

# Organic Spectroscopy Laboratory: Utilizing IR and NMR in the Identification of an Unknown Substance

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Confirming the structures of organic compounds using IR and NMR spectra is a mainstay of the undergraduate organic laboratory curriculum (1–7). Determining the identity of an unknown substance using these techniques is rarer (8–10). This laboratory experiment, which emphasizes the interpretation of both IR and NMR data in the elucidation of the structure of an unknown compound, has been developed to fill this void. This experiment is ideally suited to the sophomore-level organic chemistry sequence, can be performed in one three-hour laboratory period, and reinforces the concepts of IR and NMR spectroscopy discussed in the lecture portion of the course. Additionally, the laboratory only requires small quantities of substances for the successful completion of the lab; therefore, waste management and handling precautions are minimized. This experiment provides for hands-on use of instrumentation by students. This may prove an excellent opportunity for those departments acquiring instrumentation through laboratory curriculum improvement grants.

## Experimental Procedure

Each student in the laboratory is assigned two unknown organic compounds: one is a liquid and the other is a solid. The unknowns contain one of the following functional groups: alcohol, aldehyde, amine, carboxylic acid, ketone, or phenol. Care is taken to ensure that each student receives two unknowns with different functional groups. Tables of candidate compounds with either the melting or boiling points are provided to each student. These are sorted by functional group and state (solid or liquid). The steps required for the proper identification of these two unknowns is described below.

### Physical Constant Determination

Purification of the liquid and solid unknowns will not be attempted. For the solid unknown, each student will take the melting point. When consulting the tables of possible compounds, all compounds that melt within a  $\pm 6^\circ\text{C}$  range must be considered; more if the unknown has a melting point range greater than  $2^\circ\text{C}$ . For the liquid unknown, the atmospheric pressure boiling point is provided. The student must consider all compounds within a  $\pm 12^\circ\text{C}$  range when consulting the tables of possible compounds.

### Infrared Spectra

The infrared spectra of the solid and liquid unknowns are obtained. The solid unknown must be prepared as a mull with nujol or as a KBr pellet. The IR is interpreted to determine the functional group(s) present. This is the most important aspect of the experiment thus far. If the IR is interpreted incorrectly, then the wrong candidate compounds will be selected. Proper interpretation will lead the student to consider compounds in the appropriate table (these are sorted by state and functional group). Besides functional group analysis, it is important to look for other evidence of

structural features in the molecule, such as whether an aromatic ring is present. The infrared portion of the report sheet is filled out and, along with the IR spectrum, turned in to the instructor for grading. This process can be iterative. For instance, the student may misinterpret the IR spectrum and choose the wrong functional group family. The instructor can then choose to provide a hint to place the student on the right track. The student will reanalyze the data and resubmit the report sheet. This, of course, would result in some point deduction. Additionally, the student may correctly choose the right functional group, but the unknown compound is not on the list of possible candidates supplied by the student on the report sheet. The instructor can suggest that the student expand the list of candidates by considering a larger melting point range. It must be noted that some organic compounds are hygroscopic and therefore may give an  $-\text{OH}$  peak (due to water) in the IR spectrum. The student must be informed of this possibility. However, it is reasonable to expect that the student can determine, on their own, whether or not absorption around  $\sim 3300\text{ cm}^{-1}$  is due to the sample being wet.

### Nuclear Magnetic Resonance Spectra

After the IR portion of the experiment has been graded the structures of all possible candidates determined by IR interpretation are drawn and the NMR spectrum for each is predicted. Then a  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR of each unknown is acquired by the student. However, if time or appropriate instrumentation is an issue, the instructor can choose to supply the  $^{13}\text{C}$ -NMR spectrum or both the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra (simulated NMR spectra for all unknowns are available in the Supplemental Material<sup>W</sup>).<sup>1</sup> These spectra are to be interpreted by the student; that is, they determine how many peaks are present, the multiplicity, chemical shift, coupling constants, and the integration for each peak. From this analysis, as much structural information about the unknown as possible is determined. Comparison of the actual NMR spectra with the predicted spectra should allow for the selection of a likely candidate. The report sheet for the NMR portion of the experiment is filled out, and all data (including the IR spectrum and IR report sheet) are given to the instructor for grading.

### Hazards

There are 81 different organic compounds used as unknowns in this experiment. In general, these compounds are flammable, toxic, irritants, corrosive, or mutagens. Please refer to the Supplemental Material,<sup>W</sup> which lists the hazards for each unknown specifically.

### Results and Discussion

A typical example for a solid unknown, using the procedure above, is provided here. The melting point of an unknown solid has a range of  $60\text{--}62^\circ\text{C}$ . An infrared spectrum taken in nujol shows a carbonyl peak at about  $1700\text{ cm}^{-1}$

(Figure 1). Of the six possible functional groups, three can be immediately discarded: the unknown is not an alcohol, an amine, or a phenol. Of the remaining three (all of which would contain the carbonyl stretch), the lack of an  $\text{-OH}$  stretch denies the existence of the carboxylic acid functionality. The absence of the Fermi doublet near  $2850$  and  $2750\text{ cm}^{-1}$  would rule out an aldehyde. The compound then is most likely a ketone. The presence of peaks just above  $3000\text{ cm}^{-1}$  (and partially obscured by nujol), the peaks in the finger print region of the spectrum, and the fact that the carbonyl stretch is well below  $1700\text{ cm}^{-1}$  points strongly to an aromatic ketone.

In the table of solid ketones (comprising 30 compounds), all that have melting points within  $\pm 6\text{ }^\circ\text{C}$  ( $54\text{--}68\text{ }^\circ\text{C}$ ) of the experimental value are considered. The report sheet for the IR portion of the experiment is filled out, including the functional group suspected for the unknown (with notations on the IR spectrum to support this premise), and the list of possible candidates from the appropriate table. Of the 30 possibilities, only 6 meet the melting point criteria: 4-methylbenzophenone, 2-indanone, phenacyl chloride, benzyl phenyl ketone, 1,1-diphenylacetone, and benzalacetophenone (this number will vary depending upon the particular unknown).

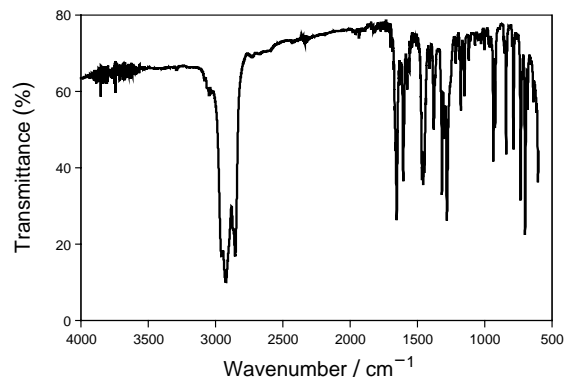
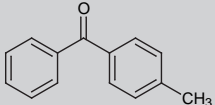
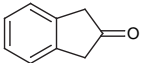
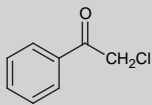
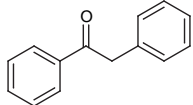
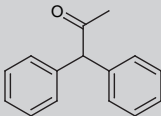
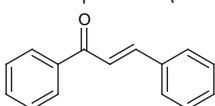


Figure 1. IR spectrum for unknown solid (taken in nujol).

ketone, 1,1-diphenyl-acetone, and benzalacetophenone (this number will vary depending upon the particular unknown).

After receiving the graded IR report sheet, a table (Table 1) for the unknown possibilities is prepared by the student.

**Table 1. Structures of Unknown Possibilities and the Predicted Signals in the NMR Spectra**

Candidate (mp)	$^1\text{H-NMR}$ Prediction	$^{13}\text{C-NMR}$ Prediction
4-Methylbenzophenone ( $54\text{ }^\circ\text{C}$ ) 	2 signals: $\sim 2.5\text{ ppm}$ (s, 3H) ( $\text{-CH}_3$ ) $\sim 7.5\text{ ppm}$ (m, 9H) (aromatic)	10 signals: $8\text{--}30\text{ ppm}$ ( $\text{-CH}_3$ ) $110\text{--}150\text{ ppm}$ (aromatic) $200\text{--}220\text{ ppm}$ ( $\text{C=O}$ )
2-Indanone ( $58\text{ }^\circ\text{C}$ ) 	2 signals: $\sim 3.7\text{ ppm}$ (s, 4H) ( $\text{-CH}_2$ ) $\sim 7.5\text{ ppm}$ (s, 4H) (aromatic)	5 signals: $20\text{--}45\text{ ppm}$ ( $\text{-CH}_2$ ) $110\text{--}150\text{ ppm}$ (aromatic) $200\text{--}220\text{ ppm}$ ( $\text{C=O}$ )
Phenacyl chloride ( $59\text{ }^\circ\text{C}$ ) 	2 signals: $\sim 4.5\text{ ppm}$ (s, 2H) ( $\text{-CH}_2\text{Cl}$ ) $\sim 7.5\text{ ppm}$ (m, 5H) (aromatic)	6 signals: $40\text{--}65\text{ ppm}$ ( $\text{-CH}_2\text{Cl}$ ) $110\text{--}150\text{ ppm}$ (aromatic) $200\text{--}220\text{ ppm}$ ( $\text{C=O}$ )
Benzyl phenyl ketone ( $60\text{ }^\circ\text{C}$ ) 	2 signals: $\sim 3.7\text{ ppm}$ (s, 2H) ( $\text{-CH}_2$ ) $\sim 7.5\text{ ppm}$ (m, 10H) (aromatic)	10 signals: $20\text{--}45\text{ ppm}$ ( $\text{-CH}_2$ ) $110\text{--}150\text{ ppm}$ (aromatic) $200\text{--}220\text{ ppm}$ ( $\text{C=O}$ )
1,1-Diphenylacetone ( $61\text{ }^\circ\text{C}$ ) 	3 signals: $\sim 2.2\text{ ppm}$ (s, 3H) ( $\text{-CH}_3$ ) $\sim 5.1\text{ ppm}$ (s, 1H) ( $\text{-CH}$ ) $\sim 7.5\text{ ppm}$ (s, 10H) (aromatic)	7 signals: $8\text{--}30\text{ ppm}$ ( $\text{-CH}_3$ ) $30\text{--}60\text{ ppm}$ ( $\text{-CH}$ ) $110\text{--}150\text{ ppm}$ (aromatic) $200\text{--}220\text{ ppm}$ ( $\text{C=O}$ )
Benzalacetophenone ( $62\text{ }^\circ\text{C}$ ) 	3 signals: $\sim 5.5\text{ ppm}$ (d, 1H) ( $\text{-CH}$ vinyl) $\sim 6.5\text{ ppm}$ (d, 1H) ( $\text{-CH}$ vinyl) $\sim 7.5\text{ ppm}$ (m, 10H) (aromatic)	11 signals: $100\text{--}145\text{ ppm}$ ( $\text{-CH}$ alkene) $110\text{--}150\text{ ppm}$ (aromatic) $200\text{--}220\text{ ppm}$ ( $\text{C=O}$ )

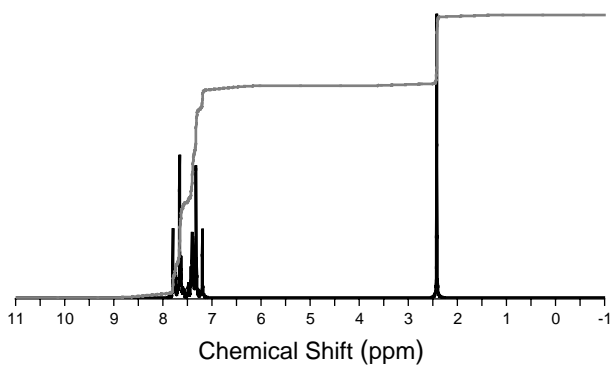


Figure 2.  $^1\text{H}$  NMR spectrum for unknown solid.

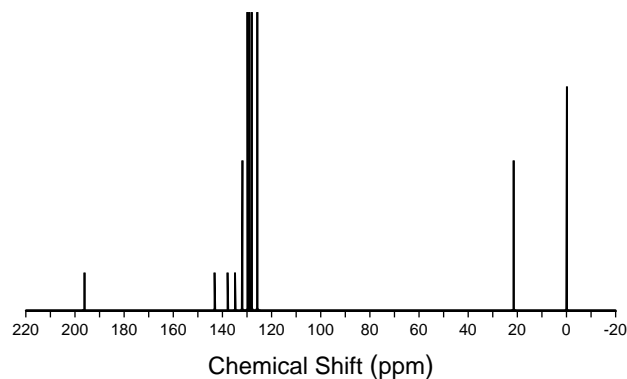


Figure 3.  $^{13}\text{C}$ -NMR spectrum for unknown solid.

This table contains structures of the six candidate compounds and predicted NMR spectra for each. This should be as complete an analysis as possible, including the number of anticipated peaks, the relative chemical shift for each peak, the multiplicity of each peak, and coupling constants, if possible. The instructor determines the depth of this analysis.

After the NMR analysis for each unknown is completed, a detailed analysis of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra (Figures 2 and 3, respectively) for the unknown solid is performed. The  $^1\text{H}$ -NMR shows two peaks: 2.4 ppm (s, 3H) and 7.5 ppm (m, 9H). The  $^{13}\text{C}$ -NMR shows ten peaks indicating ten different types of carbon atoms in the sample: one peak at 22 ppm, eight peaks between 120–145 ppm, and one peak at 196 ppm. A comparison of these results with the predictions for each candidate leads to the conclusion that the unknown has to be 4-methylbenzophenone. For completeness, a rationalization for how the other candidates were ruled out should be included in the report. This may involve more than just counting the anticipated peaks, but also the relative chemical shifts for each peak, the multiplicity of each peak, and coupling constants for split peaks where appropriate.

## Conclusions

This laboratory experiment gives the undergraduate valuable experience in the following: (i) acquisition of both liquid and solid IR spectra, as well as in the acquisition of NMR spectra, (ii) interpretation of IR spectra for the presence of various functional groups, (iii) determining  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra from the structures of compounds, (iv) interpretation of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, and (v) using the chemical literature to ascertain structures of compounds from the chemical names. In addition, this laboratory also addresses the problem of the availability of an NMR spectrometer for student use. Although it is preferred that the student obtain all spectra, providing the student with a  $^{13}\text{C}$ - or  $^1\text{H}$ -NMR does not diminish the usefulness of the experiment. Most instructors would agree that it is virtually impossible to have a large number of students acquire a  $^1\text{H}$ -NMR of a sample in one laboratory period, let alone a  $^{13}\text{C}$ -NMR spectrum. Students can observe the use of the NMR spectrometer by the instructor if this is deemed necessary. A possible compromise solution for the problems associated with NMR spectrometer use and availability may be to insist that chemistry majors in the course obtain their own spectra, while nonmajors can be given the opportunity as time permits. This is a decision best made by individual instructors or departments.

Finally, the experiment can be adjusted by the instructor to include more (or fewer) functional groups, or to incorporate more chemical compounds currently in the local chemical stores. It is not necessary to use only the unknowns described here. Instructors can choose to exclude the use of  $^{13}\text{C}$ -NMR analysis, however the use of the provided  $^{13}\text{C}$ -NMR spectra allows for flexibility on this issue.

## Supplemental Material

A detailed student handout, which includes the experimental procedure, a solved example, and tables of possible unknowns (sorted by functional group and state) and instructors' notes, which contain the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra for each unknown used in the experiment, lists of all hazards for each unknown, and lists of equipment, supplies, and other reagents necessary for the experiment are available in this issue of *JCE Online*.

## Note

1. All  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were simulated using HNMR and CNMR Spectrum Generator 4.5 (Chemist's Version) available from Advanced Chemistry Development, 90 Adelaide St. W. Suite 702, Toronto, ON M5H 3V9. If genuine spectra are preferred then the instructor can either obtain them directly, or download the spectra from various Web resources such as the Integrated Spectral Data Base System for Organic Compounds: <http://www.aist.go.jp/RIODB/SDBS/> (accessed Jun 2005).

## Literature Cited

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