

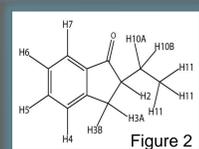
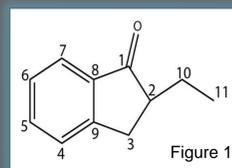
NMR ASSIGNMENTS FOR 2-ETHYL-1-INDANONE

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Introduction-

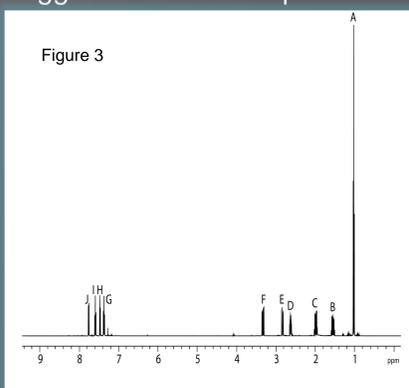
2-ethyl-1-indanone is a bicyclic hydrocarbon compound composed of an indane ring structure, a carbonyl functional group, and an ethyl side chain. Derivatives of 2-ethyl-1-indanone are used in the pharmaceutical industry and photonics. It has a molecular weight of $160.21 \text{ g}\cdot\text{mol}^{-1}$ and boiling point of 67°C . The IUPAC designation for the molecule is 2-ethylindan-1-one. Absolute stereochemistry at C2 is unresolved.



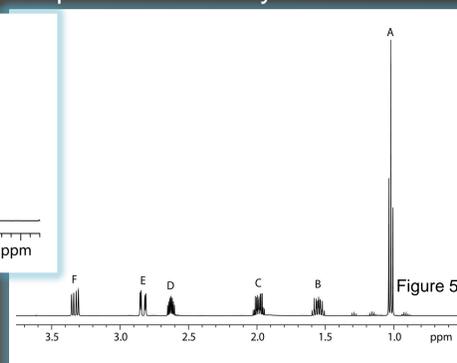
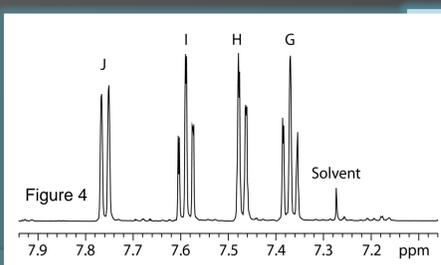
^1H NMR 1D Spectrum-

The 1D ^1H NMR of 2-ethyl-1-indanone is shown in figure 3, with expanded views of the aromatic and aliphatic regions in figures 4 and 5, respectively. The data was recorded at 500 MHz (^1H) with a spectral width of 4807.69 Hz and 8192 complex points. In figure 3 resonance A is an upfield triplet at 1.022 ppm. This suggests that it is the shielded methyl group that is being split by the two protons of the methylene on the ethyl side chain. Therefore, resonance A corresponds to the protons of C11. There are two methylene carbons in 2-ethyl-1-indanone, C3 and C10. Each methylene will have two nonequivalent protons. The electron density around C10 is predicted to be greater than that around C3, and thus the methylene protons at C10 should be upfield of those at C3. Therefore, peaks B and C can be assigned to the protons of C10. The fine structure of these resonances also suggests a more complex multiplet than the other possible peaks,

which is indicative of their position next to a methyl group. Based on splitting patterns, peaks F and E can be assigned to the protons on the other methylene, C3. They are both a doublet of doublets, which is caused by geminal coupling to one another as well as coupling to the proton at C2. One of the methylene protons on C3 will be cis to H2 and the other will be gauche. Peak E displays a large

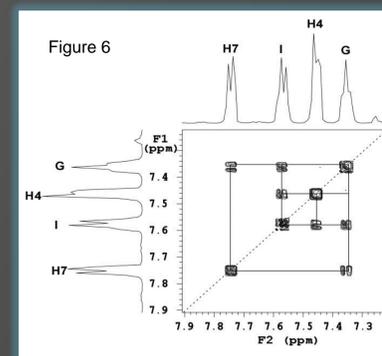


geminal coupling to its methylene proton partner and a much smaller gauche coupling to the methine proton at C2. Peak F displays a large geminal coupling to its methylene partner and a smaller cis coupling to the methine proton on C2. Peak F is therefore assigned to the methylene proton that is cis and E is assigned to the proton that is gauche with respect to H2. The remaining aliphatic resonance, peak D, must be the proton on the methine C2. This is supported by its chemical shift value and the multiplet fine structure. In the aromatic region there are four proton resonances. Peak J, the most downfield resonance, is a doublet. Its splitting pattern suggests that it is adjacent to one proton. Due to the inductive effects of the carbonyl and the splitting pattern, peak J can be assigned to H7. The other doublet in the aromatic region, peak H, must be H4. H4 shows a small splitting in each of the doublet branches, which is caused by longer range coupling. Peaks I and G are H5 and H6. They are both pseudo-triplets, arising from the two approximately equal vicinal couplings to adjacent protons. Definitive assignment of H5 and H6 remains unresolved at this point in the analysis.



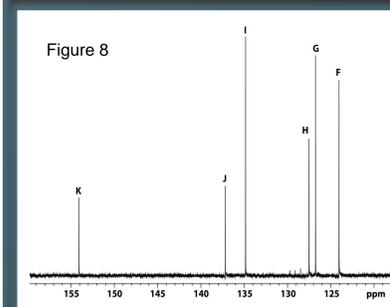
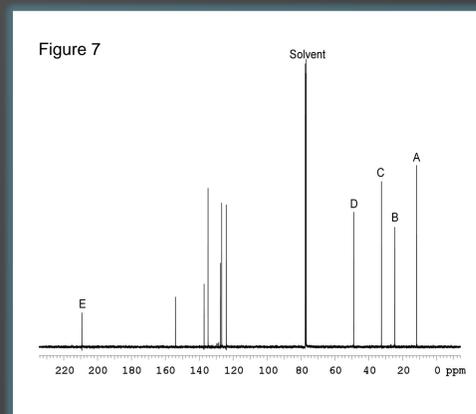
COSY Spectrum-

Figure 6 shows the aromatic region of a COSY experiment. This spectrum was recorded at 800 MHz (^1H) with a spectral width of 12755.1 Hz and 1024 complex points. By analyzing the off-diagonal peaks the ambiguities from the 1D ^1H NMR can be resolved. H7 is only coupled to peak G. The only adjacent proton to H7 is H6; therefore, peak G is H6. Peak I is coupled to two protons, H4 and the newly established H6. All proton resonances are now assigned.



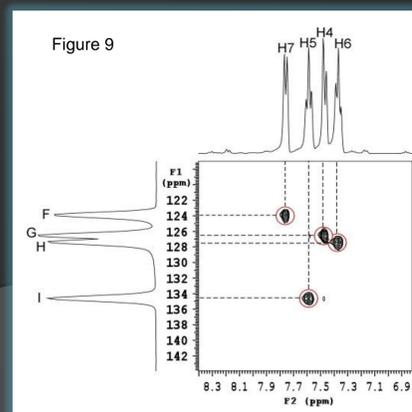
^{13}C NMR 1D Spectrum-

Figure 7 shows the result of the 1D ^{13}C NMR experiment. The spectrum was recorded at 500 MHz (^1H) with a spectral width of 31250 Hz and 32768 complex points. Peak E, which is the furthest downfield, corresponds to the carbonyl carbon, C1. The region between 120 and 155 ppm corresponds to the aromatic carbons (expanded in figure 8). Due to the proximity of the carbonyl group the quaternary carbon resonances corresponding to C8 and C9 are expected to be further downfield than the other aromatic carbons. C8, which is the nearest to the carbonyl, would correspond to peak K. Therefore peak J is assigned to C9. Assignment of the remaining aromatic carbon resonances remains ambiguous. The aliphatic resonances can be assigned based on their chemical shifts. Peak A, which has the lowest chemical shift, can be assigned to the methyl group, C11. Peaks B and C are the methylene carbons, C10 and C3. C3 is further downfield due to the inductive effects of both the carbonyl and aromatic ring. Therefore, peak C is C3 and peak B is C10. This leaves peak D to be C2, which makes sense based on the known range of methine chemical shifts. The aromatic region will be assigned using the gHMQC experiment.



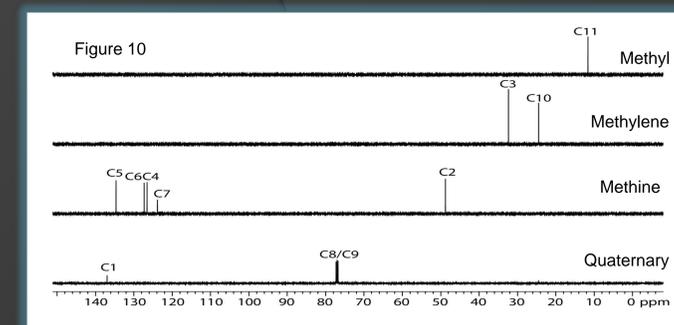
gHMQC Spectrum-

The two-dimensional gHMQC spectrum for the aromatic region of 2-ethyl-1-indanone is shown in Figure 9. This spectrum was recorded at 500 MHz (^1H) with a spectral width of 4807.69 Hz in the direct dimension and 21378.9 Hz in the indirect dimension. There were 1024 complex points. Figure 9 shows correlations between the directly bound ^1H and ^{13}C nuclei. The ^1H assignments that have already been made are mapped to the F2 projection of the HMQC. The correlations present in the HMQC spectrum resolve the ambiguities in the aromatic carbon assignments. Therefore, peak F correlates to H7, showing that peak F is C7. Peak G correlates to H4, and is therefore C4. Following this logic peak H is C6, and peak I is C5.



^{13}C DEPT Spectra-

Figure 10 shows the sub-spectrum series from a ^{13}C DEPT experiment. These data were recorded at 500 MHz (^1H) with a spectral width of 31250 Hz and 1024 complex points. The DEPT experiment shows the hybridization states of the ^{13}C nuclei in 2-ethyl-1-indanone. By comparing this spectrum with figure 6, the carbon assignments previously made can be reinforced. For example, peaks J and K were assigned to the quaternary carbons C8 and C9. In this spectrum the peaks corresponding to C8 and C9 are shown in the quaternary state. It also clarifies any ambiguities between C2 and C3. Similar comparisons can be made for the remaining resonances.



Results and Conclusion-

Using the experiments described above, complete proton and carbon assignments have been made for 2-ethyl-1-indanone. ^1H resonances were assigned using the 1D ^1H NMR and COSY experiments. ^{13}C resonances were assigned by inspection of the ^{13}C 1D NMR and gHMQC spectra. The ^{13}C DEPT was used to confirm the previously made carbon assignments. The following is a complete list of all ^1H and ^{13}C chemical shift values (ppm) of the molecule 2-ethyl-1-indanone.

^1H NMR Assignments (ppm)									
H2	H3A	H3B	H4	H5	H6	H7	H10A	H10B	H11
2.628	2.833	3.331	7.470	7.370	7.59	7.758	1.982	1.555	1.022

^{13}C NMR Assignments (ppm)										
C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
209.23	48.97	32.55	126.76	134.84	127.51	124.05	154.06	137.17	24.69	11.83

References and Acknowledgements-

Claridge, Timothy D. *High-Resolution NMR Techniques in Organic Chemistry*. Second ed. Oxford: Elsevier, 2009. Print.

NMRAnalyst Sample Application: 2-Ethyl-1-indanone. ScienceSoft, 1999. Web. 21 Feb. 2013.

<<http://www.sciencesoft.net/2-ethyl-1-indanone/index.html>>.

2-ETHYL-1-INDANONE. *ChemicalBook---Chemical Search Engine*. N.p., 2010. Web. 21 Feb. 2013. <http://www.chemicalbook.com/ChemicalProductProperty_EN_CB9127759.htm>.

"NMR Spectral Assignment." N.p., n.d. Web. 21 Feb. 2013. <http://chem.rutgers.edu/sites/default/files/Chem_542_Spring2010_Lecture_10.pdf>.