied, as heat, it first goes to getting the hexane chains apart or away from one another and then into the vapor phase. 2,2-dimethylbutane is a branched hexane constitutional isomer. Because of the high degree of branching the chains cannot get close to one another, and thus are not held together as tightly as in hexane. When energy is supplied as heat, it does not have to initially get the chains apart from one another, since they are not held so closely together, resulting in the lower boiling point.

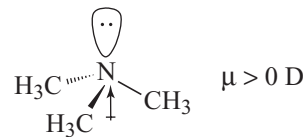
2.40 (a) and (b) are polar and hence are able to dissolve ionic compounds. (c) and (d) are non-polar and will not dissolve ionic compounds.



2.42 (a) Dimethyl ether: There are four electron pairs around the central oxygen: two bonding pairs and two nonbonding pairs. We would expect *sp*³ hybridization of the oxygen with a bond angle of approximately 109.5° between the methyl groups.

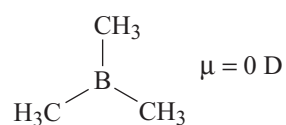


(b) Trimethylamine: There are four electron pairs around the central nitrogen: three bonding pairs and one nonbonding pair. We would expect *sp*³ hybridization of the nitrogen with a bond angle of approximately 109.5° between the methyl groups.

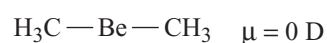


FAMILIES OF CARBON COMPOUNDS 31

- (c) Trimethylboron: There are only three bonding electron pairs around the central boron. We would expect sp^2 hybridization of the boron with a bond angle of 120° between the methyl groups.



- (d) Dimethylberyllium: There are only two bonding electron pairs around the central beryllium atom. We would expect sp hybridization of the beryllium atom with a bond angle of 180° between the methyl groups.



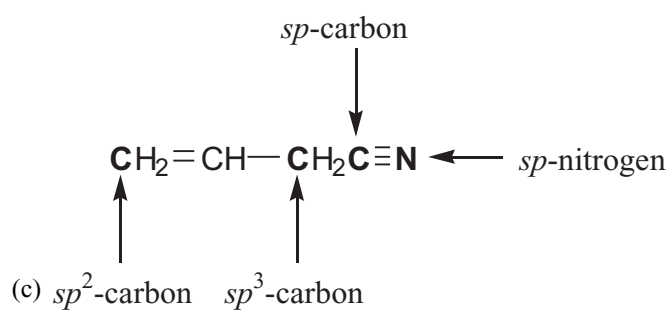
- 2.43 This is a special case of a Lewis acid (Ag^+) – Lewis base (alkene) reaction. The product

can be represented by $\left[\begin{array}{c} \diagup \text{C} \diagdown \\ \parallel \\ \text{C} \\ \parallel \\ \text{C} \\ \diagdown \end{array} \text{Ag} \right]^+$. The filled π orbital of the alkene overlaps with the

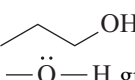
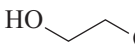
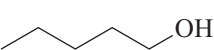

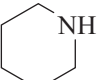
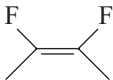
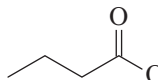
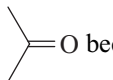

empty $5s$ orbital of Ag^+ to form a σ bond. A π bond results from the overlap of the filled $4d$ orbital of Ag^+ with an empty antibonding π^* orbital of the alkene.

- 2.44 Without one (or more) polar bonds, a molecule cannot possess a dipole moment and, therefore, it cannot be polar. If the bonds are directed so that the bond moments cancel, however, the molecule will not be polar even though it has polar bonds.

- 2.45 Indicate the hybridization around the **bold type** atoms in the following compounds:



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- 2.46 (a)  because its molecules can form hydrogen bonds to each other through its $\text{—}\ddot{\text{O}}\text{—H}$ group.
- (b)  because with two $\text{—}\ddot{\text{O}}\text{—H}$ groups, its molecules can form more hydrogen bonds with each other.
- (c)  because its molecules can form hydrogen bonds to each other.
- (d)  OH [same reason as (c)].
- (e)  because its molecules can form hydrogen bonds to each other through the $\text{—}\ddot{\text{N}}\text{—H}$ group.
- (f)  because its molecules will have a larger dipole moment. (The trans compound will have $\mu = 0$ D.)
- (g)  OH [same reason as (c)].
- (h) Nonane, because of its larger molecular weight and larger size, will have larger van der Waals attractions.
- (i)  because its carbonyl group is far more polar than the double bond of .

IR Spectroscopy

- 2.47 (a) The alcohol would have a broad absorption from the O—H group in the 3200 to 3500 cm^{-1} region of its IR spectrum. The ether would have no such absorption.
- (c) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alcohol would have a broad absorption due to its hydroxyl group in the 3200 to 3500 cm^{-1} region of its IR spectrum.
- (d) Same rationale as for (a).
- (e) The secondary amine would have an absorption near 3300 to 3500 cm^{-1} arising from N—H stretching. The tertiary amine would have no such absorption in this region since there is no N—H group present.
- (g) Both compounds would exhibit absorptions near 1710 to 1780 cm^{-1} due to carbonyl stretching vibrations. The carboxylic acid would also have a broad absorption somewhere between 2500 and 3500 cm^{-1} due to its hydroxyl group. The ester would not have a hydroxyl absorption.

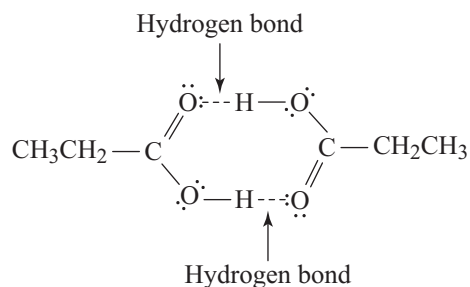
FAMILIES OF CARBON COMPOUNDS 33

(i) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alkene would have no such absorption but would have an absorption between 1620 and 1680 cm^{-1} due to $\text{C}=\text{C}$ stretching.

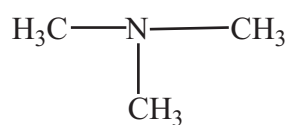
2.48 The infrared spectrum of *cis*-4-octene exhibits an absorption peak near 1500 cm^{-1} due to $\text{C}=\text{C}$ stretching, however, *trans*-4-octene shows no absorption in that region. Explain.

trans-4-octene is symmetric such that when the molecule undergoes vibration there is very little change in the net dipole moment. In order for a band to be IR active there must be a change in the net dipole moment during the vibration. In *cis*-4-octene this high degree of symmetry is missing and there is a change in the net dipole moment during the course of the vibration, leading to the observed band at 1500 cm^{-1} .

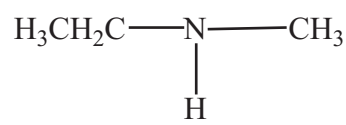
2.49



2.50 Explain how IR spectroscopy can be used to distinguish between the following two compounds:



and



$\text{C}_3\text{H}_9\text{N}$

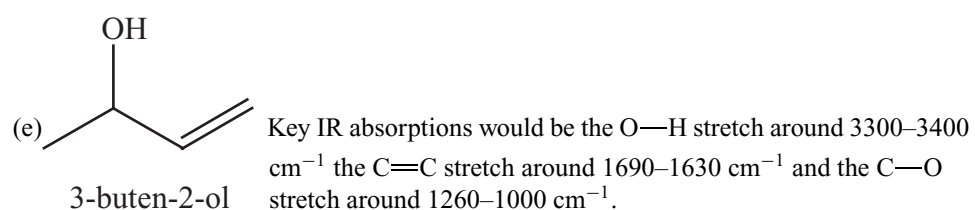
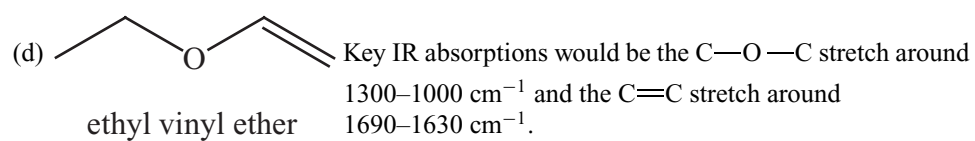
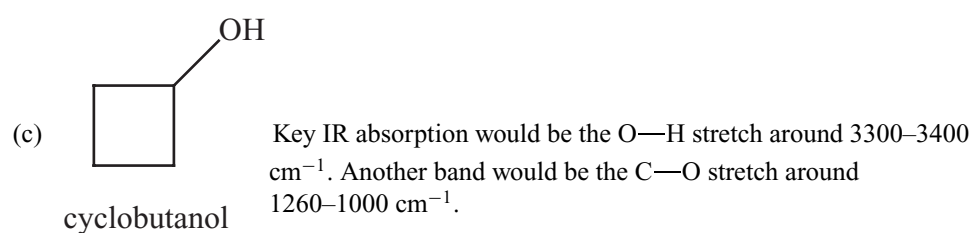
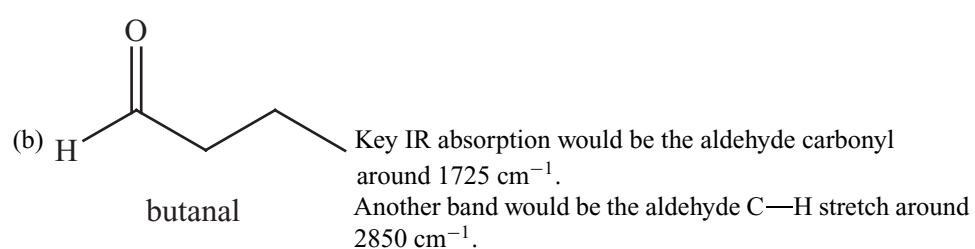
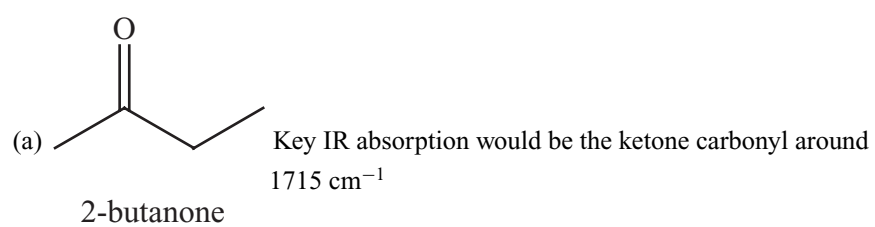
$\text{C}_3\text{H}_9\text{N}$

Trimethyl amine is a tertiary amine; there are no hydrogens on the nitrogen. Ethyl methyl amine is a secondary amine; with one hydrogen on the nitrogen. One could use IR spectroscopy to distinguish between these two compounds, by looking for the $\text{N}-\text{H}$ stretching band around $3300\text{--}3400\text{ cm}^{-1}$. There would be no such band for trimethyl amine while there would be one for ethyl methyl amine.

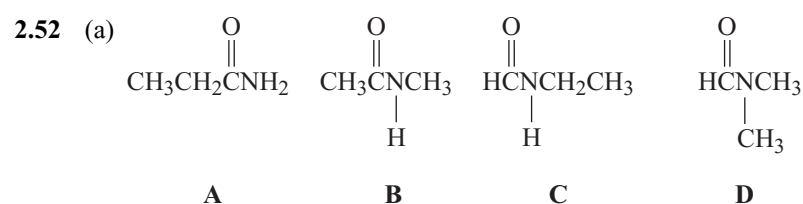
Multiconcept Problems

2.51 Write structural formulas for five compounds with the formula $\text{C}_4\text{H}_8\text{O}$ and classify each according to its functional group. Predict IR absorption frequencies for the functional groups you have drawn.

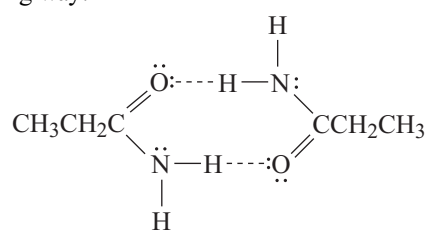
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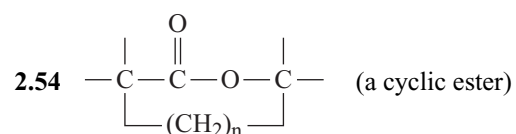
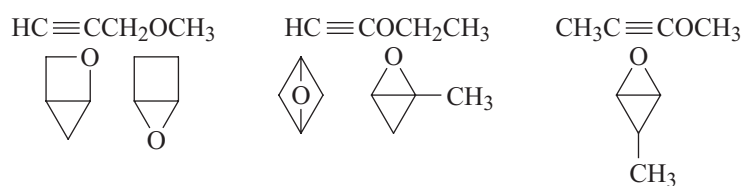
- (b) **D**, because it does not have a hydrogen that is covalently bonded to nitrogen and, therefore, its molecules cannot form hydrogen bonds to each other. The other molecules all have a hydrogen covalently bonded to nitrogen and, therefore, hydrogen-bond formation is possible. With the first molecule, for example, hydrogen bonds could form in the following way:



- (c) All four compounds have carbonyl group absorption at about 1650 cm^{-1} , but the IR spectrum for each has a unique feature.
A shows two N—H bands (due to symmetrical and asymmetrical stretching) in the $3100\text{--}3400\text{ cm}^{-1}$ region.
B has a single stretching absorption band in that same region since it has only a single N—H bond.
C has two absorption bands, due to the H—C bond of the aldehyde group, at about 2820 cm^{-1} and 2920 cm^{-1} , as well as one for the N—H bond.
D does not absorb in the $3100\text{--}3500\text{ cm}^{-1}$ region, as the other compounds do, since it does not possess a N—H bond.

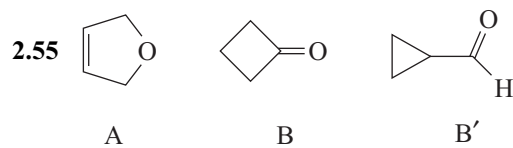
- 2.53 The molecular formula requires unsaturation and/or one or more rings. The IR data exclude

the functional groups: —OH , C=O and C=C . Oxygen (O) must be present in an ether linkage and there can be either a triple bond or two rings present to account for the low hydrogen-to-carbon ratio. These are the possible structures:

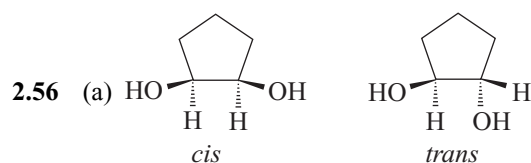


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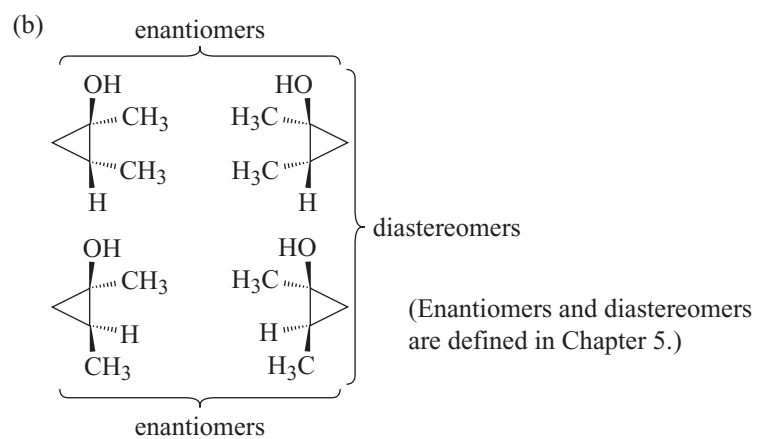
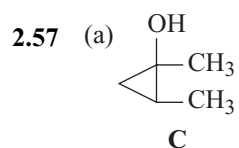
Challenge Problems



The 1780 cm^{-1} band is in the general range for $\text{C}=\text{O}$ stretching so structure B' is considered one of the possible answers, but only B would have its $\text{C}=\text{O}$ stretch at this high frequency (B' would be at about 1730 cm^{-1}).

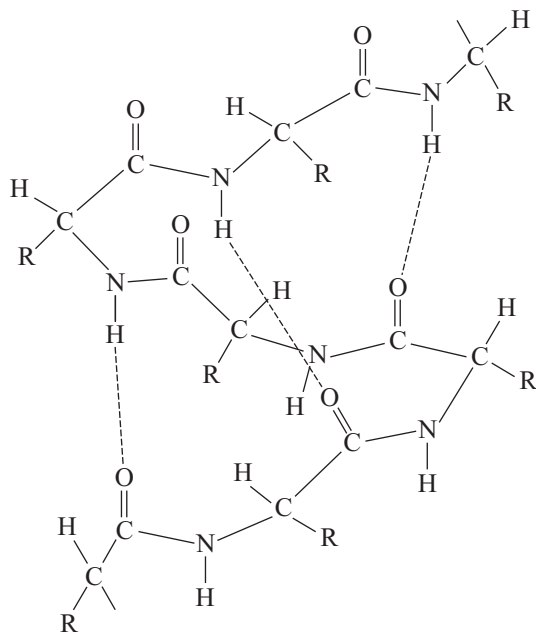


(b) The cis isomer will have the 3572 cm^{-1} band because only in it are the two hydroxyl groups close enough to permit intramolecular hydrogen-bonding. (Intermolecular hydrogen-bonding is not possible at high dilution in a non-polar solvent like CCl_4 .)



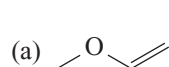
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2.58 The helical structure results from hydrogen bonds formed between amide groups—specifically between the carbonyl group of one amide and the N—H group of another.

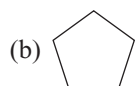
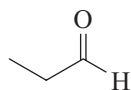


QUIZ

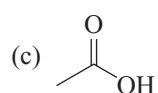
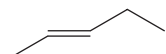
2.1 Which of the following pairs of compounds is *not* a pair of constitutional isomers?



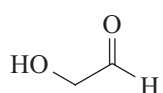
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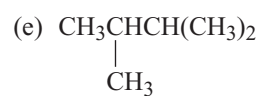
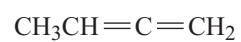
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and



and



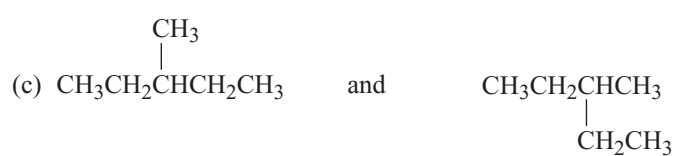
and



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2.2 Which of the answers to Problem 2.1 contains an ether group?

2.3 Which of the following pairs of structures represents a pair of isomers?



(d) More than one of these pairs are isomers.

2.4 Give a bond-line formula for each of the following:

(a) A tertiary alcohol with the formula $\text{C}_5\text{H}_{12}\text{O}$

(b) An *N,N*-disubstituted amide with the formula $\text{C}_4\text{H}_9\text{NO}$

(c) The alkene isomer of $\text{C}_2\text{H}_2\text{Cl}_2$ that has no dipole moment

(d) An ester with the formula $\text{C}_2\text{H}_4\text{O}_2$

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(e) The isomer of $C_2H_2Cl_2$ that cannot show cis-trans isomerism

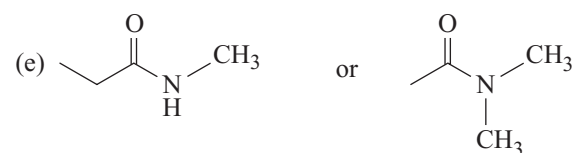
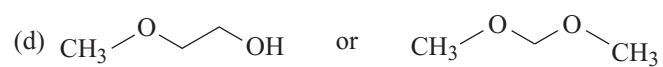
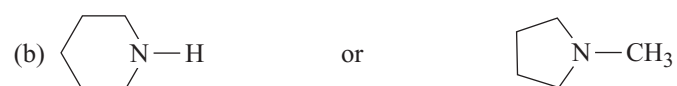
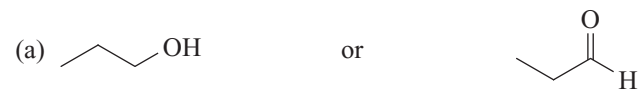
(f) The isomer of C_3H_8O that would have the lowest boiling point

(g) The isomer of $C_4H_{11}N$ that would have the lowest boiling point

2.5 Write the bond-line formula for a constitutional isomer of the compound shown below that does not contain a double bond.



2.6 Circle the compound in each pair that would have the higher boiling point.



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2.7 Give an acceptable name for each of the following:

