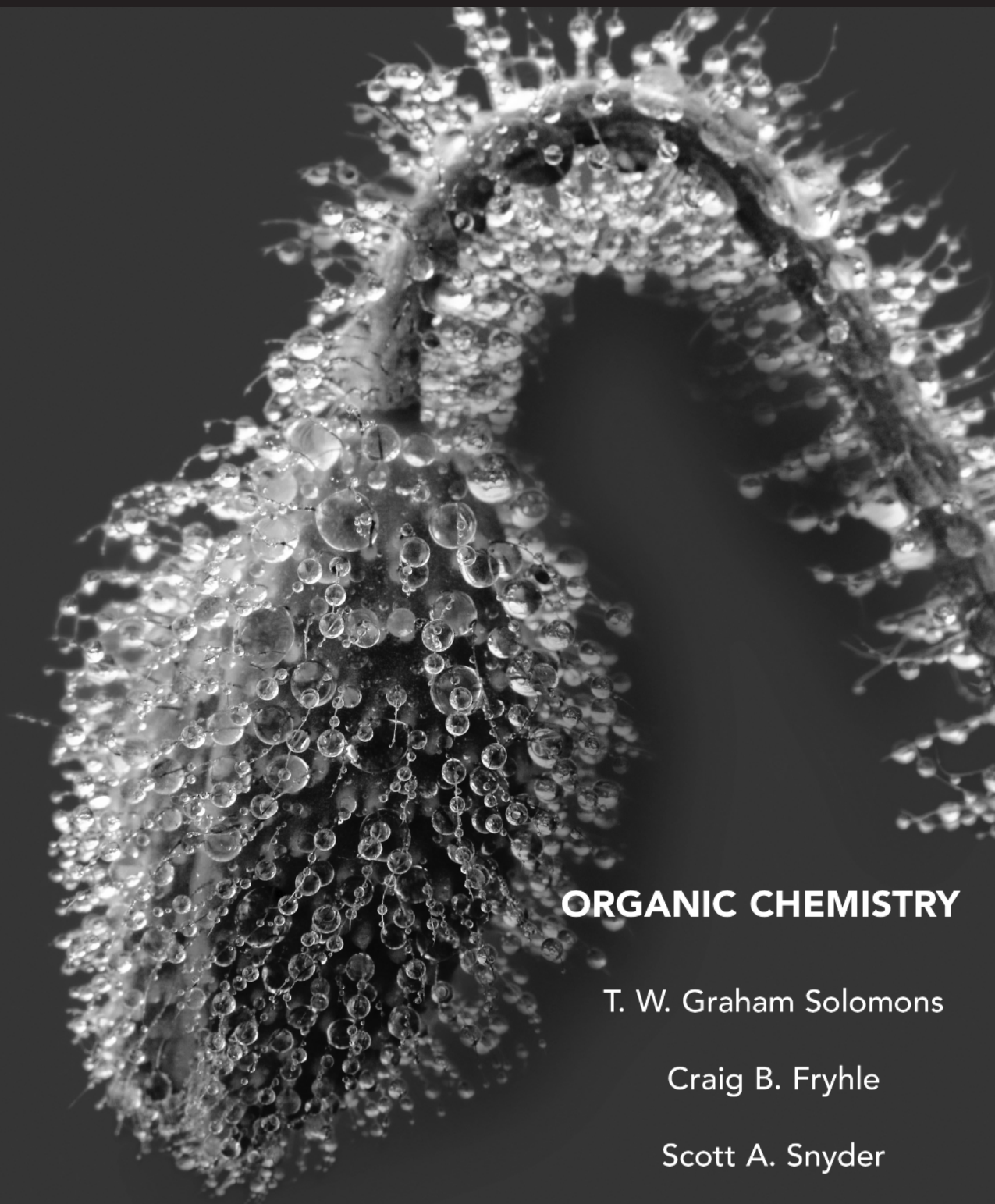# Study Guide and Solutions Manual to Accompany

T.W. Graham Solomons / Craig B. Fryhle / Scott A. Snyder / Jon Antilla

ORGANIC CHEMISTRY

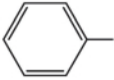T. W. Graham Solomons

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Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8–1.2
2° Alkyl, RCH_2R	1.2–1.5
3° Alkyl, R_3CH	1.4–1.8
Allylic, $R_2C{=}C{-}CH_3$ with R	1.6–1.9
Benzylic, $ArCH_3$	2.2–2.6
Alkyl chloride, RCH_2Cl	3.6–3.8
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Ketone, $RCCH_3$ (O)	2.1–2.6
Aldehyde, RCH (O)	9.5–10.5
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH{-}R$	5.2–5.7
Aromatic, ArH	6.0–8.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alcohol hydroxyl, ROH	0.5–6.0[a]
Carboxylic, $RCOH$ (O)	10–13[a]
Phenolic, $ArOH$	4.5–7.7[a]
Amino, $R{-}NH_2$	1.0–5.0[a]

[a]The chemical shifts of these protons vary in different solvents and with temperature and concentration.

Approximate carbon-13 chemical shifts

TYPE OF CARBON ATOM	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-C{-}X$ ($X = Cl$, Br, or $N-$)	10–65
Alcohol or ether, $-C{-}O$	50–90
Alkyne, $-C{\equiv}$	60–90
Alkene, $C{=}$	100–170
Aryl,	100–170
Nitriles, $-C{\equiv}N$	120–130
Amides, $-C(O){-}N-$	150–180
Carboxylic acids, esters, $-C(O){-}O$	160–185
Aldehydes, ketones, $-C(O)-$	182–215

STUDY GUIDE AND SOLUTIONS MANUAL
TO ACCOMPANY

ORGANIC CHEMISTRY

ELEVENTH EDITION

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STUDY GUIDE
AND
SOLUTIONS MANUAL
TO ACCOMPANY
ORGANIC
CHEMISTRY

ELEVENTH EDITION

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Cover Image	© Gerhard Schulz/Age Fotostock America, Inc.

This book was set in 10/12 Times Roman by Aptara Delhi and printed and bound by Bind-Rite. The cover was printed by Bind-Rite.

ACKNOWLEDGMENTS

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Methanol

CH_3OH

Now let's consider a molecule that incorporates structural aspects of both water and methane. Methanol (CH_3OH), or methyl alcohol, is such a molecule. In methanol, a central carbon atom has three hydrogens and an O–H group bonded to it. Three of the four valence electrons of the carbon atom are shared with a valence electron from the hydrogen atoms, forming three C—H bonds. The fourth valence electron of the carbon is shared with a valence electron from the oxygen atom, forming a C–O bond. The carbon atom now has an octet of valence electrons through the formation of four covalent bonds. The angles between these four covalent bonds is very near the ideal tetrahedral angle of 109.5°, allowing maximum separation between them. (The valence orbitals of the carbon are sp^3 hybridized.) At the oxygen atom, the situation is very similar to that in water. The oxygen uses its two unpaired valence electrons to form covalent bonds. One valence electron is used in the bond with the carbon atom, and the other is paired with an electron from the hydrogen to form the O–H bond. The remaining valence electrons of the oxygen are present as two nonbonding pairs, just as in water. The angles separating the four groups of electrons around the oxygen are thus near the ideal angle of 109.5°, but reduced slightly in the C–O–H angle due to repulsion by the two nonbonding pairs on the oxygen. (The valence orbitals of the oxygen are also sp^3 hybridized since there are four groups of valence electrons.) A Lewis structure for methanol is shown below, along with a three-dimensional perspective drawing.
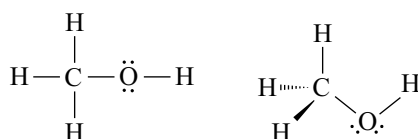
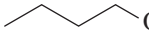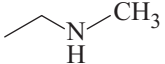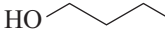## THE "CHARACTER" OF THE PUZZLE PIECES

With a mental image of the three-dimensional structures of water, methane, and methanol, we can ask how the structure of each, as a "puzzle piece," influences the interaction of each molecule with identical and different molecules. In order to answer this question we have to move one step beyond the three-dimensional shape of these molecules. We need to consider not only the location of the electron groups (bonding and nonbonding) but also the distribution of electronic charge in the molecules.

First, we note that nonbonding electrons represent a locus of negative charge, more so than electrons involved in bonding. Thus, water would be expected to have some partial negative charge localized in the region of the nonbonding electron pairs of the oxygen. The same would be true for a methanol molecule. The lower case Greek δ (delta) means "partial."
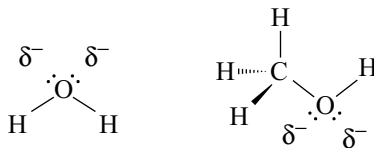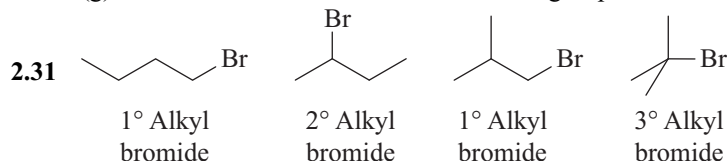
22   FAMILIES OF CARBON COMPOUNDS

2.25 (a) ∕∖∕∖OH would boil higher because its molecules can form hydrogen bonds to each other through the $-\overset{..}{\underset{..}{O}}-$H group.

(b) ∕∖N(H)CH$_3$ would boil higher because its molecules can form hydrogen bonds to each other through the $-\overset{..}{\underset{|}{N}}-$H group.

(c) HO∕∖∕∖OH because by having two $-\overset{..}{\underset{..}{O}}-$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.
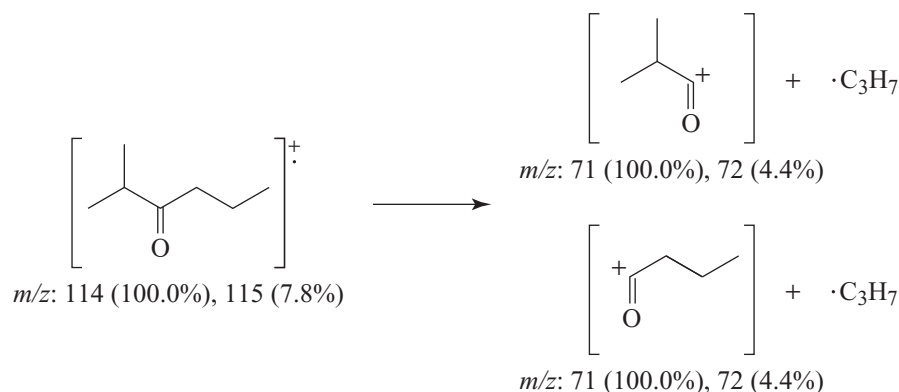
Functional Groups and Structural Formulas

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

2.31
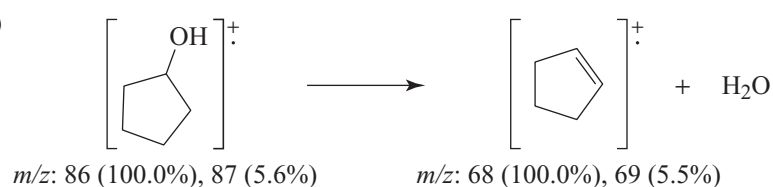
1° Alkyl bromide	2° Alkyl bromide	1° Alkyl bromide	3° Alkyl bromide

9.34 (a)

m/z: 114 (100.0%), 115 (7.8%)

m/z: 71 (100.0%), 72 (4.4%)

m/z: 71 (100.0%), 72 (4.4%)

(b)

m/z: 86 (100.0%), 87 (5.6%) m/z: 68 (100.0%), 69 (5.5%)

(c)

m/z: 142 (100.0%), 143 (10.0%) m/z: 58 (100.0%), 59 (3.4%)
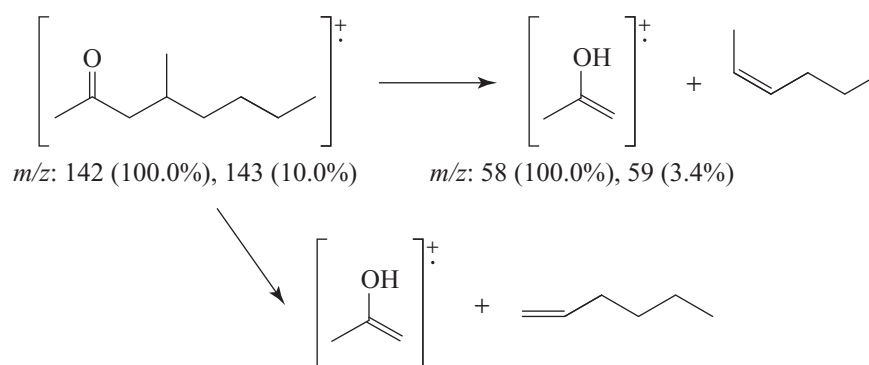
9.35 First calculate the expected masses of the compound shown for $C_6H_4 + {}^{79}Br + {}^{35}Cl$ (M) $= 190$ m/z, $C_6H_4 + {}^{37}Cl + {}^{79}Br$ (M+2) $= 192$ m/z or $C_6H_4 + {}^{35}Cl + {}^{81}Br$ (M+2) $= 192$ m/z, and $C_6H_4 + {}^{37}Cl + {}^{81}Br$ (M+4) $= 194$ m/z.

The relative ratio of ${}^{79}Br$ and ${}^{81}Br$ is 1:1 and ${}^{35}Cl$ and ${}^{37}Cl$ is 3:1. Therefore if you have 1 bromine and 1 chlorine in the molecule we must simplify the expression of (3:1)(1:1) = 3:4:1.

The ratio of the peaks will be M (190), M+2 (192), M+4 (194) = (3:4:1) or (77%: 100%: 24%).

**9.36** Ethyl bromide will have a significant M+2 for the ${}^{81}Br$ isotope at 110. The ratio of the peak at m/z 108 and m/z 110 will be approximately 1:1. The spectrum will also show peaks at M+1 and M+3 for the presence of a ${}^{13}C$ isotope (2.2 %)

Methoxybenzene will have a small peak, M+1, for the ${}^{13}C$ isotope (7.8 %)

9.37 The ion, $CH_2 \stackrel{+}{=} NH_2$, produced by the following fragmentation.
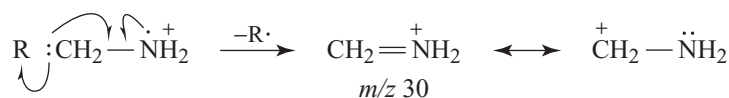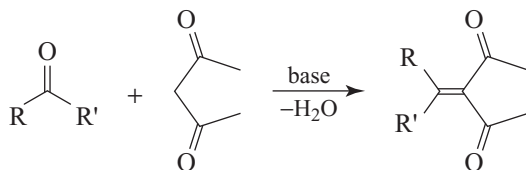
**472   CONDENSATION AND CONJUGATE ADDITION REACTIONS**

(c)
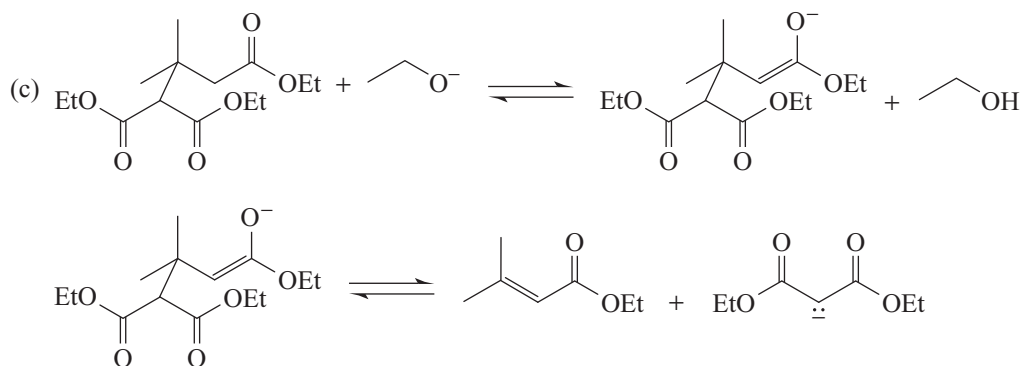
The Michael reaction is reversible, and the reaction just given is an example of a reverse Michael reaction.

19.42   Two reactions take place. The first is a reaction called the Knoevenagel condensation, initiated by attack of the conjugate base of the dicarbonyl compound on the ketone,

Then the α,β-unsaturated diketone reacts with a second mole of the active methylene compound in a Michael addition.
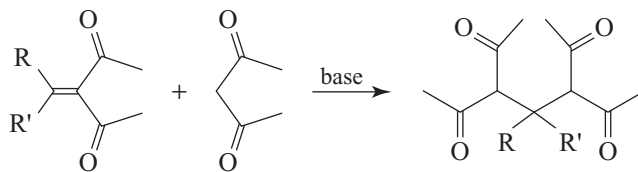
19.43
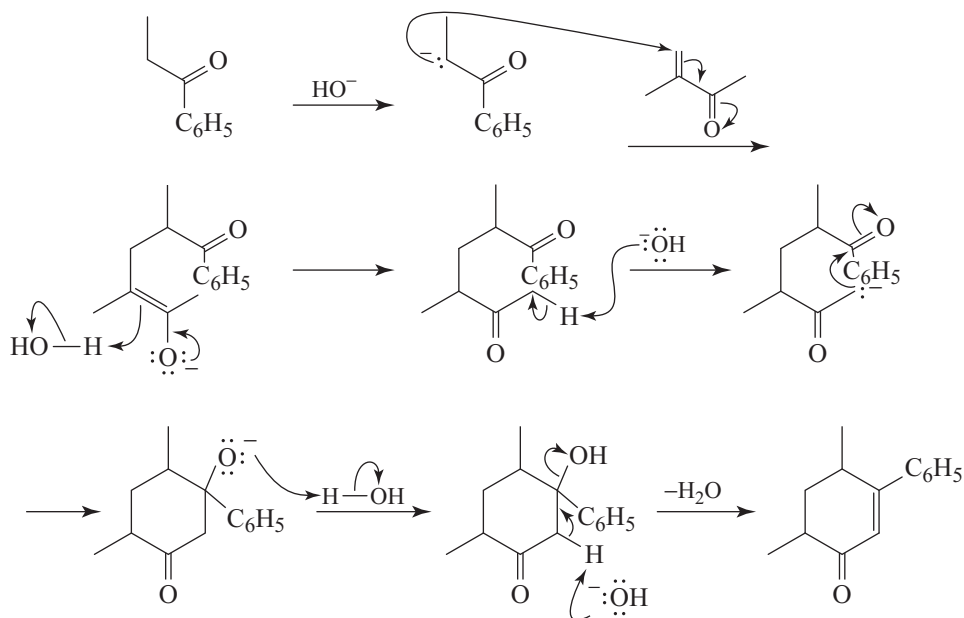
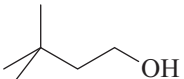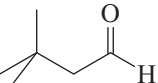## EXERCISE 12

12.1 (b)   **12.2** (a)

12.3   A = ——≡Li   or   ——≡MgBr
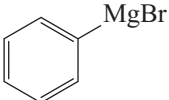
   B = NaH
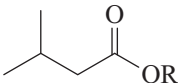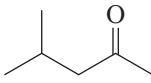
   C = CH₃I

12.4   A =

   B = PCC or Swern oxidation

   C =

   D =
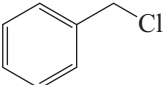
12.5   A =

   or

      (if excess CH₃MgBr is used)

EXERCISE 13

13.1 (d)   **13.2** (c)   **13.3** (c)   **13.4** (c)   **13.5** (b)

EXERCISE 14

14.1 (e)   **14.2** (a)   **14.3** (b)   **14.4** (b)

14.5

      14.6   Azulene

EXERCISE 15

15.1 (a)   **15.2** (a)   **15.3** (b)