

## 6.9: SPECTROSCOPY OF CARBOXYLIC ACIDS AND NITRILES

### OBJECTIVES

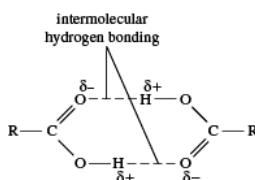
After completing this section, you should be able to

1. identify the two characteristic infrared absorptions displayed by all carboxylic acids.
2. state the approximate  $^1\text{H}$  NMR absorption of a carboxylic acid proton.
3. use infrared and NMR spectroscopy data to assist in the identification of an unknown carboxylic acid, with or without the assistance of a table of characteristic absorptions.

### SPECTROSCOPY OF CARBOXYLIC ACIDS

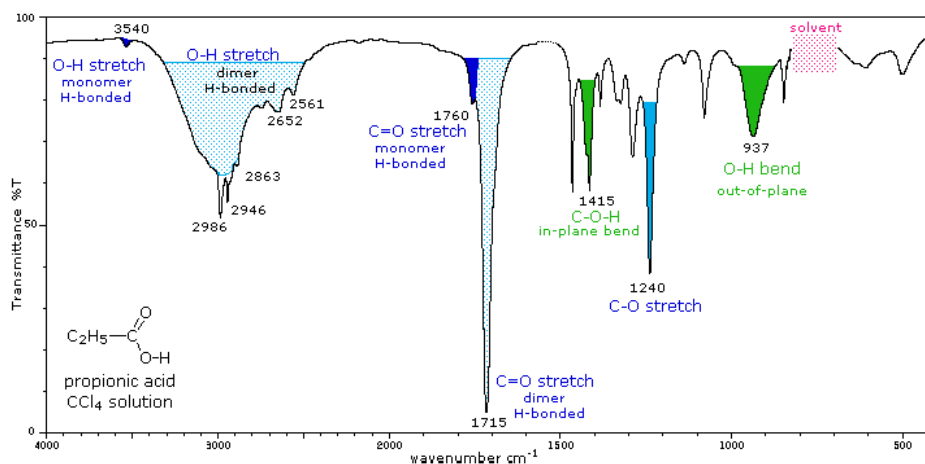
#### INFRARED SPECTROSCOPY

The carboxyl group is associated with two characteristic infrared stretching absorptions which change markedly with hydrogen bonding. The spectrum of propionic acid (propanoic acid) dissolved in  $\text{CCl}_4$ , shown below, is illustrative. Carboxylic acids exist predominantly as hydrogen bonded dimers in condensed phases.



#### The Hydrogen Bonding Dimer of Carboxylic Acids

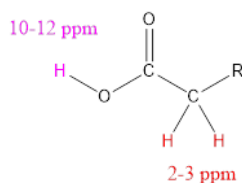
The O-H stretching absorption for such dimers is very strong and broad, extending from  $2500$  to  $3300\text{ cm}^{-1}$ . This absorption overlaps the sharper C-H stretching peaks, which may be seen extending beyond the O-H envelope at  $2990$ ,  $2950$  and  $2870\text{ cm}^{-1}$ . The smaller peaks protruding near  $2655$  and  $2560\text{ cm}^{-1}$  are characteristic of the dimer. In ether solvents a sharper hydrogen bonded monomer absorption near  $3500\text{ cm}^{-1}$  is observed, due to competition of the ether oxygen as a hydrogen bond acceptor. The carbonyl stretching frequency of the dimer is found near  $1710\text{ cm}^{-1}$ , but is increased by  $25\text{ cm}^{-1}$  or more in the monomeric state. Other characteristic stretching and bending absorptions are marked in the spectrum.



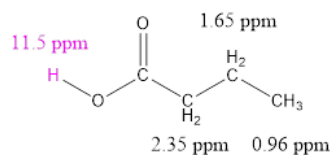
#### The Infrared Spectrum of Propanoic Acid

#### $^1\text{H}$ NUCLEAR MAGNETIC SPECTROSCOPY

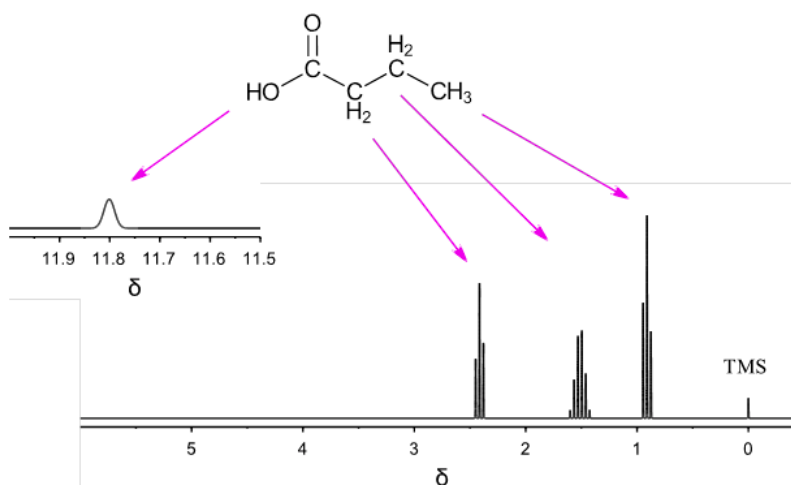
The acidic O-H protons of carboxylic acids are highly deshielded due to the electronegativity of oxygen and anisotropy from the  $\text{C}=\text{O}$  carbonyl bond. They tend to be among the least shielded protons appearing far downfield in the  $10\text{--}12\text{ ppm}$  region which is considered distinctive for carboxylic acids. Due to hydrogen bonding the proton of a carboxylic acid often appears as a broad singlet and adding  $\text{D}_2\text{O}$  causes the signal to disappear due to hydrogen-deuterium exchange. Protons on carbons adjacent to a carboxylic acid absorb in the  $2\text{--}3\text{ ppm}$  region. Some deshielding occurs due to the fact that the carbonyl oxygen is pulling electron density away from the carbonyl carbon which inductively pulls electron density away from the adjacent carbon.



### The Typical $^1\text{H}$ Peaks for a Carboxylic Acid



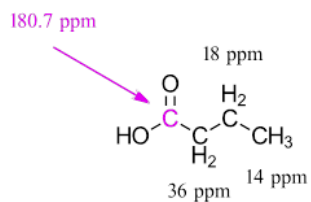
### The $^1\text{H}$ Peaks for Butanoic Acid



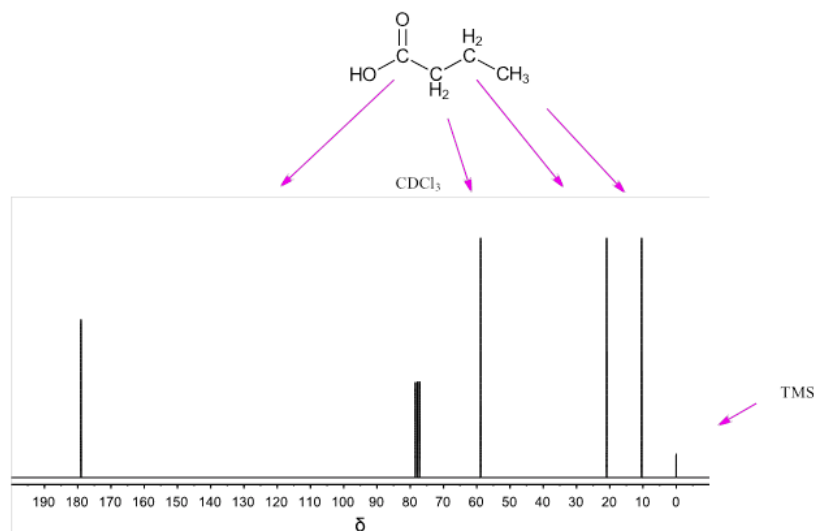
### A $^1\text{H}$ NMR Spectra for Butanoic Acid

### $^{13}\text{C}$ NUCLEAR MAGNETIC SPECTROSCOPY

The carbonyl carbon of a carboxylic acid is strongly deshielded (160-180 ppm) due to the presence of the highly electronegative oxygen. However, they are not as deshielded as the carbonyl carbon of an aldehyde or ketone (180-220 ppm).



### The $^{13}\text{C}$ Peaks for Butanoic Acid



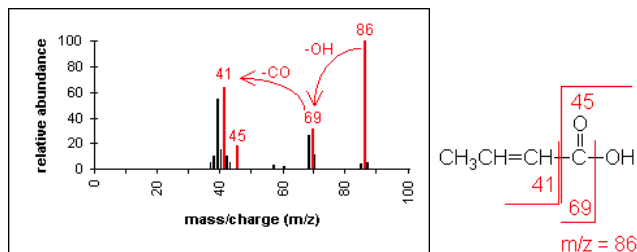
A  $^{13}\text{C}$  NMR Spectra for Butanoic Acid

### UV/VIS SPECTROSCOPY

Without additional conjugation, carboxylic acids absorb at about 210 nm, which is too low to be useful.

### MASS SPECTROMETRY

In short chain acids, peaks due to the loss of OH (molecular ion less 17) and COOH (molecular ion less 45) are prominent due to cleavage of bonds next to C=O.

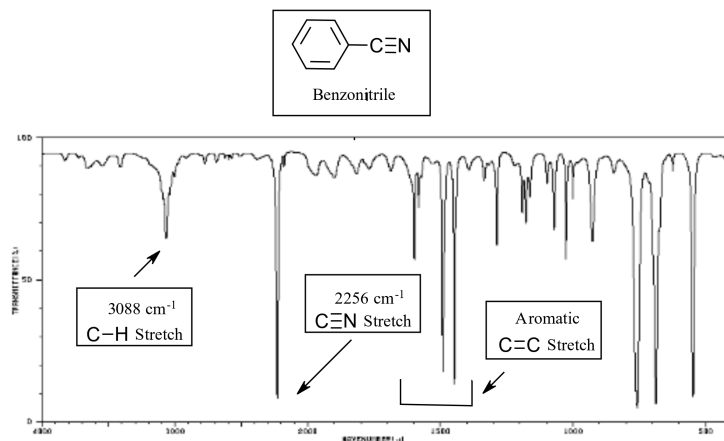


The Fragmentation of 2-Butenoic acid ( $\text{C}_4\text{H}_6\text{O}_2$ ): MW = 86.09

### SPECTROSCOPY OF NITRILES

#### INFRARED SPECTROSCOPY

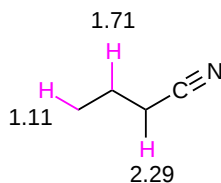
The CN triple bond stretch of nitriles appears in a distinctive region of an IR spectra, near  $2250\text{ cm}^{-1}$ . One of the only other absorptions to appear in this region is the CC triple bond stretch of an alkyne ( $2100\text{--}2250\text{ cm}^{-1}$ ).



Infrared Spectrum of Benzonitrile

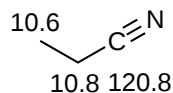
## <sup>1</sup>H NUCLEAR MAGNETIC SPECTROSCOPY

Protons on carbons adjacent to a nitrile absorb in the 2-3 ppm region. Some deshielding occurs due to the fact that the sp hybridized nitrile carbon is more electronegative than the adjacent sp<sup>3</sup> hybridized carbon.



## <sup>13</sup>C NUCLEAR MAGNETIC SPECTROSCOPY

The nitrile carbon absorbs in the 115–120 ppm region which is not as far downfield as a typical carbonyl carbon (180–220 ppm).

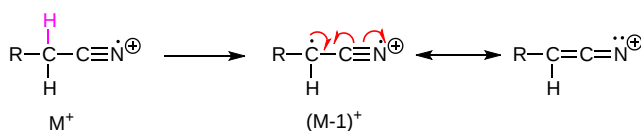


## UV/VIS SPECTROSCOPY

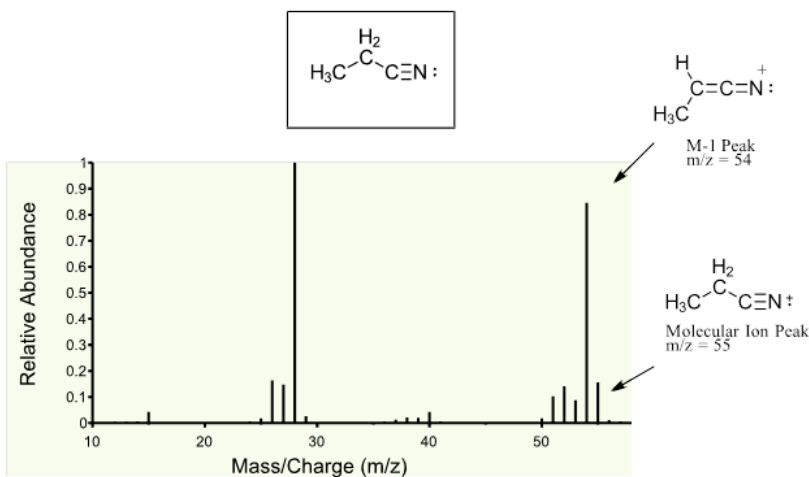
Most nitriles do not show absorption above 200 nm which does not make UV/Vis spectroscopy a useful tool to characterize them.

## MASS SPECTROMETRY

The molecular ion (M<sup>+</sup>) peaks of simple nitriles are often weak or not present in a mass spectra. There is often a M-1 peak due to the loss of a -H.



### Mechanism for the Formation of a M-1 Peak in Mass Spectra

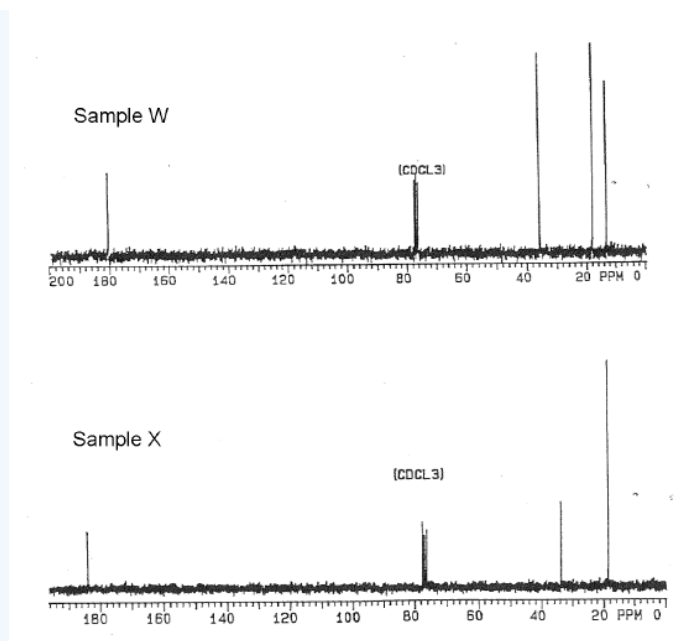


## Mass Spectra of Propanenitrile

### ? EXERCISE

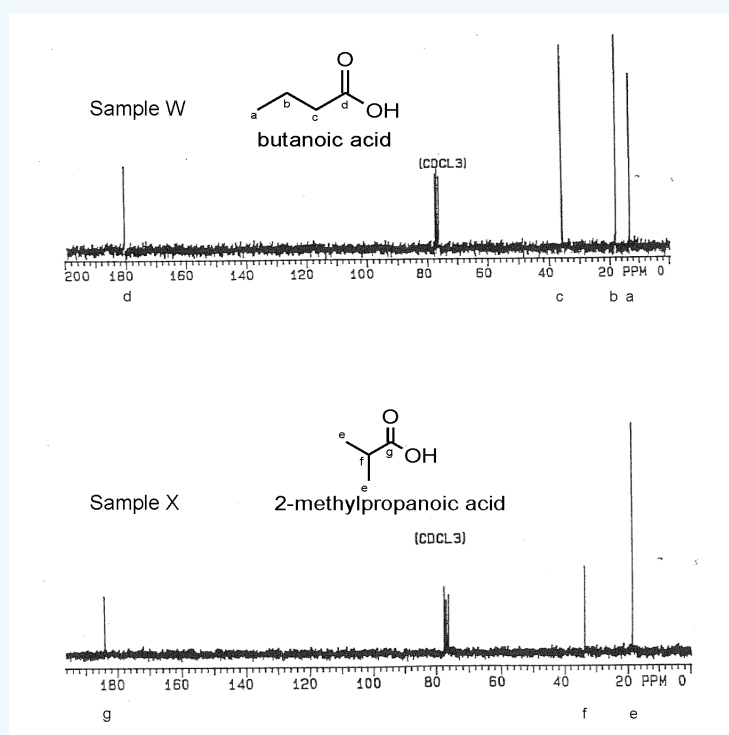
1. Sample W is a reactant for a wide range of biochemical processes. Sample X was isolated from vanilla beans. Elemental analysis indicated the compounds are structural isomers with the composition: 54.52% C, 9.16% H and 36.32% O. The IR spectrum for each compound showed a broad absorption from 3500 - 2500 cm<sup>-1</sup> and a strong band near 1710 cm<sup>-1</sup>. The <sup>1</sup>H NMR is being serviced, so only the <sup>13</sup>C NMR spectra shown below were available.

Name and draw the bond-line structures for Samples W and X and correlate the <sup>13</sup>C NMR spectral signals to their respective compounds.



Answer

1.



IR spectrum of benzonitrile. Source: SDBSWeb : <http://riodb01.ibase.aist.go.jp/sdbs/> (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

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