Structure Elucidation: Qualitative and Spectroscopic Methods (IR, NMR, MS) of Structure Determination in Organic Compounds

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Introduction

Structure elucidation is a product of qualitative and quantitative techniques. With the emergence of dynamic technologies, spectroscopic methods have made the procedures and processes for structure elucidation easier and convenient (1). Most of these methods use light, magnetic energy and electromagnetic waves as their sources of energy. Through the use of different spectroscopic instruments or coupling them, it is possible to obtain all the necessary information to determine the structure of a given product. The infrared spectroscopy operates by the use infrared radiation. The sample is bombarded with the radiation resulting into absorption of photons which causes changes in the molecular vibrations in the components of the sample (2). Given that infrared radiations are a part of the electromagnetic spectrum, they have properties of frequency (ν) and wavelength (λ) that are related by the speed of light (2). Infrared spectroscopy provides a wide range of sharp lines that appear at different fingerprint regions indicating the presence of a unique functional group in the structure.

Nuclear magnetic resonance (NMR) is among the most widely used techniques in structure elucidation. The NMR works by the principle of energy absorption by molecules placed in a region of magnetic field (3). The NMR spectroscopy is involved in the elucidation of odd number elements, for example, 1H, 13C, 15N, 19F, and 31P (1). Proton NMR is used to detect the number of hydrogens in the vicinity of a particular proton. The magnetic field strength determines the nature of the chemical shift from the standard, Tetramethylsilane (TMS). The chemical shift is measured in terms of ppm on a scale of zero to 10. Atoms that are more shielded have the lowest chemical shift; they are said to be upfield, while the less shielded are downfield.

Mass spectrometry is a technique where a compound in solution is bombarded with a high-energy beam of electrons and consequent fragmentation of various ions. The fragments are passed through a vacuum where the use of an electromagnet manipulates their flight mechanisms and characteristics (4).

Depending on the mass and the level and the angle of deflections, the fragments are separated. The results of the mass spectrometry are presented in terms of mass-to-charge ratio – a parameter that is the most useful in the analysis of the results (4). Through the use of mass-to-charge ratio and the relative abundances, the molecular formula of the compound is determined.

Results and Discussion

Qualitative Analysis

The qualitative results indicate that the compound is organic. The compound was insoluble in water and soluble in diethyl ether. This means that the compound is non-polar and organic. The DNPH derivatization test for the test of aldehydes and ketones yielded a crystal with a melting point of 134-154°C. Such high melting points suggest that the compound is more likely to be a ketone. The tertiary alcohol test using chromic acid was negative; the blue color solution was absent. The absence of a blue color suggests the presence of the chromium sulfate and its absence negates the presence of an aldehyde in the mixture (1).

The iodoform test was positive; there was a formation of a clear yellow solution. Iodoform tests are used to determine the presence of a methyl ketone or an aldehyde in the solution. This confirms that there is an aldehyde or a ketone functional group in the compound (5). This is in line with the miscibility test results that confirm the presence of an organic compound. Therefore, the compound is made of carbons, hydrogens, and at least one oxygen atom. The DNPH test indicates the presence of ketones and aldehydes through the formation of a precipitate. In the DNPH test, ketones form oils; however, the reagents used in the process solidify the oils into a precipitate. Besides, the test may indicate the presence of allylic alcohols that are easily oxidized by the DNP reagent to form aldehydes and indicate positive results (6). The ketone has a carbonyl group at the second carbon; this is suggested by the presence of a methyl ketone in the structure. Further, the ketone has more than four carbon atoms in the structure.

Spectroscopic Techniques

1H NMR

There were four significant signals from the NMR spectrum. All the signals were upfield ranging from around 0.8 to 2.4 ppm. The number of peaks from downfield to upfield was three, one, six and three. Their intensities were low except for the single peak indicating the lower frequencies. The NMR signal indicates the probability of five carbon atoms or more in the overall structure. There are four carbons bonded to hydrogens and one carbonyl group. Having more than five carbons in the structure would suggest having some protons in the same chemical environment. If the protons were in the same chemical environments, they would have given the same chemical shifts given that they were subjected to the same magnitude of the magnetic field. The magnitude of the signals indicates the frequencies through which the chemical shift was produced. The frequencies determine the energy states between the alpha and beta states (7). The protons in the unknown compound are more shielded; hence, there are lower frequencies which result in lower energy differences and lower chemical shifts.

The peaks indicate that three protons produce only one signal at 2ppm given that they border the carbonyl which has no hydrogens. Similarly, there are protons which are shielded by five protons, probably CH3 and CH2 groups. The peak is upfield, which suggests a high level of shielding. Therefore, the group may be a CH2 one surrounded by CH3 and CH2 groups. There are three peaks on the far right, near zero; this suggests that there are two protons surrounded by a greater cloud of electrons. This means that the level of shielding may be much higher than that caused by hydrogen atoms. The two protons are near the carbonyl group which shields them from a greater chemical shift (2). Lastly, the three peaks on the far left, more downfield, indicate a carbonyl with two protons that are not very shielded.

Infrared (IR)

The absorption wave numbers represent the carbon-hydrogen bonds at 3000-3100 wave numbers; the signal for alkyl groups is medium. 2000-2200 cm-1 indicates strong signals for carbon-hydrogen single bonds which are attached not only to other hydrogens but also to bigger groups apart from hydrogens (5). The presence of carbonyl is not shown on the printout but expected to absorb between 1640-1800 cm-1.

The results on the band absorption positions on the IR spectrum correspond to and agree with the chemistry of alkyl and carbonyl groups, thus confirming the speculation of CH2 and CH3 groups in the unknown compound (5).

Mass spectrometry (MS)

The mass spectrometer spectrum indicates that the highest possible mass number of the compound is 86; the molecular ion peak is at 86. Therefore, the sum of all the mass numbers of the carbonyl and alkynes suggested by the IR and NMR add up to 86 since the mass-to-charge ratio is highest at 86 (8). All peaks represent ion fragments that result from the bombardment of the unknown material with a beam of electrons. The unknown compound is 86 in mass composed of one carbonyl and alkyl groups. The most probable structure will have five carbon atoms, ten hydrogens, and one oxygen atom.

5C + 10H + 1O = 86
5(12) + 10(1) + 1(16) = 86

From other spectroscopic results and qualitative analysis, the structure is linear, has a ketone and a carbonyl at the second carbon.

Molecular structure: CH3CH2CH2C(0)CH3.

Conclusion

The qualitative methods used greatly assisted in the determination of key properties and both chemical and physical characteristics. The miscibility test was used to determine the polarity and the nature of the compound confirming that it was indeed an organic compound. The DNPH tests were used to determine the presence of ketone or aldehyde functional groups. Although the test was not substantive to differentiate between ketones and aldehydes, the melting point confirmed the presence of a ketone. The test was confirmed through the reaction with chromic acid negating the presence of aldehydes in the compound. Finally, the iodoform test confirmed the presence of a methyl ketone. The IR band absorption positions confirmed the presence of alkyl groups in the structure without other carbon-hydrogen bonds, for example, alkenes and alkynes. The mass spectrometer confirmed the mass number of the compound and its overall structure. Through the relative abundance of the ion, the fragmentation patterns confirm that the structure is linear.

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