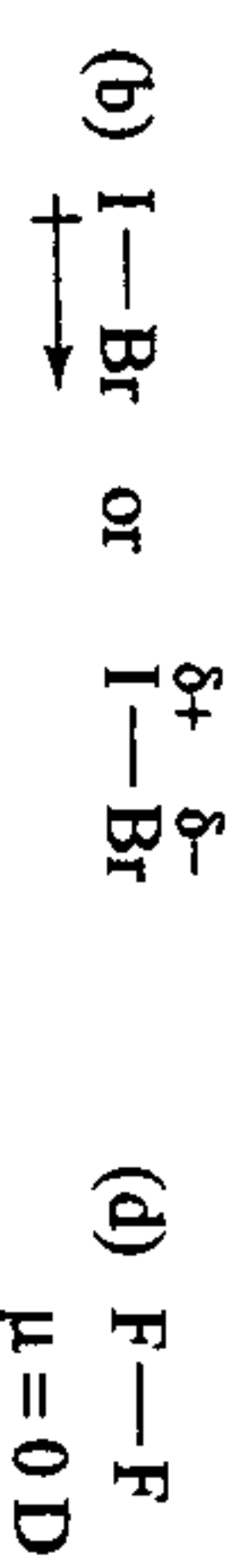
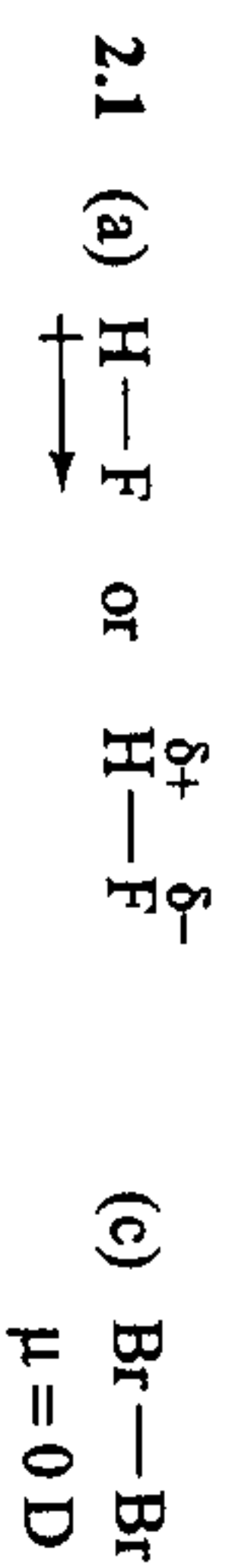
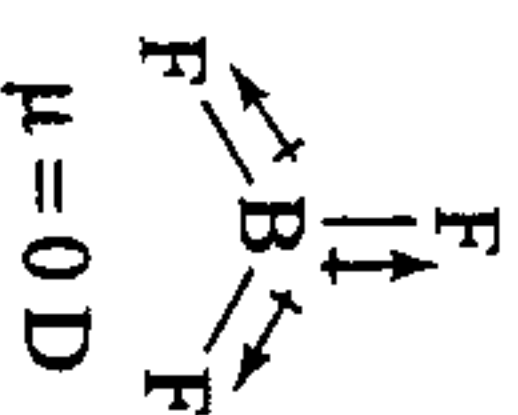


2 REPRESENTATIVE CARBON COMPOUNDS: FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY

SOLUTIONS TO PROBLEMS

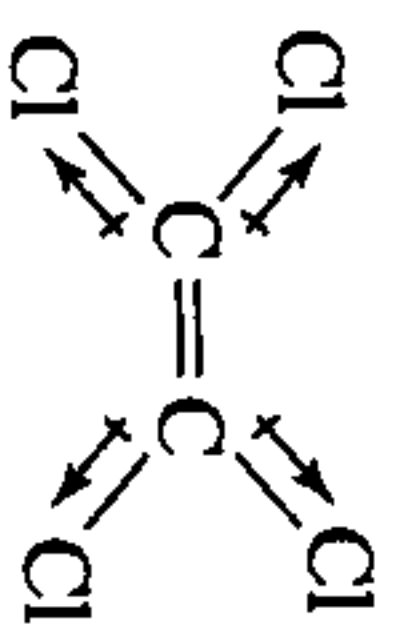


2.2 VSEPR theory predicts a planar structure for BF_3 .

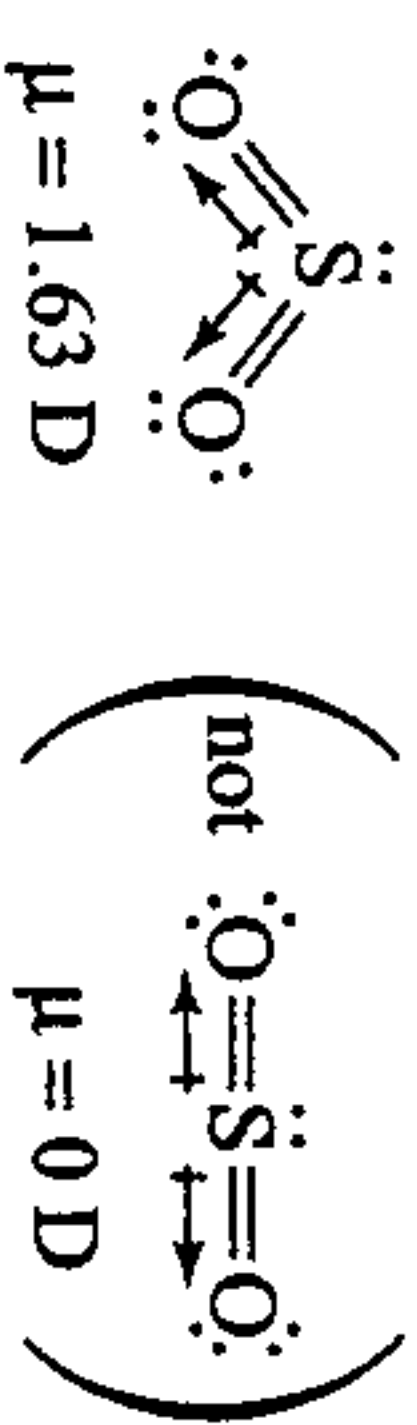


The vector sum of the bond moments of a trigonal planar structure would be zero, resulting in a prediction of $\mu = 0 \text{ D}$ for BF_3 . This correlates with the experimental observation and confirms the prediction of VSEPR theory.

2.3 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.

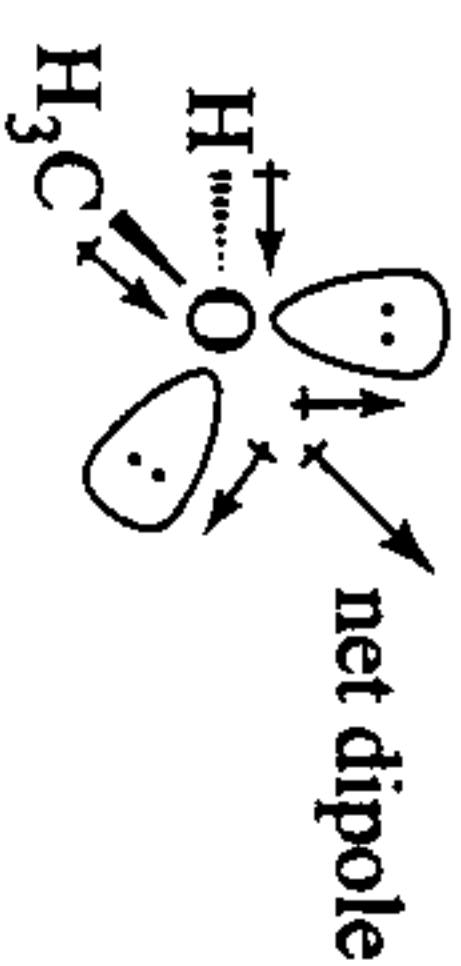


2.4 The fact that SO_2 has a dipole moment indicates that the molecule is angular, not linear.

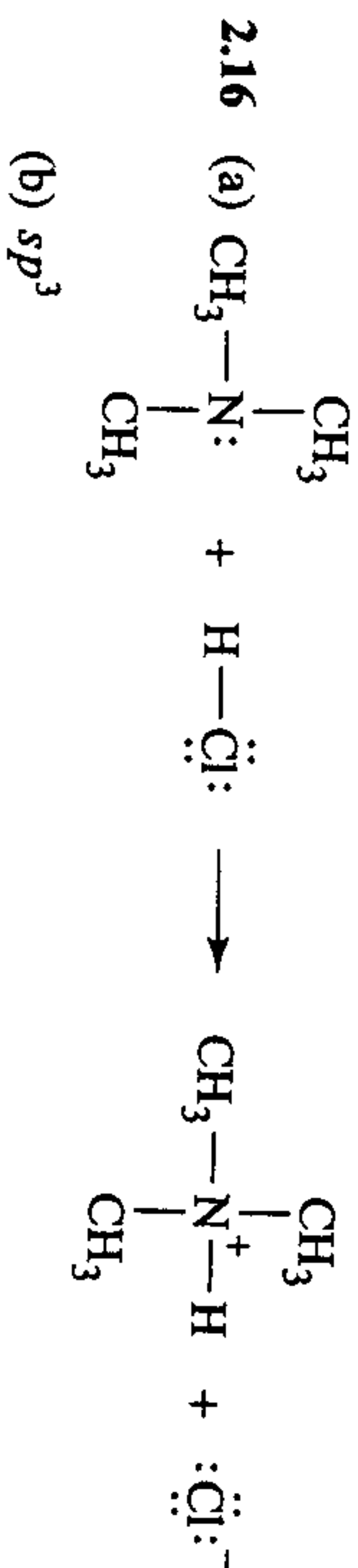
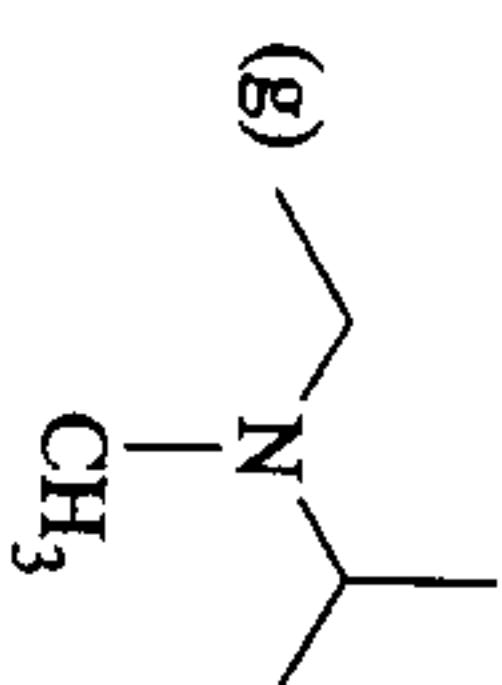
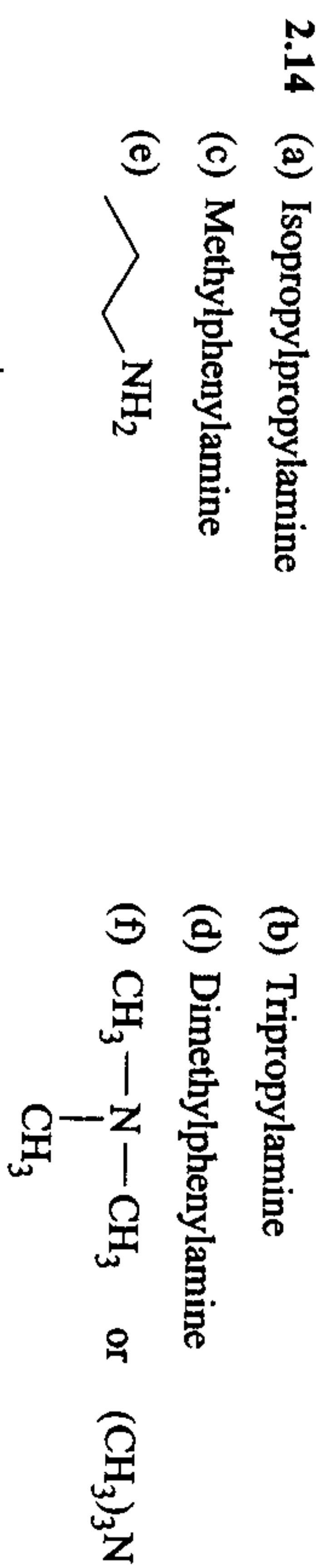
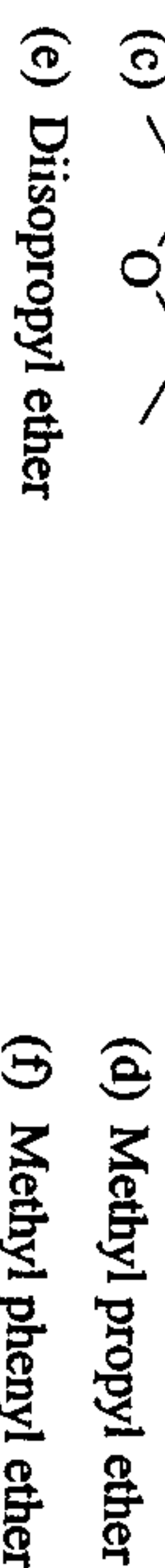
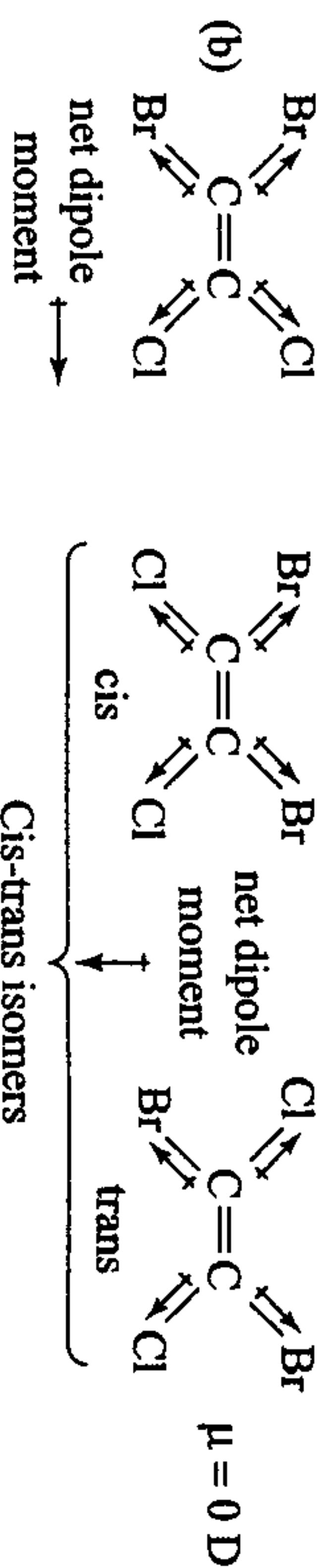
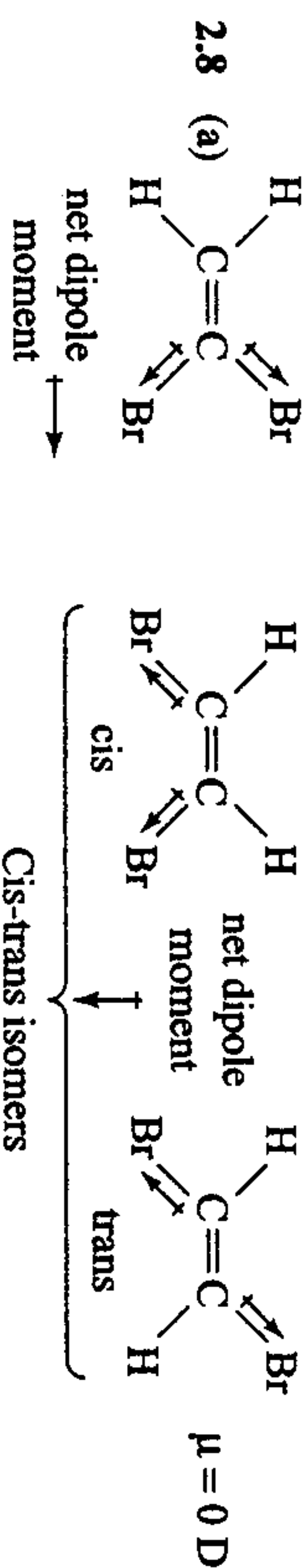
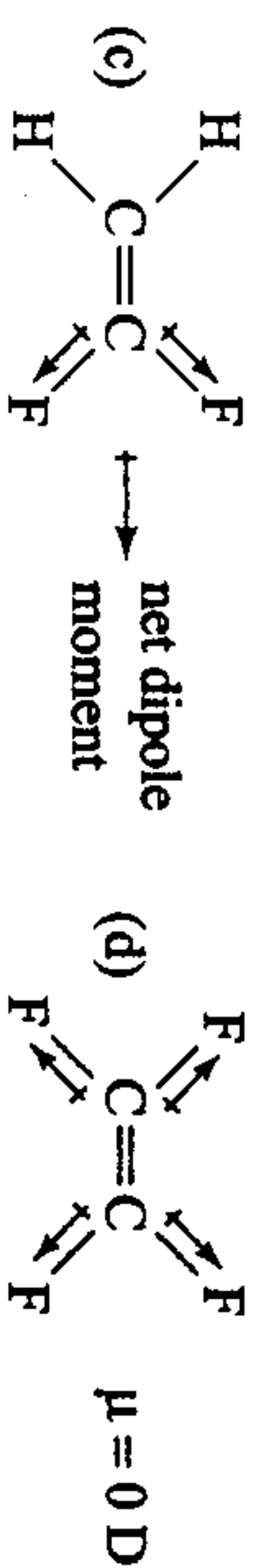
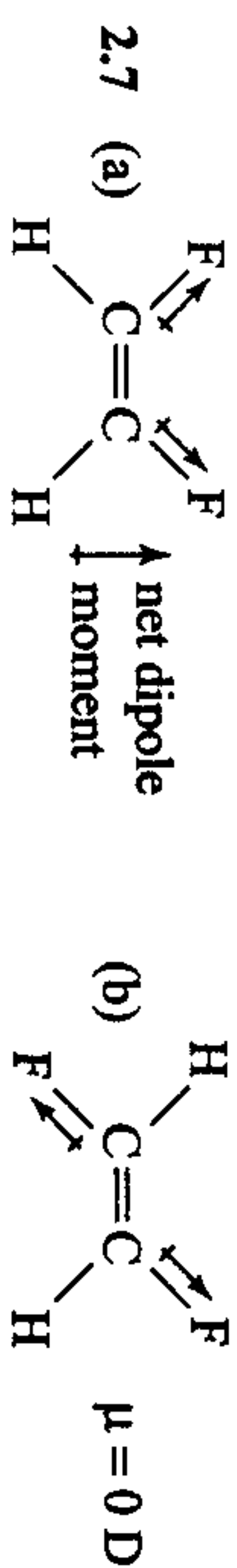
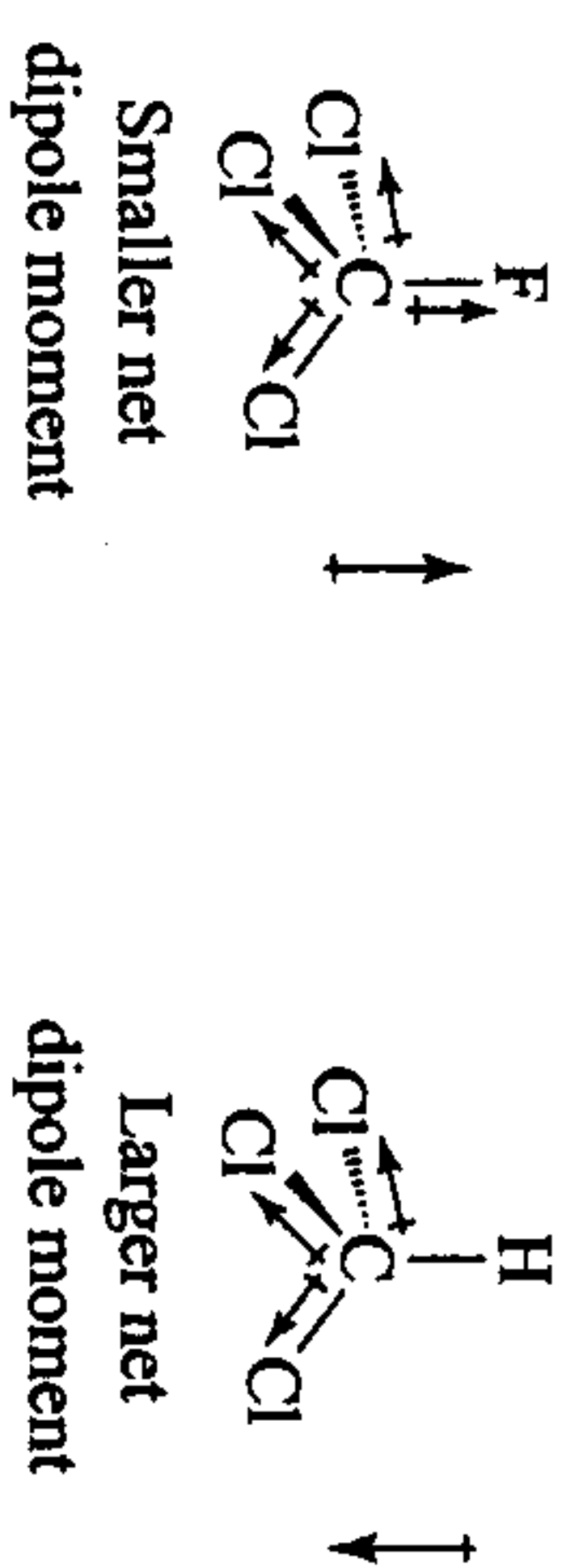


An angular shape is what we would expect from VSEPR theory, too.

2.5 Again, this is what VSEPR theory predicts.



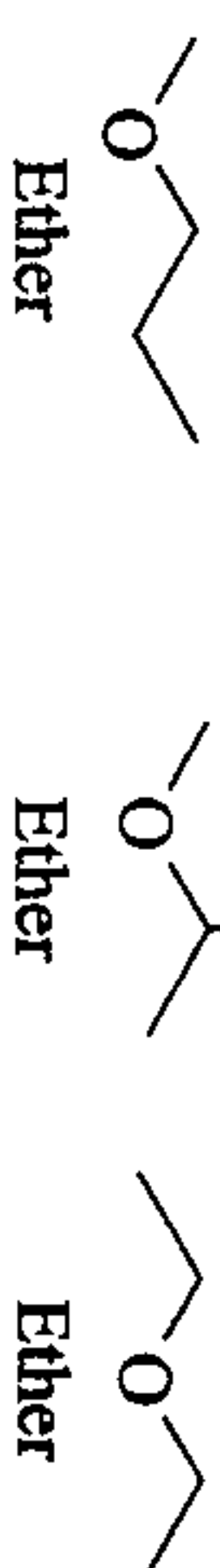
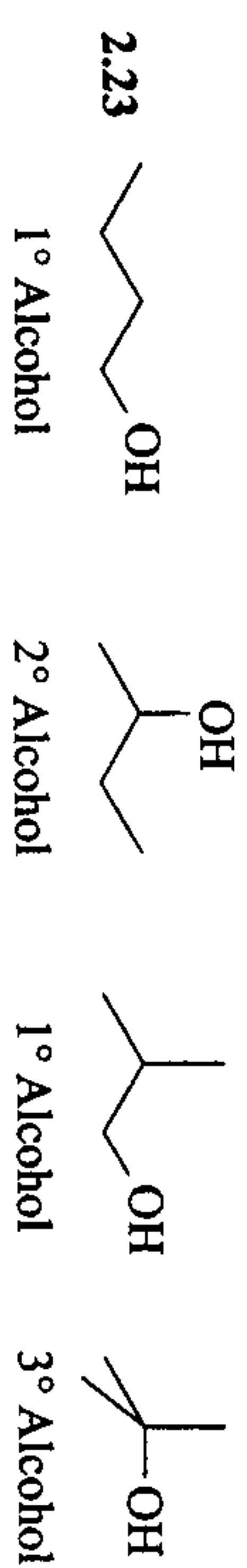
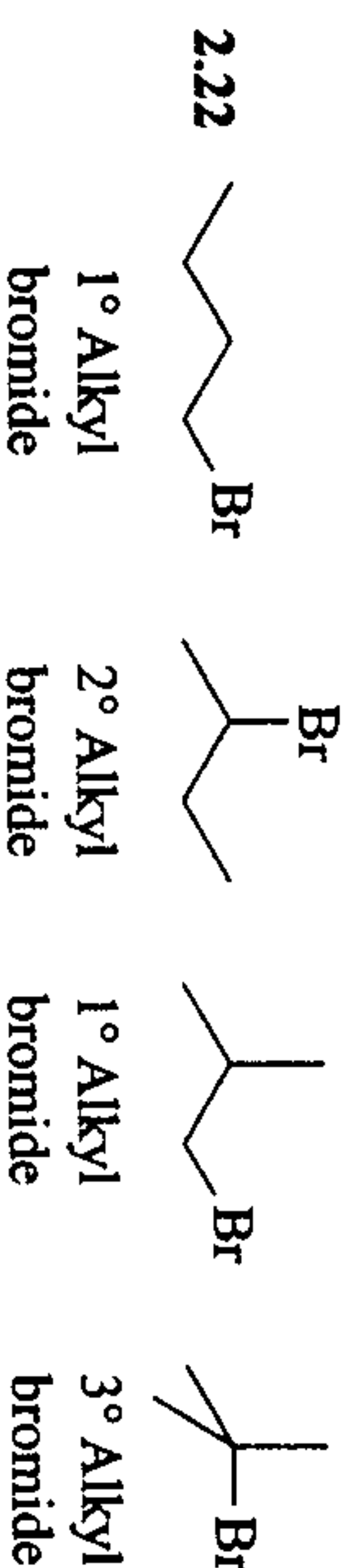
2.6 In CFCl_3 , the large C—F bond moment opposes the C—Cl moments, leading to a net dipole moment in the direction of the fluorine. Because hydrogen is much less electronegative than fluorine, no such opposing effect occurs in CHCl_3 ; therefore, it has a net dipole moment that is larger and in the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



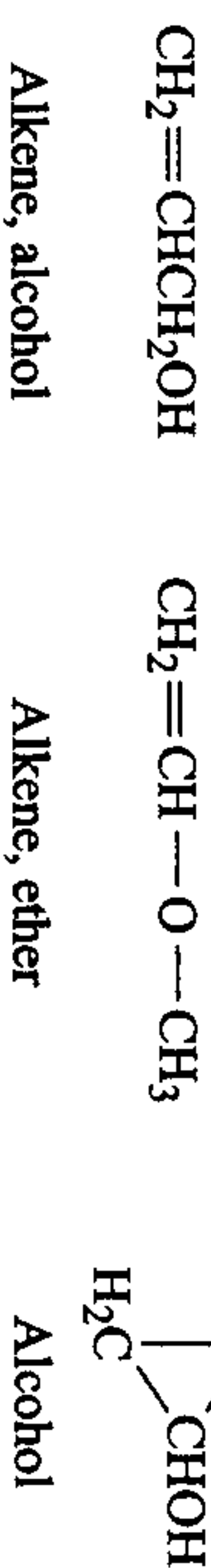
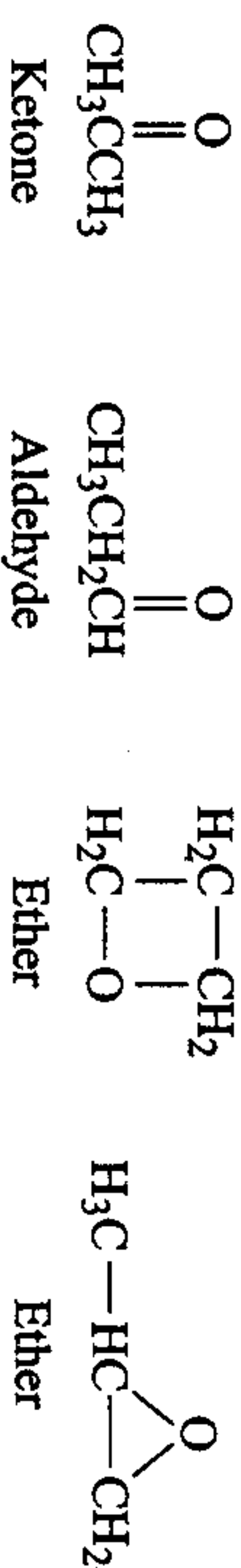
- 2.17 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ would boil higher because its molecules can form hydrogen bonds to each other through the $\text{—}\ddot{\text{O}}\text{—H}$ group.
 (b) $\text{CH}_3\text{CH}_2\text{NHCH}_3$ would boil higher because its molecules can form hydrogen bonds to each other through the $\text{—}\ddot{\text{N}}\text{—H}$ group.
 (c) $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$ because by having two $\text{—}\ddot{\text{O}}\text{—H}$ groups, it can form more hydrogen bonds.
- 2.18 Cyclopropane would have the higher melting point because its cyclic structure gives it a rigid compact shape that would permit stronger crystal lattice forces.
- 2.19 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.

Exercises

- 2.20 (a) Ketone (b) Alkyne (c) Alcohol (d) Aldehyde
 (e) Alcohol (f) Alkene
- 2.21 (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



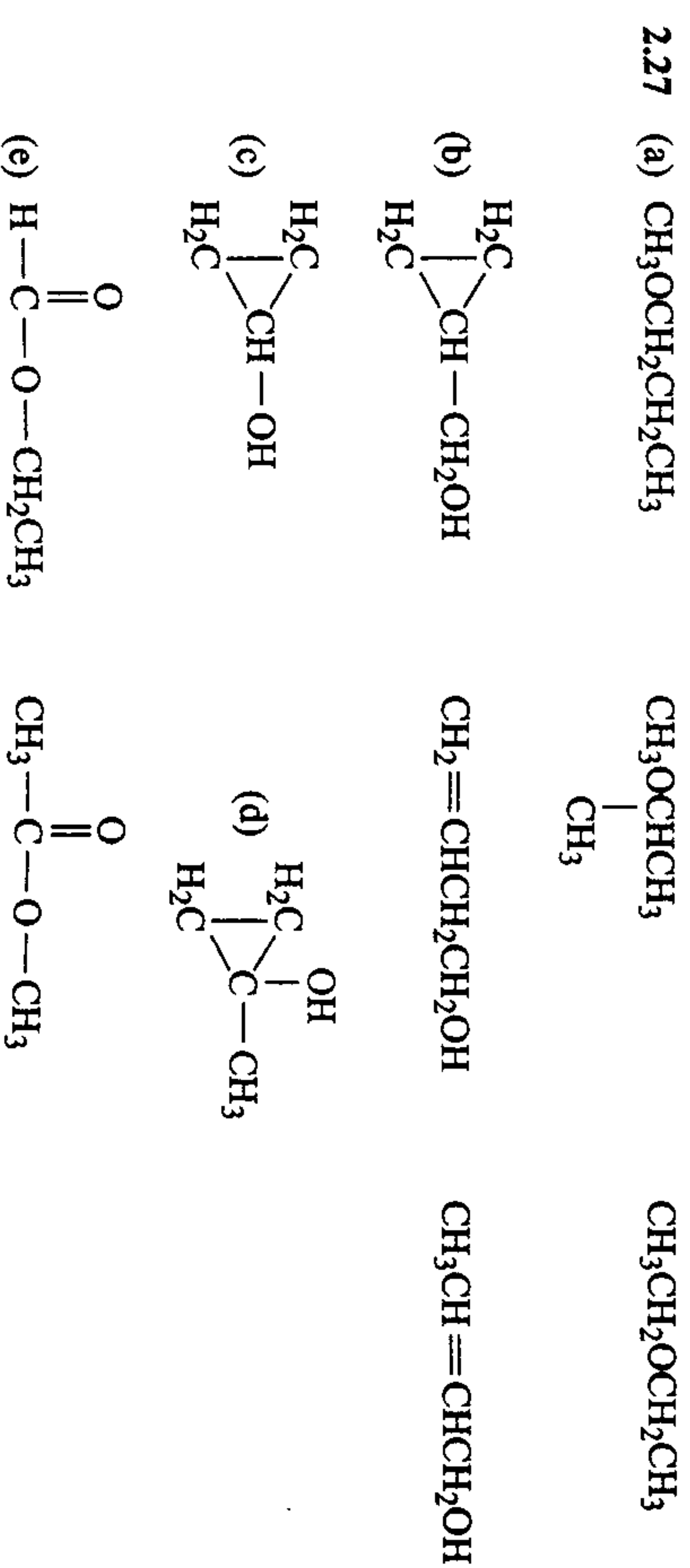
- 2.24 Any four of the following:

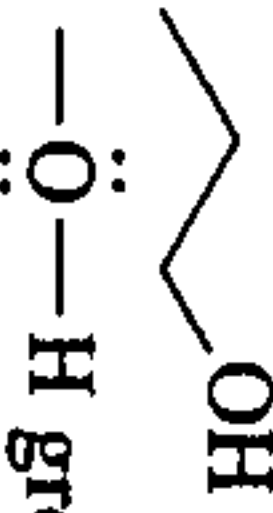





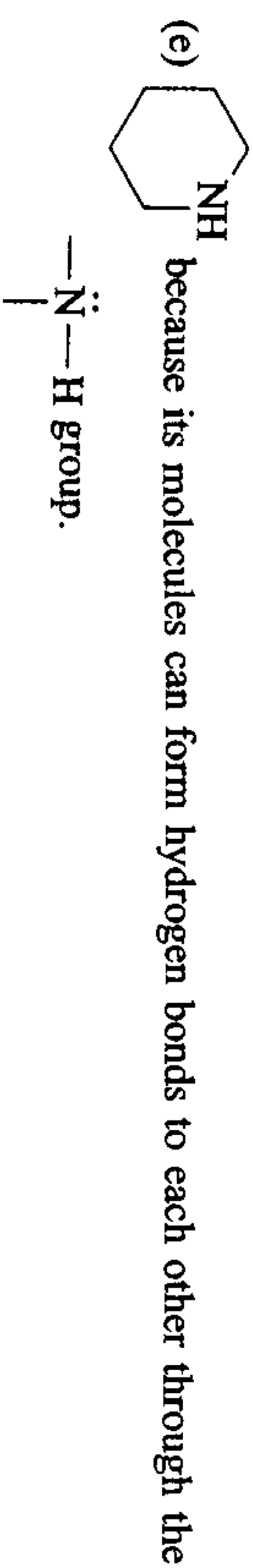
The ketone carbonyl absorption is in the 1680–1750 cm^{-1} range; that for the aldehyde is found in the 1690–1740 cm^{-1} region. The C—O absorption for the ethers is observed at about 1125 cm^{-1} . The C=C absorption occurs at approximately 1650 cm^{-1} . Absorption for the (hydrogen-bonded) O—H group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

- 2.25 (a) 1° (b) 2° (c) 3° (d) 3° (e) 2°
 2.26 (a) 2° (b) 1° (c) 3° (d) 2° (e) 2° (f) 3°

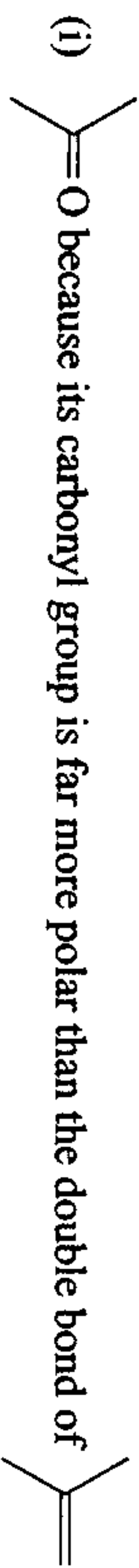
Problems



- (f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{Br}$ $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{Br}$
 CH_3 CH_3 CH_3
 $\text{CH}_3-\text{C}-\text{CH}_2-\text{Br}$
 CH_3
- (g) $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3$ $\text{CH}_3\text{CHCHCH}_3$
 Br Br Br
- (h) $\text{CH}_3\text{CH}_2-\text{C}-\text{Br}$ CH_3 $\text{CH}_3\text{CH}_2\text{CHCH}$
 CH_3 CH_3
- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$ $\text{CH}_3\text{CHCH}_2\text{CH}$ $\text{CH}_3\text{CH}_2\text{CHCH}$
 CH_3 CH_3 CH_3
- (j) $\text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3$ $\text{CH}_3\text{CHCCH}_3$
 O O O
- (k) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ CH_3CHNH_2
- (l) $\text{CH}_3\text{CH}_2\text{NHCH}_3$ (m) $(\text{CH}_3)_3\text{N}$
- (n) $\text{H}-\text{C}-\text{NHCH}_3$ $\text{CH}_3-\text{C}-\text{NH}_2$
 O O
- 2.28 (a)  because its molecules can form hydrogen bonds to each other through its —O—H group.
- (b)  because with two —O—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)].



(h) Nonane, because of its larger molecular weight and larger size, will have larger van der Waals attractions.



2.29 (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.

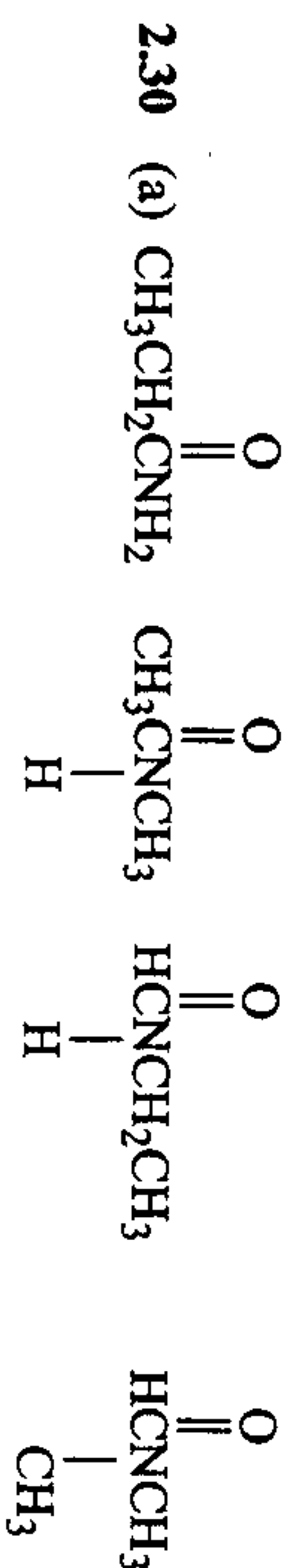
(c) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alcohol would have a broad absorption due to its hydroxyl group in the 3200 to 3500 cm^{-1} region of its IR spectrum.

(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.

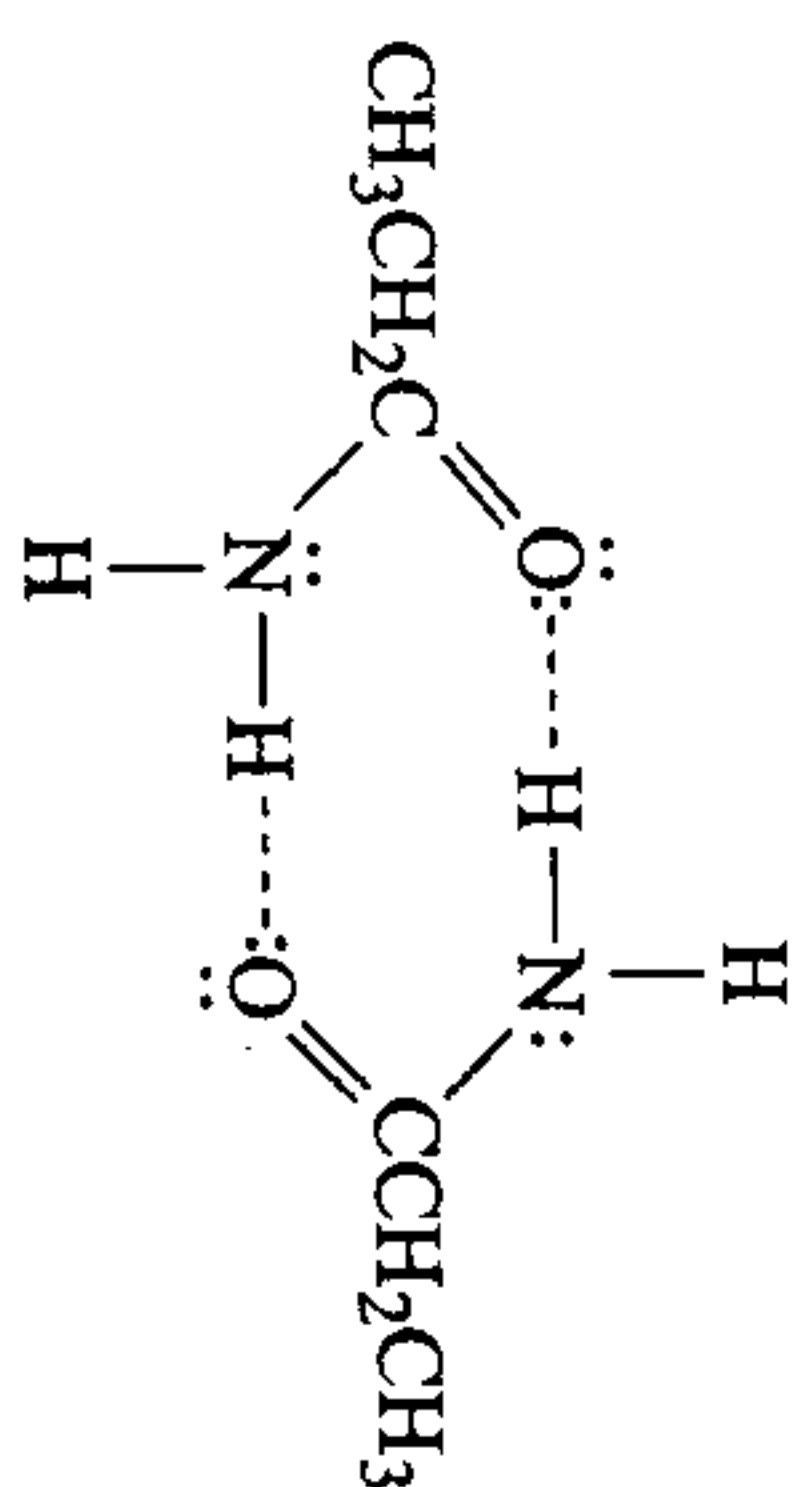
(g) Both compounds would exhibit absorptions near 1710 to 1780 cm^{-1} due to carbonyl stretching vibrations. The carboxylic acid would also have a broad absorption somewhere between 2500 and 3500 cm^{-1} due to its hydroxyl group. The ester would not have a hydroxyl absorption.

(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.



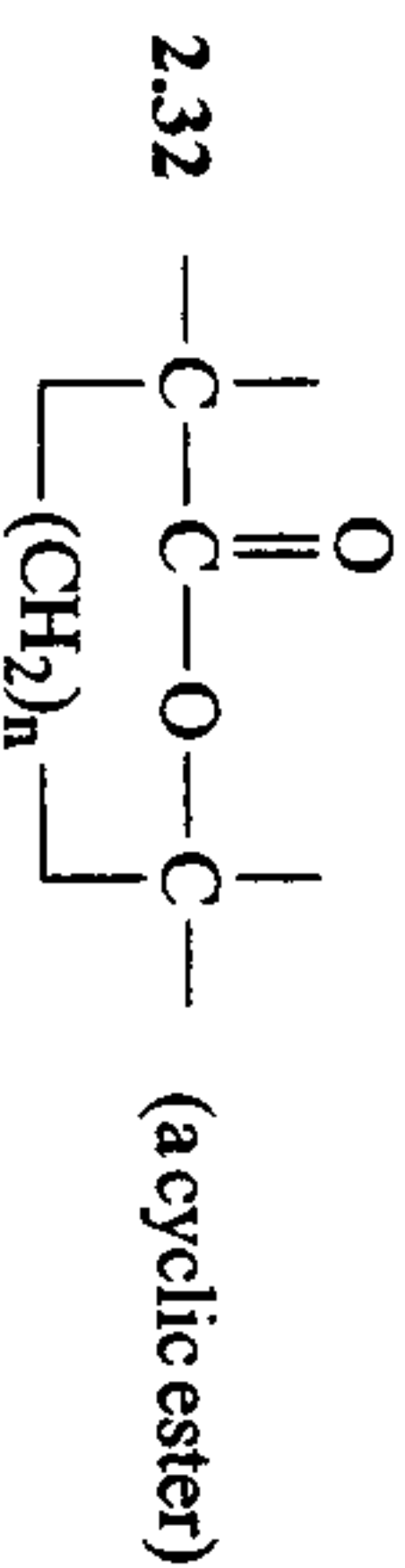
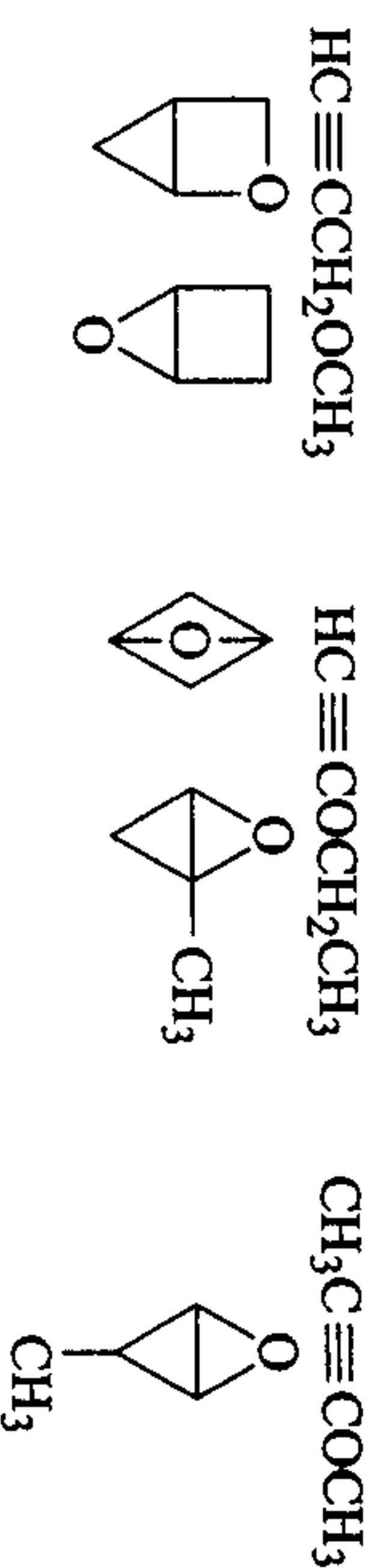
(b) D, because it does not have a hydrogen that is covalently bonded to nitrogen and, therefore, its molecules cannot form hydrogen bonds to each other. The other molecules all have a hydrogen covalently bonded to nitrogen and, therefore, hydrogen-bond

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.

- 2.31 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:

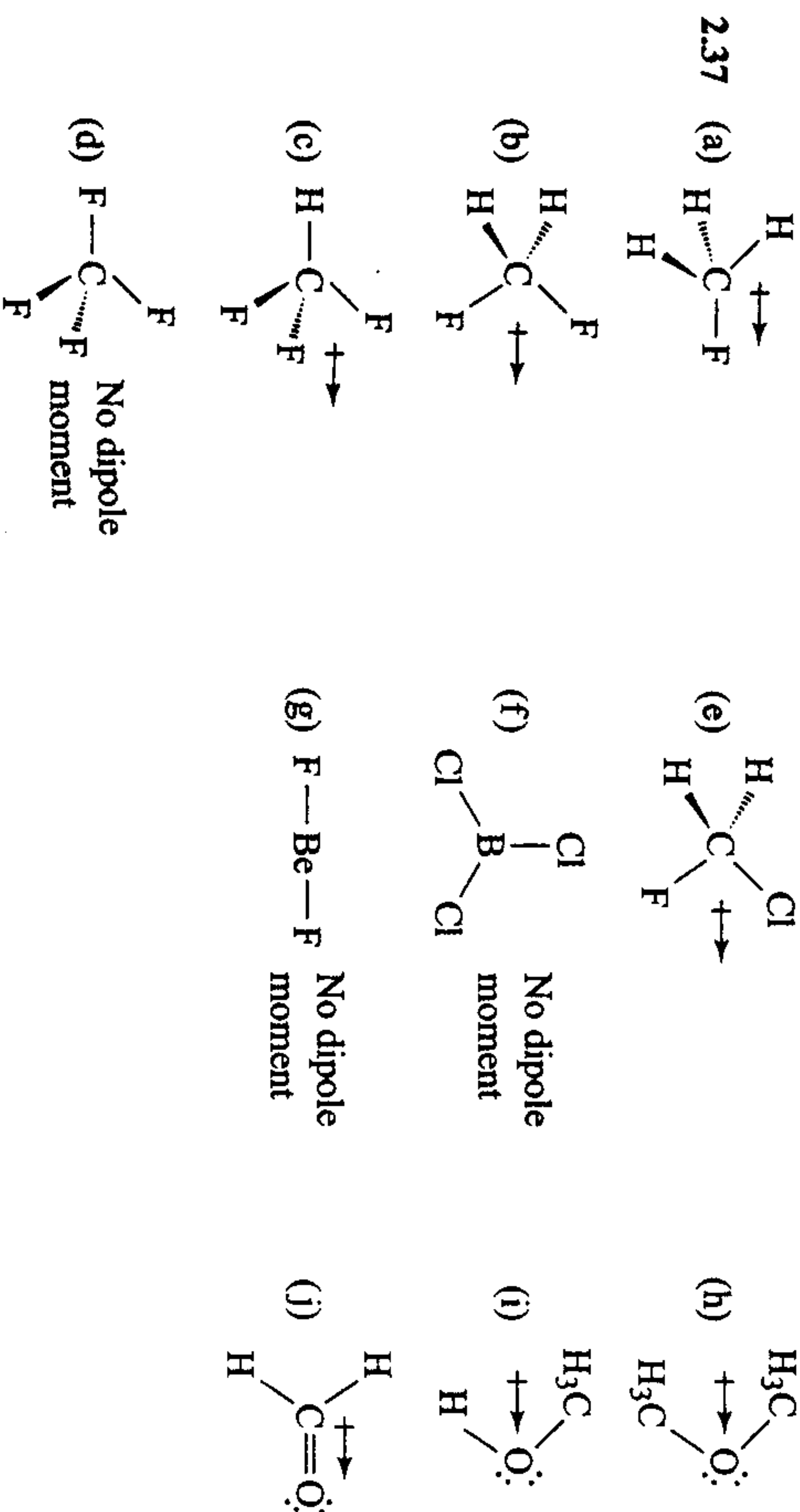


- 2.33 The attractive forces between hydrogen fluoride molecules are the very strong dipole-dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge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

- 2.34 The *cis* isomer is polar while the *trans* isomer is nonpolar ($\mu = 0\text{ D}$). 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.

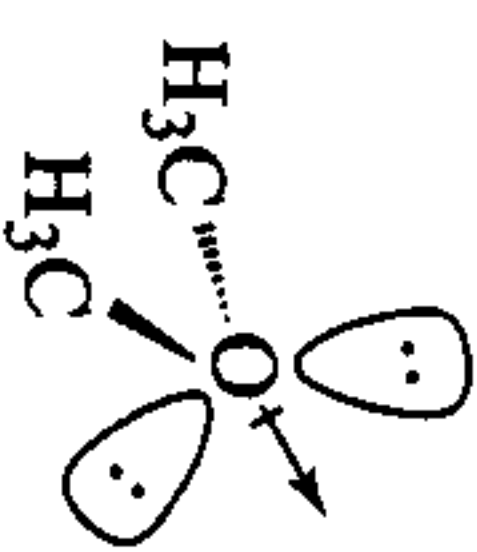
- 2.35 Because of its ionic character—it is a true salt—the compound is water-soluble. The organic cation and the bromide ion are well-solvated by water molecules in a fashion similar to sodium bromide. The compound also is soluble in solvents of low polarity such as diethyl ether (though less so than 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 forces (van der Waals forces) between these alkyl groups and ether molecules.

- 2.36 (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.

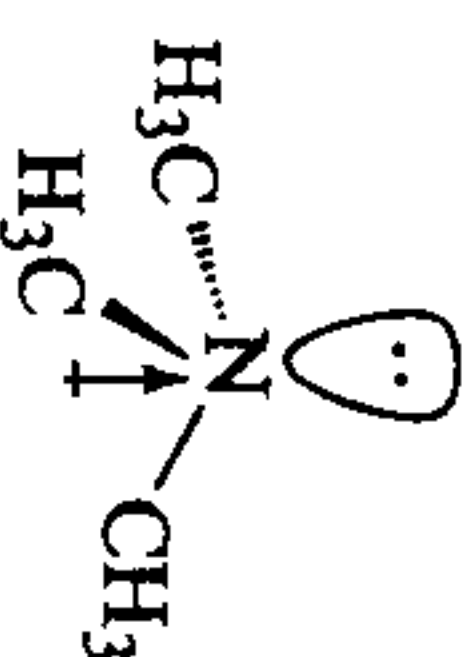


- 2.38 For absorption in the infrared to occur there must be a change in the molecular dipole moment during the stretching process. The 3-hexyne molecule is symmetrical about the triple bond and so there is no change in the dipole moment accompanying the stretching. Hence, there is no IR absorption.

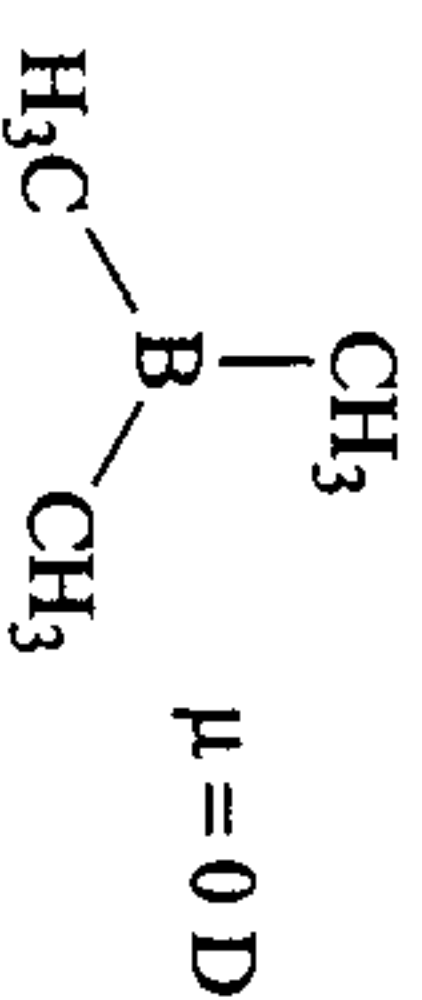
- 2.39 (a) Dimethyl ether: There are four electron pairs around the central oxygen: two bonding pairs and two nonbonding pairs. We would expect sp^3 hybridization of the oxygen with a bond angle of approximately 109.5° between the methyl groups.



- (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.



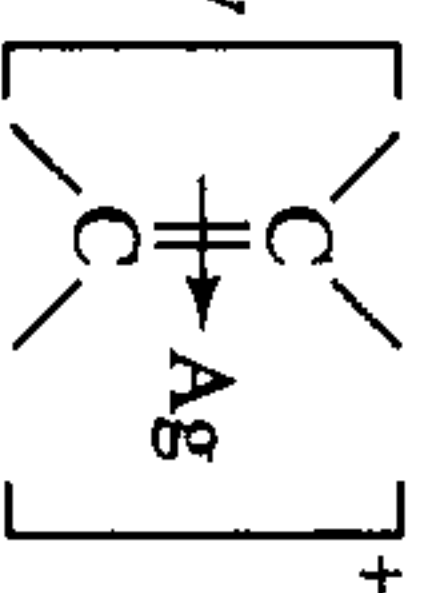
(c) Trimethylboron: There are only three bonding electron pairs around the central boron. We would expect sp^2 hybridization of the boron with a bond angle of 120° between the methyl groups.



(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.



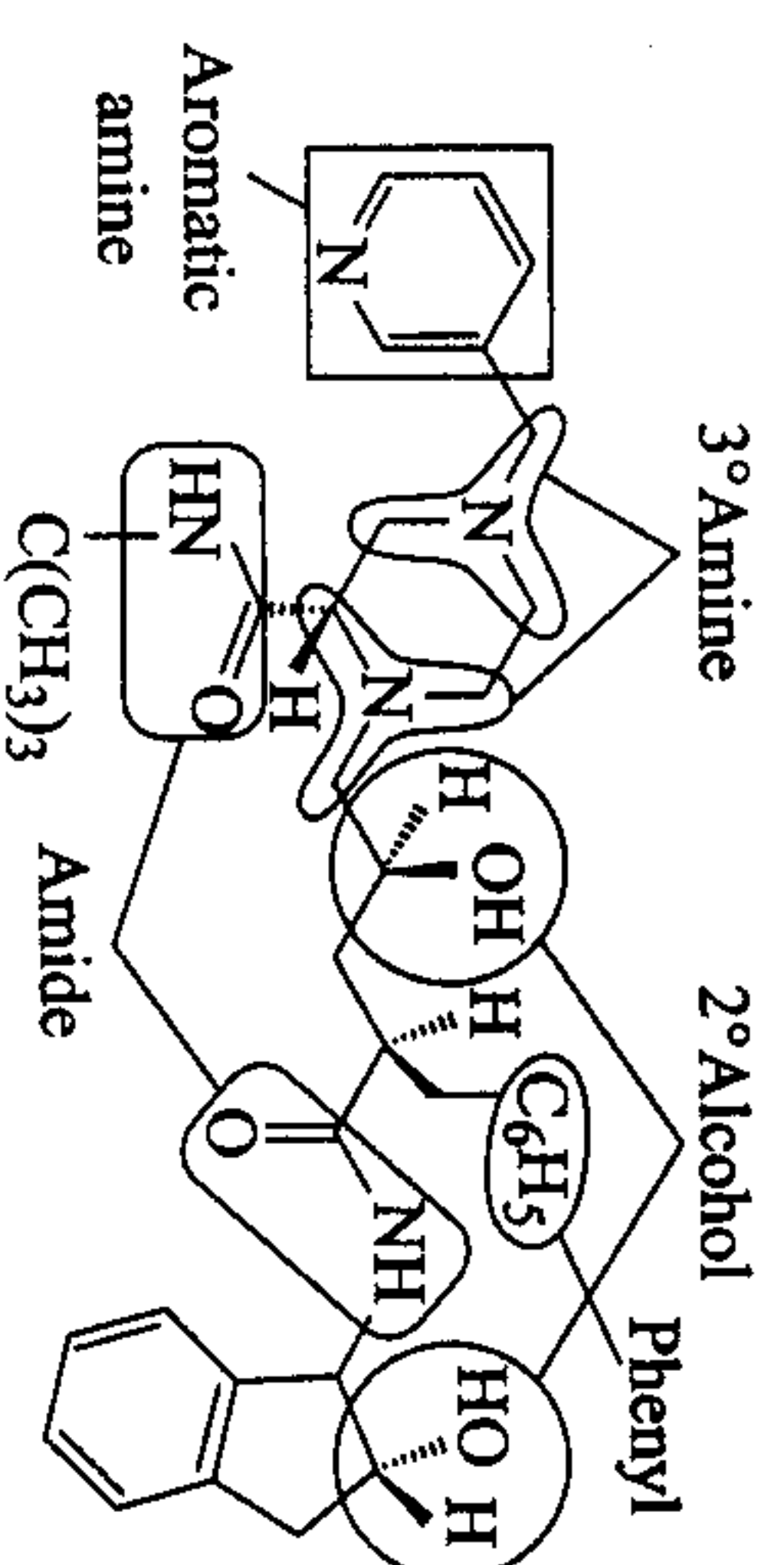
2.40 This is a special case of a Lewis acid (Ag^+) — Lewis base (alkene) reaction. The product can be represented by



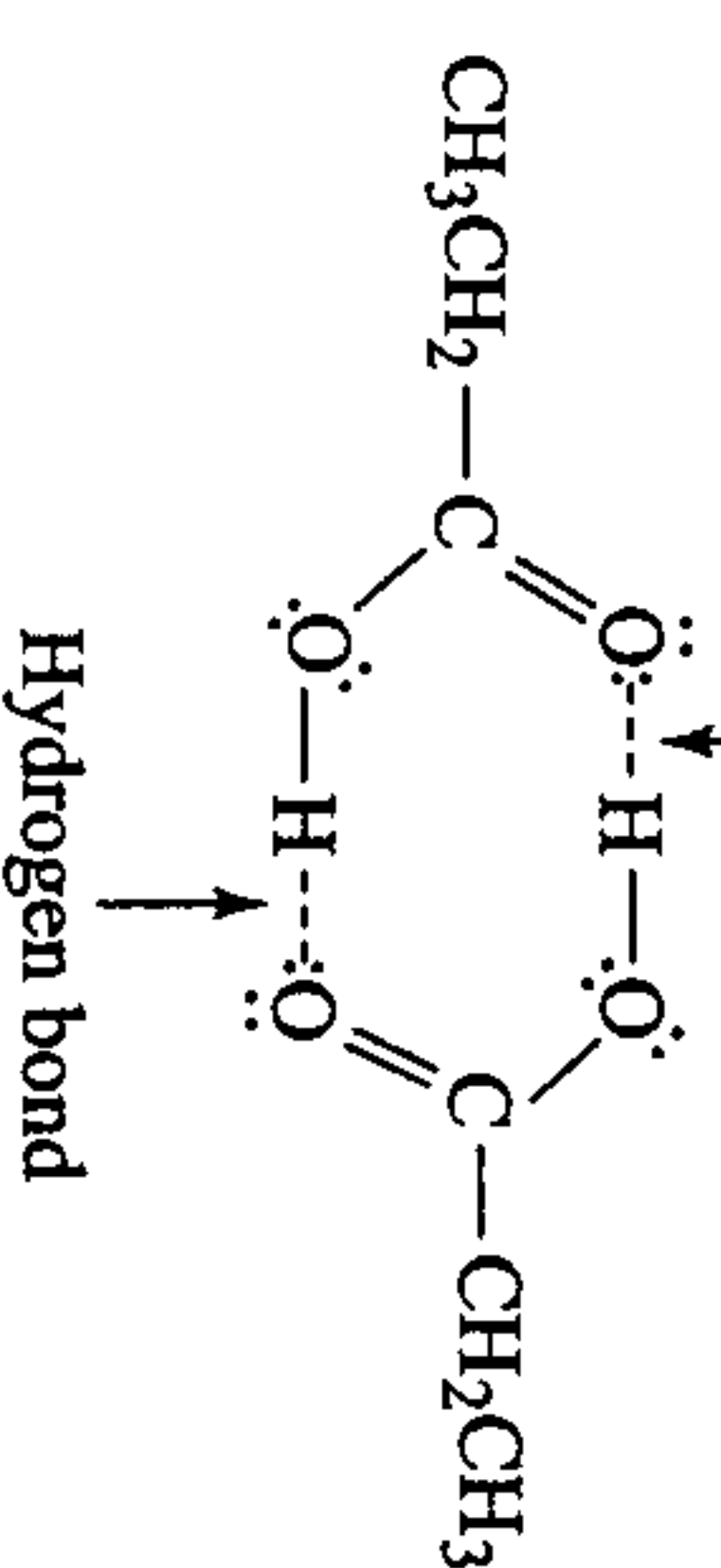
The filled π orbital of the alkene overlaps with the empty $5s$ orbital of Ag^+ to form a σ bond. A π bond results from the overlap of the filled $4d$ orbital of Ag^+ with an empty antibonding π^* orbital of the alkene.

2.41 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.

2.42 Citrixivan has the following functional groups:



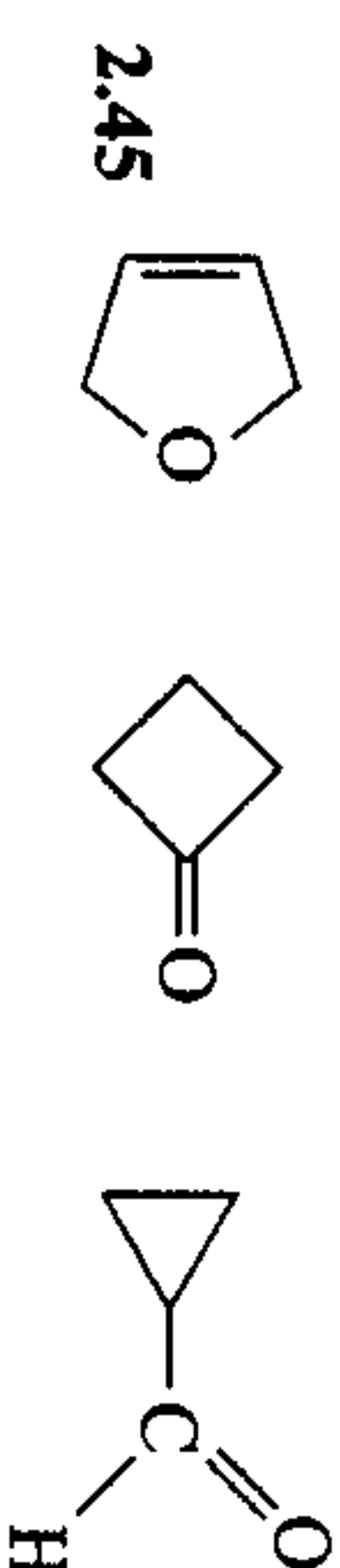
2.43



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

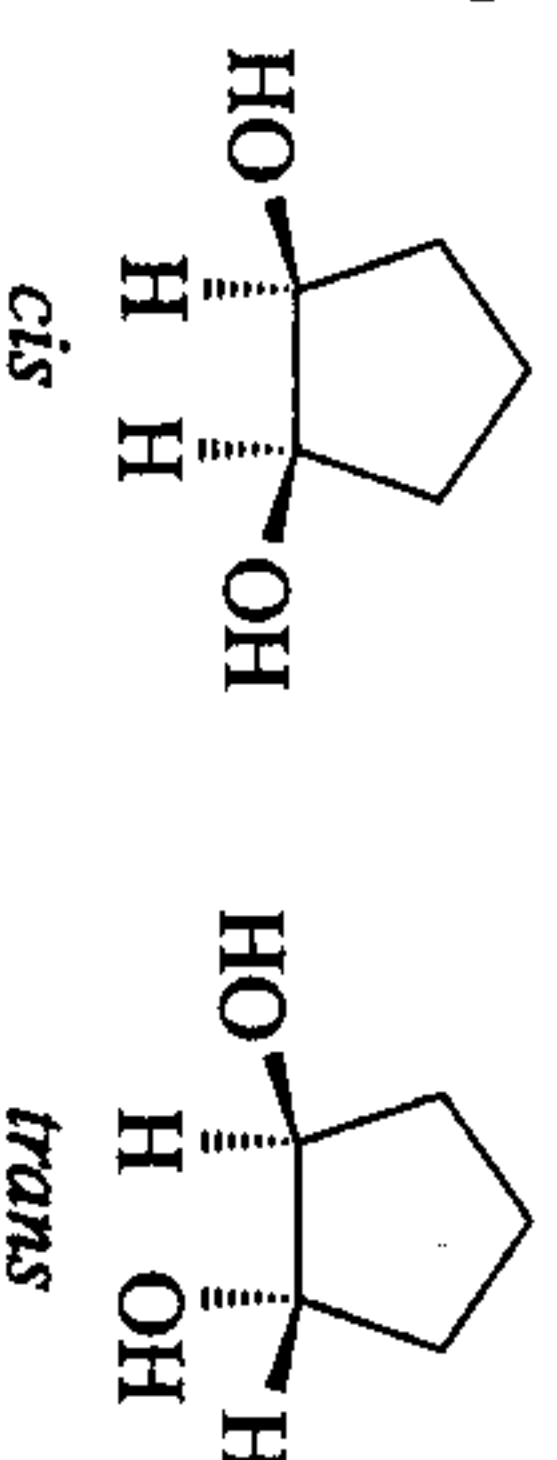


Challenge Problems



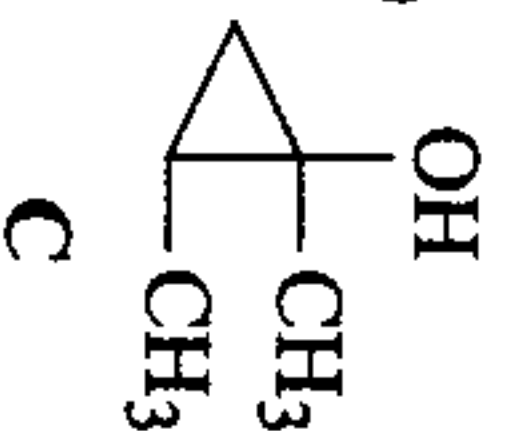
The 1780 cm^{-1} band is in the general range for $\text{C}=\text{O}$ stretching so structure B' is considered one of the possible answers, but only B would have its $\text{C}=\text{O}$ stretch at this high frequency (B' would be at about 1730 cm^{-1}).

2.46 (a)

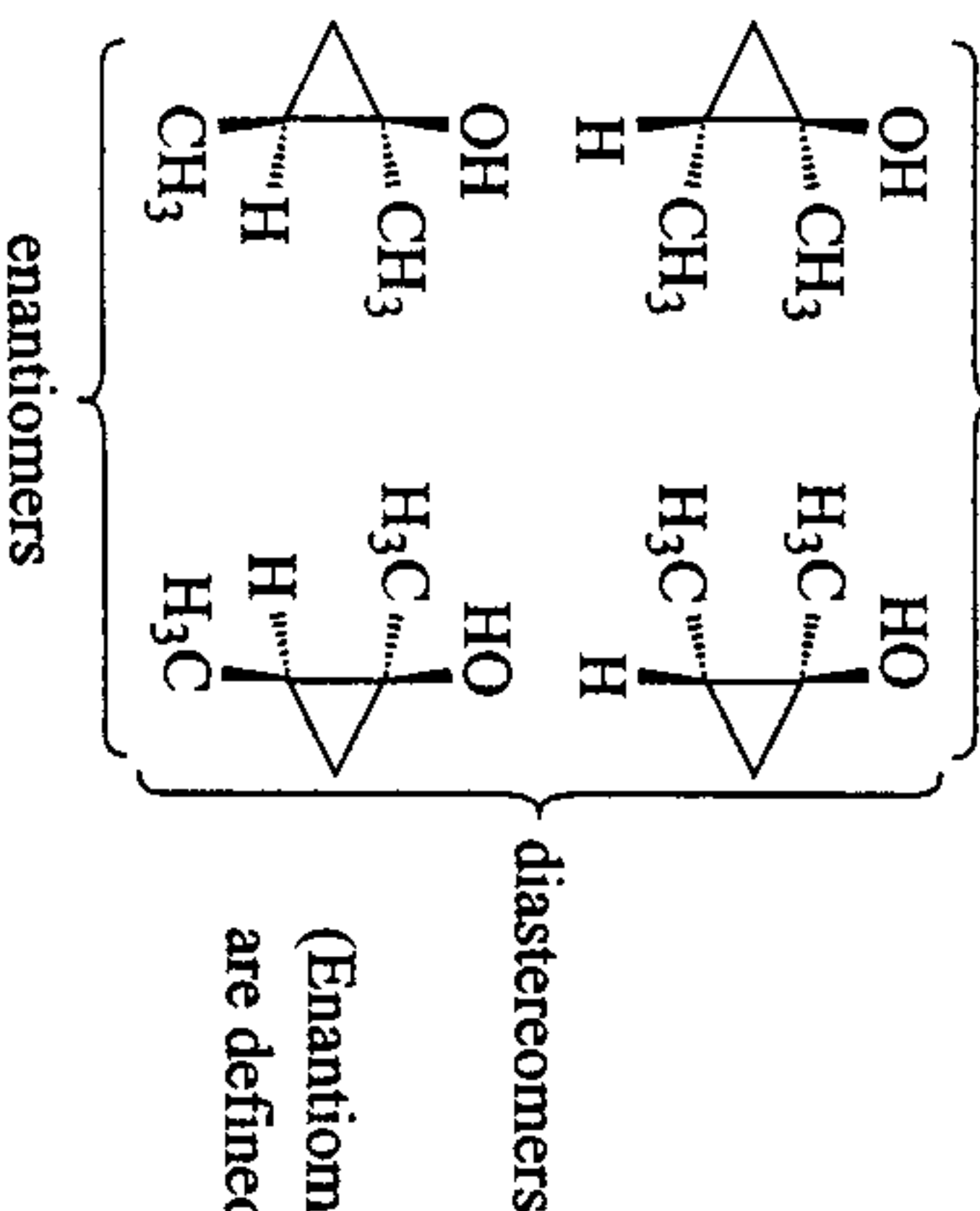


(b) The cis isomer will have the 3572 cm^{-1} band because only in it are the two hydroxyl groups close enough to permit intramolecular hydrogen-bonding. (Intermolecular hydrogen-bonding is not possible at high dilution in a non-polar solvent like CCl_4 .)

2.47 (a)



(b) enantiomers



(Enantiomers and diastereomers are defined in Chapter 5.)