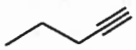
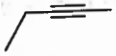
2 FAMILIES OF CARBON COMPOUNDS: FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY

SOLUTIONS TO PROBLEMS

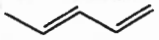
2.1 Although you were only asked to provide two possible constitutional isomers, below are the structures of all the possible products, including some unique forms of alkene bonding that you will encounter in later sections of the text.



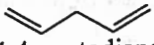
1-pentyne



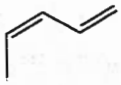
2-pentyne



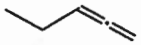
trans-1,3-pentadiene



1,4-pentadiene



cis-1,3-pentadiene



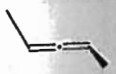
1,2-pentadiene

(compounds with adjacent double bonds are called allenes: see Section 5.18)



2,3-pentadiene

(and its non-superposable mirror image stereoisomer: see Section 5.3 regarding enantiomers and 5.18 regarding allenes)



2,3-pentadiene

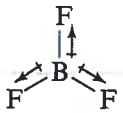
2.2 (a) $\underset{\longrightarrow}{\text{H—F}}$ or $\overset{\delta+}{\text{H}}—\overset{\delta-}{\text{F}}$

(b) $\underset{\longrightarrow}{\text{I—Br}}$ or $\overset{\delta+}{\text{I}}—\overset{\delta-}{\text{Br}}$

(c) Br—Br, $\mu = 0$ D

(d) F—F, $\mu = 0$ D

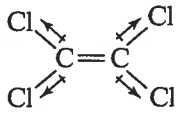
2.3 VSEPR theory predicts a trigonal planar structure for BF_3.



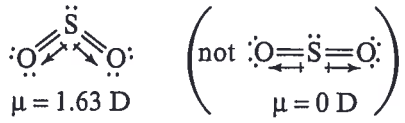
$\mu = 0$ D

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

2.4 The shape of $CCl_2{=}CCl_2$ (below) is such that the vector sum of all of the C—Cl bond moments is zero.



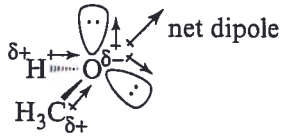
2.5 The fact that SO_2 has a dipole moment indicates that the molecule is angular, not linear.



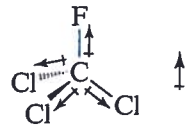
$\mu = 1.63$ D (not $\mu = 0$ D)

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

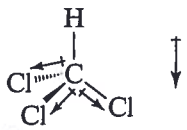
2.6 VSEPR theory predicts the following.



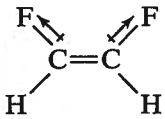
2.7 In $CFCl_3$ the large C—F bond moment opposes the C—Cl moments, leading to a net dipole moment in the direction of the fluorine. Because hydrogen is much less electronegative than fluorine, no such opposing effect occurs in $CHCl_3$; therefore, it has a net dipole moment that is larger and in the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

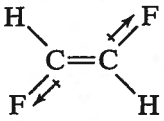


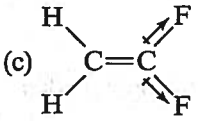
Smaller net dipole moment

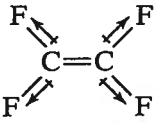


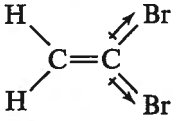
Larger net dipole moment

2.8 (a)  net dipole moment

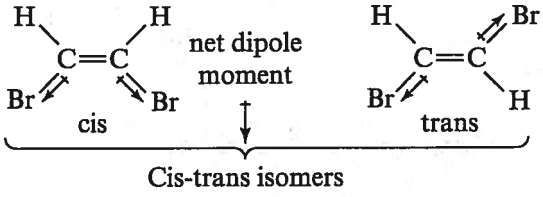
(b)  $\mu = 0$ D

(c)  net dipole moment

(d)  $\mu = 0$ D

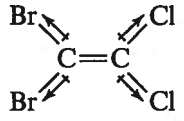
2.9 (a) 

net dipole moment

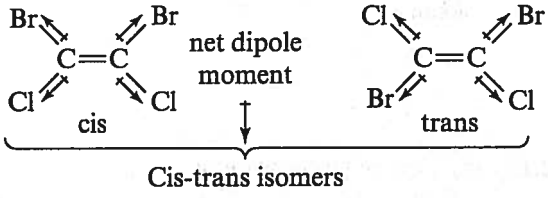


$\mu = 0$ D

Cis-trans isomers

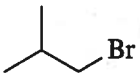
(b) 

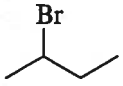
net dipole moment

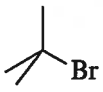


$\mu = 0$ D

Cis-trans isomers

2.10 (a) and 

(b) 

(c) 

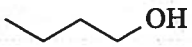
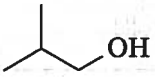
2.11 (a) 

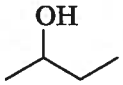
(b) 

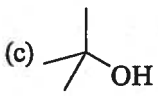
(c) Propyl bromide

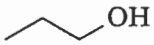
(d) Isopropyl fluoride

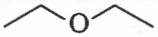
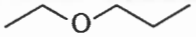
(e) Phenyl iodide

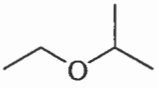
2.12 (a)  and 

(b) 

(c) 

2.13 (a)  (b) 

2.14 (a)  (b) 

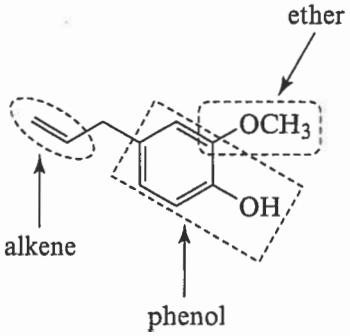
(c) 

(d) Methyl propyl ether

(e) Diisopropyl ether

(f) Methyl phenyl ether

2.15

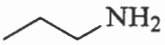


2.16 (a) Isopropylpropylamine

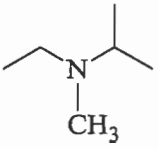
(b) Tripropylamine

(c) Methylphenylamine

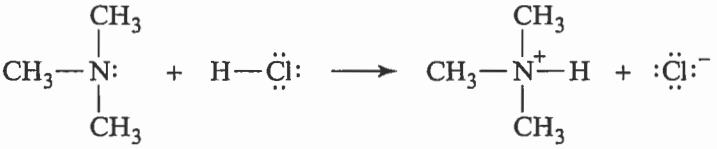
(d) Dimethylphenylamine

(e) 

(f) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{N}}}}-CH_3$ or $(CH_3)_3N$

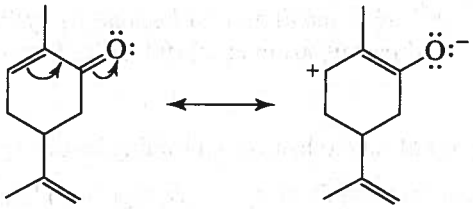
(g) 

2.17 (a) (e) only (b) (a, c) (c) (b, d, f, g)

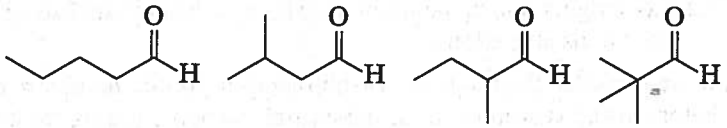
2.18 (a) 

(b) sp^3

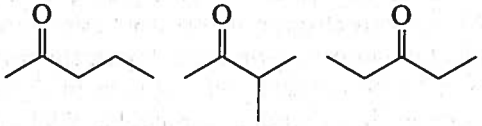
2.19



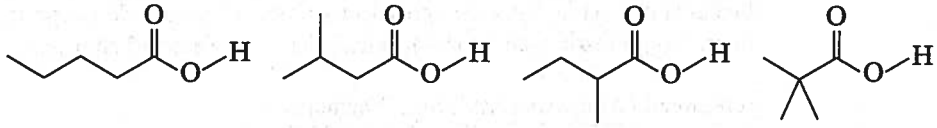
2.20 (a)



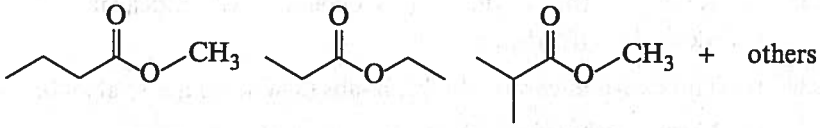
(b)



2.21

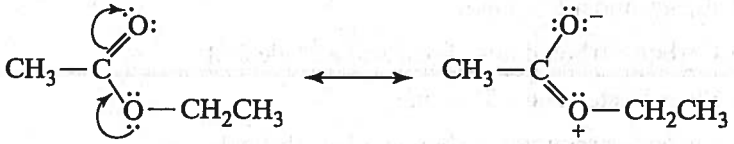


2.22



+ others

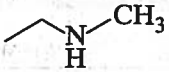
2.23



2.24



2.25 (a)  would boil higher because its molecules can form hydrogen bonds to each other through the —Ö—H group.

(b)  would boil higher because its molecules can form hydrogen bonds to each other through the —N—H group.

(c) HO  OH because by having two —Ö—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

2.29 (a) Ketone (b) Alkyne (c) Alcohol (d) Aldehyde
(e) Alcohol (f) Alkene

2.30 (a) Three carbon-carbon double bonds (alkene) and a 2° alcohol

(b) Phenyl, carboxylic acid, amide, ester, and a 1° amine

(c) Phenyl and a 1° amine

(d) Carbon-carbon double bond and a 2° alcohol

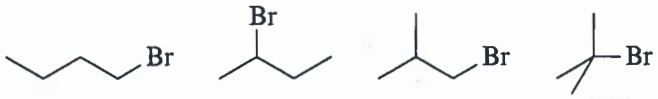
(e) Phenyl, ester, and a 3° amine

(f) Carbon-carbon double bond and an aldehyde

(g) Carbon-carbon double bond and 2 ester groups

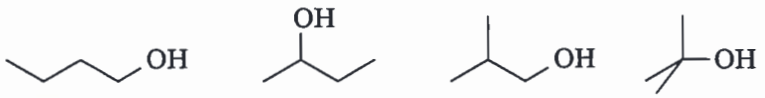
To say that the benzene/aromatic ring or cycle is the "phenyl" functional group is incorrect. The functional group is called the benzene/aromatic ring or cycle.

2.31

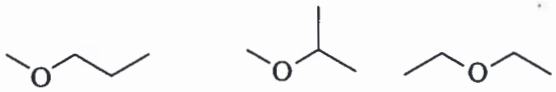


1° Alkyl bromide | 2° Alkyl bromide | 1° Alkyl bromide | 3° Alkyl bromide

2.32



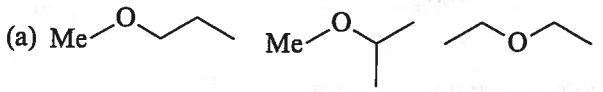
1° Alcohol | 2° Alcohol | 1° Alcohol | 3° Alcohol

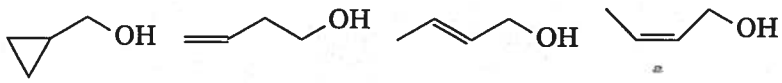


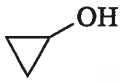
Ether | Ether | Ether

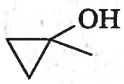
2.33 (a) 1° (b) 2° (c) 3° (d) 3° (e) 2°

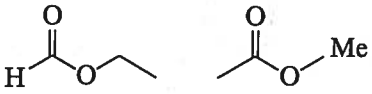
2.34 (a) 2° (b) 1° (c) 3° (d) 2° (e) 2° (f) 3°

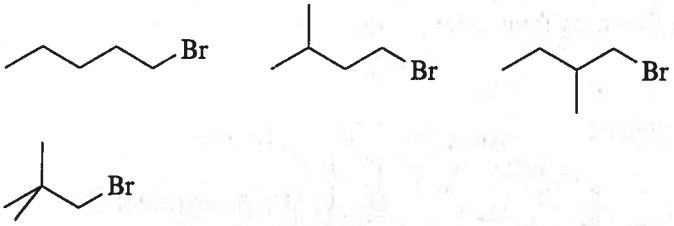
2.35 (a) 

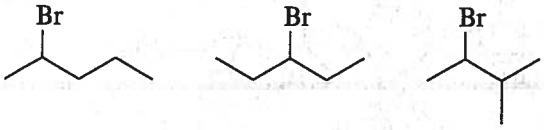
(b) 

(c) 

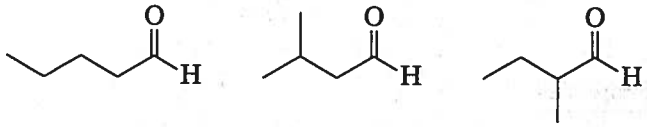
(d) 

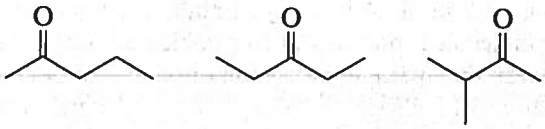
(e) 

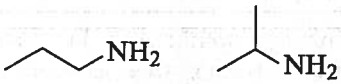
(f) 

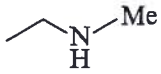
(g) 

(h) 

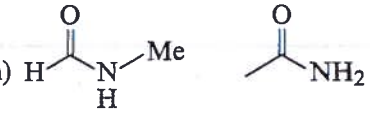
(i) 

(j) 

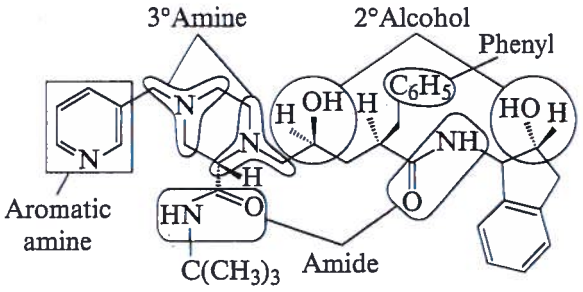
(k) 

(l) 

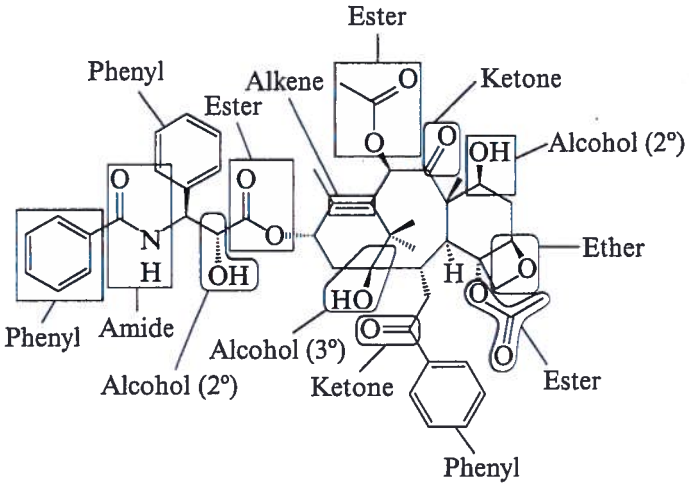
(m) Me_3N

(n) 

2.36 Crixivan has the following functional groups:



2.37 The following formula is for Taxol, a natural compound with anticancer activity. Taxol has the following functional groups.



Physical Properties

2.38 (a) The O—H group of Vitamin A is the hydrophilic portion of the molecule, but the remainder of the molecule is not only hydrophobic but much larger. Attractive dispersion forces between the hydrophobic region of one Vitamin A molecule and another outweighs the effect of hydrogen bonding to water through a single hydroxyl group. Hence, Vitamin A is not expected to be water soluble.

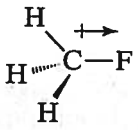
(b) For Vitamin B_3, there are multiple hydrophilic sites. The carbonyl oxygen and the O—H of the acid function as well as the ring nitrogen can all hydrogen bond to water. Since the hydrophobic portion (the ring) of the molecule is modest in size, the molecule is expected to be water soluble.

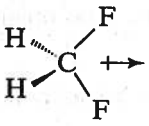
2.39 The attractive forces between hydrogen fluoride molecules are the very strong dipole-dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of 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.)

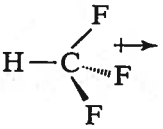
2.40 The cis isomer is polar while the trans isomer is nonpolar ($\mu = 0$ D). The intermolecular attractive forces are therefore greater in the case of the cis isomer, and thus its boiling point should be the higher of the two.

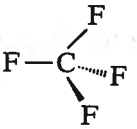
2.41 Because of its ionic character—it is a salt—the compound is water-soluble. The organic cation and the bromide ion are well-solvated by water molecules in a fashion similar to sodium bromide. The compound also is soluble in solvents of low polarity such as diethyl ether (though less so than in water). The hydrophobic alkyl groups can now be regarded as lipophilic—groups that seek a nonpolar environment. Attractive forces between the alkyl groups of different cations can be replaced, in part, by attractive dispersion forces between these alkyl groups and ether molecules.

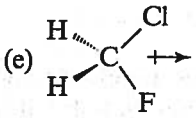
2.42 (a) and (b) are polar and hence are able to dissolve ionic compounds. (c) is non-polar and will not dissolve ionic compounds.

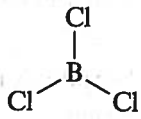
2.43 (a) 

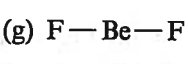
(b) 

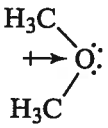
(c) 

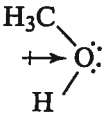
(d)  No dipole moment

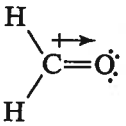
(e) 

(f)  No dipole moment

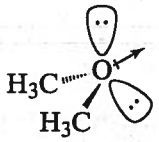
(g)  No dipole moment

(h) 

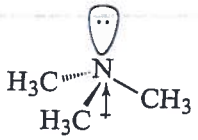
(i) 

(j) 

2.44 (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.

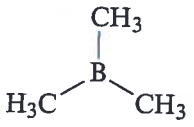
 $\mu > 0$ D

(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.



$\mu > 0$ D

(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.

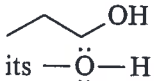


$\mu = 0$ D

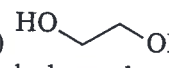
(d) Carbon dioxide: There are four bonding electron pairs around the central carbon atom. We would expect *sp* hybridization of the carbon atom with a bond angle of 180° between the oxygen atoms.

O=C=O $\mu = 0$ D

2.45 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.

2.46 (a) 

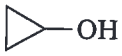
because its molecules can form hydrogen bonds to each other through its —Ö—H group.

(b) 

because with two —Ö—H groups, its molecules can form more hydrogen bonds with each other.

(c) 

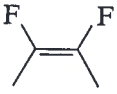
because its molecules can form hydrogen bonds to each other.

(d) 

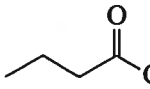
[same reason as (c)].

(e) 

because its molecules can form hydrogen bonds to each other through the —N̈—H group.

(f) 

because its molecules will have a larger dipole moment. (The trans compound will have $\mu = 0$ D.)

(g)  [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.

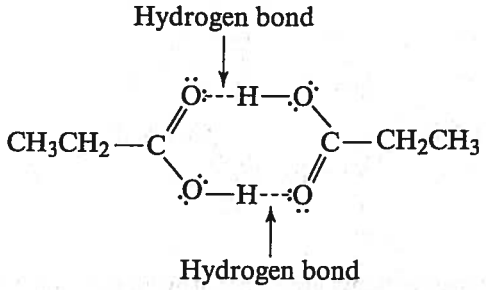
(d) Same rationale as for (a).

(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.

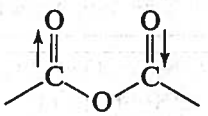
(g) Both compounds would exhibit absorptions near 1710 to 1780 cm^{-1} due to carbonyl stretching vibrations. The carboxylic acid would also have a broad absorption somewhere between 2500 and 3500 cm^{-1} due to its hydroxyl group. The ester would not have a hydroxyl absorption.

(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 C=C stretching.

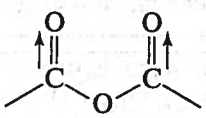
2.48



2.49 There are two peaks as a result of the asymmetric and symmetric stretches of the carbonyl groups.



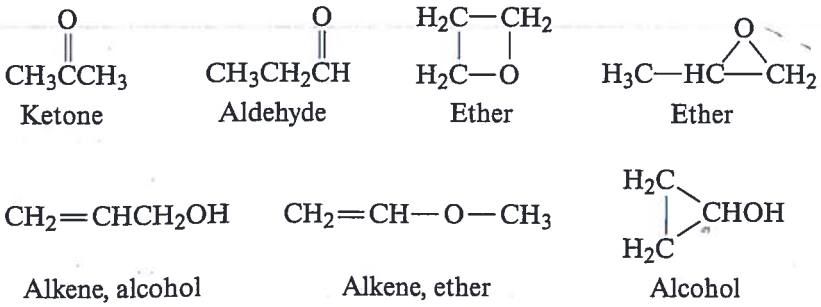
asymmetric



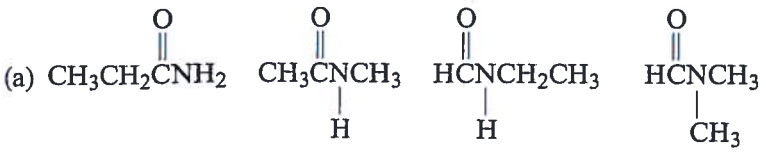
symmetric

Multiconcept Problems

2.50 Any four of the following:

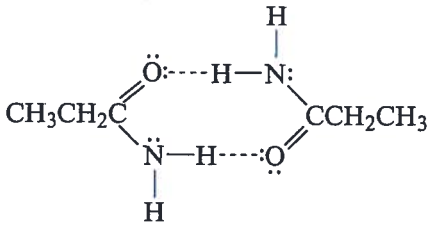


The ketone carbonyl absorption is in the 1680–1750 cm^{-1} range; that for the aldehyde is found in the 1690–1740 cm^{-1} region. The C—O absorption for the ethers is observed at about 1125 cm^{-1}. The C=C absorption occurs at approximately 1650 cm^{-1}. Absorption for the (hydrogen-bonded) O—H group takes the form of a broad band in the 3200–3550 cm^{-1} region.

2.51 (a) 

A **B** **C** **D**

(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:



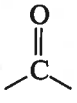
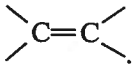
(c) All four compounds have carbonyl group absorption at about 1650 cm^{-1}, but the IR spectrum for each has a unique feature.

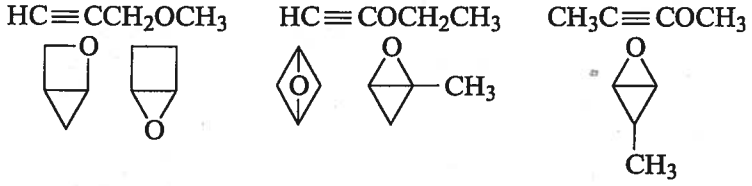
A shows two N—H bands (due to symmetrical and asymmetrical stretching) in the 3100–3400 cm^{-1} region.

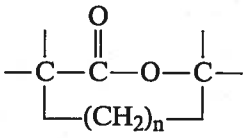
B has a single stretching absorption band in that same region since it has only a single N—H bond.

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.

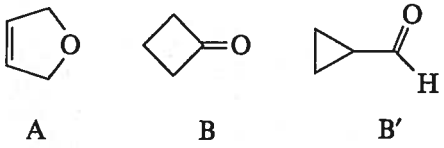
D does not absorb in the 3100–3500 cm^{-1} region, as the other compounds do, since it does not possess a N—H bond.

2.52 The molecular formula requires unsaturation and/or one or more rings. The IR data exclude the functional groups: —OH,  and . Oxygen (O) must be present in an ether linkage and there can be either a triple bond, a double bond and one ring, or two rings present to account for the low hydrogen-to-carbon ratio. These are the possible structures:



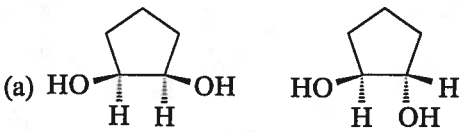
2.53  (a cyclic ester)

Challenge Problems

2.54 

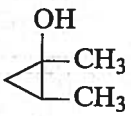
A B B′

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

2.55 (a) 

cis *trans*

(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 minimal at high dilution.)

2.56 

C