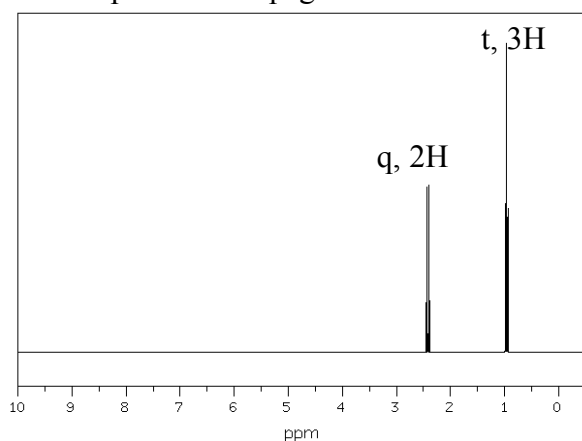


Chem 2061 Fall 2005  
 Chapter 13 assignment  
 Due Friday, Nov 4

Answer the following questions on a separate sheet of paper.

- You should have found that the compounds from the last assignment were amines, one tertiary, and one secondary, with the same formula,  $C_6H_{15}N$ . Use the following NMR spectra to positively assign their identities. Draw the structures and identify the inequivalent protons with letters. Then make a table containing the proton letter, chemical shift, number of hydrogens, and multiplicity.

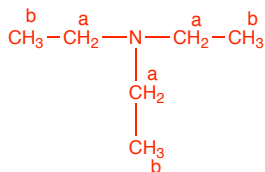
The compound from page 1:



In this spectrum we see two resonances so there are only two different types of hydrogens in the compound. The formula contains 15 hydrogens so the actual number of hydrogens in the molecule must be three times their integral ratios shown on the spectrum (i.e. there are 6 of one type, and 9 of another type).

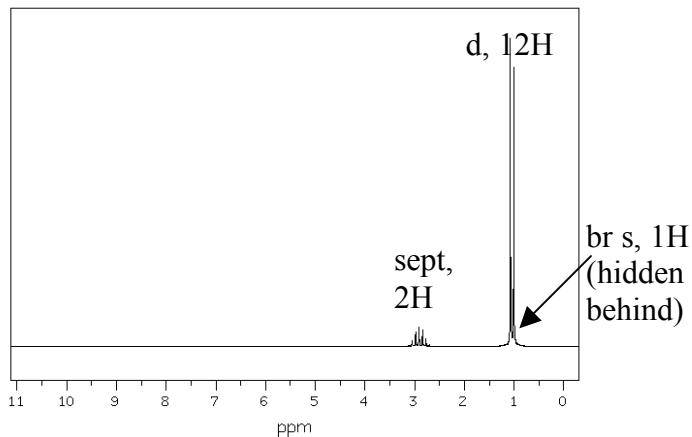
The resonance around 2.4 ppm is a quartet, so there must be three protons on the adjacent carbon, and the resonance around 0.9 ppm is a triplet so there must be two protons on the adjacent carbon. These are the only two resonances so they must be coupled to each other. This is a classic ethyl group signature. The spectrum shows one ethyl group, but we have 10 more hydrogens to account for. This must only mean that there are three equivalent ethyl groups in the molecule.

The structure is triethylamine,  $(CH_3CH_2)_3N$ .



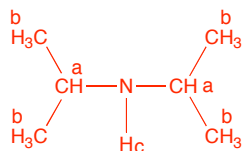
H	$\delta$ (ppm)	#H	m
a	2.4	6	q
b	0.9	9	t

The compound from page 2:



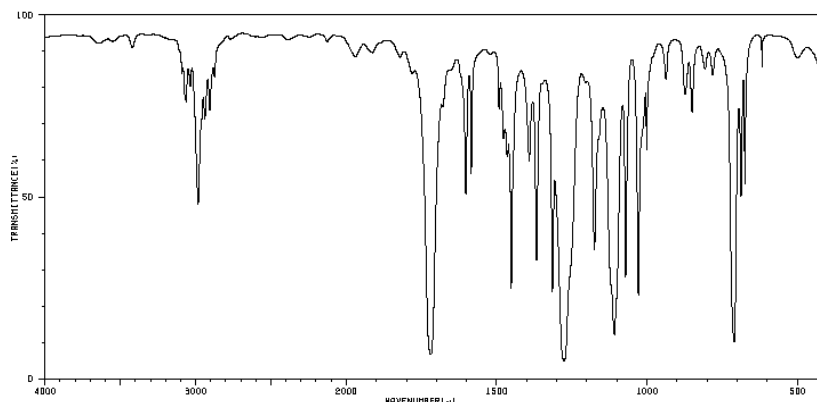
There are three resonances: a septet, a doublet, and a broad singlet. The broad singlet must be an N–H proton. This fits with the prediction of a 2° amine from the IR spectrum of the last assignment.

The septet at 2.8 ppm must have 8 hydrogens on adjacent carbons, and the doublet at 1.0 must have 1 hydrogen on adjacent carbons. This is a signature isopropyl pattern. Since one isopropyl group contains 6 + 1 hydrogens, we must have two of them in our structure. Those plus the N–H give us our total, and our compound is diisopropylamine,  $[(\text{CH}_3)_2\text{CH}]_2\text{NH}$ .



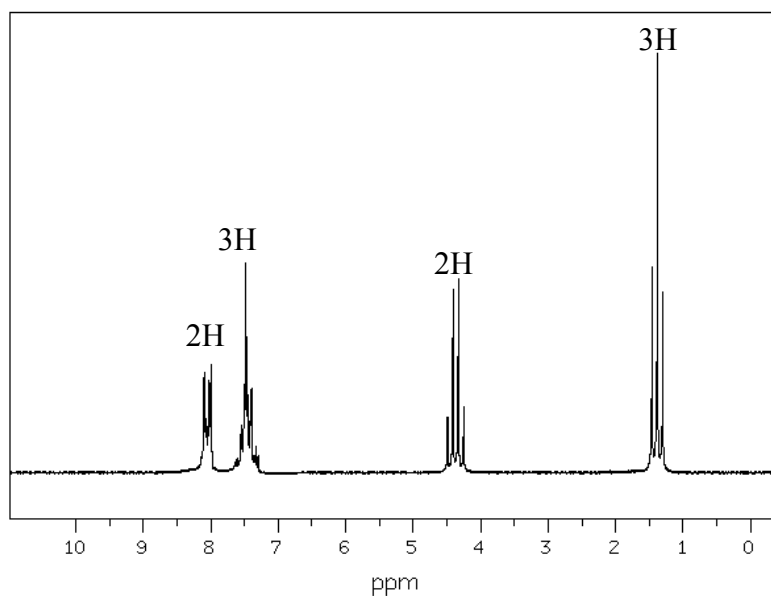
H	$\delta$ (ppm)	#H	m
a	2.8	2	sept
b	1.0	12	d
c	0.9	1	s

2. Use the following spectra to identify an unknown compound, and construct a table for the NMR resonances like in question 1. Its formula is  $C_9H_{10}O_2$ .



Note the carbonyl stretch around  $1710\text{ cm}^{-1}$ . What type of carbonyl is this usually associated with?

$1710\text{ cm}^{-1}$  is the standard carbonyl stretch frequency we associate with normal isolated ketones, aldehydes, or carboxylic acids.

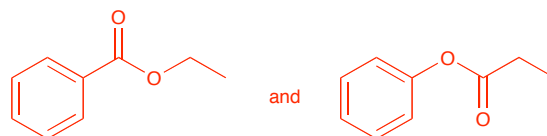


Does the NMR spectrum agree with your prediction of the type of carbonyl?

The 5 protons between 7 and 8.5 ppm are aromatic, indicating a monosubstituted phenyl group. There is also an ethyl group from the characteristic quartet and triplet. This accounts for 8 carbons and 10 hydrogens; 1 carbon and 2 oxygens to go. There must be a carbonyl (from the IR) so the remaining oxygen must be next to the carbonyl, making an ester. But, a normal ester carbonyl IR absorption is higher, at  $1740\text{ cm}^{-1}$  or so. This does not agree. How can this be??

The correct structure must account for the frequency of the carbonyl absorption **and** the NMR resonance with chemical shift 4.3 ppm. Explain your reasoning.

There are two possible orientations of the ester. One with the aromatic ring attached to the carbonyl and one with the ethyl attached to the carbonyl:



The chemical shift of the CH<sub>2</sub> in the ethyl will distinguish these. On the left compound, the CH<sub>2</sub> should be between 3 and 4.5 ppm or so, on the right compound it should be between 2 or 3 ppm. The spectrum shows the quartet at 4.3 ppm, so the left compound must be correct.

But what about the carbonyl IR absorption? Recall that starting with the baseline of 1710 cm<sup>-1</sup> as a “standard” carbonyl, this frequency can be shifted up if it’s an ester, or shifted down if the carbonyl is conjugated. A *conjugated ester*, as we see in the left compound, therefore will have these two effects in opposition, and we will be left with a carbonyl around the standard position.

Incidentally, the right compound is an isolated ester, which would have the expected carbonyl IR frequency around 1740 cm<sup>-1</sup>.