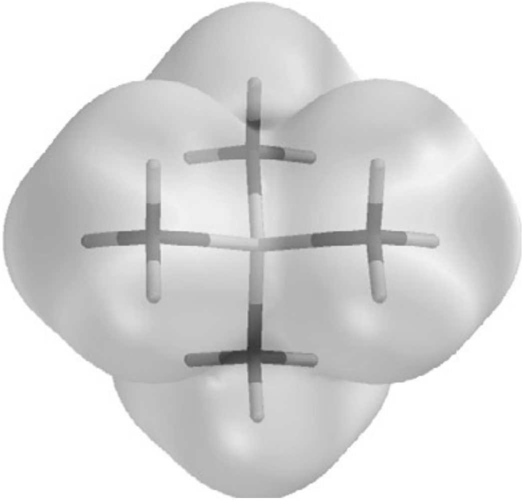


CHAPTER 13

SPECTROSCOPY

SOLUTIONS TO TEXT PROBLEMS

13.1 The field strength of an NMR spectrometer magnet and the frequency of electromagnetic radiation used to observe an NMR spectrum are directly proportional. Thus, the ratio 4.7 T/200 MHz is the same as 1.41 T/60 MHz. The magnetic field strength of a 60-MHz NMR spectrometer is 1.41 T.

13.2 The ratio of ^1H and ^{13}C resonance frequencies remains constant. When the ^1H frequency is 200 MHz, ^{13}C NMR spectra are recorded at 50.4 MHz. Thus, when the ^1H frequency is 100 MHz, ^{13}C NMR spectra will be observed at 25.2 MHz.

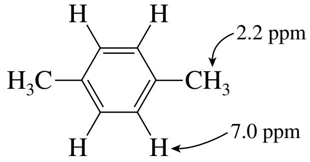
13.3 (*a*) Chemical shifts reported in parts per million (ppm) are independent of the field strength of the NMR spectrometer. Thus, to compare the ^1H NMR signal of bromoform ($CHBr_3$) recorded at 300 MHz with that of chloroform ($CHCl_3$) recorded at 200 MHz as given in the text, the chemical shift of bromoform must be converted from hertz to parts per million. The chemical shift for the proton in bromoform is

$$\delta = \frac{2065 \text{ Hz}}{300 \text{ MHz}} = 6.88 \text{ ppm}$$

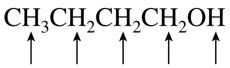
(*b*) The chemical shift of the proton in bromoform (δ 6.88 ppm) is less than that of chloroform (δ 7.28 ppm). The proton signal of bromoform is farther upfield and thus is **more shielded** than the proton in chloroform.

13.4 In both chloroform ($CHCl_3$) and 1,1,1-trichloroethane (CH_3CCl_3) three chlorines are present. In CH_3CCl_3, however, the protons are one carbon removed from the chlorines, and thus the deshielding effect of the halogens will be less. The ^1H NMR signal of CH_3CCl_3 appears 4.6 ppm **upfield** from the proton signal of chloroform. The chemical shift of the protons in CH_3CCl_3 is δ 2.6 ppm.

13.5 1,4-Dimethylbenzene has two types of protons: those attached directly to the benzene ring and those of the methyl groups. Aryl protons are significantly less shielded than alkyl protons. As shown in text Table 13.1 they are expected to give signals in the chemical shift range δ 6.5–8.5 ppm. Thus, the signal at δ 7.0 ppm is due to the protons of the benzene ring. The signal at δ 2.2 ppm is due to the methyl protons.



13.6 (*b*) Four nonequivalent sets of protons are bonded to carbon in 1-butanol as well as a fifth distinct type of proton, the one bonded to oxygen. There should be five signals in the ^{1}H NMR spectrum of 1-butanol.



$$\underset{\uparrow}{CH_3}\underset{\uparrow}{CH_2}\underset{\uparrow}{CH_2}\underset{\uparrow}{CH_2}\underset{\uparrow}{OH}$$

Five different proton environments
in 1-butanol; five signals

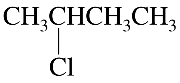
(*c*) Apply the "proton replacement" test to butane.

$CH_3CH_2CH_2CH_3$

Butane

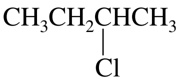
$ClCH_2CH_2CH_2CH_3$

1-Chlorobutane



$$CH_3\underset{\displaystyle Cl}{C}HCH_3CH_3$$

2-Chlorobutane



$$CH_3CH_2\underset{\displaystyle Cl}{C}HCH_3$$

2-Chlorobutane

$CH_3CH_2CH_2CH_2Cl$

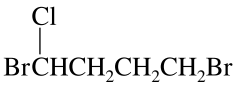
1-Chlorobutane

Butane has **two** different types of protons; it will exhibit **two** signals in its ^{1}H NMR spectrum.

(*d*) Like butane, 1,4-dibromobutane has two different types of protons. This can be illustrated by using a chlorine atom as a test group.

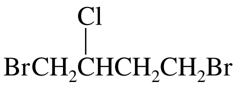
$BrCH_2CH_2CH_2CH_2Br$

1,4-Dibromobutane



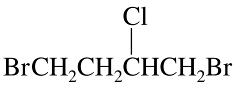
$$Br\overset{\displaystyle Cl}{C}HCH_2CH_2CH_2Br$$

1,4-Dibromo-1-chlorobutane



$$BrCH_2\overset{\displaystyle Cl}{C}HCH_2CH_2Br$$

1,4-Dibromo-2-chlorobutane



$$BrCH_2CH_2\overset{\displaystyle Cl}{C}HCH_2Br$$

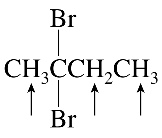
1,4-Dibromo-2-chlorobutane

$$BrCH_2CH_2CH_2\overset{\displaystyle Cl}{C}HBr$$

1,4-Dibromo-1-chlorobutane

The ^{1}H NMR spectrum of 1,4-dibromobutane is expected to consist of two signals.

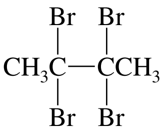
(*e*) All the carbons in 2,2-dibromobutane are different from each other, and so protons attached to one carbon are not equivalent to the protons attached to any of the other carbons. This compound should have **three** signals in its ^{1}H NMR spectrum.



$$\underset{\uparrow}{CH_3}\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}\underset{\uparrow}{CH_2}\underset{\uparrow}{CH_3}$$

2,2-Dibromobutane has three
nonequivalent sets of protons.

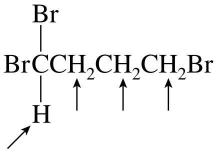
(*f*) All the protons in 2,2,3,3-tetrabromobutane are equivalent. Its ^{1}H NMR spectrum will consist of one signal.



$$CH_3\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}-\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}CH_3$$

2,2,3,3-Tetrabromobutane

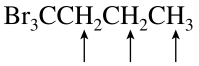
(*g*) There are **four** nonequivalent sets of protons in 1,1,4-tribromobutane. It will exhibit four signals in its ^{1}H NMR spectrum.



$\mathrm{Br}\overset{\mathrm{Br}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{CH_2CH_2CH_2Br}$

1,1,4-Tribromobutane

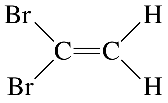
(*h*) The seven protons of 1,1,1-tribromobutane belong to three nonequivalent sets, and hence the ^{1}H NMR spectrum will consist of three signals.



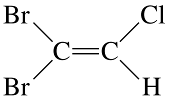
$Br_3CCH_2CH_2CH_3$

1,1,1-Tribromobutane

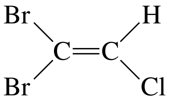
13.7 (*b*) Apply the replacement test to each of the protons of 1,1-dibromoethene.



1,1-Dibromoethene



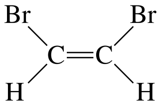
1,1-Dibromo-2-chloroethene



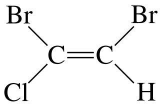
1,1-Dibromo-2-chloroethene

Replacement of one proton by a test group (Cl) gives exactly the same compound as replacement of the other. The two protons of 1,1-dibromoethene are equivalent, and there is only one signal in the ^{1}H NMR spectrum of this compound.

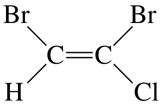
(*c*) The replacement test reveals that both protons of *cis*-1,2-dibromoethene are equivalent.



cis-1,2-Dibromoethene



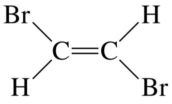
(*Z*)-1,2-Dibromo-1-chloroethene



(*Z*)-1,2-Dibromo-1-chloroethene

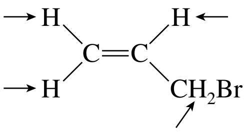
Because both protons are equivalent, the ^{1}H NMR spectrum of *cis*-1,2-dibromoethene consists of one signal.

(*d*) Both protons of *trans*-1,2-dibromoethene are equivalent; each is cis to a bromine substituent.

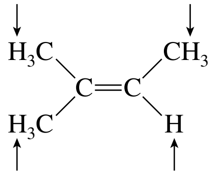


trans-1,2-Dibromoethene
(one signal in the ^{1}H NMR spectrum)

(*e*) **Four** nonequivalent sets of protons occur in allyl bromide.



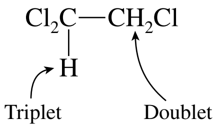
Allyl bromide (four signals in the ^{1}H NMR spectrum) (*f*) The protons of a single methyl group are equivalent to one another, but all three methyl groups of 2-methyl-2-butene are nonequivalent. The vinyl proton is unique.



2-Methyl-2-butene (four signals in the ^1H NMR spectrum)

13.8 (*b*) The three methyl protons of 1,1,1-trichloroethane (Cl_3CCH_3) are equivalent. They have the same chemical shift and do not split each other's signals. The ^1H NMR spectrum of Cl_3CCH_3 consists of a single sharp peak.

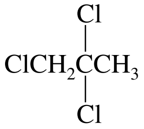
(*c*) Separate signals will be seen for the methylene (CH_2) protons and for the methine (CH) proton of 1,1,2-trichloroethane.



1,1,2-Trichloroethane

The methine proton splits the signal for the methylene protons into a doublet. The two methylene protons split the methine proton's signal into a triplet.

(*d*) Examine the structure of 1,2,2-trichloropropane.

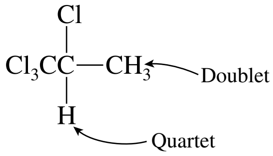


$$ClCH_2\overset{Cl}{\underset{Cl}{C}}CH_3$$

1,2,2-Trichloropropane

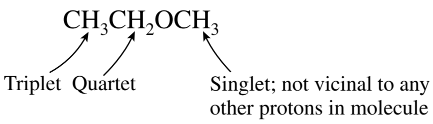
The ^1H NMR spectrum exhibits a signal for the two equivalent methylene protons and one for the three equivalent methyl protons. Both these signals are sharp singlets. The protons of the methyl group and the methylene group are separated by more than three bonds and do not split each other's signals.

(*e*) The methine proton of 1,1,1,2-tetrachloropropane splits the signal of the methyl protons into a doublet; its signal is split into a quartet by the three methyl protons.

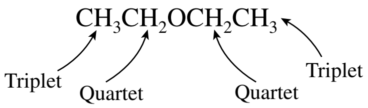


1,1,1,2-Tetrachloropropane

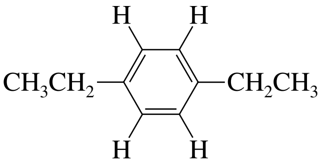
13.9 (*b*) The ethyl group appears as a triplet–quartet pattern and the methyl group as a singlet.



(*c*) The two ethyl groups of diethyl ether are equivalent to each other. The two methyl groups appear as one triplet and the two methylene groups as one quartet.



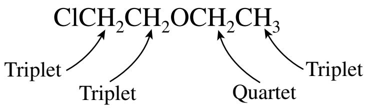
(*d*) The two ethyl groups of *p*-diethylbenzene are equivalent to each other and give rise to a single triplet–quartet pattern.



Three signals:
CH_3 triplet;
CH_2 quartet;
aromatic H singlet

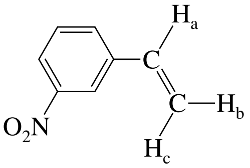
All four protons of the aromatic ring are equivalent, have the same chemical shift, and do not split either each other's signals or any of the signals of the ethyl group.

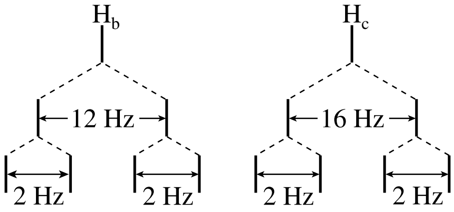
(*e*) Four nonequivalent sets of protons occur in this compound:



Vicinal protons in the $ClCH_2CH_2O$ group split one another's signals, as do those in the CH_3CH_2O group.

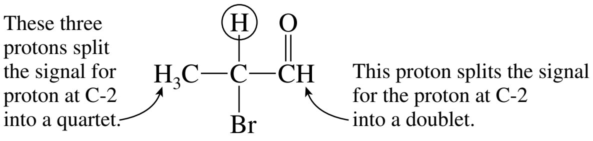
13.10 Both H_b and H_c in *m*-nitrostyrene appear as doublets of doublets. H_b is coupled to H_a by a coupling constant of 12 Hz and to H_c by a coupling constant of 2 Hz. H_c is coupled to H_a by a coupling constant of 16 Hz and to H_b by a coupling constant of 2 Hz.



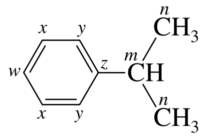


(diagrams not to scale)

13.11 (*b*) The signal of the proton at C-2 is split into a quartet by the methyl protons, and each line of this quartet is split into a doublet by the aldehyde proton. It appears as a doublet of quartets. (*Note:* It does not matter whether the splitting pattern is described as a doublet of quartets or a quartet of doublets. There is no substantive difference in the two descriptions.)

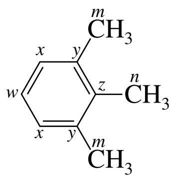


13.12 (*b*) The two methyl carbons of the isopropyl group are equivalent.



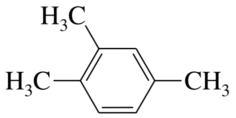
Four different types of carbons occur in the aromatic ring and two different types are present in the isopropyl group. The ^{13}C NMR spectrum of isopropylbenzene contains **six** signals.

(*c*) The methyl substituent at C-2 is different from those at C-1 and C-3:



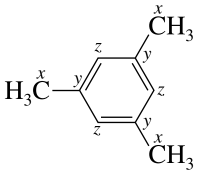
The four nonequivalent ring carbons and the two different types of methyl carbons give rise to a ^{13}C NMR spectrum that contains **six** signals.

(*d*) The three methyl carbons of 1,2,4-trimethylbenzene are different from one another:



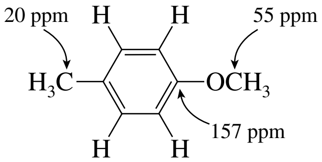
Also, all the ring carbons are different from each other. The nine different carbons give rise to **nine** separate signals.

(*e*) All three methyl carbons of 1,3,5-trimethylbenzene are equivalent.

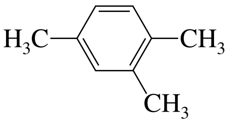


Because of its high symmetry 1,3,5-trimethylbenzene has only **three** signals in its ^{13}C NMR spectrum.

13.13 sp^3-Hybridized carbons are more shielded than sp^2-hybridized ones. Carbon *x* is the most shielded, and has a chemical shift of δ 20 ppm. The oxygen of the OCH_3 group decreased the shielding of carbon *z*; its chemical shift is δ 55 ppm. The least shielded is carbon *y* with a chemical shift of δ 157 ppm.



13.14 The ^{13}C NMR spectrum in Figure 13.22 shows nine signals and is the spectrum of 1,2,4-trimethylbenzene from part (*d*) of Problem 13.12. Six of the signals, in the range δ 127–138 ppm, are due to the six nonequivalent carbons of the benzene ring. The three signals near δ 20 ppm are due to the three nonequivalent methyl groups.



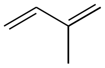
1,2,4-Trimethylbenzene

13.15 The infrared spectrum of Figure 13.31 has no absorption in the 1600–1800-cm^{-1} region, and so the unknown compound cannot contain a carbonyl (C═O) group. It cannot therefore be acetophenone or benzoic acid.

The broad, intense absorption at 3300 cm^{-1} is attributable to a hydroxyl group. Although both phenol and benzyl alcohol are possibilities, the peaks at 2800–2900 cm^{-1} reveal the presence of hydrogen bonded to sp^3-hybridized carbon. All carbons are sp^2-hybridized in phenol. The infrared spectrum is that of **benzyl alcohol.**

13.16 The energy of electromagnetic radiation is inversely proportional to its wavelength. Since excitation of an electron for the $\pi \rightarrow \pi^*$ transition of ethylene occurs at a shorter wavelength (λ_{max} = 170 nm) than that of *cis, trans*-1,3-cyclooctadiene (λ_{max}= 230 nm), the HOMO–LUMO energy difference in ethylene is **greater.**

13.17 Conjugation shifts λ_{max} to longer wavelengths in alkenes. The conjugated diene 2-methyl-1,3-butadiene has the longest wavelength absorption, λ_{max} = 222 nm. The isolated diene 1,4-pentadiene and the simple alkene cyclopentene both absorb below 200 nm.



2-Methyl-1,3-butadiene
(λ_{max} = 222 nm)

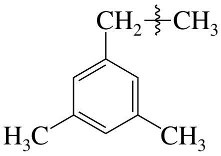
13.18 (*b*) The distribution of molecular-ion peaks in *o*-dichlorobenzene is identical to that in the para isomer. As the sample solution to part (*a*) in the text describes, peaks at *m*/*z* 146, 148, and 150 are present for the molecular ion.

(*c*) The two isotopes of bromine are ^{79}Br and ^{81}Br. When both bromines of *p*-dibromobenzene are ^{79}Br, the molecular ion appears at *m*/*z* 234. When one is ^{79}Br and the other is ^{81}Br, *m*/*z* for the molecular ion is 236. When both bromines are ^{81}Br, *m*/*z* for the molecular ion is 238.

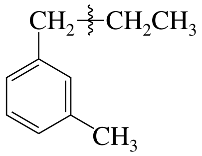
(*d*) The combinations of ^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br in *p*-bromochlorobenzene and the values of *m*/*z* for the corresponding molecular ion are as shown.

(^{35}Cl, ^{79}Br) *m*/*z* = 190
(^{37}Cl, ^{79}Br) or (^{35}Cl, ^{81}Br) *m*/*z* = 192
(^{37}Cl, ^{81}Br) *m*/*z* = 194

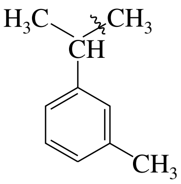
13.19 The base peak in the mass spectrum of alkylbenzenes corresponds to carbon–carbon bond cleavage at the benzylic carbon.



Base peak: $C_9H_{11}^+$
m/*z* 119



Base peak: $C_8H_9^+$
m/*z* 105



Base peak: $C_9H_{11}^+$
m/*z* 119

13.20 (*b*) The index of hydrogen deficiency is given by the following formula:

$$\text{Index of hydrogen deficiency} = \tfrac{1}{2}(C_nH_{2n+2} - C_nH_x)$$

The compound given contains eight carbons (C_8H_8); therefore,

$$\begin{aligned}\text{Index of hydrogen deficiency} &= \tfrac{1}{2}(C_8H_{18} - C_8H_8)\\ &= 5\end{aligned}$$

The problem specifies that the compound consumes 2 mol of hydrogen, and so it contains two double bonds (or one triple bond). Since the index of hydrogen deficiency is equal to 5, there must be three rings.

(*c*) Chlorine substituents are equivalent to hydrogens when calculating the index of hydrogen deficiency. Therefore, consider $C_8H_8Cl_2$ as equivalent to C_8H_{10}. Thus, the index of hydrogen deficiency of this compound is 4.

$$\begin{aligned}\text{Index of hydrogen deficiency} &= \tfrac{1}{2}(C_8H_{18} - C_8H_{10})\\ &= 4\end{aligned}$$

Since the compound consumes 2 mol of hydrogen on catalytic hydrogenation, it must therefore contain two rings.

(*d*) Oxygen atoms are ignored when calculating the index of hydrogen deficiency. Thus, C_8H_8O is treated as if it were C_8H_8.

$$\begin{aligned}\text{Index of hydrogen deficiency} &= \tfrac{1}{2}(C_8H_{18} - C_8H_8)\\ &= 5\end{aligned}$$

Since the problem specifies that 2 mol of hydrogen is consumed on catalytic hydrogenation, this compound contains three rings.

(*e*) Ignoring the oxygen atoms in $C_8H_{10}O_2$, we treat this compound as if it were C_8H_{10}.

$$\begin{aligned}\text{Index of hydrogen deficiency} &= \tfrac{1}{2}(C_8H_{18} - C_8H_{10})\\ &= 4\end{aligned}$$

Because 2 mol of hydrogen is consumed on catalytic hydrogenation, there must be two rings.

(*f*) Ignore the oxygen, and treat the chlorine as if it were hydrogen. Thus, C_8H_9ClO is treated as if it were C_8H_{10}. Its index of hydrogen deficiency is 4, and it contains two rings.

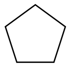
13.21 Since each compound exhibits only a single peak in its ^1H NMR spectrum, all the hydrogens are equivalent in each one. Structures are assigned on the basis of their molecular formulas and chemical shifts.

(*a*) This compound has the molecular formula C_8H_{18} and so must be an alkane. The 18 hydrogens are contributed by six equivalent methyl groups.

$$(CH_3)_3CC(CH_3)_3$$

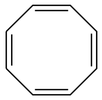
2,2,3,3-Tetramethylbutane
(δ 0.9 ppm)

(*b*) A hydrocarbon with the molecular formula C_5H_{10} has an index of hydrogen deficiency of 1 and so is either a cycloalkane or an alkene. Since all ten hydrogens are equivalent, this compound must be cyclopentane.



Cyclopentane
(δ 1.5 ppm)

(*c*) The chemical shift of the eight equivalent hydrogens in C_8H_8 is δ 5.8 ppm, which is consistent with protons attached to a carbon–carbon double bond.



1,3,5,7-Cyclooctatetraene
(δ 5.8 ppm)

(*d*) The compound C_4H_9Br has no rings or double bonds. The nine hydrogens belong to three equivalent methyl groups.

$(CH_3)_3CBr$

tert-Butyl bromide (δ 1.8 ppm)

(*e*) The dichloride has no rings or double bonds (index of hydrogen deficiency = 0). The four equivalent hydrogens are present as two —CH_2Cl groups.

$ClCH_2CH_2Cl$

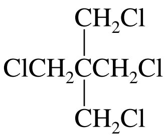
1,2-Dichloroethane (δ 3.7 ppm)

(*f*) All three hydrogens in $C_2H_3Cl_3$ must be part of the same methyl group in order to be equivalent.

CH_3CCl_3

1,1,1-Trichloroethane (δ 2.7 ppm)

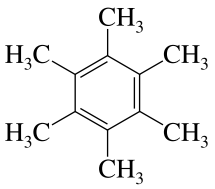
(*g*) This compound has no rings or double bonds. To have eight equivalent hydrogens it must have four equivalent methylene groups.



$$C(CH_2Cl)_4$$

1,3-Dichloro-2,2-di(chloromethyl)propane
(δ 3.7 ppm)

(*h*) A compound with a molecular formula of $C_{12}H_{18}$ has an index of hydrogen deficiency of 4. A likely candidate for a compound with 18 equivalent hydrogens is one with six equivalent CH_3 groups. Thus, 6 of the 12 carbons belong to CH_3 groups, and the other 6 have no hydrogens. The compound is hexamethylbenzene.

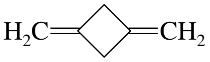


A chemical shift of δ 2.2 ppm is consistent with the fact that all of the protons are benzylic hydrogens.

(*i*) The molecular formula of $C_3H_6Br_2$ tells us that the compound has no double bonds and no rings. All six hydrogens are equivalent, indicating two equivalent methyl groups. The compound is 2,2-dibromopropane, $(CH_3)_2CBr_2$.

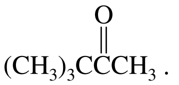
13.22 In each of the parts to this problem, nonequivalent protons must *not* be bonded to adjacent carbons, because we are told that the two signals in each case are singlets.

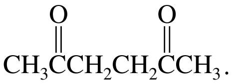
(*a*) Each signal corresponds to four protons, and so each must result from two equivalent CH_2 groups. The four CH_2 groups account for four of the carbons of C_6H_8, leaving two carbons that bear no hydrogens. A molecular formula of C_6H_8 corresponds to an index of hydrogen deficiency of 3. A compound consistent with these requirements is



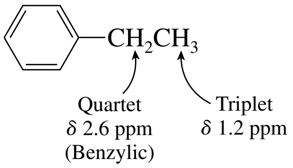
The signal at δ 5.6 ppm is consistent with that expected for the four vinylic protons. The signal at δ 2.7 ppm corresponds to that for the allylic protons of the ring.

(*b*) The compound has a molecular formula of $C_5H_{11}Br$ and therefore has no double bonds or rings. A 9-proton singlet at δ 1.1 ppm indicates three equivalent methyl groups, and a 2-proton singlet at δ 3.3 ppm indicates a CH_2Br group. The correct structure is $(CH_3)_3CCH_2Br$.

(*c*) This compound ($C_6H_{12}O$) has three equivalent CH_3 groups, along with a fourth CH_3 group that is somewhat less shielded. Its molecular formula indicates that it can have either one double bond or one ring. This compound is  $(CH_3)_3C\overset{\displaystyle O}{\overset{\|}{C}}CH_3$.

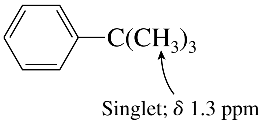
(*d*) A molecular formula of $C_6H_{10}O_2$ corresponds to an index of hydrogen deficiency of 2. The signal at δ 2.2 ppm (6H) is likely due to two equivalent CH_3 groups, and the one at δ 2.7 ppm (4H) to two equivalent CH_2 groups. The compound is  $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3$.

13.23 (*a*) A 5-proton signal at δ 7.1 ppm indicates a monosubstituted aromatic ring. With an index of hydrogen deficiency of 4, C_8H_{10} contains this monosubstituted aromatic ring and no other rings or multiple bonds. The triplet–quartet pattern at high field suggests an ethyl group.



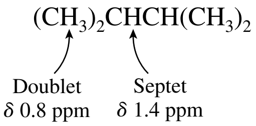
Ethylbenzene

(*b*) The index of hydrogen deficiency of 4 and the 5-proton multiplet at δ 7.0 to 7.5 ppm are accommodated by a monosubstituted aromatic ring. The remaining four carbons and nine hydrogens are most reasonably a *tert*-butyl group, since all nine hydrogens are equivalent.



tert-Butylbenzene

(*c*) Its molecular formula requires that C_6H_{14} be an alkane. The doublet–septet pattern is consistent with an isopropyl group, and the total number of protons requires that two of these groups be present.

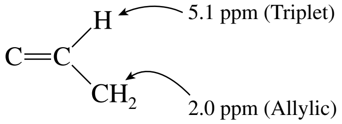


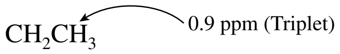
2,3-Dimethylbutane

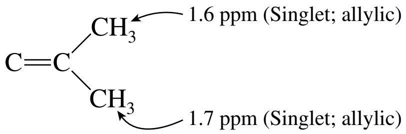
Back Forward Main Menu TOC Study Guide TOC Student OLC MHHE Website

Note that the methine (CH) protons do not split each other, because they are equivalent and have the same chemical shift.

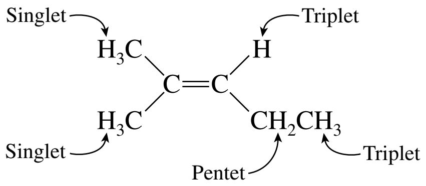
(*d*) The molecular formula C_6H_{12} requires the presence of one double bond or ring. A peak at δ 5.1 ppm is consistent with —C═CH, and so the compound is a noncyclic alkene. The vinyl proton gives a triplet signal, and so the group C═CHCH$_2$ is present. The ^{1}H NMR spectrum shows the presence of the following structural units:





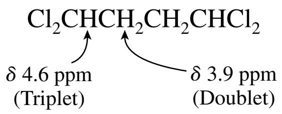


Putting all these fragments together yields a unique structure.



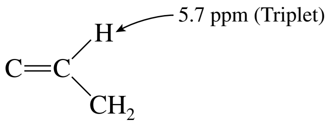
2-Methyl-2-pentene

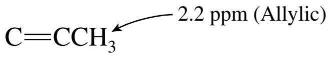
(*e*) The compound $C_4H_6Cl_4$ contains no double bonds or rings. There are no high-field peaks (δ 0.5 to 1.5 ppm), and so there are no methyl groups. At least one chlorine substituent must therefore be at each end of the chain. The most likely structure has the four chlorines divided into two groups of two.


$Cl_2CHCH_2CH_2CHCl_2$

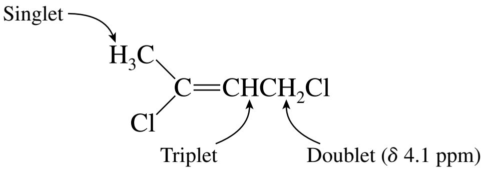
1,1,4,4-Tetrachlorobutane

(*f*) The molecular formula $C_4H_6Cl_2$ indicates the presence of one double bond or ring. A signal at δ 5.7 ppm is consistent with a proton attached to a doubly bonded carbon. The following structural units are present:





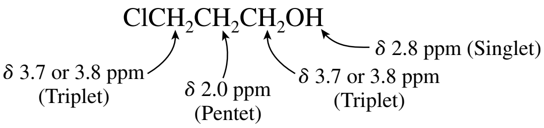
For the methyl group to appear as a singlet and the methylene group to appear as a doublet, the chlorine substituents must be distributed as shown:



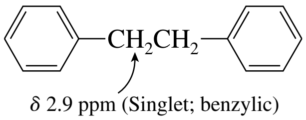
1,3-Dichloro-2-butene

The stereochemistry of the double bond (*E* or *Z*) is not revealed by the ^1H NMR spectrum.

(*g*) A molecular formula of C_3H_7ClO is consistent with the absence of rings and multiple bonds (index of hydrogen deficiency = 0). None of the signals is equivalent to three protons, and so no methyl groups are present. Three methylene groups occur, all of which are different from each other. The compound is therefore:



(*h*) The compound has a molecular formula of $C_{14}H_{14}$ and an index of hydrogen deficiency of 8. With a 10-proton signal at δ 7.1 ppm, a logical conclusion is that there are two monosubstituted benzene rings. The other four protons belong to two equivalent methylene groups.

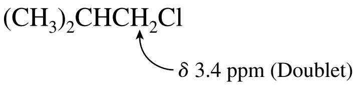


1,2-Diphenylethane

13.24 The compounds of molecular formula C_4H_9Cl are the isomeric chlorides: butyl, isobutyl, *sec*-butyl, and *tert*-butyl chloride.

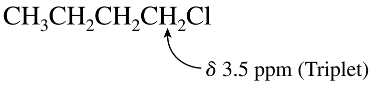
(*a*) All nine methyl protons of *tert*-butyl chloride $(CH_3)_3CCl$ are equivalent; its ^1H NMR spectrum has only one peak.

(*b*) A doublet at δ 3.4 ppm indicates a $—CH_2Cl$ group attached to a carbon that bears a single proton.



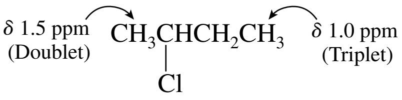
Isobutyl chloride

(*c*) A triplet at δ 3.5 ppm means that a methylene group is attached to the carbon that bears the chlorine.



Butyl chloride

(*d*) This compound has two nonequivalent methyl groups.



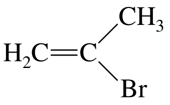
$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$

sec-Butyl chloride

13.25 Compounds with the molecular formula C_3H_5Br have either one ring or one double bond.

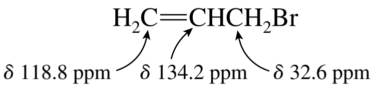
(*a*) The two peaks at δ 5.4 and 5.6 ppm have chemical shifts consistent with the assumption that each peak is due to a vinyl proton ($C{=}CH$). The remaining three protons belong to an allylic methyl group (δ 2.3 ppm).

The compound cannot be $CH_3CH{=}CHBr$, because the methyl signal would be split into a doublet. Isomer A can only be



2-Bromo-1-propene

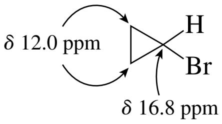
(*b*) Two of the carbons of isomer B have chemical shifts characteristic of sp^2-hybridized carbon. One of these bears two protons (δ 118.8 ppm); the other bears one proton (δ 134.2 ppm). The remaining carbon is sp^3-hybridized and bears two hydrogens. Isomer B is allyl bromide.



$H_2C{=}CHCH_2Br$

Allyl bromide

(*c*) All the carbons are sp^3-hybridized in this isomer. Two of the carbons belong to equivalent CH_2 groups, and the other bears only one hydrogen. Isomer C is cyclopropyl bromide.

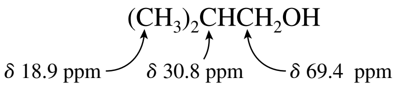


Cyclopropyl bromide

13.26 All these compounds have the molecular formula $C_4H_{10}O$. They have neither multiple bonds nor rings.

(*a*) Two equivalent CH_3 groups occur at δ 18.9 ppm. One carbon bears a single hydrogen. The least shielded carbon, presumably the one bonded to oxygen, has two hydrogen substituents.

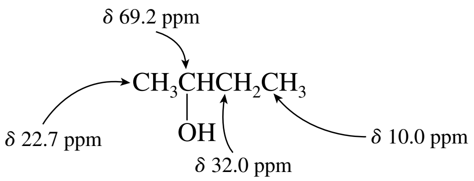
Putting all the information together reveals this compound to be isobutyl alcohol.



$(CH_3)_2CHCH_2OH$

Isobutyl alcohol

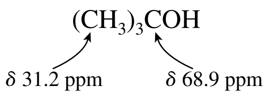
(*b*) This compound has four distinct peaks, and so none of the four carbons is equivalent to any of the others. The signal for the least shielded carbon represents CH, and so the oxygen is attached to a secondary carbon. Only one carbon appears at low field; the compound is an alcohol, not an ether. Therefore;



$CH_3CH(OH)CH_2CH_3$

sec-Butyl alcohol

(*c*) Signals for three equivalent CH_3 carbons indicate that this isomer is *tert*-butyl alcohol. This assignment is reinforced by the observation that the least shielded carbon has no hydrogens attached to it.

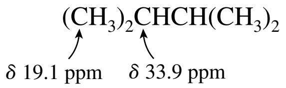


$(CH_3)_3COH$

tert-Butyl alcohol

13.27 The molecular formula of C_6H_{14} for each of these isomers requires that all of them be alkanes.

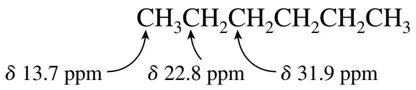
(*a*) This compound contains only CH_3 and CH carbons.



$(CH_3)_2CHCH(CH_3)_2$

2,3-Dimethylbutane

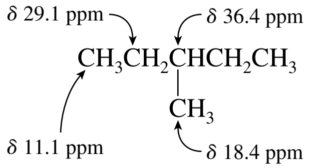
(*b*) This isomer has no CH carbons, and two different kinds of CH_2 groups.



$CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

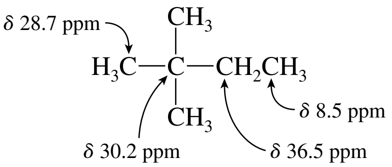
(*c*) CH_3, CH_2, and CH carbons are all present in this isomer. There are two different kinds of CH_3 groups.



$CH_3CH_2CH(CH_3)CH_2CH_3$

3-Methylpentane

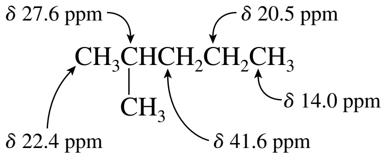
(*d*) This isomer contains a quaternary carbon in addition to a CH_2 group and two different kinds of CH_3 groups.



$H_3C{-}C(CH_3)_2{-}CH_2CH_3$

2,2-Dimethylbutane

(*e*) This isomer contains two different kinds of CH_3 groups, two different kinds of CH_2 groups, and a CH group.

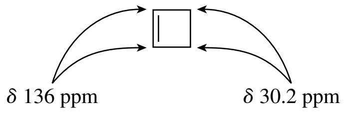


$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_3$

2-Methylpentane

13.28 The index of hydrogen deficiency of the compound C_4H_6 is 2. It can have two double bonds, two rings, one ring and one double bond, or one triple bond.

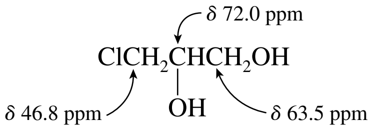
The chemical shift data indicate that two carbons are sp^3-hybridized and two are sp^2. The most reasonable structure that is consistent with ^{13}C NMR data is cyclobutene.



Cyclobutene

The compound cannot be 1- or 2-methylcyclopropene. Neither of the carbon signals represents a methyl group.

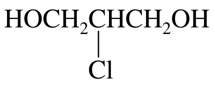
13.29 Each of the carbons in the compound gives its ^{13}C NMR signal at relatively low field; it is likely that each one bears an electron-withdrawing substituent. The compound is



$ClCH_2\underset{\substack{|\\ OH}}{C}HCH_2OH$

3-Chloro-1,2-propanediol

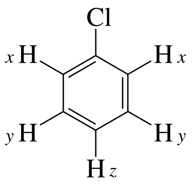
The isomeric compound 2-chloro-1,3-propanediol



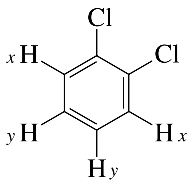
$HOCH_2\underset{\substack{|\\ Cl}}{C}HCH_2OH$

cannot be correct. The C-1 and C-3 positions are equivalent; the ^{13}C NMR spectrum of this compound exhibits only two peaks, not three.

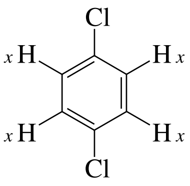
13.30 (*a*) All the hydrogens are equivalent in *p*-dichlorobenzene; therefore it has the simplest ^1H NMR spectrum of the three compounds chlorobenzene, *o*-dichlorobenzene, and *p*-dichlorobenzene.



Chlorobenzene
(three different kinds of protons)

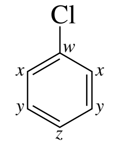


o-Dichlorobenzene
(two different kinds of protons)

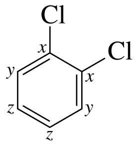


p-Dichlorobenzene
(all protons are equivalent)

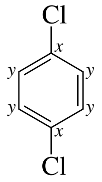
(*b–d*) In addition to giving the simplest ^1H NMR spectrum, *p*-dichlorobenzene gives the simplest ^{13}C NMR spectrum. It has two peaks in its ^{13}C NMR spectrum, chlorobenzene has four, and *o*-dichlorobenzene has three.



Chlorobenzene
(four different kinds of carbon)



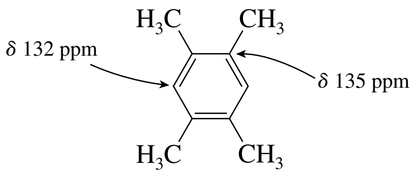
o-Dichlorobenzene
(three different kinds of carbon)



p-Dichlorobenzene
(two different kinds of carbon)

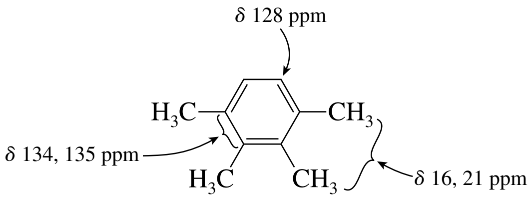
13.31 Compounds A and B ($C_{10}H_{14}$) have an index of hydrogen deficiency of 4. Both have peaks in the δ 130–140-ppm range of their ^{13}C NMR spectra, so that the index of hydrogen deficiency can be accommodated by a benzene ring.

The ^{13}C NMR spectrum of compound A shows only a single peak in the upfield region, at δ 20 ppm. Thus, the four remaining carbons, after accounting for the benzene ring, are four equivalent methyl groups. The benzene ring is symmetrically substituted as there are only two signals in the aromatic region at δ 132 and 135 ppm. Compound A is 1,2,4,5-tetramethylbenzene.



1,2,4,5-Tetramethylbenzene
(Compound A)

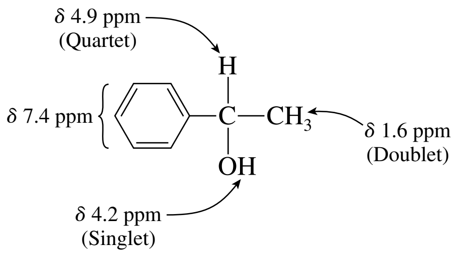
In compound B the four methyl groups are divided into two pairs. Three different carbons occur in the benzene ring, as noted by the appearance of three signals in the aromatic region (δ 128–135 ppm). Compound B is 1,2,3,4-tetramethylbenzene.



1,2,3,4-Tetramethylbenzene
(Compound B)

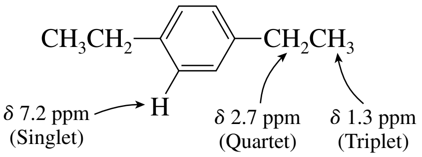
13.32 Since the compound has a 5-proton signal at δ 7.4 ppm and an index of hydrogen deficiency of 4, we conclude that six of its eight carbons belong to a monosubstituted benzene ring. The infrared spectrum exhibits absorption at 3300 cm^{-1}, indicating the presence of a hydroxyl group. The compound is an alcohol. A 3-proton doublet at δ 1.6 ppm, along with a 1-proton quartet at δ 4.9 ppm, suggests the presence of a CH_3CH unit.

The compound is 1-phenylethanol.



1-Phenylethanol

13.33 The peak at highest m/z in the mass spectrum of the compound is $m/z = 134$; this is likely to correspond to the molecular ion. Among the possible molecular formulas, $C_{10}H_{14}$ correlates best with the information from the ^{1}H NMR spectrum. What is evident is that there is a signal due to aromatic protons, as well as a triplet–quartet pattern of an ethyl group. A molecular formula of $C_{10}H_{14}$ suggests a benzene ring that bears two ethyl groups. Because the signal for the aryl protons is so sharp, they are probably equivalent. The compound is *p*-diethylbenzene.



p-Diethylbenzene

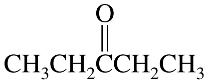
13.34 There is a prominent peak in the infrared spectrum of the compound at 1725 cm^{-1}, characteristic of C═O stretching vibrations.

The ^{1}H NMR spectrum shows only two sets of signals, a triplet at δ 1.1 ppm and a quartet at δ 2.4 ppm. The compound contains a CH_3CH_2 group as its only protons.

Its ^{13}C NMR spectrum has three peaks, one of which is at very low field. The signal at δ 211 ppm is in the region characteristic of carbons of C═O groups.

If one assumes that the compound contains only carbon, hydrogen, and one oxygen atom and that the peak at highest m/z in its mass spectrum (m/z 86) corresponds to the molecular ion, then the compound has the molecular formula $C_5H_{10}O$.

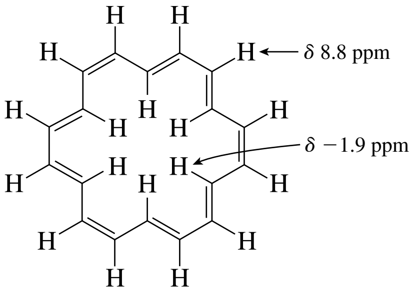
All the information points to the conclusion that the compound has the structure shown.



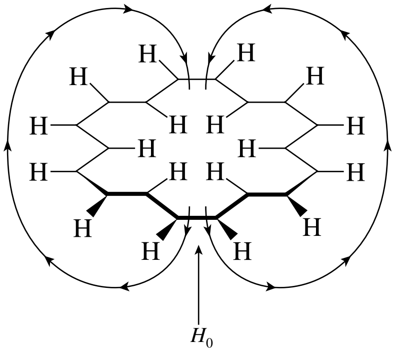
$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3$$

3-Pentanone

13.35 [18]-Annulene has *two* different kinds of protons; the 12 protons on the outside periphery of the ring are different from the 6 on the inside.



These different environments explain why the ^{1}H NMR spectrum contains two peaks in a 2:1 ratio. The less intense signal, that for the interior protons, is more shielded than the signal for the outside protons. This results from the magnetic field induced by the circulating π electrons of this aromatic ring, which reinforces the applied field in the region of the outside protons but opposes it in the interior of the ring.

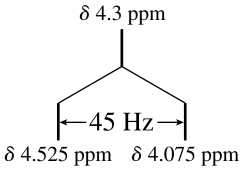


Protons inside the ring are shielded by the induced field to a significant extent—so much so that their signal appears at δ −1.9 ppm.

13.36 (*a*) The nuclear spin of ^{19}F is $\pm\frac{1}{2}$, that is, the same as that of a proton. The splitting rules for ^{19}F–^{1}H couplings are the same as those for ^{1}H–^{1}H. Thus, the single fluorine atom of CH_3F splits the signal for the protons of the methyl group into a **doublet.**

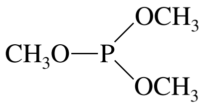
(*b*) The set of three equivalent protons of CH_3F splits the signal for fluorine into a **quartet.**

(*c*) The proton signal in CH_3F is a doublet centered at δ 4.3 ppm. The separation between the two halves of this doublet is 45 Hz, which is equivalent to 0.225 ppm at 200 MHz (200 Hz = 1 ppm). Thus, one line of the doublet appears at δ (4.3 + 0.225) ppm and the other at δ (4.3 − 0.225) ppm.



13.37–13.38 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual.* You should use *Learning By Modeling* for these exercises.

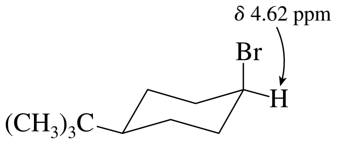
13.39 Because ^{31}P has a spin of $\pm\frac{1}{2}$, it is capable of splitting the ^{1}H NMR signal of protons in the same molecule. The problem stipulates that the methyl protons are coupled through three bonds to phosphorus in trimethyl phosphite.



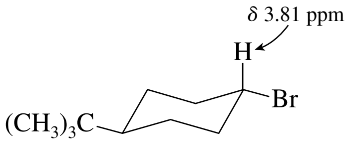
(*a*) The reciprocity of splitting requires that the protons split the ^{31}P signal of phosphorus. There are 9 equivalent protons, and so the ^{31}P signal is split into ten peaks.

(*b*) Each peak in the ^{31}P multiplet is separated from the next by a value equal to the ^{1}H–^{31}P coupling constant of 12 Hz. There are nine such intervals in a ten-line multiplet, and so the separation is 108 Hz between the highest and lowest field peaks in the multiplet.

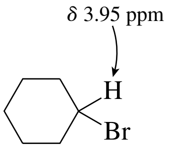
13.40 The trans and cis isomers of 1-bromo-4-*tert*-butylcyclohexane can be taken as models to estimate the chemical shift of the proton of the CHBr group when it is axial and equatorial, respectively, in the two chair conformations of bromocyclohexane. An axial proton is more shielded (δ 3.81 ppm for *trans*-1-bromo-4-*tert*-butylcyclohexane) than an equatorial one (δ 4.62 ppm for *cis*-1-bromo-4-*tert*-butylcyclohexane).



cis-1-Bromo-4-*tert*-butylcyclohexane;
less shielded



trans-1-Bromo-4-*tert*-butylcyclohexane;
more shielded

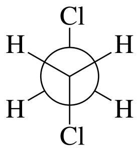


Bromocyclohexane

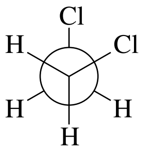
The difference in chemical shift between these stereoisomers is 0.81 ppm. The corresponding proton in bromocyclohexane is 0.67 ppm more shielded than in the equatorial proton in *cis*-1-bromo-4-*tert*-butylcyclohexane. The proportion of bromocyclohexane that has an axial hydrogen is therefore 0.67/0.81, or 83%. For bromocyclohexane, 83% of the molecules have an equatorial bromine, and 17% have an axial bromine.

13.41 The two staggered conformations of 1,2-dichloroethane are the anti and the gauche:

Anti conformation
has center of symmetry.



Anti



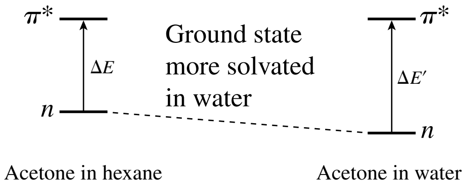
Gauche

The species present at low temperature (crystalline 1,2-dichloroethane) has a center of symmetry and is therefore the anti conformation. Liquid 1,2-dichloroethane is a mixture of the anti and the gauche conformations.

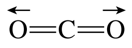
13.42 (*a*) Energy is proportional to frequency and inversely proportional to wavelength. The longer the wavelength, the lower the energy. Microwave photons have a wavelength in the range of 10^{-2} m, which is longer than that of infrared photons (on the order of 10^{-5} m). Thus, microwave radiation is lower in energy than infrared radiation, and the separation between rotational energy levels (measured by microwave) is less than the separation between vibrational energy levels (measured by infrared).

(*b*) Absorption of a photon occurs only when its energy matches the energy difference between two adjacent energy levels in a molecule. Microwave photons have energies that match the differences between the rotational energy levels of water. They are not sufficiently high in energy to excite a water molecule to a higher vibrational or electronic energy state.

13.43 A shift in the UV-Vis spectrum of acetone from 279 nm in hexane to 262 nm in water is a shift to shorter wavelength on going from a less polar solvent to a more polar one. This means that the energy difference between the starting electronic state (the **ground** state, *n*) and the excited electronic state (π^*) is *greater* in water than in hexane. Hexane as a solvent does not interact appreciably with either the ground or the excited state of acetone. Water is polar and solvates the ground state of acetone, lowering its energy. Because the energy gap between the ground state and the excited state increases, it must mean that the ground state is more solvated than the excited state and therefore more polar than the excited state.

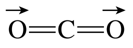


13.44 The dipole moment of carbon dioxide is zero and does not change during the symmetric stretching vibration. The symmetric stretch is not "infrared-active." The antisymmetric stretch generates a dipole moment in carbon dioxide and is infrared-active.



$\overleftarrow{O}{=}C{=}\overrightarrow{O}$

Symmetric stretch: no change in dipole moment



$\overrightarrow{O}{=}C{=}\overrightarrow{O}$

Antisymmetric stretch: dipole moment present as a result of unequal C—O bond distances

13.45 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual.* You should use *Learning By Modeling* for these exercises.

SELF-TEST

PART A

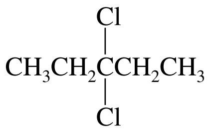
A-1. Complete the following table relating to ^{1}H NMR spectra by supplying the missing data for entries 1 through 4.

	Spectrometer frequency	*Chemical shift*	
		ppm	**Hz**
(*a*)	60 MHz	______ 1	366
(*b*)	300 MHz	4.35	______ 2
(*c*)	______ 3	3.50	700
(*d*)	100 MHz	______ 4	of TMS

A-2. Indicate the number of signals to be expected and the multiplicity of each in the ^1H NMR spectrum of each of the following substances:

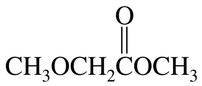
(*a*) $BrCH_2CH_2CH_2Br$

(*b*)



$CH_3CH_2\overset{Cl}{\underset{Cl}{C}}CH_2CH_3$

(*c*)



$CH_3OCH_2\overset{O}{\overset{\|}{C}}OCH_3$

A-3. Two isomeric compounds having the molecular formula $C_6H_{12}O_2$ both gave ^1H NMR spectra consisting of only two singlets. Given the chemical shifts and integrations shown, identify both compounds.

Compound A: δ 1.45 ppm (9H)
δ 1.95 ppm (3H)

Compound B: δ 1.20 ppm (9H)
δ 3.70 ppm (3H)

A-4. Identify each of the following compounds on the basis of the IR and ^1H NMR information provided

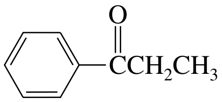
(*a*) $C_{10}H_{12}O$:
IR: 1710 cm^{-1}
NMR: δ 1.0 ppm (triplet, 3H)
δ 2.4 ppm (quartet, 2H)
δ 3.6 ppm (singlet, 2H)
δ 7.2 ppm (singlet, 5H)

(*b*) $C_6H_{14}O_2$:
IR: 3400 cm^{-1}
NMR: δ 1.2 ppm (singlet, 12H)
δ 2.0 ppm (broad singlet, 2H)

(*c*) $C_{10}H_{16}O_6$:
IR: 1740 cm^{-1}
NMR: δ 1.3 ppm (triplet, 9H)
δ 4.2 ppm (quartet, 6H)
δ 4.4 ppm (singlet, 1H)

(*d*) C_4H_7NO:
IR: 2240 cm^{-1}
3400 cm^{-1} (broad)
NMR: δ 1.65 ppm (singlet, 6H)
δ 3.7 ppm (singlet, 1H)

A-5. Predict the number of signals and their approximate chemical shifts in the ^{13}C NMR spectrum of the compound shown.



A-6. How many signals will appear in the ^{13}C NMR spectrum of each of the three C_5H_{12} isomers?

A-7. The ^{13}C NMR spectrum of an alkane of molecular formula C_6H_{14} exhibits two signals at δ 23 ppm (4C) and 37 ppm (2C). What is the structure of this alkane?

PART B

The following three problems refer to the ^1H NMR spectrum of $CH_3CH_2OCH_2OCH_2CH_3$.

B-1. How many signals are expected?

(*a*) 12 (*b*) 5 (*c*) 4 (*d*) 3

B-2. The signal farthest downfield (relative to TMS) will be a

(*a*) Singlet
(*b*) Triplet
(*c*) Doublet
(*d*) Quartet

B-3. The signal farthest upfield (closest to TMS) will be a

(*a*) Singlet (*c*) Doublet

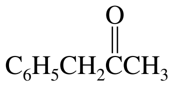
(*b*) Triplet (*d*) Quartet

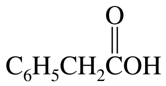
B-4. The relationship between magnetic field strength and the energy difference between nuclear spin states is

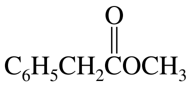
(*a*) They are independent of each other.
(*b*) They are directly proportional.
(*c*) They are inversely proportional.
(*d*) The relationship varies from molecule to molecule.

B-5. An infrared spectrum exhibits a broad band in the 3000–3500-cm^{-1} region and a strong peak at 1710 cm^{-1}. Which of the following substances best fits the data?

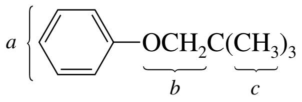
(*a*) $C_6H_5CH_2CH_2OH$

(*c*)

$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_3$

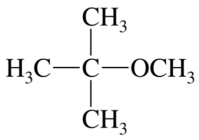
(*b*)

$C_6H_5CH_2\overset{O}{\overset{\|}{C}}OH$

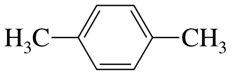
(*d*)

$C_6H_5CH_2\overset{O}{\overset{\|}{C}}OCH_3$

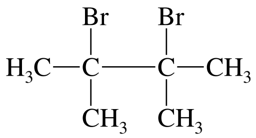
B-6. Considering the ^1H NMR spectrum of the following substance, which set of protons appears farthest downfield relative to TMS?



B-7. Which of the following substances does *not* give a ^1H NMR spectrum consisting of only two peaks?

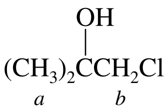
(*a*)

$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3$

(*c*)


(*b*)

$H_3C-\underset{CH_3}{\overset{Br}{C}}-\underset{CH_3}{\overset{Br}{C}}-CH_3$

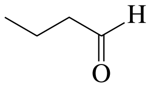
(*d*) None of these
(all satisfy the spectrum)

B-8. The multiplicity of the *a* protons in the ^1H NMR spectrum of the following substance is

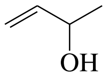

$\underset{a}{(CH_3)_2}\overset{OH}{C}\underset{b}{CH_2}Cl$

(*a*) Singlet (*b*) Doublet (*c*) Triplet (*d*) Quartet

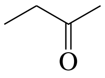
B-9. An unknown compound C_4H_8O gave a strong infrared absorption at 1710 cm^{-1}. The ^{13}C NMR spectrum exhibited four peaks at δ 9, 29, 37, and 209 ppm. The ^1H NMR spectrum had three signals at δ 1.1 (triplet), 2.1 (singlet), and 2.3 (quartet) ppm. Which, if any, of the following compounds is the unknown?



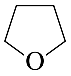
(*a*)



(*b*)



(*c*)

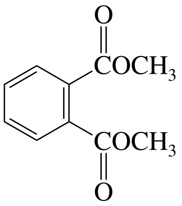


(*d*)

None of these

(*e*)

B-10. How many signals are expected in the ^{13}C NMR spectrum of the following substance?

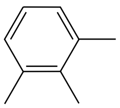


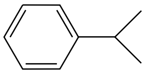
(*a*) 5 (*b*) 6 (*c*) 8 (*d*) 10

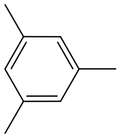
B-11. Which one of the following has the *greatest* number of signals in its ^{13}C NMR spectrum? (The spectrum is run under conditions in which splitting due to ^{13}C–^{1}H coupling is not observed.)

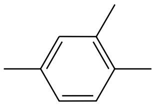
(*a*) Hexane
(*b*) 2-Methylpentane
(*c*) 1-Hexene
(*d*) *cis*-3-Hexene
(*e*) 1,5-Hexadiene

B-12. Which of the following C_9H_{12} isomers has the *fewest* signals in its ^{13}C NMR spectrum?

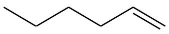

(*a*)

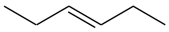

(*b*)

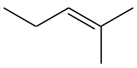

(*c*)

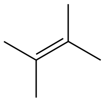

(*d*)

B-13. Which of the following compounds would best fit a ^{13}C NMR spectrum having peaks at δ 16, 21, 32, 36, 115, and 140 ppm?

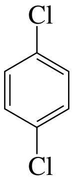
(*a*)


(*c*)


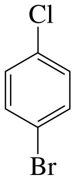
(*b*)


(*d*)


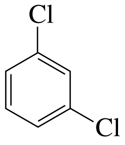
B-14. Which of the following compounds would have the *fewest* peaks in its ^{13}C NMR spectrum?



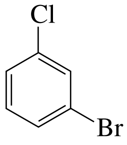
(*a*)



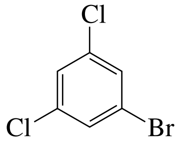
(*b*)



(*c*)



(*d*)



(*e*)

B-15. Which of the compounds in the previous problem would have the *most* peaks in its ^{13}C NMR spectrum?

Back Forward Main Menu TOC Study Guide TOC Student OLC MHHE Website