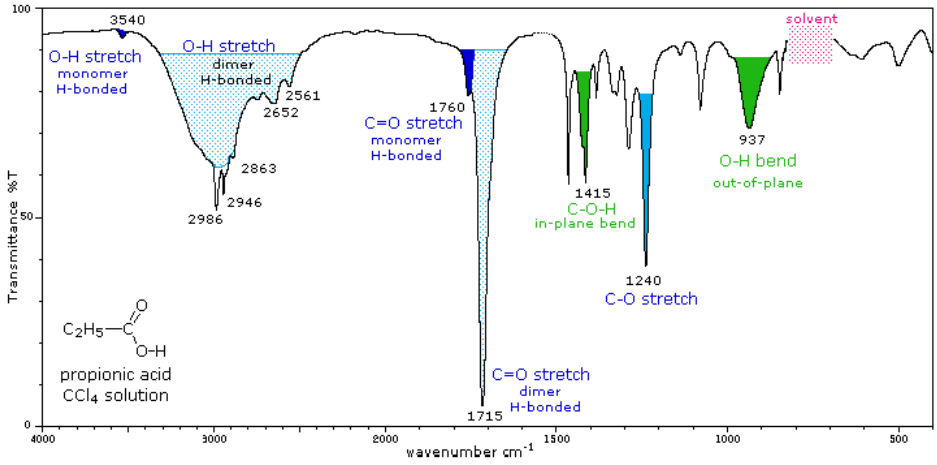
21.3: SPECTROSCOPY OF CARBOXYLIC ACIDS

IR

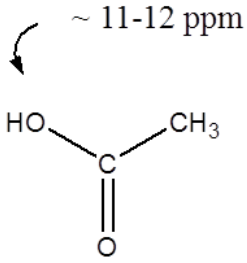
The carboxyl group is associated with two characteristic infrared stretching absorptions which change markedly with hydrogen bonding. The spectrum of a CCl_4 solution of propionic acid (propanoic acid), shown below, is illustrative. Carboxylic acids exist predominantly as hydrogen bonded dimers in condensed phases. The O-H stretching absorption for such dimers is very strong and broad, extending from 2500 to 3300 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 cm^{-1}. The smaller peaks protruding near 2655 and 2560 are characteristic of the dimer. In ether solvents a sharper hydrogen bonded monomer absorption near 3500 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 cm^{-1}, but is increased by 25 cm^{-1} or more in the monomeric state. Other characteristic stretching and bending absorptions are marked in the spectrum.

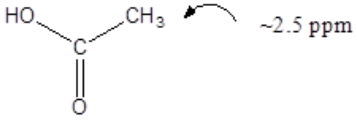


NMR

The combination of anisotropy and electronegativity causes the O-H hydrogen in a carboxylic acid to be very deshielded.



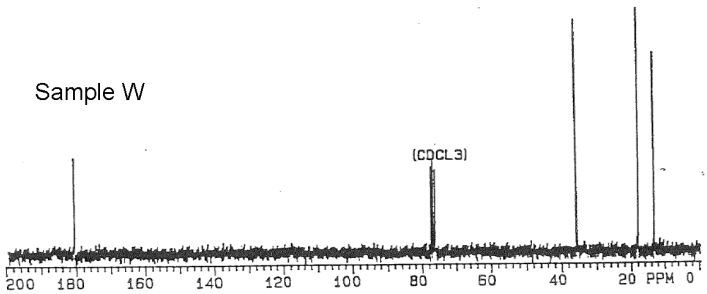
Hydrogen environments adjacent to a carboxylic acid are shifted to the region of 2.5-3.0 ppm.Deshielding occurs due to the fact that the sp2 hybridized carbon the the carboxylic acid is more electronegative than a sp3 hybridized carbon.

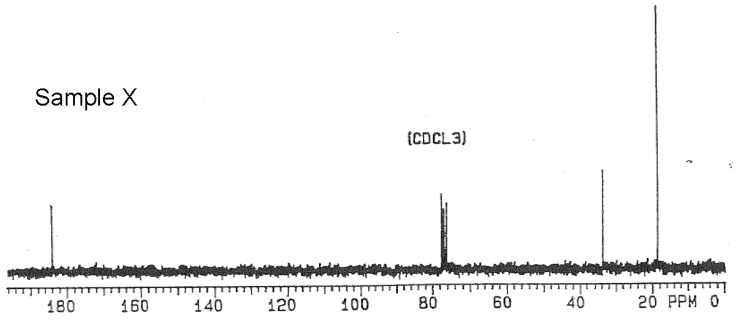


Exercise

2. 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-1 and a strong band near 1710 cm-1. The ^{1}H NMR is being serviced, so only the ^{13}C NMR spectra shown below were available.

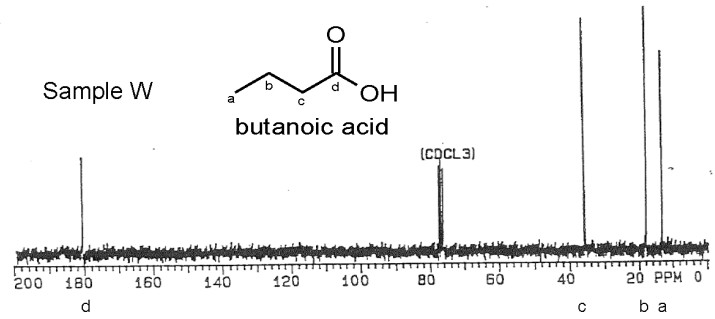
Name and draw the bond-line structures for Samples W and X and correlate the 13C NMR spectral signals to their respective compounds.

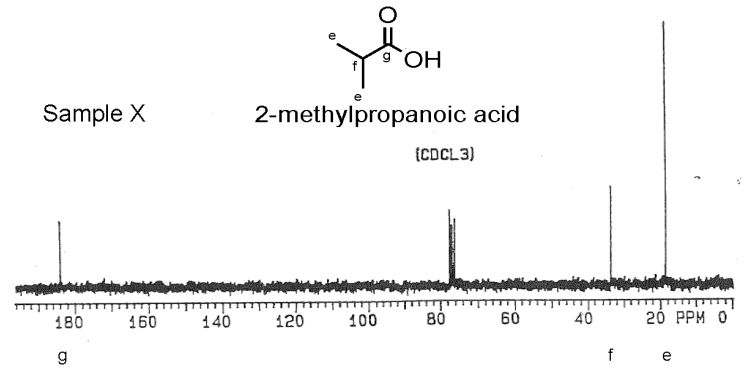




Answer

2.





CONTRIBUTORS AND ATTRIBUTIONS

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